DEGRADATION AND PRESERVATION
OF ARTEFACTS
IN SYNTHETIC PLASTICS

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The Desert Roses, growing in wasteland, appear like an elegant and fascinating girl in a desolate country. They spontaneously form following the mixing of sand and water under the action of pressure and heat.

Men by using synthetic plastics tried to produce objects similar in shape to the natural Roses of desert by imitating the basic principles spontaneously applied by nature.

Nevertheless the Roses of desert, uncontaminated by any human contact, seem to be made by some kind of supra-natural forces, and thus they are hardly imitable by men.

_t.m.r.w.a.m.l.e.m._
PREFACE

In a previous book the most relevant aspects concerning the chemistry of degradation and conservation of plastic artefacts of pre-synthetic “era” that is based on natural or artificial polymers were reviewed [1].
In particular the main internal and external factors generating damages and the most important mechanisms leading to the deterioration, together with prevention and protection measures, were analysed. In that book the following families of plastics were taken into consideration:

--- Plastics based on natural pre-formed polymers with protein structure (horn and hoof, bois durci and casein);
--- Plastics deriving from natural low molecular mass molecules that following process transform in macromolecules (i.e. Shellac);
--- Ebonite (hard rubber) and soft-rubbers obtained from transformation of natural rubber;
--- Plastics derivatives from chemical alteration of natural cellulose (celluloid, cellulose acetate).

With the discovery and commercialization of the “Bakelite” by Leo Hendrik Baekeland (1908-1909) begun the “era” of synthetic plastics that is materials obtained by polymers deriving by polymerization reactions of low molecular substances (monomers).
Since then a relevant number of new classes of synthetic polymers (i.e. Polymers Man-Made) were invented.
The introduction on the market of those new materials was interesting not only from industrial, scientific and economic point of view but also because of the deep impact they had on most of social aspects. As matter of fact the fast growing use of plastics products determined great changes in the people daily way of life.

![Image of Gino Bramieri with a plate of food, caption: "FIGURE 1: The famous Italian comic actor Gino Bramieri while advertises new products manufactured in polypropylene (MOPLEN), around the early years 1960s [2]."]
The demand of objects manufactured in plastics increased tremendously during all the 20th century. For such a reason this century past to the history as the “Century of Plastics.”

In such a contest the introduction on the market of the early thermosetting resins (phenol-formaldehyde, urea (thiourea)-formaldehyde, and melamine-formaldehydes) and the early thermoplastic polymers (polyvinylchloride, poly (methyl methacrylate), polystyrene) represented a mile-stone. Plastics, first by imitating and afterwards by substituting many traditional materials (wood, metal and glass), become day after day part of almost all aspect of the people life (see figure 1) [2,3].

As the industrial development of plastic increased designers, architects, engineers and artists made profit of the availability of these polymer-based materials with innovative properties to manufacture artefacts valuable for their refined design and also for their artistic content (see examples in figure 2).

Around the 1960s it was observed as many Pop art objects were manufactured by using a large variety of commercial plastics.

**FIGURE 2:** The designer Eero Aarnio and some of his famous and elegant plastic furniture. **Left:** Copacabana Table 1991. **Right:** Mushroom, 1960 [4].

At the begin of the “Plastic revolution” designers and manufacturers started in using plastics, essentially for their low production cost and easy processing, as materials in substitution of more prized or scarce natural materials as, gemstones, ivory and wood (see the case of costume jewels, statues, radio cabinets, etc.) [5].

Because of their relatively low cost plastic artifacts, assumed not as much of value than similar objects made of more costly traditional materials, were quite often considered as disposable. During the last few decades not only this position drastically changed but it was observed as plastic objects were more and more collected and found place in various modern art museums or in museums dedicated to the history of science, technology and industrial development.
With the rapid increase in the collections of the number of artifacts in plastics several problematic issues, concerning their preservation, including, storage and displaying conditions, direct restoration and non-direct protection measures against the major factors of degradation, dramatically came out. Due to the specificity of the plastic materials conservators have to face a new challenge connected to a wide variety of problems associated with the care and with the management of materials which behave quite dissimilarly in comparison with more traditional materials.

In the present book along the line of the first one [1] the most relevant aspects concerning the conservation of artifacts manufactured by synthetic polymers ( early thermosetting resins: Bakelite, Urea/Melamine-formaldehyde and early thermoplastic resins: Polyvinylchloride, Polymethylmethacrylate, Polystyrene, and Polyurethanes ) are reviewed taking into consideration the main intrinsic chemical and physical peculiarities of such materials together with their very complex degradation behavior.

The main goals may be summarized as follows:
1 ) To clarify the relationships between molecular structure of those polymers and the mechanisms of the processes induced by the most effective internal and external factors of degradation.
2 ) To point out the influence of additives on the above mentioned processes and mechanisms.
3 ) To critically analyze the measures so far applied for the conservation and protection of plastic objects especially in relation to the conditions of display and storage.
4 ) To put into evidence the difficulties encountered in managing with the preservation of plastic objects, which due to their organic nature in comparison to traditional materials ( ceramics, glasses, metal, etc.) are characterized by a relatively short life span.

The polymers belonging to the chosen families are components of plastics, which were used for the manufacturing of objects with high value both from historical and artistic point of view, and for such a reason now a day's find place in many museums.

For each of the plastics taken into consideration the following critical points were analyzed and reviewed:
--- Appropriate techniques for the identification of plastics and their main components;
--- Suitable practices for surveying plastics in collections;
--- Methodologies for the assessment of polymer degradation and types of damage;
--- Procedures for recognizing the main factors affecting polymer degradation;
--- Analysis of deterioration products and study of degradation processes;
--- Solution to polymer degradation;
--- Best practices for preserving plastics pieces in Museums.

It is hoped that the present book will help conservators in finding out some useful answers to the wide range of problems associated with the care, treatment and maintenance of valuable artifacts in plastics.

< Plastic objects have now become highly collectable, and are sold for considerable sums alongside other antiques and works of art. It has to be acknowledged that one day plastics will be as important as any other material in a collection of art and design > [6].
REFERENCE

1) E. Martuscelli, <The chemistry of degradation and conservation of plastic artefacts of pre-synthetic “era” based on natural or artificial polymers>, Palazzo Spinelli Restauro, PAIDEIA-Firenze (2010).
   <La Montecatini dal secondo dopoguerra alla fine>.
3) E. Martuscelli, <Le plastiche nel terzo millennio>, Ricerca e Futuro, 23, 46 (2002).
CHAPTER-FIRST

PHENOL FORMALDEHYDE RESINS: THE FIRST SYNTHETIC PLASTICS:

SYNTHESIS, PROCESSING AND PROPERTIES (Bakelite, "the Material of Thousand Uses")

The development by Leo Baekeland (figure 1), of the earliest synthesis and process suitable to be exploited at industrial level for the production of objects made of the phenol formaldehyde resins (polyoxybenzylmethyleneglycolanhydride), represented, de facto, the start of the so called "Synthetic Era" of plastic industry.

FIGURE 1: Dr. Leo Baekeland (Belgian–American industrial chemist (1863–1944), living in Yonkers, New York in its laboratory while working at the development of the phenol formaldehyde resins, called on its honor as "Bakelite", the first Man-made plastic.

The various scientific and technological achievements leading to the final set-up of the synthesis and process of Bakelite are hereafter summarized [1,2,3,4,5,6].

1872: Adolf Bayer, the very famous German chemist, found that phenol, in presence of concentrated hydrochloric acid, was capable to react with simple aldehydes (formaldehyde and acetaldehyde). The resultant resinous and bituminous products of the condensation reaction, according to the Bayer record, were materials useless and untreatable with no practical utility.

1883: Products with similar properties of those obtained by Bayer were synthesised, but in alkaline conditions, by A. Michael.

1890–1889: Lederer and O. Manasse, independently, noted that ortho and para hydroxylbenzylalcohols are intermediate products of the condensation reaction between phenol and formaldehyde.

W. Kleberg, Bayer pupil, evidenced the following aspects of the condensation reaction:

1) During the reaction a relatively large amount of heat is generated.
2) The resinous products of the reaction at RT slowly become insoluble in the common solvents, not fusible and then untreatable.
3) The large volume of gases and vapours emitted in the course of the setting phase gives rise to highly porous and fragile materials.

1889: Arthur Smith filed the first patent where the procedures of obtaining phenol-formaldehyde based resins, suitable to substitute the hard rubber (Hebanite) were described. Nevertheless besides its claims the products were considered of poor practical utility.

1902-1903: The German chemist, A. Luft developed an innovative method for the condensation reaction of phenol and formaldehyde essentially based on the following procedure:

a) Phenol and formaldehyde are first mixed in sulphuric acid and the mixture is heated up in a vessel fitted with a reflux condenser. In the course of such operation the coagulation of a viscous mass occurs.

b) The product of the reaction after washing show plastic characteristics. When the solvent is completely removed, then the dried mass results to be very fragile.

c) The dried mass could be shaped by compression moulding, nevertheless the objects due to their inherent fragility showed poor competitiveness against similar artefacts made by materials such as celuloid and other natural plastics.

1903-1906: W. H. Story experimented a new process where the phenol was allowed to react with formaldehyde, the latter being previously dissolved in water at high temperature. The highly viscous mass, so obtained, was suitable to be shaped by compression molding and set at about 100°C. The product of the reaction resulted to be soluble in alcohol and acetone. Thus it was considered for applications in the field of the surface coating.

It must be pointed out that all the process developed before the Baekeland discovery were unsuccessful from practical point of view essentially because the cured final materials denoted a high level of porosity and of brittleness. Such inconvenient was related to difficulties encountered in controlling the various parameters of the condensation reaction (pressure, temperature and concentration of components) and the rapid evolution of water vapors.

1905-1912: Leo Baekeland achievements.

In 1905 Leo Baekeland starts a rigorous, systematic investigation finalized at studying the influence of all the different factors governing the violent phenol-formaldehyde condensation reaction with the main aim at obtaining products suitable to be shaped by compression molding and then cured to get objects with reproducible and useful performances, and then capable to compete with similar items made by more traditional materials.

The above objectives were fulfilled through the following accomplishments:

- The optimisation of the monomers as well as of catalyst concentration and type.
- The lowering of the curing time by selecting suitable higher setting temperature.
- The obtaining of void-free materials through the use of relatively more elevated values of the pressure.
- The utilization of filler as wood-flour or asbestos, to implement the mechanical properties and particularly to lower the fragility of shaped objects.

The above achievements in the first procedure developed by Baekeland were described in the famous "heat-pressure patents" (Baekeland; 1907a, 1907b).

< His patent shows that he had virtually complete understanding of the reaction and could control it. Among other things he found methods by which the resin could be mixed with sawdust and colorants to produce moulding powder which, when subjected in a mould to heat and pressure,
would produce a solid, infusible, insoluble moulded shape with excellent mechanical and electrical properties. He called his material Bakelite.... > [6].

The whole heat-pressure process was described in details, as follows, in reference [7].

< Resinoid may be prepared by boiling one molecular equivalent of formaldehyde, as formalin or 40% solution, in a vessel fitted with a reflux condenser to prevent loss of formaldehyde. It is usual to add a small amount of alkali or acid to act as catalyst...After one hour or two the resinoid forms and separates from watery layer.... The mass is run out of the vessel and cooled rapidly. The resinoid is used in this stage in moulding powders or varnishes and is in what is known as the unfinished or the "A stage". It is soluble in acetone and alcohols.......

If this A stage material is heated for an hour or more at 95-100°C...., it will change to a leathery intermediate "B stage", ...insoluble in alcohol and acetone. When heated for a short time longer the B stage will change into the final or "C stage", ...insoluble and permanently hard, even when hot > [6].

Thus it can be seen that, besides details and implementations, the process of bakelite-like resins is essentially based on the steps, schematically represented in figure 2 [8].

![Diagram of Bakelite production process](image)

**FIGURE 2**: Schematic representation of the main steps concerning the process for shaping objects in Bakelite thermosetting resins [8].
< The whole industry of moulding phenolic and other thermo-setting plastics is based on the fact that in the A stage the material is workable and can be moulded, and by further heat treatment it loses plasticity and becomes permanently hard > [7].

The equipment (digester) used for the preparation of the earlier Bakelite resins is reproduced in figure 3-a), while in figure 3-b) is schematically described the "Bakelizer", the apparatus used for the curing process [9].

*FIGURE 3-a: Digester apparatus used for the production of the earlier Bakelite resins.  
< It is steam jacketed and provided with a large valve at the bottom for drawing off the product. At right is shown a super heater for steam. At left is a condenser so constructed as to permit distillation in vacuum. The manhole at the top of the digester is an essential feature. Digester may be made of steel and may be cylindrical instead of spherical > [9].

Backeland presented the results of its research for the first time at the "Meeting of the New York Section of the American Chemical Society" on the 5th of February 1909. Some of the main characteristics of the Bakelite were presented as follows: 
< Perfectly insoluble, infusible, unaffected by almost all chemicals and excellent insulator for heat and electricity...far superior to Shellac and Hard Rubber > [2].

On September 1910 Bakeland founded The "General Bakelite Company" and a factory was then established at Perth Amboy, New Jersey. In this company essentially raw materials suitable to be, by compression moulding devices, successively shaped in cured objects, were produced and distributed. The Company in 1939 merged with the Union Carbide and Carbon Corporation (now the Union Carbide Corporation) [10].
FIGURE 3-b: The scheme of the apparatus, named “Bakelizer”, used to cure under controlled conditions the early phenol formaldehyde resins. *It is a container in which phenol formaldehyde resins can be heated under pressure. Carbon dioxide... is supplied to the bakelite to create a pressure of several atmospheres on the resin which is undergoing hardening. Sufficient pressure is applied to counteract the tendency of the resin to become spongy due to the escape of gas when heat is applied.* [9].

FIGURE 4: Early semiautomatic presses used during the World War-I to shape objects from Bakelite compounds by compression moulding, produced by the Charles Burroughs Company (Newark, New Jersey, USA) [11].
The Bakelite Company, at that time, used to advertise their products as follows: “The advantages of hard rubber, Japanese Lacquer, Celluloid and surpassing their properties”.

Some of the most relevant physical, thermal and electrical properties of Bakelite molding compounds after curing, which contributed, in part, to the enormous success of the phenol-formaldehyde resin (henceforth PF), are described in Table 1 [1].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural strength</td>
<td>MPa</td>
<td>69 – 150</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>MPa</td>
<td>210 – 270</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>48 – 90</td>
</tr>
<tr>
<td>Impact, Izod</td>
<td>J/m</td>
<td>15 – 35 (Glass Filled)</td>
</tr>
<tr>
<td>Deflection Temp.</td>
<td>°C</td>
<td>180 – 260</td>
</tr>
<tr>
<td>Water absorption</td>
<td>%</td>
<td>0.20 – 0.50</td>
</tr>
<tr>
<td>Molded Shrinkage</td>
<td>%</td>
<td>0.40 – 1.10</td>
</tr>
<tr>
<td>Apparent density</td>
<td>g/cm³</td>
<td>Avg. 0.6</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td></td>
<td>1.40 – 1.82</td>
</tr>
</tbody>
</table>

Backeland, enthusiast of the successes, which PF resins acquired soon after its set-up of producing technologies, invented the slogan: “Bakelite, the Material of Thousand Uses”.

Early semiautomatic presses, developed by the Charles Burroughs Company (Newark, New Jersey-USA) like those shown in figure 4, were used during the World War I for shaping objects by compression moulding Bakelite mass compounds. In particular the press of figure 4-right was first used for the old bell-shaped telephone receiver housing [11].

Some of early applications of Bakelite mouldings in various industrial fields are documented by figures 5, 6 and 7 [11,12].
FIGURE 5: Some early applications of Bakelite in electrical industry [12].

FIGURE 6, left: In the production of billiard balls first Gutta-percha took the place of ivory then celluloid substituted Gutta-percha. In 1912, as shown in figure, Bakelite substituted celluloid <since it was more economical to produce and made superior products> [11].

FIGURE 7, right: An example of a hand cranked brown model 1930's Ohmmeters by Evershed and Vignoles manufactured with a body in bakelite.

PF resins are produced by a step-growth polymerization reaction which may be either acid or base catalyzed.
The molecular structure of the starting monomers, phenol and formaldehyde, are below represented. It must be pointed out that in aqueous solution, formaldehyde exists in equilibrium with methylene glycol, and that phenol is reactive towards formaldehyde only at the ortho and para positions (sites 2, 4 and 6 in the below figure) allowing up to 3 units of formaldehyde to attach to the ring [2,13, 14,15].

\[
\begin{align*}
\text{CH}_2\text{O} & \rightleftharpoons \text{HO-CH}_2\text{-OH} \\
\text{Formaldehyde} & \quad \text{Methylene Glycol}
\end{align*}
\]

Thus the theoretical functionality of phenol and formaldehyde is three and two respectively. Of course it must be underlined as the real functionality depends on the phenol-formaldehyde ratio used in the course of the reaction.

Following the findings of Baekeland, the PF resins, from a chemically point of view, may be divided in two families: Those produced by using a base catalyst in a single phase process (Resole) and those based on a two step process in an acidic medium (Novolac) [14,15].

1) Base-catalysed or Single Phase process (Resoles)

Resole-type PF resins are usually obtained following a process where a formaldehyde to phenol ratio of greater than one (= 1.15 molar ratio) is used in a basic catalyst system.
The components, phenol, formaldehyde, water and catalyst, are mixed in the desired amount, and are then heated by using an apparatus like that described in figure 8 [7].
The chemistry of the reaction is characterized by a first step where phenol reacts with methylene glycol to form methylol phenol according to the below scheme.
FIGURE 8: Apparatus used for the condensation reaction of phenol and formaldehyde. It was used for the production of Resoles and Novolacs [7].

In the following steps, as below shown, molecules of methylol phenol may react with themself forming dimers molecules.

\[
\begin{align*}
\text{OH} \quad \text{CH}_2\text{-OH} & + \quad \text{OH} \quad \text{CH}_2\text{-OH} \rightarrow \quad \text{OH} \quad \text{CH}_2\text{-OH} \quad \text{CH}_2\text{-OH} + \text{H}_2\text{O} \\
\end{align*}
\]

Alternatively they can form dibenzyl ether molecules (see below reaction).

\[
\begin{align*}
\text{OH} \quad \text{CH}_2\text{-OH} & + \quad \text{OH} \quad \text{CH}_2\text{-OH} \rightarrow \quad \text{OH} \quad \text{CH}_2\text{-O}-\text{CH}_2 \quad \text{OH} \quad \text{CH}_2\text{-OH} + \text{H}_2\text{O} \\
\end{align*}
\]

On the other hand methylol phenol, as hereafter shown, by reacting with phenol may form a methylene bridge [2,13,14].
The excess of formaldehyde gives rise to the presence in the reacting mass of a sufficient number of reactive methyol and dibenzyl ether groups. \textit{At this point the resin is starting to crosslink, to form the highly extended 3-dimensional web of covalent bonds which is typical of polymerised phenolic resins} \cite{14}.

In the real industrial practice the rate of the polymerization and curing reaction is drastically reduced by a rapid cooling \textit{before substantial degree of cross-linking occurs to allow for further reaction in compounding and final molding of the finished part} \cite{15}.

Resoles are then commercialised as powders, following dehydration, or in a wet state by maintaining in the mass a certain amount of water. It is important to note that Resoles, due to the fact that even at RT the polymerisation reaction keeps still ongoing, even if at much slower rates, present a \textit{limited shelf lives dependent on the resin character, storage conditions and application} \cite{14}.

\textit{By manipulating the phenol to aldehyde monomer ratio, pH, catalyst type, reaction temperature, reaction time, and amount of distillation, a variety of resin structures demonstrating a wide range of properties are possible. The typical number average molecular weight (Mn) of a straight phenol resol resin is between 200 and 450} \cite{14}.

Thus, according to reference \cite{16} Resole may be defined as:

\textit{A thermosetting resin composition in its unformed and uncured state, but containing all of necessary materials for hardening upon heating. Also called “A-stage resin”} \cite{16}.

\section{Acid-catalysed or Two-Phase Process (Novolacs)}

Novolacs resins are obtained by using conditions characterized by an acid catalyst and a molar ratio of formaldehyde to phenol of less than one. Due to the fact that the reaction occurs with phenol excess such a resin will not completely crosslink (polymerize) without the addition of a suitable curing agent \cite{2,14,15}.

According to ASTM, a novolac is a PF resin which, unless a source of methylene groups is added, remains permanently thermoplastic (thermoplastic phenolic) \cite{16}.

The chemical processes involved in the formation of novolacs may be summarised as follows \cite{2,13,14,15}.

The initial phase sees the reaction between methylene glycol and phenol (figure 9).

The reaction, as schematically shown in figure 10, keeps on going by involving additional phenol while water is released.

\textit{The reaction creates a methylene bridge at either the ortho position or the para position of the phenol aromatic rings. The “rule of thumb” is that the para position is approximately twice as reactive as the ortho position, but there are twice as many ortho sites (two per phenol molecule) so the fractions of ortho-ortho, para-para and ortho-para bridges are approximately equal. Branching occurs because reaction can occur at any of three sites on each ring. As the reaction continues, the random orientations and branching quickly result in an extremely complex mixture of polymers of different sizes and structures. The reaction stops when the formaldehyde reactant is exhausted, often leaving up to 10\% of un-reacted phenol} \cite{14}.
FIGURE 9: Initial phase of novolacs formation (see text) [14].

FIGURE 10: Chemical reactions involved in the formation of novolacs (see text) [14].

The final phase consists in removing from the molten resin the excess of phenol and water by distillation [14].

Thus the novolac resins, due to the specific conditions of reaction used are essentially chain-linear oligomers whose molecular structure, almost free of crosslinks, is hereafter shown.

It must be considered that the above molecular structure is highly simplified as it take into consideration only the case where the phenolic nuclei are connected by methylene bridges in ortho positions. In the real practice the phenolic nuclei are connected by methylene bridges in both ortho and para positions, and this occurs essentially in a random manner. Thus, according to the conditions of reaction and the length of molecules, a large number of isomeric oligomers are possible [15-a].
The novolacs, due to the lack of formaldehyde, may transform in the final cross-linked structure only if a cross-linking agent is added. For such a reason the novolacs are labeled as "two-stage" or "two-step" products.

Some of the main characteristics of a standard phenol novolac resin are hereafter summarized:
- Number average molecular weight (Mn) between 250 and 900 (Mn of ~500 corresponding to five linked phenol rings);
- Amorphous thermoplastics, solid at room temperature;
- Soften and flow between 65°C - 105°C;
- Soluble in many polar organic solvents (e.g., alcohols, acetone), but not in water.

The novolacs are commercialized in a semi-reacted oligomeric status. When the compounder or molder decides to complete the reaction of polymerization, to obtain a network-based molecular structure, similar to that depicted in figure 11, a curing agent containing formaldehyde must be added to the novolacs. Usually this is accomplished by adding hexamethylenetetramine, HEXA (see molecular structure in figure 12) a substance that when is heated decomposes forming formaldehyde and ammonia. At a relatively high temperature while the ammonia outgases the formaldehyde combines with the unreacted phenol still present in the novolacs. Following such a process novalac undergoes cross-linking and the mass set assuming all properties of a thermostetting solid polymer (infusible, scratch and water resistant).

![Diagram of phenolic resin and Bakelite](image)

**FIGURE 11. left:** Simplified view depicting, in a planar view, the networking-based structure of cured Resoles or Novolacs phenolformaldehyde resins (Bakelite).

**FIGURE 12. right:** Molecular structure of Hexamethylenetetramine (HEXA), see text [13,14].

< Ground and blended with the resin, hexa serves as a convenient source of formaldehyde when heated to molding and curing temperatures. A special attribute of hexa is that it reacts directly with resin and phenol without producing appreciable amounts of free formaldehyde. Hexa cures the resin by further linking and polymerizing the molecules to an infusible state......., the resulting polymer is not a long straight chain but rather a complex three-dimensional polymer network of extreme molecular weight. This tightly cured bonding network of aromatic phenolics accounts for the cured materials’ hardness, and heat and solvent resistant properties > [14].
The reaction between phenol and HEXA, representing the formula of hexamethylenetetramine as \( \text{N}=(\text{CH}_2\text{—N—CH}_2) \), may be described according to the reacting scheme shown in Figure 13:

\[
2\text{C}_6\text{H}_5\text{OH} + \text{N}=(\text{CH}_2\text{—N—CH}_2) \rightarrow \text{HO—C}_6\text{H}_4\text{—OCH}_2\text{—C}_6\text{H}_4\text{—CH}_2\text{NH}_2 + \text{HN—(CH}_2\text{—N—CH}_2) \\
\text{and a second reaction may occur:} \\
2\text{C}_6\text{H}_5\text{OH} + \text{HN—(CH}_2\text{—N—CH}_2) \rightarrow \text{NH}_2\text{—C}_6\text{H}_4\text{—OCH}_2\text{—C}_6\text{H}_4\text{OH} + \text{H}_2\text{N—(CH}_2\text{—N—CH}_2}
\]

**FIGURE 13**: See text.

The reaction keeps on going until all the \( \text{CH}_2 \) groups have combined with phenol. Ammonia is released as a by-product [9].

With the use of suitable pigments, resoles or novolacs powders molding, with various colorations, may be formulated and sold to the molders for shaping coloured artefacts [17].

It has been ascertained from literature that some specific catalysts are capable to tailor the polymerization reaction in novolac process in order to obtain essentially ortho-ortho oligomers (see below figure).

Following such a mechanism the more reactive para positions are preserved. Consequently the novolac resins produced by using these catalysts are characterized by a lower time of curing if compared to the standard casually linked resins [14].

PF resins partially polymerized, and still in a liquid state, have been prepared to be used in casting producing technologies.

The process of casting, referring to figure 14, is described as follows in reference [8]:

> *Thermosetting plastics of phenol type can be used for casting by making use of the liquid state at which polymerization has not gone far enough to build up long thread molecules. As polymerization continues, the material sets in the mould. The temperatures used in the final setting operation are usually lower than those used in compression molding (\( \sim 70-80\text{°C} \))>* [8].

It is interesting to point out that through casting it is possible to shape objects showing better colors than those produced by molding. Such a behavior is accounted for by assuming that pigments, due to the mild processing conditions are less likely to be degraded [8].
The first industrial casting phenol resin was commercialized only after 1923 under the trade name “Leukorit” [12]. These resins found applications in the production of artifacts were decorative, color and appearance were requested [12].

**FIGURE 14**: The casting process used for liquid thermosetting still uncured resins (see text) [8].

PF resins have also the capability to be processed by lamination giving the opportunity to produce laminated materials having superior properties if compared with those simply filled or molded [8]. In the reinforced plastic industry the term “Laminate” < refers mainly to superimposed layers of resin-impregnated or resin-coated fabrics or fibrous reinforcements which have been bonded together, usually by heat and pressure to form a single piece > [16].

Following the representation in figure 15 the various steps of a lamination process involving liquid uncured PF resins are below described.
-- **First step** - A fabric (cotton cloth, asbestos, glass fiber mat, nylon, etc.) is passed through a bath containing an impregnated solution of uncured PF resins. After impregnation the fabric is first dried and then cut into sheets (see figure 15-top).
-- **Second step** - The sheets are stacked between the plates of a press (figure 15-bottom, left).
-- **Third step** - The stacked sheets heated under pressure consolidate into a single panel following the set of the resin [8].

Early gears manufactured by lamination processes are shown in figure 16 [11].
FIGURE 15: The scheme of the lamination process used to manufacture laminates based on thermosetting resins (for details see text) [8].

FIGURE 16: The early gears developed in 1912, by Frank Conrad (Westinghouse) were manufactured by lamination processes based on phenolic resins, *<and a very large market developed therefrom>* [11].
3) **Characteristics and properties of cured phenol formaldehyde resins.**

The highly cross linked structure of cured PF resins is highly responsible of many of their properties (for example: hardness, thermal stability, resistance against chemical attack and solvation, etc.). Some of the most interesting, and applicative properties of PF resins, taking into account also the data reported in tables 2 to 5) are below described.

**High Temperature Performance**
thermoset PF are capable to tolerate, even at relatively high temperatures, mechanical load undergoing only low deformation or creep. Thus they are qualified in providing enough rigidity to keep structural integrity and dimensional stability even under severe thermo-mechanical stresses [14].

**Chemical Resistance**
PF are materials highly resistant to corrosive chemical agents (gasoline, alcohol, oil, glycol, brake fluid, various hydrocarbons, and also weak acids and bases), and this occurs even at elevated temperatures [14].

**Smoke and Toxicity**
Usually PF, following burning, generate smoke with a low level of toxicity. Essentially hydrogen, hydrocarbons, water vapor, and carbon dioxide are produced. Inorganic fillers, often used as reinforcing agents, improve the fire resistance of the cured resins [14].

**Carbon and Char Yield**
PF, at temperatures above their decomposition point, exhibit a relatively higher char yields. *In an inert atmosphere at high temperatures (300 - 1,000°C), phenol resin will convert to a structural carbon known as vitreous carbon. In many ways, this material behaves similar to ceramic and may actually contribute to structural integrity when exposed to fire situations.* [14].

**Capability to act as matrix in composites with various fillers and fibers acting as reinforcing agents.**
PF due to their chemical composition, structure and manufacturing characteristics have been, since the beginning of their development, used as polymer matrix in composite where various types of reinforcing agents may be utilized. As matter of fact such resins show good compatibility and degree of adhesion with several kinds of fibers and fillers. PF-based composites exhibit:

--- Superior strength at elevated temperatures.
--- Better resistance against environmental factors of deterioration.
--- Higher flame resistance.

Such composites, nowadays, may be manufactured by means of different processes as:

- Resin Transfer Molding;
- Pultrusion and Profile Extrusion;
- Filament Winding;
- Hand Lay-up.
FIGURE 17: <These bobin ends were the first molded Bakelite parts. They were produced (in 1907) of a phenolic asbestos combination by Broonton Rubber Company for Weston Electrical Instrument Company > [11].

It is interesting to underline that the first molded PF components were manufactured, for applications in the electrical industry, in 1907, starting from compounds containing as reinforcing agents asbestos or wood floor (see example in figure 17) [11].

4) Historical overview of applications of phenol formaldehyde resins

Especially since the Bakelite patents expired in 1926 many firms were established all around the world producing and commercializing resins with different characteristics and then suitable to be used in many different fields.

PF resins, with different structure, physical state and chemical composition and with various additives, were produced and commercialized tailored to the manufacture and curing process. Thus from application point of view PF resins may be broadly classified in:

--- PF for Molding;
--- PF for Casting;
--- PF for Lamination.

The main characteristics and relevant fields of application of the above PF families are summarized and compared through the data reported in tables 2, 3 and 4 [8].

Many application properties of PF molding compounds may be drastically improved by using various types of additives, fillers and pigments. General-purpose PF molding, generally those obtained through a two step procedure, are multicomponent formulated materials containing as fillers, mica, clay, wood floor, cellulose, mineral fibers and chopped fabric [15-b].

Engineering grade PF molding compounds, used for more sophisticated applications, are usually formulations based on novolacs reinforced with glass or carbon fibers [15-b].

The presence of fillers (table 5), as described in a following chapter, determines the enhancement of several important properties (for example: the resistance to creep under loads at elevated temperatures) [15-a].
**TABLE 2:** Main characteristics of **compression molded**
phenol formaldehyde resins [8].

<table>
<thead>
<tr>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour:</td>
</tr>
<tr>
<td>General Physical</td>
</tr>
<tr>
<td>Properties:</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Water:</td>
</tr>
<tr>
<td>Heat:</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Solvents and chemicals:</td>
</tr>
<tr>
<td>Light:</td>
</tr>
<tr>
<td>Age:</td>
</tr>
<tr>
<td>Electrical:</td>
</tr>
</tbody>
</table>

**TABLE 3:** Main characteristics of **laminated**
and **cast** phenol formaldehyde resins [8].

1. **Laminated Plastics.**
   - Properties generally related to those of moulded plastics.
   - Improved strength and dimensional stability.
   - Improved impact resistance.

2. **Cast Resins.**
   - Colour: Good. Transparent and may be colourless.
   - General Physical Properties:
     - Hard and rigid. (Contd. p. 102.)
   - Good dimensional stability under normal conditions.
   - Tend to be brittle, with low impact strength.
   - Easily machined and polished.
   - Other Properties:
     - Generally similar to those of moulded plastics.
TABLE 4: Some of the most relevant applications of compression moulded, laminated and cast phenol formaldehyde resins [8].

(1) **Moulding Materials.**
A wide range of moulding powders is available, in which the composition of the resin, fillers etc. is varied to provide mouldings suitable for many purposes. Compression and transfer processes commonly used.
Examples of Uses: Electrical equipment; caps; handles; buttons; radio cabinets; furniture; knobs; vacuum cleaners; cameras; ash trays; engine ignition equipment.

(2) **Laminated Material.**
Laminated sheets, rods and tubes are made in great variety from fabric, paper, wood veneers etc. impregnated with phenolic resins, providing a range of materials of widely differing properties.
Examples of Uses: Electrical equipment; building panels; gears and bearings; chemical equipment; airplane parts; clutch and brake linings; jigs and dies.

(3) **Cast Resins.**
Phenolic resins of several types are produced for casting and potting.
Examples of Uses: Imitation jewellery; ornaments; handles and knobs; advertising displays; instrument panels; jigs and dies.

TABLE 5: Fillers commonly used in the formulation of Phenol formaldehyde resins. In table are indicated for each of the filler the corresponding effect expected [8].

<table>
<thead>
<tr>
<th>Filler</th>
<th>Effects on Plastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asbestos</td>
<td>Good resistance to high temperature.</td>
</tr>
<tr>
<td></td>
<td>Good dimensional stability.</td>
</tr>
<tr>
<td></td>
<td>Low expansion.</td>
</tr>
<tr>
<td></td>
<td>Low moisture absorption.</td>
</tr>
<tr>
<td>Barytes</td>
<td>Good resistance to acid.</td>
</tr>
<tr>
<td>Carbon</td>
<td>Good electrical conductivity.</td>
</tr>
<tr>
<td>Cotton fibre or cloth</td>
<td>Good shock resistance.</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>Good surface hardness and resistance to moisture.</td>
</tr>
<tr>
<td>Graphite</td>
<td>Good resistance to friction.</td>
</tr>
<tr>
<td>Mica</td>
<td>Good electrical resistance, dimensional stability and low moisture absorption.</td>
</tr>
<tr>
<td>Paper pulp forms</td>
<td>Good impact resistance.</td>
</tr>
<tr>
<td>Wood flour</td>
<td>General purpose filler.</td>
</tr>
</tbody>
</table>
Phenolic moulding compounds, usually formulated by mixing uncured PF resins (either based on novolacs or resoles) with 50-60% fillers, reinforcements, pigments, and additives, due to their characteristics (for example, high heat resistance, excellent dimensional stability and fire performance, excellent electrical resistance, strength at high temperatures, creep resistance under load, chemical and corrosion resistance, dimensional and thermal stability, and resistance to water and solvents and cost-effectiveness) since the beginning competed with aluminium, steel, other thermoset compounds, and high-heat thermoplastics in many applicable fields (in household appliances, business equipment, wiring devices, automotive electrical systems, etc.) [18].

In the automotive industry moulding compounds based on PF were used for the production of drive pulleys, fuel rails, intake manifolds, and water pump housings, while in the corrosion industry, they were employed for tank liners, scrubbers, ducting, and piping, especially for salt water and hot chlorinated solvents [18].

PF resins were also extensively used in wood industry where they were utilized <as binders in the manufacture of hardboard, plywood, particle board, and oriented strand board> [18]. Decorative laminates, produced by first impregnating Kraft paper with uncured PF resins, followed by curing at high temperature and pressure, have been used in kitchen countertops and vertical panel applications [18].

The development of low viscosity PF made possible to realize fiber-glass-reinforced composites, with high strength-to-weight ratios, by using techniques as hand lay-up, spray-up, filament winding, resin transfer moulding, pultrusion; and press moulding [18].

Advanced composites with PF resin as matrix, also for their outstanding fire performance (flammability, smoke generation, and smoke toxicity), found applications in the transportation sector especially for the manufacturing of <in vehicle panels and seats due to increasing concerns about the safety of both drivers and passengers> [18].

In general the properties of materials based on cured PF plastics widely vary according to the type of process used for their manufacturing. This is documented by the data in table 6 where the values of the heat deflection temperature for several PF-based products are compared [15-a].

<table>
<thead>
<tr>
<th>Type of phenoplast</th>
<th>Heat-distortion temperature, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast</td>
<td>79.0</td>
</tr>
<tr>
<td>Molded, one type</td>
<td>121.0</td>
</tr>
<tr>
<td>Molded, second type</td>
<td>159.0</td>
</tr>
<tr>
<td>Laminate, asbestos-paper</td>
<td>154.3</td>
</tr>
<tr>
<td>Laminate, Kraft paper</td>
<td>193.0</td>
</tr>
<tr>
<td>Laminate, fine cotton-fabric</td>
<td>193.5</td>
</tr>
<tr>
<td>Laminate, Fiberglass-fabric</td>
<td>200.0</td>
</tr>
<tr>
<td>Laminate, for postforming</td>
<td>103.0</td>
</tr>
</tbody>
</table>
A summary of the very large range of possibilities offered by processes basically similar to those developed by Baekeland is given by the flow chart represented in figure 18 where the operations involved in the production of various types of PF-based materials are delineated according to a block diagram where the several pathways leading the initial compounds, resultant from the starting condensation phase, towards the ultimate stage of finished products are described [15-a].

**FIGURE 18:** Flow sheet representing the manufacture of the various types of phenol formaldehyde resins [15-a].
Some of the main operations indicated in the flow sheet of figure 18 are, as in the course of production practice, photographically reproduced in figure 19 [5,15-a].

**FIGURE 19:** Production steps of phenol formaldehyde resins. 
Top left- Installation of the kettle ( digester or reactor ). Top right- Resin discharging to cooling floor. After cooling fragile sheets are obtained and transformed by grinding in pellets or powders ( bottom left ). Bottom right- The uncured compound is shaped in the final artifact by means of a metallic press at about 150°C, and under high pressure [5,15-a].
PF resins have been partly replaced by cheaper and less brittle plastics, but still nowadays they find applications in many sectors, where they compete successfully with other thermoset plastics and with metals and wood. This is confirmed by the increasing worldwide PF demand, by the overall thermoset market share and by the annual growth data as reported in table 7 [19].

**TABLE 7**: Worldwide phenolic resins demand (ktonnes), period 1989-2004. Market share against other thermoset resins is also indicated together with annual growth 89/99 and 99/04 [19].

<table>
<thead>
<tr>
<th></th>
<th>1989 Market share (%)</th>
<th>1999 Market share</th>
<th>2004 Market share</th>
<th>% Annual Growth 89/99</th>
<th>% Annual Growth 99/04</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2849</td>
<td>19</td>
<td>3607</td>
<td>18.4</td>
<td>4270</td>
</tr>
</tbody>
</table>

**FIGURE 20, left**: World consumption of phenolic resins by country (2007) [20].

**FIGURE 21, right**: World consumption of phenol monomer by end use [21].

In reference [20] the present still relevant role of the PF plastics is commented as follows:

"The developed regions (North America, Western Europe and Japan) accounted for 65% of phenol resins consumption in wood adhesive applications. Over 70% of phenol resins for insulation were consumed in the United States and Western Europe. Asia consumed 34% of the phenol resins used for molding compounds and phenol resins used for laminates were consumed primarily in Western Europe and Other Asia (65%). Wood adhesives will continue to
have the largest market share and will drive phenol resin consumption on a global scale. The developing regions of Central and South America, Central and Eastern Europe, and Asia (excluding Japan) will experience the largest growth in this application. Phenol resin consumption for molding compounds will grow primarily in Other Asia as more molding operations operate in the region > [20] (see figure 20).

Another indication of the relevance of PF resins on the present plastic market (see table 8) comes out from figure 21 from which it emerges as in 2008 about 26.5% of the total global consumption of phenol is used for the production of phenol resins [21].

![Table 8: Fields of applications in nowadays market for phenolic resins [15-b].](image)

To document the significant function had by PF plastics, since their early development, in the applications in several sectors, often in substitution of materials such as metals, wood, ceramics and other plastics, some artifacts with particular historical, cultural and also artistic value are heretofore photographically reproduced. The various artifacts are shown according to the different applicative sectors.

1) **TELEPHONY**
Bakelite was, since the beginning of its history, widely used in the field of telephony as demonstrated by the reproductions of two models shown in figure 22 and 23 [22,23].

II) **RADIO AND TELEVISION CABINETS**
The application of PFRs in the manufacturing, by compression-molding, of radio cabinets, in substitution of wood, goes back to 1933 when the Bakelite Corporation started the production of
such items (see the exemplars in figure 24 and 25) [24].

<Thermosetting plastics were suited to radio cabinets because they resisted heat generated by radio tubes. It wasn't long before colorful, modernistic Catalin radios began to make their appearance. The Catalin Corporation made all the radio cases for Fada> [24].

**FIGURE 22, left:** <In 1927 Bell Telephone Company began to produce phones with a cradle handset in black Bakelite. This revolutionized the telecommunications industry by combining the receiver and speaker into one unit> [22].

**FIGURE 23, right:** This telephone model in bakelite was introduced in 1934. A <large numbers remained in use into the 1950s and a few until around 1970> [23]. This Bakelite telephone is now considered as iconic art deco phones in the UK.

**FIGURE 24, left:** <This bright orange radio is a good example of the stylized Streamline Modern design which became so popular during the late 1930s and early 1940s. Helen Golubic collection> [24].

**FIGURE 25, right:** Radio Siemens, with cabinet in black bakelite, 1930 [5].
An advertisement from the *Evening World Publication*, appeared on November 1924, concerning radios with cabinets in bakelite, is reproduced in figure 26 [25]. Cabinets for early televisions were also obtained by compression moulding of PF resins (see figure 27) [5].

**FIGURE 26.** left: advertisement of radios with cabinet in bakelite from the *Evening World Publication*, November 1924 [25].

**FIGURE 27.** right: Early television set with cabinet manufactured in bakelite commercialised by the Bush Company [5].

**FIGURE 28:** Industrial presses used for the manufacture of radio cabinets by moulding of phenoformaldehyde resins [5].
Molding industrial presses once used for the production of radio and television cabinets in PF plastics are shown in figure 28 [5].

It must be pointed out how since 1920 artists and designers actively participate in defining new and elegant forms and colors for the objects made in bakelite. This, combined also with innovative molding procedures, greatly contributed to the success of bakelite in many different application fields.

III ) PHOTOGRAPHY
The first application of PF as laminates in the field of camera for photography occurred on 1915 when George Eastman produced < the Model 1-A Autographic Kodak special, whose bellows extended from a case with two side panel molded from bakelite-impregnated paper > [26] ( see figure 29 ).
Latest exemplaries of folding camera, ≈1929 and 1930, are shown respectively in figure 30 and 31 [27].

![Figure 29 left: Autographic Kodak with end panels manufactured in "Pressed Bakelized Paper" ( laminate, 1915 ) [26].](image1)

![Figure 30, centre: A strut-folding camera with the body made of black/dark-brown bakelite ( RAJAR No 6, APEM Ltd, UK, ≈1929 ) [27].](image2)

![Figure 31 right: A strut-folding camera with the body in brown/marbled Bakelite ( No 2, Hawkette, Kodak, UK, 1930's ) [27].](image3)

IV) COSTUME JEWELRY
PF resins were also widely used for the fabrication of costume jewelry ( i.e. decorative artifacts suitable to be worn on clothes or on the body, such as rings, necklaces, dress clips, brooches, earrings, etc. ).

< The bracelets that attracted collectors of so-called Bakelite jewelry fifty years later were sliced off from cast tubes, machined for ornament, and then polished. Catalin's color range and easy fabrication lent itself to rings, buttons, earrings, and brooches > [26].
In 1936 about < two thirds of all costume jewelry made in the United States was fabricated from cast phenolic resin. Collectors today may wonder why this jewelry commands such high prices. The answer lies in the fabricating process, which was labor-intensive and lengthy > [28].

The procedure for the manufacture of custom jewelry based on cast resins is below described.

1 ) Molds are fabricated by dipping a steel master into molten lead.
2 ) Suitable liquid uncured PF resins, after formulation with colorants or pigments, are carefully poured into the mold cavity by hand.
3 ) Once filled, the molds are wheeled into a oven kept at ≈ 80°C until the resin set ( the curing time depends upon color: dark red and blue, three to four days, while whites takes six to eight days ).
4 ) After curing the cast resin is removed from the lead molds using air hammers [28].

< To make jewelry components, shaped or hollow phenolic rods were cut into individual pieces ( much like a loaf of bread is sliced ) and then carved and machined by hand for added adornment. ( Phenolic resin had the great advantage of being able to withstand heat and friction generated by milling machines, lathes and sanding belts. ) Once the decorative carving was complete, pieces were finished by tumbling or were buffed on a polishing wheel > [28].

As shown by figure 32 on “The Gift & Art Shop Publication” already on 1923 bakelite custom jewelry was advertised.

Examples of custom jewelry in bakelite are shown in the figures 33 and 34 [28,29].

FIGURE 33: (Left)-Carved brooches or pins in bakelite spotlighting various motifs <a popular style during late 1930s. All jewelry courtesy of Helen Golubic collection> [28].
(Right)-Carved and colorful bracelets in bakelite. They were <cast into hollow tubes and then sliced into individual pieces. The blanks were then machined by hand with lathes, drills and sanding wheels. The final products were polished either by tumbling or buffing> [28].

FIGURE 34: (Left)-A painstakingly carved teal-colored Bakelite dress clip, ≈ (1930) [30].
(Right)-Necklace and ring in bakelite (UK-1930) [31].
BAKELITE, DESIGN AND ART

According to reference [26] the great success of Bakelite as plastics of mass production, must be attributed essentially to the synergic combination of three main factors:

1) Economic (related to the possibility of minimize costs of production and to the feasibility of obtain lighter weight objects with dimensional precision and stability).

2) Public Faith in Technological Progress <as a counterforce to economic and social stagnation> [26].

3) Twentieth-century Culture of Modernism, <artists, designers, and visionaries were articulating the meaning of technical and industrial modernity. They not only celebrated plastic among wonders but also showed manufacturers how to use plastic in idealized machine-age design modes> [26].

In agreement with S. Katz [32] with the development of bakelite a bridge between Art and Industry was thrown. As matter of fact the artifacts in bakelite may be considered as the first family of synthetic objects through which was possible to realize a union between the opposite properties of Art and Industry.

The above statement was supported in reference [33] as follows:

< In the 1920s a whole new range of color was introduced and thermosetting plastics took off to invade every area of modern life. Now cast into tubes, rods and sheets it could be made into almost anything. Reds, greens, yellows and oranges appeared in everyone's kitchens and around the home with dinnerware, cooking utensils, clocks, radios and telephones all in bright, vibrant colors. Jewellery, and designer objects made from Bakelite, Casein and Celluloid appeared at the 1925 Paris exhibition from which Art Deco got its name. The motifs of Art Deco design were expressed in the new plastics among the interiors created by the best artists and designers in each country's pavilion >[33].

The Art Déco, whose name was derived as the synthesis of the "Exposition Internationale des Arts Décoratifs et Industriels Modernes, (Paris-1925)" represented a worldwide phenomenon of the aesthetic taste that interested mostly the second and third decade of twentieth century and essentially regarded the decorative arts, the architecture, the fashion, the design and the visual arts [34].

The American Catalin Corporation of New York, established in 1927 was capable to produce and commercialize (years 1930s) PF resins with a wide variety of new colors (see figure 35 and 36). It can be affirmed that up to 70% of so-called bakelite jewelry, is made by Catalin resins and they were especially famous for their Art Deco style. The same can be said for the radio cabinets and many other artifacts, most of them designed by famous artists.

The achievements of Catalin coupled with the implementation of casting processes allowed the birth of the so called "Plastic-Art Industry". In such a contest it was widely recognized that <Bakelite was the major form of "art plastic" from the 1930s through to the 1950s....... The beauty and durability of this magic plastic began to be appreciated with luxury items produced which have survived to this day >[33].

PF resins, together with other thermosetting such as urea and melamine formaldehyde resins (see next chapters)

< became a symbol of progress and modernity by offering new opportunity for designers in products and packaging. By the late 1930s, Streamline design trends were reflected in a myriad of
plastic moldings for personal use. Shiny surfaces, modernistic curves, waterfall fronts and facades that were made to look like car grills all found their way into jewelry, small home appliances and decorative household objects > [35].

Examples of artefacts in Art Deco style manufactured in PF resins are shown also in the figures 37 and 38.

**FIGURE 35:** The development of new plastics and pigments led to the production of plastics having a wide variety of colors. In figure is shown a catalogue (1936) of the Catalin Company presenting “the colored Gem of the modern industry” based on phenolformaldehyde resins [26].

**FIGURE 36:** Bakelite custom jewelry manufactured with coloured Catalin resins [36].
FIGURE 37: Art Deco Jewelry. Right, 1930S bakelite and metal brooch [37].
Left, necklace comprised of Bakelite with decorative, metal bands, and beads that are made of silver and brass tone metals [38].
MODIFIED PHENOLIC RESINS

In order to obtain thermosetting materials with properties, somehow different to those of traditional PF, chemically modified phenol resins have been developed by substituting the phenol with other aromatic hydrocarbons as for example, cresols (see structure below), xylenols, and substituted phenols or/and formaldehyde with paraformaldehyde, and furfural.

Phenol resins with specific properties were also synthesized by condensation reaction between phenols derivatives of diphenylpropane and the colophony, a natural resin extracted from conifers like the pine, spruce and larch. The main component of colophony is the abietic acid whose molecular structure is below described [39].
Other important modified PF resins were based on lignin-resol and lignin-novolac products. *Due to the increase of phenol cost, researchers have been working to partially substitute this monomer by natural polymers that present similar structure in the resin without modification of resin properties. One of these possible substitutes, among other natural compounds, is lignin, a polydisperse natural polymer constituted mainly by propane units, which present a structure close to that of phenolic resin* [40].

Usually in the production of those resins, lignosulfonate derivatives of lignin are used as comonomers. In order to increase their reactivity against phenol and formaldehyde the lignosulfonates are modified by methylation and phenolation. The mechanism of the reactions which lead to the synthesis of lignin-novolac resins where lignin has been substituted by lignosulfonates is depicted in figure 39 [40].

**FIGURE 39:** Chemical mechanism for the synthesis of lignosulfonates-novolac resins [40].
Since the early 1970s Bakelite artifacts became highly collectable and most of them nowadays find place in many important private and public museums as they testify the evolution of the scientific, technical and of uses and customs of people and countries.

Beside the advantages presented by PF resins when compared to other materials nevertheless such a resins presented some peculiar disadvantages [41,42]. For example the opacity of samples obtained from molding powders (only dull colors could be taken), the noticeable smell and relative fragility. These difficulties <were partly overcome by the development, in 1920 of the urea-formaldehyde resins, which were translucent and would take bright pigments> [41].
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22) Published January (2009).
CHAPTER SECOND

SYNTHESIS, PROCESSING AND PROPERTIES OF AMINO-PLASTICS (UREA-FORMALDEHYDE AND MELAMINE-FORMALDEHYDE RESINS)

Urea-formaldehyde and melamine-formaldehyde resins, commonly named amino-plastics, both belong to the family of thermosetting plastics. The advantages of this amino-plastics against the phenol-formaldehyde resins lie in the fact that white or pale colored or almost transparent moldings can be produced from molding powders in which they act as binders. The same light color and translucency can also be obtained in laminated sheets, and the surface lamina can be printed or decorated to produce permanent and weather-proof effects [1].

Thus different from the dark colored phenol resins, the cellulose filled urea plastics were practically colorless.
The main scientific and technological achievements allowing the development and the production of the above amino-plastics are hereafter summarized [1,2,3,4].
1828: Wöhler produced urea (a white crystalline substance readily soluble in water) by synthesis from its inorganic components.
1834: Liebig isolated melamine.
1884: The condensation of urea and formaldehyde was described by Tolens.
1889-1896: Ludy, in 1889 and Goldsmith, in 1896, investigated about the possibility to get resins from urea and formaldehyde.
1908: Mono- and dimethyl urea were isolated by Einhorn and Hamburger.
1918: The first British Patent on urea formaldehyde adhesives was issued to H. John, an Austrian chemist.
1921: Frits Pollak, an Austrian chemist, announced that it was possible by heating urea and formaldehyde in the presence of a base to obtain a colorless liquid capable to set under heating and pressure becoming a hard infusible transparent mass, insoluble in acids and alkalies. Moreover he reported that the molding properties of this urea-formaldehyde resin could be implemented by using as fillers, wood flour. Moreover he claims that the resin was suitable to impregnate wood, paper or fabric.
1923: Pollak and K. Ripper separately patented in USA their procedures to obtain urea-formaldehyde resins.
1921-1923: Other patents on urea resins were issued to the German chemists H. Goldschnitz and O. Teuss.
1925-1926: First a patent was granted to Rossier, who in 1926 introduced the first commercial urea-formaldehyde resin under the trade name of <Beetle resins>.
1929: The American Cyanamid Company started manufacturing Beetle-urea plastics.
1932: Plaskon Company Inc. was established following the interest of the Toledo Scale Company in to producing lightweight, white scale housing.
1933: Carlton Ellis was granted additional patents where improvements concerning process and properties were claimed.
The same year the Toledo Scales Company sponsored a project, named Plaskon, at the Mellon Institute finalized at the development of urea molding compounds.
Palmer Griffith (Cyanamide Company) while producing dicyanamide observed the presence as by-product of melamine that treated with formaldehyde formed a resin like material. This resin compounded with paper pulp was transformed in moldable thermosetting mass.
1935-36: Patents concerning the synthesis and process of melamine formaldehyde plastics were granted to Henkel and Co. Melamine-formaldehyde resins were introduced into the market.

1937: American Cyanamid initiated full-scale production of cellulose-filled melamine-formaldehyde molding compounds. These colorless resins were commercialized under the trade names of Cymel and Resimene.

1941: A. Gans and G. Widmer refined the procedures to obtain the just-above mentioned materials.

**FIGURE 1:** Left- Different colored urea formaldehyde molding powder compounds nowadays on the market [5].

**FIGURE 2:** Right- Salt and pepper shakers, biscuit cutter, toy car, and west-clock travel alarm all made by molding urea formaldehyde powder compounds [3].

**FIGURE 3:** Left- < Radio cabinet molded of Plaskon urea formaldehyde. Designed by Harold Van Doren and John Gordon Rideout for the Air King Products Company, 1933 > [3].

**FIGURA 4:** Right- Dinnerware obtained by molding, with built-in decoration, melamine formaldehyde compounds [4].
In reference [4] the innovative properties of urea-formaldehyde and melamine-formaldehyde plastics (henceforth, UF and MF respectively) against phenol-formaldehyde are described as follows:

< Whereas the phenolics offered only a limited range of dark colors, the amino plastics brought in all the brilliant colors of the spectrum > [4] (see figure 1).

In a 1927 issue of the Plastics & Molded Products Magazine some of the properties the Beetle urea formaldehyde molding compounds were pointed out as follows:

< Noting that Beetle contained no coal-tar chemicals, ...colorless in its pure state, light-fast, nonflammable, capable of being boiled and immersed in cold water without crazing or cracking-perfect, in other words, for cups, saucers, plates, and flatware handles. Above all, its "many beautiful translucent shades" offered the possibility of reproducing artistic shapes in delicate shades and colors > [3].

Early applications of UF and MF in the production of tableware, toys, alarm clocks and finely designed radio cabinets obtained by molding of powders are shown in figure 2, 3 and 4 [1,3,4]. The basic manufacturing process of UF and MF molding compounds, in the form of powders or granules is depicted in figure 5 [4].

**FIGURE 5:** The various steps of the manufacturing process leading to urea/melamine formaldehyde molding compounds [4].
The process may be schematized as follows:

1) The urea or melamine are added to a water solution of formaldehyde (45-50%) in a steel autoclave where they are allowed to react, at a relatively high temperature, with formation of a resin that is syrup in consistency.

2) The so obtained syrup is first concentrated till it contains 50-60% of resin and then is mixed with cellulose (wood meal or paper pulp) in a suitable mixer (see figure 5). It must be pointed out that in order to manufacture white or translucent artifacts the filler must be very pure.

3) The syrup containing a cellulose based filler is transformed first in a slightly wet mass that is broken into small pieces and then dried to form a molding powder.

4) In the final phase the resin powder is conveniently mixed with pigments and dyes and other additives and then transformed in granular or powder compounds for shipment to molders [1,6].

It must be underlined that, as in all thermosetting plastics, the soluble or formable precursor used for the manufacture of the final products by molding, <must be sufficiently stable to ship and handle and yet it must be sufficiently reactive to go to the final stage in a short time without the use of severe conditions of cure> [8]. In order to fulfill such objective the moldable compound is stabilized by suitably controlling the pH value <so that it will produce a powder, which keeps well in store without polymerizing> [1].

Thus acid substances, capable to act as catalysts, are added to the precursor compounds for the reaction of setting that will occur on heating under pressure, in the mold where the artifacts will be shaped.

Typical old apparatus and equipments used for the preparation of UF and MF powder compounds are reproduced in figure 6 [7].

**FIGURE 6: Left-** Autoclave once used for the preparation of the urea/melamine formaldehyde syrup. **Center-** Mixer for the preparation of compounds containing cellulose-based filler. **Right-** Typical dryer tower for urea/melamine formaldehyde resins [7].
THE CHEMISTRY OF THE PROCESS THAT LEADS TO THE UREA/MELAMINE FORMALDEHYDE UNCURED RESINS

The two important families of amino-plastics are obtained by a step-condensation reaction between formaldehyde with urea (a white crystalline substance readily soluble in water) or melamine (a solid crystalline trimer of cyanamide). As results from their chemical structure, below depicted, urea and melamine are a di-functional and a tri-functional amine respectively.

Urea-Formaldehyde Resins

The chemistry of the overall process that leads to the formation first of uncured moldable UF precursor and successively to the set of UF material is hereafter discussed. It is well known that the synthesis of urea-formaldehyde resin takes place in two stages. The trend of the reactions involved, as well as the nature of products obtained, is essentially determined by the following factors:

The concentration of hydrogen ions;
The relative amount of reagents;
The temperature.

In the first stage of the reaction between urea and formaldehyde, and under acidic conditions, a bisamidine and methylol derivatives (see molecular structures below) are formed [9].

\[
\text{Bisamidine} \\
\text{N}_2\text{H}_2\text{O-CH}_2\text{N-CH}_2\text{N-CH}_2\text{N-CH}_2\text{NH-CO-NH}_2 \\
\text{methylol derivatives} \\
\text{N}_2\text{H}_2\text{O-CH}_2\text{N-CH}_2\text{N-CH}_2\text{NH-CO-NH}_2 \\
\text{CH}_2\text{OH}
\]
In agreement with what above reported, Chiavarini, Bigatto and Conti by means of NMR spectroscopy, combined with chemical analyses, demonstrated that

<In the first step of the condensation (at 95°C and mildly acid reaction), the reaction takes place quickly with the formation of methylene linkages (\(=N—CH_2—N=\)) and, to a minor extent, of methylol groups (\(=N—CH_2OH\)) > [10].

When the first stage reaction occurs under neutral or alkaline conditions, depending upon the ratio of reactants, mono-(ratio aldehyde/urea = 1/1) or dimethylolurea (ratio aldehyde/urea = 2/1) are formed (see scheme below) [9].

The second stage of UF synthesis lies in the condensation of the methylolureas to low molecular weight oligomers. In the normal industrial practice those reactions are activated by heating and by acid catalysts [11,12,13,14].

In reference [11] the mechanism are described as follows.

<The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of:
- methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules;
- methylene ether linkages by the reaction of two methylol groups;
- methylene linkages from methylene ether linkages by the splitting out of formaldehyde;
- methylene linkages by the reaction of methylol groups splitting out water and formaldehyde in the process > [11].
Some of the possible condensation reactions leading, at the end, to a cross-linked polymer network are shown in figure 7 [12,13].

\[
\begin{align*}
\text{HN-CH}_2\text{OH} & \quad \text{N=CH}_2 \\
\text{O} & \quad \text{O} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{OH} & \quad \text{OH} \\
\text{N-CH}_2\text{OH} + \text{H}_2\text{O} & \rightarrow \\
\text{N-CH}_2\text{N} + \text{HCHO} + \text{H}_2\text{O} \\
\text{N-CH}_2\text{OH} + \text{H}_2\text{O} & \rightarrow \\
\text{N-CH}_2\text{N} + \text{HCHO} + \text{H}_2\text{O}
\end{align*}
\]

**FIGURE 7:** Possible condensation reactions leading to the cross-linked urea formaldehyde resins [12,13].

The details of a typical industrial method of UF resins production is described as follows in reference [9].

A common used manufacturing procedure is to allow urea and formaldehyde in a ratio of 1/1.3 to 1/1.8 to react at RT in the presence of a weakly alkaline catalyst such as ammonia, calcium hydroxide or dilute sodium hydroxide solution to form water-soluble mono- and dimethylureas. The solution is then boiled and partially dehydrated under vacuum to yield viscous syrup. To this, fillers (usually paper pulp or wood flour) and pigments are added and the resulting product dried to a fine powder.

The powder is mixed with an acid catalyst such as dimethyl oxalate, an amine hydrochloride or a salt of ethyl hydrogen sulphate, and under molding conditions of temperature and pressure, the acid liberated from this additives induces the requisite cross-linking [9].

The final process of curing of the UF resins molding powders is, as a rule, performed at a temperature of ~140-160 °C and a pH < 5, while the pressure is in the range of 200-350 Kg/cm², and the setting time is around 2mins for a thickness of the artifact walls of ~ 2.5mm [7].

The reactions happening in the course of this phase, leading to a cross-linked polymeric network (see figure 8) are similar to those occurring during the acid condensation of the methylureas [11,15].

The uncuried liquid syrup works also as strong-bonding glue for plywood. During the Second World War this type of plywood, due to its high moisture resistance, was used for making aircrafts. Successively they found applications for the manufacture of boats, furniture and wall paneling [6].
It is important to point out that the molding characteristics of the uncured UF resins, as well as the properties of the post-hardened materials depend upon the choice of fillers, lubricants, pigments and dyes. Moreover it must be also underlined as the curing rate may influence the final behavior of the set resins.

Hereafter the main agents used as fillers, lubricants, catalysts and colorants are briefly described especially concerning the case of UF molding powders.

1) **Fillers**

As previously written cellulose fibers in the form of wood flour or paper pulp are usually used. It must be remembered that in some cases also asbestos fibers were used; of course this filler was employed before its harmfulness was established. Pulp obtained from highly bleached wood or cotton represents the highest grade and are appropriate to produce translucent products [1,7].

2) **Lubricants**

Neutral substances (zinc or magnesium stearate) are used.

3) **Catalysts or accelerators**

The role of catalysts relies on the fact that, as widely proved, the set conditions are highly favored by the presence in the molding mass of substances able to produce acid conditions. A dry acid like oxalic acid, ground into the powder, would be safe so long as the powder did not become moist and begin to harden before entering the mold > [1].

From above it is possible to generalize that the most appropriate catalyst < is one which does not produce acid conditions until the powder is hot and in the mold, and a number of such salts and esters are recorded in the patent literature > [1].

4) **Colorants**

Mineral pigments or lake colorants were used. In the case of UF resins, contrary to the case of phenol-formaldehyde resins, essentially light and translucent and transparent colors are demanded. Moreover it must be pointed out that the process of coloration for UF resins occurs in the dry state.

![Figure 8](image.png)

**FIGURE 8:** Network-like molecular structure of post-cured urea formaldehyde thermosetting plastics (planar view) [15].

Most of the main characteristics of UF resins, together with their applications as syrup, molding powders and as laminated are outlined in table 1 [6].
TABLE 1: Data panel concerning urea formaldehyde thermosetting plastics [6].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>UREA-FORMALDEHYDE PLASTICS DATA PANEL</th>
<th>Applications</th>
<th>Electrical</th>
<th>Good insulation, with resistance to wearing. Electrical properties do not deteriorate appreciably when moisture is absorbed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour: Good</td>
<td></td>
<td></td>
<td></td>
<td>A range of materials is produced for many purposes.</td>
</tr>
<tr>
<td>General Physical Properties:</td>
<td>Vary greatly depending on fillers, laminating materials, etc.</td>
<td>(1) Beads and Amathet</td>
<td>Examples of Uses: Foundry core production; surface coatings; finishes for textiles, paper, etc.; adhesives; lamination.</td>
<td></td>
</tr>
<tr>
<td>Hard and rigid. Scratch resistant.</td>
<td></td>
<td></td>
<td></td>
<td>(2) Moulding Materials. A wide range of moulding powders is produced, in all shades including white; translucent or opaque. Used for compression and transfer moulding.</td>
</tr>
<tr>
<td>Strong and tough if appropriate filler used. Slight shrinkage may follow moulding.</td>
<td></td>
<td></td>
<td></td>
<td>Examples of Uses: Electrical equipment, e.g. plugs, switches, etc.; buttons; buckles; cosmetic jars; bottle tops; knobs and handles; cups, saucers and plates; toys; clocks; radio cabinets; lighting fittings; kitchen equipment.</td>
</tr>
<tr>
<td>Heavier than water (S.C. 1.4 – 1.6).</td>
<td></td>
<td></td>
<td></td>
<td>(3) Laminated Materials. Sheets and panels are made in a great variety of colours and patterns from urea-formaldehyde resins and fabric, paper, wood veneers, etc.</td>
</tr>
<tr>
<td>Water: Absorption takes place, with loss of dimensional stability and increase in brittleness.</td>
<td></td>
<td></td>
<td></td>
<td>Examples of Uses: Lighting fittings; building panels; signs.</td>
</tr>
<tr>
<td>Heat: Thermosetting, and do not soften. Good stability to moderate temperatures, and perform satisfactorily over range 70° F. to 170° F.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Densify and decompose at higher temperatures. Burn with difficulty. Solvents and chemicals: Good resistance to most solvents and common chemicals. Unaffected by detergents, cleaning fluids (e.g., carbon tetrachloride), gasoline (petrol), nail polish and removers, alcohol, oil, greases.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light: No effect. Age: Slight deterioration.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 2: Urea formaldehyde and phenol formaldehyde resins competed in the production of telephones.
The two samples shown were <Designed in Sweden in 1947, attributed to Gerard Kiljan. These specimens were made in Brazil in the 1960s. The cream one (left) is made of Plaskon (Urea Formaldehyde) and the black (right) is Bakelite (Phenol Formaldehyde), two of the noblest plastics> [16].
From the data panel of table 1 it emerges as UF resins, as thermosetting materials, were used, since the beginning of their introduction on the market, in applications demanding resistance to heat and mechanical stresses, and hardness. Moreover, they were valued also for giving the opportunity to produce artifacts made in a wide range of the most attractive and brilliant colors. Inevitably, the UF plastics have found important outlets in the tableware and crockery trade. They are made into all sorts of decorative and ornamental articles for home > [6] (see figure 4).

UF resins, as shown by figures 9 and 10, competed with phenol-formaldehyde resins in the production of telephones and radio cabinets [16,17].

![Figure 10: Left-This radio was made in Brazil but similar designs were made in USA too, probably in the 40s. Made of Plaskon (urea formaldehyde) plastics >[17]. Right- sandwich box processed in ureic resin “Bandalasta” developed in England in the late 1920s. <This box was part of a fantastic pic-nic set made by Brookes & Adams, England (1930) >[18].](image)

**Thiourea-Formaldehyde Resins**

Thiourea-Formaldehyde Resins (TUF) are obtained by substituting in the process of condensation with formaldehyde urea with thiourea (thiocarbamide [SC(NH₂)₂], a colorless crystalline substance soluble in water and melting at 172°C) [1]. The chemical mechanisms occurring during the preparation of TUF resins are essentially similar to those of UF resins.

The TUF resins, developed by Rossiter (British Cyanides Co. Ltd.), present, in comparison with UF, the hereafter listed characteristics.

1. A more high stability.
2. The molding powders show a higher clearness and elasticity.
3. A lower rate of curing (high curing time).
4. Possibility to avoid the use of external catalyst. As matter of fact by heating the uncured TUF resin may develop sulfocyanic acid able to act as internal catalyst for the curing reaction.
5. Possibility to be used without fillers [7].
In practice, due also to the higher cost of TUF resins, suitable mixtures of urea and thiourea are used. According to reference [1] this procedure allows the production of better quality artifacts.

**Melamine Formaldehyde Resins**

Thermosetting melamine formaldehyde resin (MF) were developed, before World War II, making profit of the capability of melamine, a tri-functional amine whose molecular structure was above described, to react with formaldehyde, under neutral or alkaline conditions, forming methylol amines (analogous to methylolureas) together with low molecular weight substances having in their molecules reactive functional methyol groups (-CH₂OH). The mixture so obtained in this first stage is in the state of syrup similar in consistency to that obtained in the first stage of UF resin production. The heating of this syrup under acidic conditions produces further condensation and polymerization and at longer times, following the formation of cross-links, the mass set assuming a tri-dimensional network structure typical of thermosetting post-cured resins. This liquid syrup, following addition of an acidic catalyst and accelerator, can be used, as it is for impregnation in the fields of surface coating, textile and paper finishing as well as in lamination. Solid MF molding powders or granules, as for UF, are prepared first by direct mixing of the syrup with fillers (especially paper pulp), colorants and other additives followed by drying and pulverizing processes. The various chemical steps in MF resin production are schematically described in figure 11.

![Chemical reactions occurring during the production of melamine formaldehyde resins. Bottom: planar structure of the post cured resin based on a tridimensional network (see text).](image)
Most of the main characteristics of MF resins, together with their applications as syrup, molding powders and as laminates are outlined in table 2 [6].

**TABLE 2:**
Data panel of Melamine Formaldehyde thermosetting plastics [6]

*Characteristics.*

<table>
<thead>
<tr>
<th>Properties</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Are generally similar to those of urea-formaldehyde plastics, with improved resistance to heat (up to 220° F, continuous operating temperature). Water absorption is lower, and there is less tendency to shrinkage after molding. Melamine-formaldehyde plastics are usually harder than urea-formaldehyde plastics. Their physical properties are excellent, with even greater arc-resistance than the UF plastics.</td>
<td></td>
</tr>
</tbody>
</table>

*Applications.*

1. **Resins and Syrups.**
   - A range of resins and syrups is produced. Applications are similar to those of urea-formaldehyde resins.
   - Examples of Uses: Surface coating, textile and paper finishes, lamination.

2. **Molding Materials.**
   - A wide range of melamine-formaldehyde molding powders is produced, with fillers of all types, providing a variety of properties. They are used primarily for compression and transfer molding.
   - Examples of Uses: Electrical equipment, tableware, handles, tools.

3. **Laminated Materials.**
   - Laminates are produced from fabrics, paper, wood veneers, etc., bonded with melamine-formaldehyde resins, in a manner similar to urea-formaldehyde laminates.
   - Examples of Uses: Electrical equipment, building panels.

In reference [6] and [19] the properties exhibited by MF resins were compared with those of UF, TUF and PF. The resulting advantages are hereafter summarized.

< 1 ) Melamine's heat resistance was superior to that of phenolics and much better than that of ureas.

II ) Melamine could be produced in light colors as varnish or as molding material or as a translucent overlay for decorative laminates.

III ) Melamine resin had amazing abrasion resistance and could be used easily in place of TUF. Its moisture resistance was superior to that of TUF > [19].

< MF plastics after setting are harder, more heat resisting and less affected by water than UFs. And they possess excellent electrical properties > [6].

Due the above performances MF resins were applied in several sectors as can be deduced also by the data in table 2. Some significant examples of MF applications are evidenced through the reproductions reported in the figures 12 and 13 [7,19,20,21,22].
MF due to their peculiar mechanical properties (hardness and impact resistance) were widely used to make non-breakable plastic crockery i.e., cups and plates. Some of them were characterized by elegant design and very fine colorations (see figure 13) [21,22]. Moreover it must be pointed out as MF resins show lower water absorption and enhanced resistance to heat and chemicals in comparison to UF plastics. 

*The later properties have led to their use in domestic laminates on furniture and counter surfaces>* [9].

![Image of early applications of Melamine formaldehyde resins.](image)

**FIGURE 12:** Early applications of Melamine formaldehyde resins.
*Top-left:* Distributor housing for aircraft (highly arc resistant, used during the World War II) manufactured in MF with mineral fillers [19].
*Top-right:* Pick-up for record player in melamine formaldehyde resin ≈ 1950s [7].
*Bottom-left:* Hair dryer in melamine resin ≈ 1950s [7].
FIGURE 13: Right: Pale green divided bowls, creamers and cups with various colors, manufactured in melamine formaldehyde plastics (designed for Boonton by Belle Kogan in the 1950's) [21]. Left: Melamine tan and gold dogwood and wheat bread or dessert vintage plates [22].

TABLE 3: Properties of thermosetting formaldehyde based resins [13].

<table>
<thead>
<tr>
<th>Property</th>
<th>Melamine-Formaldehyde α-cellulose</th>
<th>Phenol-Formaldehyde Wood or Cotton</th>
<th>Urea-Formaldehyde α-cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, g/cm³</td>
<td>1.47-1.52</td>
<td>1.25-1.30</td>
<td>1.34-1.45</td>
</tr>
<tr>
<td>Refractive index n²</td>
<td>—</td>
<td>—</td>
<td>1.54-1.56</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>7000-13,000</td>
<td>7000-8000</td>
<td>5000-9000</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>0.6-0.9</td>
<td>1.0-1.5</td>
<td>0.4-0.8</td>
</tr>
<tr>
<td>Tensile modulus, 10⁶ psi</td>
<td>12-14</td>
<td>7.5-10</td>
<td>8-17</td>
</tr>
<tr>
<td>Impact strength, ft-lb/in. of notch</td>
<td>0.24-0.35</td>
<td>0.20-0.36</td>
<td>0.24-0.60</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>350-370</td>
<td>240-260</td>
<td>260-340</td>
</tr>
<tr>
<td>Dielectric loss, 1000 cycles</td>
<td>7.8-9.2</td>
<td>4.5-6.0</td>
<td>4.4-9.0</td>
</tr>
<tr>
<td>Water absorption, 1 in. bar, 24 hr, %</td>
<td>0.015-0.036</td>
<td>0.03-0.08</td>
<td>0.04-0.20</td>
</tr>
<tr>
<td>Burning rate</td>
<td>None</td>
<td>Very slow</td>
<td>Very slow</td>
</tr>
<tr>
<td>Effect of sunlight</td>
<td>Slight</td>
<td>Darkens</td>
<td>Darkens</td>
</tr>
<tr>
<td>Effect of strong acids or bases</td>
<td>Attacked</td>
<td>Attacked</td>
<td>Attacked</td>
</tr>
<tr>
<td>Effect of organic solvents</td>
<td>Resistant</td>
<td>Resistant</td>
<td>Resistant</td>
</tr>
<tr>
<td>Clarity</td>
<td>Opaque</td>
<td>Transparent</td>
<td>Opaque</td>
</tr>
</tbody>
</table>

Some of the most relevant characteristics and properties of PF, UF, and MF resins are compared in table 3 [13].

60
REMARKS CONCERNING PRODUCTION, PROPERTIES AND APPLICATIONS OF UREA/MELAMINE FORMALDEHYDE PLASTICS IN PRESENT DAYS

UF and MF resins, as molding compounds, are still nowadays produced and widely used in many sectors. Usually, they contain as filler chemically purified cellulose fibers as well as other type of additives tailored to impart <strength and moldability, improve dimensional stability, and reduce molded-in stresses. Clarity and absence of yellow color permit the manufacture of molding compounds colors ranging from light to dark, from pastel to high chromatic, and from translucent to opaque > [23] (see figure 13 and 14).

**FIGURE 14:** Melamine formaldehyde plastics are used for the production of tableware (also known as imitation ceramic in China) with a large variety of colors [24].

The modern chemical industry is capable to supply UF and MF molding compounds characterized by a wide range of flow, stiffness, color and rate (time) of cure [23].

The processing conditions used for UF and MF are:

- **Molding temperature:** 127-171°C for UF and as high as 182°C for MF resins.
- **Compression molding pressure:** from 2000 to 8000 p.s.i. [23].

Some of the present days applications of UF and MF, cellulose filled, molding compounds are here after listed.

--- Wiring devices (circuit breakers, wall plates, receptacles);
--- Closures;
--- Electric blanket control housing;
--- Buttons, toilet seats, housing, knobs and handles [23].
Water soluble UF and MF resins find applications as adhesives and bonding agents for wood particle board, plywood, boat hull and furniture [23]. According to reference [25] UF and MF modern thermoset molding compounds < offer many advantages over basic thermoplastics, and are suitable for compression, transfer or injection molding. Applications include dinnerware, ashtrays, caps and closures for the cosmetics industry, precision medical components, electrical wall plates and switches, buttons, and much more... offer a wide range of applications for every-day living and industry > [25].

The main characteristics of the modern UF resin compounds are in reference [25] summarized as follows:
--- Economically priced;
--- Strong, glossy, and durable;
--- Not affected by fats, oils esters, ether, petrol, alcohol or acetone, nor by detergents or weak acids, and they exhibit good resistance to weak alkalis.

Moreover it must be pointed out that due to < their high mechanical strength, heat and fire resistance, and good electrical arc and tracking resistance make them an ideal plastic for numerous industrial and household applications, from doorknobs and toilet seats to electrical components and cosmetics enclosures > [25].

Concerning MF thermoset plastics it must be underlined as they have, in comparison with UF, even better resistance to heat, chemicals, moisture, electricity and scratching. Thus MF thermosts are < ideal for dinnerware, kitchen utensils, bathroom accessories, and electrical components. The molded compounds are bright, inviting, and highly resistant to scratches and staining. MF thermosts are approved for contact with foodstuffs, and they do not affect the food's flavor - even at high temperatures. They are very, very durable > [25].

Nowadays it is possible to find on the market MF thermosts with the following main characteristics:
--- High surface hardness and gloss;
--- Brilliant and precise colors, and light fastness;
--- High resistant to solvents and household chemicals [25,26,27].

By using suitable additives and plasticizers in the preparation of UF molding powders it has been possible to prepare compounds with improved stability, storage life and temperature tolerance which find application in the below listed sectors [27]:

1. Spares of electrical, balls, and closes tool cover. Appliance spares: Switch, fittings, sockets, cases.
2. Machinery spares: Knob, handle, spinning machine components, instrument shell, clock shells.
3. Ornaments: Imitation pearls, buttons and pins.
4. Vessel: Various kinds of commercial used bottles, boxes and covers.
5. Others: Toys, mahjong cards, chess, ashtrays.

The excellent moldability of UF and MF thermosts gives to designers and molders great opportunities < to express marketing concepts through fashion, color and shape, Always adapting to customers' needs> [25].
Thus it can be concluded that with modern chemical technologies it is possible to tailor the properties of UF and MF thermosets for specific and demanded applications. The above goals are practically fulfilled essentially because by changing some of the synthesis parameters of UF and MF resins it is possible to realize products with a wide range of properties (gel time, tack and spreadibility, formaldehyde emissions and durability of the cured resin). Thus by controlling the synthesis and processing conditions UF and MF resins specifically tailored for the final end use may be designed [26].
REFERENCES

CHAPTER-THIRD

METHODOLOGIES FOR THE MOLECULAR, STRUCTURAL AND PHYSICAL CHARACTERIZATION OF PHENOL (UREA/MELAMINE)-FORMALDEHYDE PLASTICS AS TOOLS FOR ASSESSING DEGRADATION

As shown in previous chapters, due to their peculiar properties, Bakelite and Urea/Melamine-Formaldehyde plastics were extensively used in the past in numerous applications, and in several industrial fields (for example, terminal boards, switches, bearings, gears, wear strips, gaskets, washers, transformers and electrical insulators, machining components, industrial laminates, radio and telephone casings, etc.) [1]. Moreover, they were also widely used for the manufacturing of products as kitchenware, consumer jewels, pipe stems, and children's toys [2].

Nowadays Bakelite, because of the cost, production difficulty and its fragility is not any longer widely used for general consumer products. Nevertheless, even today, Bakelite, by virtue of its superior heat resistance, durability and other excellent features, finds still many industrial applications in the electronics, power generation, and aerospace industries as well as in small, precision-shaped components where their specific properties are required, such as molded disc brake cylinders, saucepan handles, electrical plugs and switches, and electrical iron parts [1] (old and recent applications of Bakelite are shown in figure 1 and 2 respectively).

FIGURE 1, left: A great multi-colored Art Deco barometer partly in Bakelite (Pre-1950), an example of old application [3-a].
FIGURE 2, right: Bakelite distributor rotor in Bakelite an example of today application [2].
Formaldehyde-based resins such as urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF), and phenol formaldehyde resins (PF) still constitute the greatest majority of the adhesives used industrially today for thermosetting wood bonding [3-b].

It is well established that many kinds of artifacts in Phenol-formaldehyde (PF), especially those produced with cast phenol resins in the Art Deco style, see examples in figure 1 and 3, and in Urea/Melamine-Formaldehyde (U/M F) plastics are since few decades greatly appreciated by collectors, and are part of many collections in private and public museums [4,5].

**FIGURE 3.** left: Smiths Art Deco Bakelite Mantle Clock [4].  
**FIGURE 4.** right: Addison radio (1940) in Bakelite [5].

The preservation of those items from environmental aging deserves today a great attention. For a better understanding of the degradation behavior of objects made of Phenol-formaldehyde (PF) and Urea/Melamine-Formaldehyde (U/M F) plastics and of the best practice for their protection against the factors of deterioration it seems necessary to review the main diagnostic techniques suitable, not only for the chemical and physical characterization of the components used in the manufacturing, but also for the identification of the nature the materials used.

### A) MECHANICAL PROPERTIES OF MOULDED PHENOL-FORMALDEHYDE (PF) PLASTICS

Interesting information concerning the physical behaviour of PF and U/M F plastics, may be obtained from tensile mechanical behaviour. As can be seen by the generalized stress strain diagram reported in figure 5 (<established by continuously measuring the force developed as the sample is elongated at constant rate of extension until it breaks>; [7]), the following useful quantities may be obtained:

--- Modulus of elasticity (provided from the initial slope: is a measure of the stiffness);
--- Yield Stress (<the stress at the knee in the curve (known as the yield point) is a measure of the strength of the material and of its resistance to permanent deformation>; [7]);
--- Elongation at Yield;
--- Elongation at Break;
--- Ultimate Tensile Strength ( < the stress at the breaking point, ...is a measure of the force required to fracture the material completely > [7]);
--- Work to Break ( provided by the area under the curve; gives a rough indication of the toughness ) [6,7].

FIGURE 5: Generalized tensile stress strain diagrams for polymeric materials. The quantities obtainable from the curves are indicated [6].

The shape of the stress strain curves, in the case of polymer material, strongly depends upon its chemical, physical and structural characteristics at the temperature at which the test is performed.
As shown by figure 6 from the shape of the stress strain curve it is possible do differentiate polymers behaving as soft and tough material ( i.e. cellulose acetate at RT ) from those with hard and brittle characteristics ( for example moulded phenoplastics ).
Stress-strain diagrams in between this two extreme behaviours are presented by other families of polymers with intermediate mechanical properties ( see figure 6 ) [7].

An amorphous polymer at RT, far below its Tg ( see the case of atactic polystyrene ( Tg = 75-100°C ) and polymethylmetacyrlate ( Tg= 72°C ) ) behaves as an hard brittle material. Thus its stress-strain diagram presents an early slope symptomatic of a very high modulus, moderate strength, a low value of the elongation at break and a small area under the curve [7].
< Typical values of modulus and tensile strength are 500,000 and 10,000 psi, respectively; typical elongation is about 2 per cent. Generally, such materials exhibit elastic deformation up to the point of fracture, which is a brittle fracture > [7].

Phenol-Formaldehyde and Urea ( Melamine ) resins, as already reported, are at RT relatively stiff.
and non-ductile thus their stress-strain diagrams are similar to those of hard and brittle polymers as shown in figure 6 [6,7].

![Chart](chart.png)

**FIGURE 6:** Tensile stress-strain curves for different types of polymer materials [7].

The influence of the type of filler on the tensile mechanical behavior of PF molded resins can be followed by observing the corresponding stress-strain diagrams obtained by mechanical tensile experiments. As can be seen by the trend of the curves shown in figure 7 molded PF-based compounds exhibit a behavior typical of stiff and no ductile materials. The values of the modulus of elasticity, derived from those diagrams, are reported for each of the composites in table 1. It can be seen that the nature of filler strongly influences the mechanical behavior (mica and asbestos based compounds present best values of the elasticity modulus). Nevertheless it must be underlined that the elongation at break results to be lowered in the case of composites [6].

**TABLE 1:** Modulus of elasticity of molded phenolformaldehyde resins as function of the nature of filler used [6].

<table>
<thead>
<tr>
<th>Type of filler</th>
<th>Modulus, p.s.i.</th>
</tr>
</thead>
<tbody>
<tr>
<td>No filler</td>
<td>$8.9 \times 10^6$</td>
</tr>
<tr>
<td>Wood flour</td>
<td>$14.6 \times 10^6$</td>
</tr>
<tr>
<td>Chopped tire cord</td>
<td>$12.0 \times 10^6$</td>
</tr>
<tr>
<td>Asbestos</td>
<td>$24.3 \times 10^6$</td>
</tr>
<tr>
<td>Mica</td>
<td>$28.0 \times 10^6$</td>
</tr>
</tbody>
</table>
FIGURE 7: Tensile Stress-Strain diagrams for unfilled molded phenolformaldehyde resins and for compounds with several types of reinforcing agents [6].

Some of the most interesting physical and mechanical properties of moulded PF resins formulated for different applications are summarized in Table 2 [8].

**TABLE 2:** Physical and mechanical properties of Phenoplastics for different applications are reported [8].

<table>
<thead>
<tr>
<th>Property</th>
<th>General purpose</th>
<th>Impact</th>
<th>Non bleeding</th>
<th>Electrical</th>
<th>Heat resistant</th>
<th>Glass reinforced</th>
<th>Chemical resistant compound</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PHYSICAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.35-1.46</td>
<td>1.36-1.41</td>
<td>1.37-1.38</td>
<td>1.36-1.75</td>
<td>1.41-1.84</td>
<td>1.7-2.0</td>
<td>1.17-1.75</td>
</tr>
<tr>
<td>Water absorption, 24 hours, 1/8 inch thick (%)</td>
<td>0.6-0.7</td>
<td>0.6-0.9</td>
<td>0.8-0.9</td>
<td>0.05-0.20</td>
<td>0.30-0.35</td>
<td>0.05-0.2</td>
<td>0.20-0.40</td>
</tr>
<tr>
<td><strong>MECHANICAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength (psi)</td>
<td>6,500-7,000</td>
<td>6,000-7,000</td>
<td>6,000-7,000</td>
<td>5,000-7,000</td>
<td>5,000-6,000</td>
<td>6,000-12,000</td>
<td>7,000-9,000</td>
</tr>
<tr>
<td>Flexural modulus (10-5 psi)</td>
<td>11-13</td>
<td>12</td>
<td>10</td>
<td>17-25</td>
<td>14</td>
<td>20-30</td>
<td>10</td>
</tr>
<tr>
<td>Flexural strength (psi)</td>
<td>9,000-11,000</td>
<td>10,000</td>
<td>10,000</td>
<td>9,000-11,000</td>
<td>10,000</td>
<td>12,000-24,000</td>
<td>9,500</td>
</tr>
<tr>
<td>Impact strength, Izod (ft-lbs/in. of notch)</td>
<td>0.36-0.35</td>
<td>0.6-1.05</td>
<td>0.28</td>
<td>0.28-0.45</td>
<td>0.26</td>
<td>0.4-1.5</td>
<td>0.50</td>
</tr>
<tr>
<td>Hardness, Rockwell E</td>
<td>70-95</td>
<td>82</td>
<td>82</td>
<td>75-88</td>
<td>94</td>
<td>92-104</td>
<td>76</td>
</tr>
</tbody>
</table>

From the above data it can be observed as at the present time PF resins tailored for specific use functions can be formulated which may differ in the values of many physical and mechanical properties.
B. THERMAL PROPERTIES OF MOULDED PHENOL-FORMALDEHYDE (PF) PLASTICS

B.1) Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is suitable to follow the curing kinetics of PF and U/Mf resins making possible the determination of the total and partial heats, the cure degree and the reaction rate [9].

An example of application of DSC to the investigation of the curing reaction of Phenol-formaldehyde and Lignin-Phenol-formaldehyde resoles is described in reference [9].

![DSC thermograms](image)

**FIGURE 8:** DSC thermograms of uncured Phenol-formaldehyde and Lignin-Phenol-formaldehyde resoles performed at 9 different rate of heating as indicated in figure (°C min⁻¹) in a scanning temperature range from 30 to 250 °C. [9].
**TABLE 3:** Peaks temperatures and reaction heats of the curing process of Phenol-Formaldehyde resoles as functions of the heating rate (from top to down, 2, 4, 6, 8, 10, 12, 14, 16, and 20 °C min⁻¹). The heat of polymerisation (\( \Delta H_0 \)) is in heat per mole of formaldehyde group [9].

<table>
<thead>
<tr>
<th>( T_{p1} ) (K)</th>
<th>( T_{p2} ) (K)</th>
<th>( \Delta H_0 ) (J g⁻¹)</th>
<th>( \Delta H_0^a ) (J mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>392.7</td>
<td>422.6</td>
<td>118.0</td>
<td>3540</td>
</tr>
<tr>
<td>408</td>
<td>431</td>
<td>116.9</td>
<td>3507</td>
</tr>
<tr>
<td>415.7</td>
<td>438.7</td>
<td>122.9</td>
<td>3687</td>
</tr>
<tr>
<td>415.8</td>
<td>439.8</td>
<td>131.7</td>
<td>3951</td>
</tr>
<tr>
<td>422</td>
<td>443</td>
<td>100.0</td>
<td>3000</td>
</tr>
<tr>
<td>425.4</td>
<td>449.4</td>
<td>98.0</td>
<td>2940</td>
</tr>
<tr>
<td>426.6</td>
<td>452.3</td>
<td>121.9</td>
<td>3657</td>
</tr>
<tr>
<td>430.2</td>
<td>454.2</td>
<td>102.2</td>
<td>3066</td>
</tr>
<tr>
<td>436</td>
<td>457</td>
<td>123.2</td>
<td>3696</td>
</tr>
</tbody>
</table>

**TABLE 4:** Peaks temperatures and reaction heats of the curing process of Lignin-Phenol-Formaldehyde resoles as functions of the heating rate (from top to down, 2, 4, 6, 8, 10, 12, 14, 16, and 20 °C min⁻¹). The heat of polymerisation (\( \Delta H_0 \)) is in heat per mole of formaldehyde group [9].

<table>
<thead>
<tr>
<th>( T_{p1} ) (K)</th>
<th>( T_{p2} ) (K)</th>
<th>( \Delta H_0 ) (J g⁻¹)</th>
<th>( \Delta H_0^a ) (J mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>395</td>
<td>-</td>
<td>108.4</td>
<td>3252</td>
</tr>
<tr>
<td>401</td>
<td>419.6</td>
<td>113.6</td>
<td>3408</td>
</tr>
<tr>
<td>411</td>
<td>427.2</td>
<td>83.6</td>
<td>2508</td>
</tr>
<tr>
<td>413.4</td>
<td>430.2</td>
<td>84.4</td>
<td>2532</td>
</tr>
<tr>
<td>417.3</td>
<td>433.6</td>
<td>81.1</td>
<td>2433</td>
</tr>
<tr>
<td>420.6</td>
<td>439.5</td>
<td>63.4</td>
<td>1902</td>
</tr>
<tr>
<td>422</td>
<td>440.6</td>
<td>64.7</td>
<td>1941</td>
</tr>
<tr>
<td>427.8</td>
<td>442.2</td>
<td>76.7</td>
<td>2301</td>
</tr>
<tr>
<td>431.3</td>
<td>445.3</td>
<td>52.0</td>
<td>1560</td>
</tr>
</tbody>
</table>
As shown in figure 8 the DSC thermograms of PF and LPF resole resins are characterized by the presence of two reaction exothermic peaks.  
*The first appears at lower temperature (Tp1) and it is the result of the free formaldehyde in the resin, which can lead to a different product. The second peak (Tp2) is due to condensation reactions among the phenol and the formaldehyde, and the methylated lignosulfonate in the LPF case.* [9]  
In the table 1 the data of the reaction heats for the PF and LPF resins as function of the heating rate used are shown.  
From the thermograms of figure 8 the values of the peaks temperatures and the reactions heats of curing for both the resin type have been calculated; the results are summarized in tables 3 and 4 [9].  
It was found that the data reported in tables 3 and 4 are well fitted by means of the Borchardt–Daniels, Ozawa and Kissinger methods, which allow determining the kinetic parameters of both resins. The kinetic study has been realized to evaluate the effect of methylated ammonium lignin sulfonate in the curing process of the lignin–phenolic resins. The results showed a slightly higher activation energy for LPF resin (the activation energy (E) of PF and LPF resins is 96.3 and 119.2 kJ mol⁻¹, respectively.) [9]. Such a finding is accounted for by the presence of modified lignosulfonate.

In reference [10] the residual reactivities of three cured resole resin samples (S1, S2, and S3), synthesis conditions: F/P ratio of 2.0, alkalinity 4.5 wt%, temperature of reaction, 80, 90, 100 or 110°C), with different values of viscosity, number average molar mass (Mn), weight average molar mass (Mw), and polydispersity (PD) index (see below data) were studied in post-curing experiments by DSC with the goal of determining the extent of cure of the resins and the residual heat of curing.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Viscosity (mPa s)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>PD index</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>25</td>
<td>469</td>
<td>567</td>
<td>1.21</td>
</tr>
<tr>
<td>S2</td>
<td>457</td>
<td>1159</td>
<td>2208</td>
<td>1.91</td>
</tr>
<tr>
<td>S3</td>
<td>751</td>
<td>1268</td>
<td>2630</td>
<td>2.08</td>
</tr>
</tbody>
</table>

The absolute values of the residual heat of reaction (ΔH) in the above resin samples, pre-cured for 120-min at 80, 90, 100, and 110 °C, are reported, as function of the curing temperature (CT) in figure 9. As expected, the residual reactivities decreased as a function of curing temperature. Nevertheless it can be observed that, especially for lower CT, the value of ΔH is strongly dependent upon the molecular structure of the resole (compare the trend, in figure 9, of S3, S2 and S1 sample curves) [10]. The results are in agreement with the fact that S1 resole is characterized by lowest viscosity, M and PD values.

The above results showed that DSC technique is capable to characterize also cured thermosetting resins as far as the residual heat of curing is concerning thus giving the possibility to assess the degree of the curing reaction occurred, as well as the presence of free un-reacted components in the samples.
FIGURE 9: DSC measurements of the residual reactivities (ΔH) of pre-cured, for 120-min at 80, 90, 100, and 110 °C, phenol-formaldehyde resins S1, S2, and S3 (see characteristics in the text) [10].

C. APPLICATION OF INFRA-RED ABSORPTION SPECTROSCOPY, RAMAN SPECTROSCOPY AND SOLID STATE NMR SPECTROMETRY, TO THE CHARACTERIZATION OF (PF) RESINS

C.1) Raman spectroscopy

J. Monni and others by using a prototype Raman spectrometer were able to monitor on line the synthesis and curing of phenol-formaldehyde resol resins (F/P 2.0, alkalinity 4.5 wt%) [10]. The Raman system, described in figure 10 <...> consisted of a semiconductor diode laser, a spectrograph, a charge-coupled device (CCD) detector, and a fiber optic probe ... that allowed remote study of the synthesis and curing ... The wavelength of the excitation laser was 830 nm, and the laser power at the sample was 100mW... All measurements were performed in a darkened room in the absence of daylight > [10].

The progress of the curing was investigated isothermally (80, 90, 100, and 110 °C; for 120 min) for three resin samples having different degrees of condensation, <The synthesis and curing of the resins were started in the reactor and the advancement of the methylation and condensation reactions was followed through the window of the reactor in the wave number region of 2000–400 cm⁻¹ with use of a fiber optic probe for the data collection > [10].

The consumptions of free phenol and free formaldehyde, as well as the progress of the methylation and condensation reactions were easily monitored by following the changes in intensity of the characteristic Raman bands (see table 5).
**FIGURE 10:** The prototype Raman spectrometer developed to monitor on line and also in situ the curing of phenol-formaldehyde resol resins [10].

**FIGURE 11:** Raman spectra taken on line at different reaction time in the course of the isothermal condensation reaction (at 90°C) of a phenol-formaldehyde resol resin (F/P 2.0, alkalinity 4.5 wt%) [10].
The progress of the condensation reaction of the resole resins was followed looking at the changes in intensity of some of the typical Raman bands (see table 5 and figure 11) as a function of time and temperature.

As far as the progress of the curing reaction of the resole samples is concerned it was followed by observing the relative intensity changes of the spectral regions at 1050–995 cm⁻¹ and 950–920 cm⁻¹. The intensity ratios of these regions at the end of the curing experiments, gives a quantification of the degree of cross linking in the resins (see figure 12 and 13) [10].

**TABLE 5:** Assignements of bands observed in Raman spectra of phenol-formaldehyde resole resins [10].

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600–1610</td>
<td>ν(CC)</td>
<td>Ring</td>
</tr>
<tr>
<td>1494</td>
<td>β(HCH)</td>
<td>Formalin</td>
</tr>
<tr>
<td>1469</td>
<td>β(HCH)</td>
<td>Methylol</td>
</tr>
<tr>
<td>1438</td>
<td>β(HCH)</td>
<td>Bridge</td>
</tr>
<tr>
<td>1370</td>
<td>ν(HCO) + ν(CO)</td>
<td>Methylol</td>
</tr>
<tr>
<td>1324</td>
<td>ν(HCH)</td>
<td>Formalin</td>
</tr>
<tr>
<td>1300–1296</td>
<td>ν(HH)</td>
<td>Bridge/methylol</td>
</tr>
<tr>
<td>1268</td>
<td>ν(HH) + ν(CO)</td>
<td>Formalin/ring</td>
</tr>
<tr>
<td>1247</td>
<td>ν(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>1200–1210</td>
<td>ν(ring CH₂)</td>
<td>Ring/substituents</td>
</tr>
<tr>
<td>1174</td>
<td>β(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>1157</td>
<td>β(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>1074</td>
<td>ν(CC) + ν(OCD)</td>
<td>Ring/formalin</td>
</tr>
<tr>
<td>1046</td>
<td>ν(CO2) + ring</td>
<td>Methylol/ring</td>
</tr>
<tr>
<td>1027</td>
<td>ν(CC)</td>
<td>Ring</td>
</tr>
<tr>
<td>1002–995</td>
<td>ν(CC)</td>
<td>Ring</td>
</tr>
<tr>
<td>950–920</td>
<td>γ(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>916–912</td>
<td>ν(CO2)</td>
<td>Formalin</td>
</tr>
<tr>
<td>852</td>
<td>γ(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>818</td>
<td>ν(CC), β(CC), ν(CO)</td>
<td>Ring</td>
</tr>
<tr>
<td>793</td>
<td>γ(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>770</td>
<td>γ(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>733</td>
<td>γ(CH)</td>
<td>Ring</td>
</tr>
<tr>
<td>645</td>
<td>Ring def</td>
<td>Ring</td>
</tr>
<tr>
<td>621</td>
<td>β(CC)</td>
<td>Ring</td>
</tr>
<tr>
<td>567</td>
<td>Ring def</td>
<td>Ring</td>
</tr>
<tr>
<td>536</td>
<td>β(CC)</td>
<td>Ring</td>
</tr>
<tr>
<td>492</td>
<td>Ring def</td>
<td>Ring</td>
</tr>
<tr>
<td>400</td>
<td>Ring def</td>
<td>Ring</td>
</tr>
</tbody>
</table>

*ν* = stretching vibration; *β* = bending vibration; *ω* = wagging vibration; *def* = deformation vibration; *γ* = twisting vibration; *ring* = ring vibration; *out-of-plane* = out-of-plane vibration.

From the diagrams in figure 12 it emerges that the intensity of the Raman bands at 1050-995 cm⁻¹, indicated by an arrow, decreases with curing time while the contrary happens for that at 950-920 cm⁻¹ [10]. This finding is consistent with the trends of the curves in figure 13 where the intensity ratios of the Raman bands at 950-920 cm⁻¹ and 1050-995 cm⁻¹ as a function of curing time of a PF resole (F/P 2.0, alkalinity 4.5 wt%, with initial viscosity 457 mPas) at different temperatures (80, 90, 100, and 110°C) are reported [10].
**FIGURE 12:** Raman spectral changes (1100-850 cm$^{-1}$ region) in the course of the curing of PF resole (F/P 2.0, alkalinity 4.5 wt%) at 100°C for 120 min [10].

**FIGURE 13:** Intensity ratios of Raman bands at 950-920 cm$^{-1}$ and 1050-995 cm$^{-1}$ as a function of curing time in the setting experiments of a PF resole (F/P 2.0, alkalinity 4.5 wt%, initial viscosity 457 mPas) at different temperatures (80, 90, 100, and 110°C) [10].
From the above results it can be concluded that Raman spectroscopy is an effective and fast method for structural study of the cured, solid state resins, suitable to provide also important information concerning the state of conservation of PF artifacts.

C.2) Solid state 13C NMR

An example of application of solid state 13C NMR spectra (the high power dipolar decoupling and magic angle sample spinning methods were used during the analysis while hexamethylbenzene was the standard for the chemical shift calculations) to a cured resole PF-resin is reported in figure 14 [11]. The PF-resole (see properties in table 6) was synthesized in the presence of tetraalkylammonium hydroxides as catalysts (TMAH) by using an F/P mole ratio of 3.0 [11]. The resole product was cured at 230°C.

**TABLE 6:** Physico-chemical characteristics of the PF resole resin.

<table>
<thead>
<tr>
<th>Free phenol (%)</th>
<th>Reactive CH₂O (%)</th>
<th>Density (g/cm³)</th>
<th>Gelation time (s)</th>
<th>Water-miscibility</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53</td>
<td>5.37</td>
<td>1.115</td>
<td>118</td>
<td>1:50</td>
<td>0</td>
</tr>
</tbody>
</table>

**FIGURE 14:** A solid state 13C NMR spectrum of the PF resole after curing.
Note: the asterisked peaks (p) represent the rotational bands of the main signals [11].
The exemplary of solid state 13C NMR spectrum of cured resole is shown in Fig.14. <As can be seen, the NMR signals in the spectrum are derived either from the free resin or from the free catalyst. Hence, the catalyst remains in free state in resin >[11].

The solid state 13C NMR (CP/MAS) spectra of solid (finely grounded) post cured resole PF-resins, corresponding to three industrial resoles (A, B, C) with different F/P ratios, catalyst concentration and degree of condensation reaction, and cured at 120°C for 6h, present, as shown in figure 15, a dissimilar peaked structure [12,13].

From the examination of the diagrams in figure 15 it is possible to draw the following structural conclusions:

--- Resole A < has a high number of non substituted ortho sites, few residual hydroxymethyl groups and a higher proportion of ortho-para links than para-para >[12].
--- Resole B < has fewer free ortho sites than resole A, and a higher proportion of ortho-para links than para-para >[12].
--- Resole C < The band of free ortho sites around 115ppm is very weak. The band at 90ppm indicates the presence of polyoxymethylene chains due to the high initial F/P ratio >[12].

**FIGURE 15:** Solid state 13C NMR (CP/MAS) spectra of post-cured industrial resoles differing in F/P ratio, catalyst content and degree of condensation reaction, and cured at 120°C for 6h (see text) [12].
The results gained in reference [12] demonstrated that solid state 13C NMR (CP/MAS) is suitable to characterize solid post-cured PF resins giving information about their molecular structure and then final properties which in turn may affect their physical/chemical degradation behavior.

**C.3) Fourier Transform Infra-Red Absorption Spectroscopy (FTIR)**

Typical FTIR spectra, usually recorded in the solid state, on post-cured grounded samples of PF resins, in the form of KBr pellets, are shown in figure 16 [12]. Those spectra refer to the same three different samples of post-cured resoles (A, B, C) above mentioned (see figure 15) [12]. It can be seen that through FTIR spectroscopy it is possible to put in evidence changes in the intensity and position of bands related to the different history of the starting resoles [12].

![FTIR spectra](image)

**FIGURE 16:** FTIR spectra of solid post-cured industrial resoles differing in F/P ratio, catalyst content and degree of condensation reaction, cured at 120°C for 6h, in the 1800-700 cm⁻¹ region (see text) [12].
Some of the most relevant thermal and electrical characteristics of phenolic resins are listed in table 7 [8].

**TABLE 7:** Typical thermal and electrical properties of Phenolic resins

<table>
<thead>
<tr>
<th>Property</th>
<th>General purpose</th>
<th>Impact</th>
<th>Non bleeding</th>
<th>Electrical</th>
<th>Heat resistant</th>
<th>Glass reinforced</th>
<th>Chemical resistant compound</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>THERMAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity (10^-4 cal - cm/sec - cm^2 - °C)</td>
<td>7.1</td>
<td>7.9</td>
<td>-</td>
<td>16.0</td>
<td>-</td>
<td>-</td>
<td>8.8</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (10^-5 in./in.-°C)</td>
<td>3.95</td>
<td>3.56</td>
<td>4.40</td>
<td>2.60</td>
<td>2.80</td>
<td>1.80</td>
<td>3.60</td>
</tr>
<tr>
<td>Deflection temperature (°F) At 264 psi</td>
<td>275-360</td>
<td>270-500</td>
<td>370</td>
<td>310-400</td>
<td>330-380</td>
<td>370-550</td>
<td>360-430</td>
</tr>
<tr>
<td>Flammability rating 1/8 inch</td>
<td>V-1</td>
<td>HB</td>
<td>-</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>HB</td>
</tr>
<tr>
<td><strong>ELECTRICAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dielectric strength (V/mil) short time, 1/8 in. thick</td>
<td>350</td>
<td>350-400</td>
<td>200</td>
<td>400</td>
<td>170</td>
<td>400</td>
<td>175</td>
</tr>
<tr>
<td>Dielectric constant At 1kHz</td>
<td>5.2-5.3</td>
<td>5.2-5.4</td>
<td>-</td>
<td>4.9-6.5</td>
<td>11.7</td>
<td>4.4</td>
<td>7.8</td>
</tr>
<tr>
<td>Dissipation factor At 1kHz</td>
<td>0.04-0.05</td>
<td>0.04-0.06</td>
<td>-</td>
<td>0.025-0.10</td>
<td>0.15</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>Volume resistivity (ohm-cm) At 73°F, 50% RH</td>
<td>10-11-10-12</td>
<td>10-11-10-12</td>
<td>10-12</td>
<td>10-11-10-13</td>
<td>10-12</td>
<td>10-12</td>
<td>10-11</td>
</tr>
<tr>
<td>Arc resistance(s)</td>
<td>100</td>
<td>50</td>
<td>-</td>
<td>184</td>
<td>181</td>
<td>181</td>
<td>-</td>
</tr>
</tbody>
</table>

80
D) CHARACTERIZATION OF UREA-FORMALDEHYDE RESINS

T. Zorba et others demonstrated that Fourier transform infrared spectroscopy (FTIR in transmittance mode) and thermogravimetry (TG-DTA) may be useful also for the characterization of Urea-formaldehyde resins (UF) [14]. In the cited study, samples of two UF resins (a conventional and an innovative one) obtained through two different synthesis procedures (low formaldehyde to urea mole ratio) were analyzed and characterized in dynamic heating conditions both in their pre-polymer and cured state.

The resins are delivered in liquid or powder form (after spray drying) to the industry for the production of various wood-based panels. During this stage (hardening reaction), the resin cures completely and a more or less three-dimensional network is built up.

CHIMAR Hellas produced two UF resins following different synthesis procedures. The first one was a conventional resin, whose synthesis procedure included an alkaline methylation followed by a mild acid condensation step, while the second resin was produced according to an innovative CHIMAR technology, which included acid methylation followed by strong acid condensation stages. The dry solids for the conventional and innovative resins were 65.6 and 65.8%, respectively in the pre-polymer and 62.79 and 62.97% respectively in the cured resins. Both resins had final formaldehyde to urea (F:U) mole ratio 1.07 > [14].

The specifications of the uncured liquid resins are reported in Table 8 [14].

<table>
<thead>
<tr>
<th>Properties of pre-polymer</th>
<th>Unit</th>
<th>Conventional resin</th>
<th>Innovative resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH at 25°C</td>
<td></td>
<td>8.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Brookfield viscosity at 25°C</td>
<td>cP</td>
<td>320</td>
<td>365</td>
</tr>
<tr>
<td>Hardening time at 100°C</td>
<td>s</td>
<td>59</td>
<td>49</td>
</tr>
<tr>
<td>Water tolerance (resin/water) at 25°C</td>
<td>mL mL⁻¹</td>
<td>1/2.5</td>
<td>1/4.3</td>
</tr>
<tr>
<td>Surface tension</td>
<td>mN m⁻¹</td>
<td>71</td>
<td>72</td>
</tr>
<tr>
<td>Dry solids</td>
<td>mass/mass %</td>
<td>65.6</td>
<td>65.8</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>%</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Buffer capacity (measured with 0.1 N H₂SO₄)</td>
<td>mL</td>
<td>11.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

The FTIR absorbance spectra of the UF conventional pre-polymer and of the corresponding post-cured resin are shown in figure 17 [14]. The spectra of innovative resin appear to be very similar to those of conventional one.

The examination of the peaked structure led to the following conclusions:

--- the peaks revealed could be attributed to the characteristic functional groups of the resin such as amide I, II and C=O at 1650–1350 cm⁻¹ and CH₂OH, CH₃ and CN at 1400–1360 cm⁻¹, etc

--- The most characteristic difference between the pre-polymers and the cured resins is at the spectral area 3700–3000 cm⁻¹. The broadening of the band of the pre-polymer at ~3440 cm⁻¹,
could be attributed to pre-polymer's by products, such as water and excess formaldehyde, which allow hydrogen bonding with the reactive functional groups such as CH₂OH, NH₂ and NH.
--- The sharpening and the shifting at 3350 cm⁻¹ of this band after curing, indicate the formation of bonded NH group > [14].

**FIGURE 17:** FTIR absorbance spectra of the UF conventional pre-polymer (1, in figure) and of the corresponding post-cured resin (2, in figure) [14].

The above findings indicate that FTIR may be conveniently used for recognizing UF cured resins from the typical absorbance bands.

The post-cured UF resins were also characterized by TG-DTA thermal analysis. Solid grounded samples were heated from ambient temperature to 500°C (flow of N₂, heating rate of 5°C min⁻¹). The thermogravimetric diagrams of samples of the two UF resins after curing, together with the first derivative curves, are compared in figure 18 [14].

The first endothermic peak, around 100°C, is accounted for by loss of water humidity, while the endothermic peak with minimum between 234–242°C is attributed by many authors to the degradation of methylene-ether bridges in the resin's network [14].

Thus it can be concluded that also for UF resins the thermal behavior, followed by TG-DTA thermal analysis may give useful data which can be useful for the characterization of those thermosetting materials as components of polymer based artifacts.
**FIGURE 18:** TG-DTA diagrams. Mass (%) and heat flow vs. temperature for the totally cured urea/formaldehyde resins: 1 – the conventional resin and 2 – the innovative resin [14].
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13) L. Paolillo, I. Giudicianni, <La diagnostica nei Beni Culturali, Moderni Metodi di Indagine>,
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CHAPTER- FOURTH

1) RESISTANCE TO CHEMICAL AGENTS AND TO MICROORGANISMS AND WATER ABSORPTION OF PHENOL (UREA/MELAMINE)/FORMALDEHYDE RESINS

A ) Chemical Resistance

As can be seen also by the data reported in table 1 phenol-formaldehyde (PF) cured resins are relatively resistant to the action of most chemical agents [1,2]. At RT the unfilled post-cured PF resins (powder moulding grade) are decomposed by hot diluted alkalis and dissolved by molten phenol (with some decomposition) and naphthols but at very high temperatures. Moreover they may also be attacked by strong oxidizing acids [1,2].

<table>
<thead>
<tr>
<th>Table 1: Resistance to chemical agents of phenolic resins [2].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Inorganic saline solutions</td>
</tr>
<tr>
<td>Weak acids</td>
</tr>
<tr>
<td>Strong acids</td>
</tr>
<tr>
<td>Weak oxidizing acids</td>
</tr>
<tr>
<td>Strong oxidizing acids</td>
</tr>
<tr>
<td>Alkaline waters</td>
</tr>
<tr>
<td>Hard alkaline</td>
</tr>
<tr>
<td>Aliphatic hydrocarbon</td>
</tr>
<tr>
<td>Chlorinated hydrocarbon</td>
</tr>
<tr>
<td>Alcohol with low molecular weight (ethanol)</td>
</tr>
<tr>
<td>Ester</td>
</tr>
<tr>
<td>Ketones</td>
</tr>
<tr>
<td>Aromatic hydrocarbon (toluene)</td>
</tr>
<tr>
<td>Petrol</td>
</tr>
<tr>
<td>Mineral oil</td>
</tr>
<tr>
<td>Grease, oil</td>
</tr>
<tr>
<td>Unsaturated chlorinated hydrocarbon</td>
</tr>
<tr>
<td>Iron tri-chloride</td>
</tr>
<tr>
<td>Phenol</td>
</tr>
</tbody>
</table>

+: resistant; o: enough resistant; 5: resistant with certain conditions; -: non-resistant
The chemical resistance of filled-PF resins against reactive chemicals is influenced by the nature of the filler used. *Resins containing cellulose fillers are affected by reagents, which tend to destroy the filler, such as sulphuric acid* [1].

No solvents are known for fully cured Melamine-formaldehyde (MF) and Urea-formaldehyde (UF) resins [3].
The above data are useful as far as the choice of the cleaning procedures of PF, MF, and UF artefacts are concerned.

B) Water Absorption

Generally water resistance in polymers is evaluated by measuring under controlled and specified conditions the amount of humidity/water absorbed. A test used to determine the amount of water absorbed includes the following procedure.

*The specimens are dried in an oven for a specified time and temperature and then placed in desiccators to cool. Immediately upon cooling, the specimens are weighed. The material is then immersed in water at agreed upon conditions, often 23°C for 24 hours or until equilibrium. Specimens are removed, patted dry with a lint free cloth, and weighed. Water absorption is expressed as increase in weight percent.*

**Percent Water Absorption = [(Wet weight - Dry weight)/ Dry weight] x 100** [4].

For a given plastic artefacts the amount of water absorbed, at given conditions, depends by several factors:

--- Type of polymer component;
--- Additives;
--- Nature of fillers;
--- State of conservation;

Of course the performance of plastic materials in many cases results to be strongly affected by the amount of water absorbed in humid environments.

For example *the variation in humidity can result in the formation of a network of micro-fractures on the surface of the artefacts and alter their electrical and mechanical properties. The sensitivity to water is related to the grade of cure of phenolic resins; for example, in the case of incomplete cure, the laminates in contact with the water swell, change their size and undergo delamination* [5].

In some circumstances the absorption of water may determine an increase in the volume of plastic pieces hindering their use in applications where stable dimensions are requested.
The data reported in tables 2, 3 and 4 demonstrate as the amount of water absorption of PF resins depends upon:

--- Type of PF;
--- Type of filler;
--- Resin content [1].
### TABLE 2: Moisture absorption by phenol-formaldehyde resins at 25°C [1].

<table>
<thead>
<tr>
<th>Type of phenoplast</th>
<th>Gain during immersion in water, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hrs.</td>
</tr>
<tr>
<td>Molded, wood flour-filled</td>
<td>0.25</td>
</tr>
<tr>
<td>Cast</td>
<td>0.16</td>
</tr>
<tr>
<td>Laminated, paper-base</td>
<td>0.44</td>
</tr>
</tbody>
</table>

### TABLE 3: Effect of the type of filler on water absorption of phenol-formaldehyde resins [1].

<table>
<thead>
<tr>
<th>Type of filler</th>
<th>Filler, %</th>
<th>Resin, %</th>
<th>Water absorption after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>24 hrs. at 25°C</td>
<td>48 hrs. at 25°C</td>
</tr>
<tr>
<td>Wood flour</td>
<td>50</td>
<td>50</td>
<td>0.50</td>
</tr>
<tr>
<td>Wood flour (15%) mixed with cotton flock (50%)</td>
<td>45 (total)</td>
<td>55</td>
<td>0.60</td>
</tr>
<tr>
<td>Cotton flock</td>
<td>45</td>
<td>55</td>
<td>0.70</td>
</tr>
<tr>
<td>Wood flour (15%) mixed with asbestos (41%)</td>
<td>60 (total)</td>
<td>40</td>
<td>0.20</td>
</tr>
<tr>
<td>Asbestos</td>
<td>60</td>
<td>40</td>
<td>0.08</td>
</tr>
<tr>
<td>Mica</td>
<td>60</td>
<td>40</td>
<td>0.03</td>
</tr>
<tr>
<td>Chopped fabric</td>
<td>60</td>
<td>50</td>
<td>0.55</td>
</tr>
<tr>
<td>Cotton cord</td>
<td>50</td>
<td>80</td>
<td>1.10</td>
</tr>
</tbody>
</table>

### TABLE 4: Effect of resin content on water absorption of wood flour-filled phenol-formaldehyde resins [1].

<table>
<thead>
<tr>
<th>Wood flour, %</th>
<th>Resin, %</th>
<th>Water absorption after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>24 hrs. at 25°C</td>
</tr>
<tr>
<td>50</td>
<td>80</td>
<td>0.55%</td>
</tr>
<tr>
<td>40</td>
<td>80</td>
<td>0.51</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.15</td>
</tr>
</tbody>
</table>
J. Day and L. Sperry, investigated about the influence of matrix and filler nature upon the water absorption mechanism of laminates produced by different thermosetting resins [6].

For the study the following five different compositions of laminates were used:

1) Melamine resin, with continuous filament woven glass;
2) Phenolic resin with fine weave cotton fabric;
3) Phenolic resin with staple fiber nylon fabric;
4) Phenolic resin plasticized with tung oil and laminated with paper;
5) Phenolic resin with paper [6].

The curves representing the variation with time of the log of the rate of water absorption in grams per hour, for each of the five laminates investigated are reported in figure 1.

**FIGURE 1. left:** The log of the rate of water absorption in grams per hour, plotted as a function of time.
1, melamine resin with continuous filament woven glass. 2, phenolic resin with fine weave cotton fabric. 3, phenolic resin with staple fiber nylon fabric. 4, phenolic resin laminated with paper and plasticized with tung oil. 5, phenolic resin with paper > [6].

**FIGURE 2. right:** Grams of water absorbed in 24 hours plotted as a function of the contact angle of water on the plastic surfaces > [6].
From the observed trends it was suggested that
the main factor influencing the rate of water absorption are the chemical nature of the plastic, the
nature of the laminating filler, and the physical structure of the laminate, particularly with regard
to the completeness of bonding between the plastic and the laminated material [6].

As far as the influence of the nature of the filler upon the shape of the above-mentioned curves is
concerned it was accounted for by assuming that probably each filler may contribute
absorption in four ways: (1) the number of capillary voids in the sample due to the type of
filler, (2) the rate of wicking action of the filler, (3) the greater effective plastic absorbing surface
due to the voids, and (4) the total absorption capacity of the filler itself [6].

The values of the ultimate water absorption ( % by weight ) reported in table 5 indicate that the
phenolic resin with paper is the most absorbing laminate while phenolic resin with staple fiber
nylon fabric and phenolic resin plasticized with tung oil and laminated with paper are the less
absorbing laminates [6].

**TABLE 5:** Ultimate water absorption expressed as % by weight [6].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Our data, 840 hours</th>
<th>Manufacturer's data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.54</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>4.60</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>1.22</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>1.44</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>13.6</td>
<td>12.0</td>
</tr>
</tbody>
</table>

**FIGURE 3:** Measurements of the contact angle ( \( \theta \) ) ( \( \theta \) is defined as the
angle between the liquid/solid interface and the liquid/vapour interface )
are suitable to assess the adhesion between a liquid and a solid surface as
well as their compatibility.
*Left: \( \theta < 90^\circ \), good wetting case; Right: \( \theta > 90^\circ \) poor wetting case [7].*
As shown by figure 2 the grams of water absorbed by the laminates in 24 hours seem to decrease with the increase of the values of the contact angle of water on the plastic surfaces [6]. This means that laminates with a more hydrophobic surface (higher value of the contact angle) are more resistant to water absorption. Thus measurements of the contact angle (figure 3) may give useful information about water absorption process in plastics [7].

The behaviour against water absorption of composites obtained by mixing phenolic resin and vegetable fibres from sugar cane pulp was investigated as function of the resin content and the size of the cane pulp fibre (essentially grain sizes) keeping the pressure and moulding temperature constant. To improve the interaction between the fibre and the PF-matrix, the fibres were submitted to "mercerisation", by using NaOH solutions [5]. The morphology of the composite, together with the adhesion between PF-matrix and fibres, was investigated by scanning electron microscopy (SEM).

The SEM micrographs of the surface fractures of the composites (see figure 4) revealed a weak fibre-matrix adhesion. The interaction between the fibre and the matrix was inefficient. The fibres are released from the matrix during the fracture of the test body; this finding is also known as the "pullout" mechanism [5]. Moreover from figure 4-b it can be seen that the cane pulp fibres are not covered by the polymeric matrix (phenolic resin), indicating also weak fibre-matrix adhesion [5].

![Figure 4: Scanning electron micrographs of fracture surfaces of PF-cane fibres based composites: (a) with 69% fibres and a granulometry of 35-80 mesh (b) with 29% fibres and a granulometry of 80-170 mesh [5].](image)

The absorption of water, as demonstrated by the data shown in figure 5, resulted to be of about 12% and of 3% for the composites with higher percentage of cane pulp fibres (69%) and with a lower percentage of cane pulp fibres (29%) respectively. The pure PF matrix shows a relatively higher water resistance [5]. Such behaviour is consistent with the fact that the fibres acting as filler are highly hydrophilic. Cellulose fibres are difficult to dissolve due to their highly crystalline nature, although they tend to retain liquid in their fibrillar spaces [5].
**FIGURE 5:** Absorption of water by phenol-formaldehyde matrix and composites with different % (69 and 29%) of cane pulp fibres and grain size (80-170 or 35-80 mesh) [5].

**FIGURE 6:** Resistance to traction for samples of phenol-formaldehyde matrix and composites with different % of pulp cane fibres and grain sizes [5].

From the diagrams in figure 6 it can be seen that the PF-based composites may present values of tensile strength higher than those of plain resins (see for example the composite with 29% of fibre content and 80-70 grain size) [5]. It is interesting to observe that the composites with better mechanical performances are those with higher water resistance (compare data of figure 5 and 6) [5].
The water absorption of different type of commercial phenolic resins, recently published, are hereafter reported [8].

--- Phenolic, Unreinforced, Molded - 0.0300 - 0.500 %
--- Phenolic, Novolac, Heat Resistant Grade, Filled - 0.200 - 0.700 %
--- Phenolic, Novolac, Wood flour Filled - 0.247 - 0.640 %
--- Phenolic, Novolac, Flock Filled - 0.180 - 0.630 %
--- Phenolic, Novolac, Mineral/Fiber Filled - 0.300 - 0.400 %
--- Phenolic, Novolac, Glass Filled - 0.0300 - 0.250 %

The above data confirm that the water resistance of PF plastics is strongly dependent upon their grade and nature of the filler used.

The major applications as well as the optical, physical, thermal and chemical properties of PF, UF, and MF resins are compared through the data contained in the tables 6, 7 and 8 [9].

**TABLE 6:** The major applications as well as the optical, physical, thermal and chemical properties of phenol-formaldehyde resins [9].

| Major applications | Phenolics can be cast into rod, tubes and sheet and foamed. They can be impregnated into paper and cloth. Electrical insulation, plugs and switches, radio and television housings, telephones, cameras (e.g. Kodak’s Brownie 127), fuse box covers, bushings, gears, beads, knife handles, paperweights, billiard balls, saucepan handles and knobs, panelling (as foam).
| Optical properties | Bakelite is little used today due to cost, complexity of production and its brittleness. It is used for precision-shaped components including saucepan handles and electrical switches.
| Physical and thermal properties | Refractive index (ND 20°C) 1.54-1.58
| | Mostly available in dark, opaque colours (novolaks), though transparent, unfilled castings are formed by reacting cresols or resorcinol with formaldehyde (resoles). May be painted or decorated by electroplating.
| | Bakelite is a thermoset, hard, brittle material. Its high shrinkage on moulding and brittleness are mediated by adding fillers or reinforcing fibres. It resists burning.
| | Density (g/cm³) 1.7-2.0
| | Ignition time(s) > 300
| | Tensile strength at break (MPa) 34-62
| | Elongation at break (%) 1.5-2.0
| | Coefficient of thermal expansion (°C⁻¹ x 10⁻⁶) 68
| Chemical properties | Resistant to organic liquids but attacked by concentrated nitric and sulphuric acids and chlorine. Photo-oxidation manifests as reduction in gloss of surfaces.
| | Degree of crystallinity (%) 0
**TABLE 7:** The major applications as well as the optical, physical, thermal and chemical properties of urea-formaldehyde resins [9].

<table>
<thead>
<tr>
<th>Major applications</th>
<th>Electrical fittings, telephone handsets, radio housings, cigarette boxes, lampshades, tableware, cavity wall insulation (UFP) from 1950s until 1980 when it was discontinued due to concern over formaldehyde toxicity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical properties</td>
<td>Transparent, pale colours available.</td>
</tr>
<tr>
<td>Physical and thermal properties</td>
<td>UF is a thermostet. It is brittle and stiff, so requires filler or reinforcement. Organic fillers are required for UF because it is more sensitive to the high temperatures required for inorganic fillers than MF. High tensile strength. Low water absorption.</td>
</tr>
<tr>
<td></td>
<td>Maximum use temperature (°C) 80–140</td>
</tr>
<tr>
<td></td>
<td>Ignition time (s) &gt;300</td>
</tr>
<tr>
<td></td>
<td>Tensile strength at break (MPa) 35–75</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%) 1.5–2.0</td>
</tr>
<tr>
<td></td>
<td>Coefficient of thermal expansion (°C⁻¹ × 10⁻⁶) 68</td>
</tr>
<tr>
<td>Chemical properties</td>
<td>Highly resistant to dilute acids and alkalis but attacked by concentrated materials.</td>
</tr>
<tr>
<td></td>
<td>Degree of crystallinity (%) 0</td>
</tr>
</tbody>
</table>

**TABLE 8:** The major applications as well as the optical, physical, thermal and chemical properties of melamine-formaldehyde resins [9].

<table>
<thead>
<tr>
<th>Major applications</th>
<th>Radio housings, laminates for kitchen and bathroom surfaces, tableware, cutlery handles.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical properties</td>
<td>Transparent, pale colours available.</td>
</tr>
<tr>
<td>Physical and thermal properties</td>
<td>MF is a thermostet. It is brittle and stiff, so requires fillers or reinforcements. High tensile strength. Low water absorption.</td>
</tr>
<tr>
<td></td>
<td>Maximum use temperature (°C) 80–140</td>
</tr>
<tr>
<td></td>
<td>Ignition time(s) &gt;300</td>
</tr>
<tr>
<td></td>
<td>Tensile strength at break (MPa) 35–75</td>
</tr>
<tr>
<td></td>
<td>Elongation at break (%) 1.5–2.0</td>
</tr>
<tr>
<td></td>
<td>Coefficient of thermal expansion (°C⁻¹ × 10⁻⁶) 68</td>
</tr>
<tr>
<td>Chemical properties</td>
<td>Highly resistant to dilute acids and alkalis but attacked by concentrated materials.</td>
</tr>
<tr>
<td></td>
<td>Degree of crystallinity (%) 0</td>
</tr>
</tbody>
</table>
C ) Resistance to Micro-organisms

Under normal conditions the PF, UF and MF resins are fairly resistant to biodegradation. Nevertheless it has been observed that laminated phenolics, with cellulose fillers, suffer biodegradation. On the contrary compounds with asbestos or mica seemed to be highly resistant to the attack of fungi and other micro-organisms [1]. Artefacts exposed to the action of micro-organisms under environmental severe tropical conditions (heat and humidity) showed evidences of the growth of fungi.

Quite recently Gussie, Miller and Volk demonstrated that PF resins under some specific conditions are biodegraded by the white-rot fungus *Phanerochaete chrysosporium* [10].

![Figure 7: Scanning electron micrograph of the surface of a phenolic polymer chip (A) embedded in malt agar with *Phanerochaete chrysosporium* (Pc1) for 28 days and washed with alcohol before fixation. Jagged edged holes (A, see arrow) are present, along with smaller pockmarks in the smooth polymer surface. The major area of degradation (A, center) is mottled in appearance, with the heaviest degradation occurring at the top of the micrograph. (B) Control polymer chip embedded in malt agar without fungi. Note the glasslike appearance when the chip had been broken. No degradation was seen in B... > [10].](image-url)
Such a conclusion was based essentially upon the hereafter-reported findings:

< --- Chromatic transformation of growth medium (yellow to pink) indicated initial biodegradation of the resin 3 days after inoculation.
--- A degradation product, $^{13}$C-labelled phenol, was detected with gas chromatography-mass spectroscopy.
--- Scanning electron micrographs revealed physical evidence of degradation (see figure 7) > [10].

II) METHODS FOR THE IDENTIFICATION OF PHENOL
(UREA/MELAMINE)/FORMALDEHYDE RESINS IN COLLECTION ARTEFACTS

In previous chapters a certain number of analytical instrumental techniques, which can be used to identify the chemical structure of PF, UF and MF plastics, together with their components have been described. Some of those analytical instrumental procedures are hereafter listed.

- Fourier transform infrared spectroscopy (FTIR)
- Mass Spectrometry
- Nuclear magnetic resonance spectroscopy, NMR (in solution and solid state)
- Thermal Analysis. Differential Scanning Calorimetry and Thermogravimetry
- X-Ray Fluorescence
- X-Ray Diffraction
- Dynamic thermal mechanical analysis
- Stress-Strain behaviour in traction or in flexure modes.

To obtain reliable information suitable for the identification of the constituents of an artefact in plastics (this includes the nature of the base polymer as well as the nature and concentration of additives, fillers, pigments and colorants) it is a good practice to use several complementary techniques (11).

Some other practical chemical, mechanical and physical testing techniques used for the identification of Bakelite and urea (melamine)-formaldehyde plastics are hereafter presented and discussed.

1) The hot water test (smell test)
< The simple tried & true test for Bakelite is to hold the item under hot water for 10 seconds.... If it smells of medicinal chemicals — like an old band aid or medicine chest, that is the formaldehyde smell of old phenolic Bakelite.....it is more than likely genuine Bakelite. This test is the least likely to damage or degrade the finish on the Bakelite > [12].

< Phenolic (bakelite) will usually give off a distinct smell of carbolic acid when wet or warmed. Friction with your thumb on the dry item for 30 seconds or so can release this distinctive odour.... smells like mothballs/vicks vapour rub (camphor) it's celluloid....smells like burnt milk it's casein/galalith, a plastic derived from milk products.... if it smells clean, or like nothing at all it's lucite or acrylic > [13].
2) Flame test and burning test

Plastic materials concerning flammability are divided according to the following groups [14].

a) Flammable, the sample will support combustion when an igniting flame has been removed;
b) Self-Extinguish, the sample does not continue to burn on removal of the flame;
c) Non-Flammable, the sample does not ignite in a flame, although it may char and decompose > [14].

In the course of flammability tests also rate of burning, nature of residue, burning character are taken into consideration as they may help in recognizing polymer materials.

**FIGURE 8:** Flame test: procedures to distinguish PF, UF and MF from thermoplastics and between themselves (see text) [15].
By means of flammability test, that is destructive in nature, it is possible to distinguish PF, UF and MF from thermoplastics as well as from themselves. The flame test is usually performed on unknown plastic objects according to the modalities shown in figure 8 [15]. It can be seen that following the procedure reported in figure 8 it is possible first of all to establish if the polymer constituent is thermoplastic or thermosetting. Such a result can be afforded simply by pressing a hot rod against the sample (thermoplastics will soften, while thermosets will remain hard). The following step consists in burning a small piece of material. If the plastic belong to the family of thermosets then the flame will self extinguish; nevertheless from the colour of the flame, the odour emitted and from other characteristics it is possible to have suitable information to distinguish between PF, UF and MF resins (see figure 8).

From figure 8 it can be seen that the colour of the flame will be yellow with blue tip, yellow or yellow with green/blue edge in the case of MF, PF and UF plastics respectively [14]. As far as the odour emitted is concerned it comes out that it will be of fish like type (MF-plastics), phenol-like (PF-plastics) or formaldehyde-like in the case of UF-resins [14]. Other observed burning characteristics are also significant:
--- MF and UF may swell and crack;
--- PF may, in some cases not self extinguish [14].

3 ) Simichrome Polish test
Simichrome Polish is a non-abrasive cream used to clean metals. This test is described in reference [16] as follows:
< Take a small bit of Simichrome on a cotton swab. Rub it on an unobtrusive area. It is best to then take the other end of your cotton swab with no Simichrome on it and rub very hard against the polish you have left there to see if you get a stain. Bakelite will stain the cotton swab a yellow or brown colour. The colour will vary because of different colours of Bakelite, different formulas used to create the substance, the amount of wear and contact to air, and the type of finished used on the piece. European pieces tend to test darker, as do pieces, which were well loved and worn, > [16].

![Image](97.png)

**FIGURE 9**: Typical custom jewel made in Bakelite.
Some “Basic Observable Criteria” suitable for recognize bakelite artefacts (figure 9) are hereafter listed:

1. Bakelite has no Mould Linen.
2. Bakelite is heavier then other plastics.
3. Two pieces of Bakelite struck together will have a distinctive sound.
4. Bakelite has a unique surface, interiors usually slightly pitted. Exteriors may vary according to actually finish, use, and wear
5. Bakelite was most often hand finished. Items would have been hand sanded and polished.
6. Older pieces of Bakelite will not have "glued" hardware. [17]

4) Formaldehyde test.
This test is suitable to detect urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde.

The procedure as described in reference [18] is hereafter textually reported:

< The manufacturer’s protocol is easy to follow. However, very small or solid samples containing highly cross-linked formaldehyde such as phenol-formaldehyde and melamine-formaldehyde may give false negatives. To avoid this problem, we suggest heat-sealing the capillary end of a pipette and placing a sample the size of the dot on an “i” in the pipette. Then, place a drop of carbonate solution on half a test strip (cut in two longitudinally). The test strip will turn from yellow to pink.

Bend one end of the test strip, insert it in the pipette, and hold it in place with the Plasticine. Heat the sample in the flame of the alcohol burner. Remove the pipette from flame. If there is any formaldehyde in the sample, the test strip will turn violet within approximately ten minutes. A pink color does not indicate a positive test.

Apart from acetaldelyde and glutaraldehyde, which produce different colors, the manufacturer does not mention any substances that give a false positive.

Since this is a destructive test, we recommend using it only after a pyrolysis test has been performed to determine whether the sample is a thermosetting plastic (does not soften before burning) and the pH of the combustion vapor has been established. The combustion vapors of urea-formaldehyde and melamine-formaldehyde are alkaline (pH 9.5) while that of phenol-formaldehyde is neutral (pH ≈ 7.0). The test should be practiced using reference samples before testing a museum object. [18].>
REFERENCES

CHAPTER FIFTH

THE CONSERVATION AND RESTORATION OF ARTEFACTS MADE IN PHENOL-FORMALDEHYDE RESINS

In general the main causes of degradation of plastic artefacts are related to various types of reaction occurring in presence of environmental oxygen, water, gaseous atmospheric pollutanst, liquid acids and alkalis.
Moreover it has been quite often observed that plastic deterioration processes are initiated or also accelerated by mechanical injuries related to the use function of the objects [1].

FIGURE 1: Schematic and planar view of the cross-linked structure of post-cured phenol-formaldehyde resins [3].

The resistance of PF resins against environmental or chemical factor of degradation as well as their chemical and mechanical properties, are strongly influenced by:
--- The chemical structure of the pre-polymer ( novolacs or resoles-like ) and of the cured base polymer (especially degree of cross-links);
--- Nature and concentration of additives;
--- The presence of fillers including their chemical structure (cellulose, asbestos, etc.) and shape (fiber-like or powder-like, etc.);
--- Processing and manufacturing conditions [2,3,4].
In general Formaldehyde-based plastics, heat-resistant and waterproof, though somewhat brittle due to their thermoset nature, characterized by a three-dimensional network structure (see figure 1, [3]) are resistant, under normal conditions, against environmental factors of degradation (e.g., oxygen, water, gaseous pollutants, acid rains) and against weak liquid acids and alkalis. Nevertheless when the PF resins are filled with cellulose-based materials result to be affected by water and solutions of acids and alkalis. As a matter of facts such type of fillers in long-lasting contact with water tend to swell determining mechanical damages to the artefacts. Some recommendations concerning the conservation of artefacts made in PF plastics (some exemplary are reproduced in figure 2) are reported as follows in reference [4]:

*Any conservation treatments involving aqueous solutions should be avoided. When heated, formaldehyde plastics tend to darken and blister, but disrupted surfaces should not be abraded since this will tend to accelerate the rate of degradation. Plastics cast in pale colours discoulour and lose their gloss when exposed to ultraviolet light. Since the products of degradation include formaldehyde and ammonia, which may corrode metals, formaldehyde plastics should be stored separately from artefacts containing lead and zinc. Polyvinyl acetate adhesives can be used for repairs.* [4].

**FIGURE 2:** Artefacts in Bakelite of great historical and artistic interest.  
*Top-left:* Bakelite telephone – a common item in every office in earlier times [5].  
*Top-right:* the Sobell 439 Jelly Mould Wireless (Sobellette) walnut bakelite, from 1949.  
*Bottom:* Carving raft cast phenolic double inkwell stand, Art Deco style manufactured by J Dickinson of Great Britain (around 1946) [6].
The effects of UV light, moisture and pollutants, on Phenol-resins are hereafter summarized.

<table>
<thead>
<tr>
<th>UV radiation and excess light</th>
<th>Moisture (high relative humidity) and moisture fluctuations</th>
<th>Pollutants</th>
<th>Danger to neighbors</th>
</tr>
</thead>
<tbody>
<tr>
<td>discolored and more matte</td>
<td>discolored and more matte</td>
<td>fillers swell and surface mottles with solvents</td>
<td>phenol and formaldehyde with severe degradation</td>
</tr>
</tbody>
</table>

It is worthwhile to underline as PF resins with severe deterioration effects may release phenol and formaldehyde, which may cause degradation to neighbors objects; thus such a resins act as malignant materials.

Some suggestions about the conservation of objects manufactured in phenolic resins are given in reference [7]. Some of them are below summarized.

**Cleaning:** Usually should be performed by using washing soap in lukewarm water or alternatively a liquid cleansing agent. Detergents containing abrasive agents should be not used to avoid surface scratching.

To keep the original sheen it can be conveniently used a polish commonly used for furniture or a silicon-based spray.

In some cases the surface of the items has been coated with paints or varnishes. To ripristinate the original state such a coating must be removed. This can be afforded by using suitable solvents containing chemicals as for example di-chloromethane or methanol. In doing this operation the use of caustic soda solutions must be avoided as this agent may react with cellulose fillers.

**Scratches repairing:** The use of a dense polish or a formulation based on bee wax to fill the scratches represents the simplest method to be followed. In some cases pigments or colorant can be mixed with the polish or wax.

**Cracks restoring:** For such operation cyano-acrylates adhesives can be used.

Cyanoacrylate, <a very strong adhesive, particularly when used to bond non-porous materials or those that contain minute traces of water> is sold as liquid oligomer or pre-polymer that in presence of air moisture or of a suitable catalyst rapidly sets, in situ, <forming long, strong chains, joining the bonded surfaces together> [8]. Cyanacrylates are capable <to bond to a wide variety of surfaces to give a very fast and strong bond> [8].

The molecular structure of methyl 2-cyanoacrylate and ethyl 2-cyanoacrylate monomers used to manufacture the cyanoacrylate glues are hereafter described.

The rections of polymerization and setting of cyanoacrylate glues are schematically shown in figure 3 [8].

In case of large cracks it is convenient to fill the voids, before the application of the cyanoacrylate glue, with cellulose plaster [7].

The restored area should be suitably painted.
FIGURE 3: Polymerization and setting of cyanoacrylate adhesives [8].
REFERENCES

CHAPTER-SIXTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (VINYL CHLORIDE)

A.) HISTORY, SYNTHESIS, PROCESSING, PROPERTIES AND APPLICATIONS

A.1) HISTORY

Polyvinyl chloride, IUPAC denomination Polychloroethene (PVC), commonly referred to as “vinyl-resins” is obtained by a free radical addition polymerisation of the monomer, vinyl chloride, according to the hereafter shown scheme (in the bottom figure, representing a model of the PVC chain, the carbon atoms are in black, the hydrogen in white and the chlorine in grey).

The history of PVC can be traced back on the 19th century when the French chemist Henri Victor Regnault and Justus Baron von Liebig (figure 1) in 1835 discovered the first method for the preparation of vinyl chloride (VC) starting from ethylene (figure 2). Nevertheless it must be pointed out as almost 100 years had to pass before first industrial production of PVC was started in 1928 in USA and 1930 in Rheinfelden, Germany [1,2,3].

On 1872 E. Baumann, a German chemist found that the CV exposed to sunlight transforms in an insoluble solid mass. He could not understand at that time that the light had induced the polymerisation of VC to polyvinyl chloride.

The second procedure for the preparation of CV was developed in 1912 by the German chemist F. Klatte at the Chemische Fabrik Griesheim Elektron. Klatte was able to synthesised VC by reacting gaseous hydrogen chloride (HCl) and acetylene in presence of metal chloride (see figure 2) [1].

The chemistry of the main steps concerning the processes of CV synthesis, together with some more up to date innovative variants, is described in figure 2 [1].

The main characteristics of CV, a gas at room temperature and at normal pressure, are described in table 1 [4].

In 1913 F. Klatte of the German chemical company Griesheim-Elektron polymerised VC with organic peroxides and described the processing of PVC as a substitute for horn and for films, fibres and lacquers.
**FIGURE 1:** Henri Victor Regnault (1810–1878), the French chemist and physicist (Left) and (Right), the German chemist Justus von Liebig (1803–1873) that in 1835 discovered the vinyl chloride.

\[
\text{From ethylene} \\
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{Cl}_2 & \longrightarrow \text{ClCH} = \text{CH}_2 \text{Cl} \\
& \quad \text{1,2 dichlorethane} \\
a) \text{ treatment with caustic soda or potash} \\
\text{ClCH} = \text{CH}_2 \text{Cl} + \text{NaOH} & \longrightarrow \text{CH}_2 = \text{CHCl} + \text{NaCl} + \text{H}_2\text{O} \\
& \quad \text{vinyl chloride} \\
b) \text{ thermal or catalytic elimination of HCl} \\
\text{ClCH} = \text{CH}_2 \text{Cl} & \longrightarrow \text{CH}_2 = \text{CHCl} + \text{HCl} \\
c) \text{ treatment of trichlorethane with a metal} \\
\text{Cl}_2\text{CH} = \text{CH}_2 \text{Cl} + \text{Zn} & \longrightarrow \text{CH}_2 = \text{CHCl} + \text{ZnCl}_2 \\
& \quad \text{1,1,2 trichlorethane} \\
d) \text{ from sym. dichlorethylene} \\
\text{ClCH} = \text{CHCl} + \text{H}_2 & \longrightarrow \text{CH}_2 = \text{CHCl} + \text{HCl} \\
\text{From acetylene} \\
\text{ClH} = \text{CH} + \text{HCl} & \longrightarrow \text{CH}_2 = \text{CHCl} \\
\]

**FIGURE 2:** The main processes for the synthesis of vinyl chloride (VC) [1].
**TABLE 1: Some physical properties of vinyl chloride monomer [4].**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>-13.8°C</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless</td>
</tr>
<tr>
<td>Melting point</td>
<td>-153.7°C</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>158.4°C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>52.7 A tm</td>
</tr>
<tr>
<td>Specific weight</td>
<td>0.9121 at 20°C</td>
</tr>
</tbody>
</table>

In 1916 F. K. Ostromislensky, a Russian chemist working in Moscow, patented a process for obtaining rubber or similar substances from polymerised vinyl bromide, vinyl chloride or their methyl homologues. In his application he noted that the polymers could be prepared by the action of sunlight from the monomer alone and also in solvent such as benzene or carbon disulphide. Unaware of the influence of molecular weight on properties he divided his polymer product into α, β, and γ isomers and observed that the γ form, presumably with the highest molecular weight, did not dissolve in any solvent and had the best physical properties [2].

The attempts of Ostromislensky and Klatte to use PVC in commercial products practically failed because of difficulties in processing related to the rigid and brittle behaviour of the PVC at that time synthesised.

In 1918 a patent was issued to Du Pont [1] in which the procedure of polymerisation was described as follows:

< 26 parts by weight ( pbw ) of acetylene and 36.5 pbw of hydrogen chloride were mixed in an autoclave at 1-2 atm at 150-200°C. This yielded 36-37 pbw of VC. By further heating up to 90% of VC can be polymerised. The time can be reduced if the pressure is increased by introduction of nitrogen > [1].

The method presented as major disadvantage the large amount of heat evolved during the reaction that could not be easily dissipated. Such a heat produced thermal degradation effects on the PVC mass.

On 1922, J. Plotnikow, while working at the photochemical research laboratory of Agfa in Berlin, found that VC easily polymerises following exposure to the extreme ultraviolet rays of a quartz lamp (Photo-polymerisation). The synthesis was performed in solution of ethanol or methanol. PVC, being insoluble, precipitated as the reaction proceeded [1].

In 1926 Griesheim-Elektron allowed the PVC patents to lapse; this opened the door for other companies.

In 1926 Ostromislensky demonstrated that was possible to polymerise VC, placed in a hermetically sealed transparent container following exposure to ultraviolet rays produced by a mercury lamp. It was found that following an exposition of 12 hours at about 20°C about 90% of monomer was converted to a solid polymer; moreover it was found that the rate of conversion was dependent upon the intensity of the light [1].

The reaction could be also performed under sunlight in presence of soluble lead salts as catalyst. It was noticed that the reaction could occur also in presence of solvents (alcohol or mono chlorobenzene).
In 1926 Waldo L. Semon (1898-1999), from Hudson, Ohio, began working with PVC at the B.F. Goodrich Company in Akron. The researches of Semon were essentially finalized at finding out a cheaper formulation with performance similar to that of rubber but without its chemical instability.

At the beginning Semon <attempted to invent a method for converting a waste plastic (called polyvinyl chloride or PVC) into an adhesive that could bond metal to rubber. "People thought of PVC as worthless back then," Semon explained. "They'd throw it in the trash." Semon did not succeed with this venture, but through the process of heating the PVC he inadvertently discovered a substance that was both flexible and elastic. Applications for the PVC did not come along instantly, but over time the substance has become the world's second-best-selling plastic, generating billions of dollars in annual sales > [5].

![FIGURE 3: Waldo L. Semon, research chemist in 1937 working in the Research Laboratory (B. F. Goodrich)](image)

During the 1920s the chemical companies had to face the problem related to the fact that the PVC produced with the methods till that moment developed resulted difficult to be processed. <it>(PVC) does not soften until reaches 160°C and even then does not flow readily. It begins to decompose at about 180°C so that processing is quite a critical business > [2].

Moreover it was observed during the process, due to the heating, the release of toxic clouds of hydrochloric acid that in some cases exploded the transformation equipments used.
On 1928 the last patent dealing with photo-polymerisation of VC was issued to Du Pont [1]. The reaction of polymerisation occurred with VC in methanol solution and under a stream of a mixture of air and ozone.

On 1928 three groups of scientists, working independently, found a method to solve the above problem by developing PVC-copolymers with a lower softening point thus being much more easier to process.

< E. W. Reid, of Carbide and Carbon Chemical Corporation was the first to patent a copolymer between VC and vinyl acetate. Just one month later A. Voss and J. Dukhauser claimed a similar copolymer for I. G. Farbenindustrie and in the same period W. E. Lawson in his patent showed that Du Pont was ploughing a similar furrow > [2];

Those innovations represented the first real landmark in PVC industrial development.

On 1930 Staudinger introduced the concept of “mean molecular weight” for polymers.

On 1930 IG-Ludwigshafen copolymerised VC and vinyl ethers and acrylic esters; VC was emulsion-polymerised; PVC was stabilized with alkali salts.

On 1930 PVC was characterized by its K value (Fikentscher) that is a number calculated from dilute solution viscosity measurements used to denote degree of polymerisation according to the following relationship: \[ \log \left( \frac{v_s}{v_0} \right) = K \] where: \( v_s \) = viscosity of solution; \( v_0 \) = viscosity of the solvent and \( c \) is the concentration in g/ml.

On 1932 PVC was chlorinated (IG-Bitterfeld).

In 1933, a U.S. patent was issued to Waldo Semon, titled “Synthetic Rubber-like Composition and Method of Making same” (U.S. No. 1,929,453). The researches and the achievements described by Semon represented the second main turning point of PVC technology [1,5].

In this patent Waldo Semon, claimed < the method of manufacturing a resilient rubber-like composition that comprises dissolving insoluble polymerised PVC at an elevated temperature considerably above RT in such proportions as to form a stiff resilient gel at ordinary temperatures and causing the composition to gel by cooling it > [7,1].

in effect Semon discovered that PVC mixed at relatively high temperature with a non volatile, high-boiling point, miscible solvents (e.g. o-nitrodiphenyl ether, dibutyl phthalate, tricresyl phosphate) on cooling assumes the characteristics of a rubber-like material whose properties were not dissimilar from those of the copolymers.

It must be pointed out that the PVC and the non-volatile solvents, being miscible from thermodynamically point of view form a single homogeneous phase even after cooling at RT. Essentially Semon set up a method to plasticize PVC by mixing it with specific additives. As result more flexible and more easily processed PVC materials could be produced, which immediately achieved extensive commercial importance.

It was also observed as the content of these solvents (plasticisers) influences the final properties of the PVC-based compound.

< An increased proportion of solvent in general gives a softer more resilient and more extensible product, whereas a decrease in the proportion gives a harder product of greater strength > [1].

The material developed by Semon was commercialised as “Koroseal” as substitute of rubber.

< Used initially for seals for shock absorbers, Koroseal soon appeared as a coating for fabric raincoats and shower curtains, as a flexible tubing for bottling plants, in suspended and watch straps, and as a coating for General Electric’s Flamenol insulated wire > [8].
Semon suggested for PVC a variety of uses, including waterproofing and flooring, plastic piping and also phonograph records.

The industrialization of PVC, following the above achievements, advanced almost contemporaneously in Germany and in USA.

On 1934 a PVC pilot plant was opened in Bitterfeld (600 tons/year), another at Ludwigshafen (the same year the Wacker developed the suspension process of the VC polymerisation). These plants began large-scale production on 1937 [2].

Of great relevance as far as the industrial development of PVC is concerned were the results of the research of the German G. Wick in (around the 1935) according to which it was possible to reach the conclusions that PVC may productively be processed only at relatively high temperature (≈ 160°C). Such a finding led to the necessity to built up dedicated and special equipments different from those used from rubber industry (e.g. rubber mills, etc.).

In 1935 rigid PVC was produced in semi finishing form at the Deutsche Celluloid Fabrik in Ellensburg, at Trisdorf and Bitterfeld. I. G. Farbenindustrie rationalized the sale of these products under the trade name Vinidur (by 1938-39 about 110 tons per month were produced at Ellensburg).

The development of the PVC industry in USA, followed the discovery of the copolymerisation and plasticization methodologies. The real break through of PVC history in USA occurs in early 1937 when ICI <began to investigate the process for the manufacture of the monomer (from acetylene and hydrochloric acid) and particularly the methods of its polymerisation</b> [2]. Some years later the Distillers Company developed on 1940 a method for obtaining VC monomer based on a catalysed cracking process of ethylene dichloride (CHCl=CHCl).

In December 1940 ICI, using an emulsion polymerisation process with a water soluble catalyst and a single-component emulsifying agent (see later), established first a pilot plant capable to produce 85 tons/year of PVC and later, on 1942, opened the first PVC production unit with a capacity of 450 tons/year [2].

On 1943 the ICI was able to produce at the pilot plant set up in Runcorn the <i>first commercial batch of granular PVC</i> obtained by suspension polymerisation process [2].

Around the end of 1943 “Distillers” <i>started up their pilot plant at Tunbridge, Kent, with a capacity of 75 tons/year, producing the monomer from ethylene dichloride and polymerising it to a new type of paste polymer which in later years acquired a world wide reputation</i> [2].

It must be underlined as during the Second World War the total production of PVC-based plastics, including those of plasticisers, enormously increased, both in USA and Europe (especially in Germany).

The discovery of PVC stabilization and related stabilizers agents greatly contributed to the PVC industrial growth as well as to the increase of application fields.

In such a contest the following steps need to be remembered:

1930- PVC was stabilized with alkali salts.
1934- Frazier Groff (Union Carbide) discovered alkaline earth soaps, and Carbide & Carbon Chemicals used lead salts as heat stabilizer for PVC.
Union Carbide and Goodrich manufactured PVC on 1936. Carbide & Carbon Chemicals used Dialky1 tin soaps as stabilizers.
1947 Barium, cadmium, calcium, and zinc soaps were synergistically combined [3].

In 1962 VC was bulk-polymerised in a two-stage reactor (in 1975, a one-stage reactor was used) by St. Gobain and Pechiney (Rhone-Poulenc).
A.2 ) Progresses in the polymerisation procedures of polyvinyl chloride

From industrial point of view PVC, according to the ultimate properties and applications desired, can be obtained by using four different processes of polymerisation:
--- Suspension;
--- Emulsion;
--- Bulk or mass;
--- Solution [9].

All the above processes are based on a free-radical mechanism of the VC polymerisation occurring in presence of initiators (generally organic peroxides).

A.2.1 ) Suspension process

It is a batch process in which droplets of VC monomer, stabilized by suitable suspending agents (e.g. water-soluble celluloses and polyvinyl alcohol) are suspended in water under strong stirring [10,11,12].
The first application of the suspension polymerisation procedure to VC is to be attributed to H. Berg (Alexander Wacker) who on 1935 described <a process for the preparation of granular or powder emulsion polymer of vinyl chloride> [11,1].

According to J. Irvine <Polymerisation is begun by monomer-soluble initiators, generally peroxides, that thermally decomposes to produce free radicals. Cooling is needed to control the temperature of the exothermic polymerisation reaction>[12].

With reference to the scheme depicted in figure 4 the PVC suspension process is essentially based upon the hereafter described phases [13]:
1) Demineralised water, VC monomer, catalysts (peroxides) and protective colloids (polyvinyl alcohol or cellulose derivatives) are fed into a reactors.
2) Strong stirring gives rise to the formation of drops of monomer (average diameter of 30 - 40 μm) being suspended in water. The suspending agents act as a protective layer that stabilises the droplets against coalescence.
4) The polymerisation reaction is initiated by the formation of radicals arising from the thermal decomposition of the water soluble organic peroxides.
Even though PVC is insoluble in its monomer nevertheless VC is able to form a coherent gel by swelling the polymer. Thus as the conversion increases polymerisation continues in the gel phase.
5) The termination of the reaction is usually accomplished by either adding a chain terminator and/or venting off the un-reacted VC to the recovery plant [13].

The main factors, which control the reaction and the final properties of the obtained resin, may be summarized as follows:
--- The degree of agitation and the content of aid-suspension agent control the particle size and particle size distribution of the polymer [12].
--- The polymerisation temperature (can be varied in the range between 45°C to 85°C) controls the molecular weight of the resin (at higher temperature PVC with lower molecular weight are produced) [12].
By controlling the reaction temperature it is possible to produce different PVC-grades with smooth molecular weight distribution [13].

**FIGURE 4:** Schematic view of the suspension process used for the polymerisation of vinyl chloride monomer (VCM) to polyvinyl chloride [13].

At the end of the polymerisation, first the un-reacted VC is removed by heating under vacuum, then the resin, in the form of granular beads (diameters in the range of 50-250 μm and K-values between 50 and 75) is recovered [12,13].

<... Depending upon the ultimate application, the product may be sold as (1) a non-stabilized polymer, usually in the powder form as it is obtained from the reactor; (2) a dry powder blend with additives and/or colorants; or (3) a pelletized compound. Suspension resins are used for both rigid and flexible formulations [10].

The suspension polymerisation process, suitable to produce both homo-polymers and copolymers with a wide range of molecular weights, is extensively used today (in the USA it accounts for ≈ 80% of PVC production) [10,11].

Normally the PVC obtained by suspension technique, to be transformed in usable products, must be compounded with several types of additives.
Broadly speaking, PVC, according to the type of formulation may be grouped in two large families of materials:
--- **Flexible PVC-compounds containing plasticisers**;
--- **Rigid PVC-formulations**, which do not contain plasticisers [12,13].

Both rigid and flexible compounds need to be heat-stabilised by means of suitable substances (stabilisers) to prevent thermal degradation during the processing operations [12]. PVC resins obtained by suspension technique may be used for both rigid and flexible formulations. As can be seen from the data reported in table 1 both the applications of PVC, obtained by suspension technique as well as the corresponding processing methods depend from the K value [13].

**TABLE 1**: Applications and processing techniques of PVC resins, obtained by suspension technique, according to their K values [13].

<table>
<thead>
<tr>
<th>K value</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>Bottle blow moulding, injection moulding, extrusion of rigid foil.</td>
</tr>
<tr>
<td>60</td>
<td>Calendered and extruded crystal clear sheet and profiles, blow moulding, injection moulding</td>
</tr>
<tr>
<td>65</td>
<td>Flexible, semi rigid and rigid compositions for extrusion and calendaring,</td>
</tr>
<tr>
<td>66-68</td>
<td>Extrusion of rigid pipes and profiles</td>
</tr>
<tr>
<td>70</td>
<td>Flexible medical compositions, flexible crystal clear extrusion for packaging film, profiles, injection moulding,</td>
</tr>
<tr>
<td>80</td>
<td>Flexible sheet, cables.</td>
</tr>
</tbody>
</table>

A.2.2) **Emulsion process**

According to M. Kauffman the industrial development of an emulsion process capable to be used in the polymerisation of VC to PVC should be ascribed to the researches of H. Fikentscher and some of his colleagues (Ludwigshafen laboratories of I. G. Farbenindustrie). The process was patented on 1931 [1,14].

Emulsion polymerisation becomes the most used technique to produce fine latex particles of PVC (0.1-1.0μ) suitable for the formulation of plastisols (< A suspension of a finely divided PVC particles in a liquid plasticiser which has little or no tendency to dissolve the resin at normal temperature but becomes a solvent for the resin when is heated. At the proper temperature, the resin is completely dissolved in the plasticiser, forming a homogeneous plastic mass, which upon cooling is a more or less flexible solid. Additive, such as fillers, stabilisers and colorants are also present > [15].) or organosols (< plastisols modified with volatile solvents or diluents which evaporate upon heating [15]>.

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In the case of emulsion polymerisation, carried out in water, the initiators are water-soluble. Emulsifying agents (soaps) are used to disperse, under vigorous stirring, the VC monomer in the water phase [16].

A typical formulation of an emulsion PVC polymerisation includes:

--- **Vinyl Chloride monomer**: 42% - 48%;
--- **Water**: 52% - 58%;
--- **Surface active agent** (alkyl sulphates, alkyl sulphonates, alkylbenzenesulphonates, dialkyl sulphosuccinates, alkyl ethoxysulphates, fatty acid soaps, etc.): 0.05% - 0.4%;
--- **Catalyst** (water soluble peroxides, persulphates): 0.05% - 0.1% [13].

The mechanism of the emulsion PVC polymerisation is described as follows in reference [13] (see also figure 5 and 6).

< The surfactant when dispersed in water is in the form of spherical or rod-like micelles. Those micelles reach a "critical micelle concentration" related to the minimum surface tension the system can reach. Conventional emulsion polymerisation is carried out at a concentration above the critical micelle concentration. When vinyl chloride is added to the aqueous micelle dispersion, most of it remains in the water as large droplets, but some of it is encapsulated in the micelles, which reach a diameter of 0.05 to 5 microns. Initiator radicals generated in the aqueous phase, diffuse into the micelles to continue the reaction producing PVC radicals. As polymer chains are formed, the micelles grow by the diffusion of monomer from the aqueous phase. At 2 to 3% polymerisation the PVC particles grow much larger than the micelles and absorb all the emulsifier. Further polymerisation takes place within the polymer particles. Agitation is therefore needed to avoid the coalescence and separation of the monomer. Polymerisation continues in the polymer through diffusion of the monomer... the polymerisation reaction is strongly exothermic. The reaction is terminated by either adding a chain terminator and/or venting off the non-reacted monomer to the recovery plant. PVC lattices are colloidal, milky, dispersions of spherical particles in water, ranging in size between 0.1 and 3.0 μm. Most PVC lattices when dried and milled result in fine powders, made up of agglomerates of particles of 5 - 50 μm diameter. When mixed with plasticisers they disperse readily to form stable suspensions. During mixing most of the agglomerates are broken down into the original latex particles. Such dispersions of fine particles in plasticisers are known as plastisols or pastes > [13].

Thus the end product of the emulsion polymerisation is stable latex, which is stripped of excess VC. Such a product is spray-dried to form finished PVC with an average particle size of 1-10 μ.

PVC in a fluid form, as in plastisols or organosols, is usually manufactured through the hereafter-reported processes:

--- **Spread coating**
For applications as:
--- Thin, hard exterior coatings for residential home siding;
--- Thick, soft foamed upholstery fabrics;
--- Decorative printing and surface effects [16].

--- **Slush moulding and rotational casting**
To produce:
--- Hollow items (boots, dolls, play balls, automotive armrests and headrests) [16].
**FIGURE 5:** Mechanism of the emulsion polymerisation of vinyl chloride, see text for explanation [13].

**FIGURE 6:** The scheme of the emulsion polymerisation of vinyl chloride [13].

--- *Dipping technique*
To apply protective coatings to various items (tool handles, glass bottles, etc.). Moreover with such a technique *the plastisols can be stripped from a mould as in the manufacture of unsupported gloves* [16] (see figure 7) [17].
**FIGURE 7**: Left - Protective gloves are made by dipping a hand shaped former into a paste of PVC and plasticiser (plastisols). The former is heated in an oven; the PVC dissolves in the plasticiser and on cooling forms a rubbery film of plasticized PVC in the shape of the gloves. This is stripped away from the former [17].

Right - A set of formers or shapes from which rubber gloves are made by dipping into latex [17].

--- Spraying
Such a procedure allows the coating of large and irregular items that would be impossible to dip (tanks, drum linings, anticorrosive sealants, etc.) [16].

---

A.2.3) **Bulk or mass process**

This solvent free two stage process is described as follows in reference [13] (see also figure 8).

Vinyl chloride and an initiator (persulphate, monomer soluble peroxide) roughly at 0.015-0.1% concentration, are charged and vigorously stirred in a vertical, stainless-steel autoclave (prepolymerizer) of 8-25 m³ capacity. The pressure in the polymerisation vessel reaches 10 bars. The initiation step consists of the formation of radicals.

\[ \text{CH}_2=\text{CH}-\text{Cl} + \text{catalyst} \rightarrow \text{CH}_2=\text{CH}^\cdot \text{Cl} \]

Rapid polymerisation takes place at 62 - 75 °C to give 60μm aggregated spherical flocks composed of 0.1 μm primary particles, which form the basis for seeds in the final PVC grain. Conversion is taken to 7 - 12% in about 30 min, by which time the initiator used is exhausted and the unreacted monomer is recycled.

The slurry from the prepolymeriser is discharged in a 12 - 50 m³ autoclave, with fresh initiator and more VCM... In the second stage the 0.1 μm primary particles making up each seed grow in size, fuse together to give the final grain of PVC of 130 - 180 μm diameter. The reaction is terminated at
a predetermined stage, either by adding a chain terminator and/or venting off the unreacted monomer to the recovery plant. ...PVC produced, cannot be processed unless it is compounded > [13].

Today the mass process provides about 10% of world PVC production.

**FIGURE 8:** Scheme of the process of bulk polymerisation of vinyl chloride to PVC (see text) [13].

A.2.4) **Solution Polymerization**

I. Ostromislensky through two patents, the first on 1912 and the second on 1926, demonstrated that VC may be easily polymerised in various solvents (bromobenzene, benzene, toluene, xylene, carbon disulphide, etc.) [1]. In solution polymerisation VC monomer is dissolved, together with catalyst, in a suitable solvent, which is a non-solvent for the polymer. Thus as PVC forms it precipitates and can be easily recovered. With such a process very pure polymers or copolymers, free of suspending agents, are produced. The disadvantage is related to the fact that the polymerisation rates are normally slower than for suspension or emulsion processes [18].
A.3) MOLECULAR, CHEMICAL AND PHYSICAL PROPERTIES OF POLYVINYL CHLORIDE

Some general molecular characteristics of PVC are hereafter summarised.

![Diagram showing isotactic, syndiotactic, and atactic configurations of a vinyl polymer-chain.](image)

**Figure 9:** The possible configurations of a vinyl polymer-chain.
In the case of polyvinyl chloride (the largest groups are the chlorine atoms) the allowed most stable micro-structure are the atactic and the syndiotactic. In the figure for sake of simplicity all carbon atoms of the chains lay in a plane perpendicular to the sheet [19]. In the case of the syndiotactic configuration the Cl groups are alternatively right and left in respect to the plane of the carbon atoms (central figure). In the atactic structure they are randomly positioned (figure at right), while in isotactic configuration Cl groups are all right or all left against the plane (left figure) [19].

1) The macromolecular chains of PVC (linear with a low number of short-chain branches), as obtained from polymerisation, are predominantly atactic, but with the presence of relatively short blocks along the chains with a regular syndiotactic configuration (see figure 9) [9,19]. Such a finding accounts for the observed low crystallinity in PVC whose fraction is around the 5% [9]. It has been found that the degree of crystallinity and then the syndiotaticity of PVC increase with the decrease of polymerisation temperature [13].

2) The molecular weight (Mw) of most commercial PVC is between 100,000 – 200,000, and Mn between 45,000 – 64,000 [9]. According to other sources the number-average molecular weights (Mn) vary from 30,000 to 75,000, with values of the degree of polymerisation between 500 and 1500 [13].
3) The presence along the macromolecular backbone of bulky and electronegative chlorine atoms determines a strong polarity of the PVC chains.

4) The crystallites, deriving from the association of the syndiotactic blocks, act as physical cross-links stable even at temperature higher than the Tg which, as can be seen by the dynamical mechanical curves shown in figure 10, is around 85°C [13]. This aspect accounts for the rubbery behaviour exhibited by PVC at relatively higher temperature as well as its thermoplastic behaviour and good mechanical properties [13].

5) The micro crystallites by forming a three-dimensional physical cross-linked network impart to plasticized PVC a viscous elastic flow behaviour resembling that of a lightly cross-linked rubber molecules [13].

**FIGURE 10**: Dynamic mechanical analysis of a sample of rigid PVC [13,20].

6) The glass transition temperature of non-plasticized PVC is dependent upon the polymerisation process. Its value, generally, falls within the range of 60-90 °C.

Some of the main chemical and physical characteristics of rigid-PVC and plasticized-PVC are summarized through the data panel shown in figure 11 [17].

The main application fields, referred to the years 1960s, are summarized according to the type of the PVC used as starting material, in figure 12 [17], while the most relevant general properties of rigid PVC are listed in table 2 [21].

The photo reproductions of early devices used to process PVC are shown in figure 13 [1].
Colour: Good.

General Physical Properties:
Unplasticized: tough and horny. Good impact strength.
Plasticized: soft; flexible; rubbery. Good dimensional stability.
Heavier than water (S.G. 1.20 – 1.60).
Water: Good resistance.
Heat: Thermoplastic. Good resistance to deterioration by heat, especially unplasticized.
Burns only with great difficulty.
Solvents and chemicals: Good resistance to acids, alkalis and most common chemicals and solvents, particularly unplasticized.
Light: Some deterioration in colour.
Age: Plasticized material may tend to stiffen.
Electrical: Good insulator, particularly in low frequency range.

**FIGURE 11:** General characteristics of rigid-PVC and plasticized-PVC [17].

**TABLE 2:** General properties of the rigid PVC [21,22].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1380 kg/m³</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>2900-3300 MPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>50-80 MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>20-40%</td>
</tr>
<tr>
<td>Impact strength</td>
<td>2.5 kJ/m²</td>
</tr>
<tr>
<td>Glass temperature</td>
<td>87 °C</td>
</tr>
<tr>
<td>Melting point</td>
<td>212 °C</td>
</tr>
<tr>
<td>Vicat temperature</td>
<td>85 °C</td>
</tr>
<tr>
<td>Heat transfer coefficient</td>
<td>0.16 W/m.K</td>
</tr>
<tr>
<td>Linear expansion coefficient</td>
<td>8.10-5 /K</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.9 kJ/(kg K)</td>
</tr>
<tr>
<td>Water absorption</td>
<td>0.04-0.4</td>
</tr>
</tbody>
</table>
(1) **Emulsions; pastes.**
Polyvinyl chloride emulsions and pastes are used for
dipping, casting spreading, slush moulding, etc.
Examples of Uses: Leathercloth; gloves; conveyor
belting; toys; dolls.

(2) **Moulding Materials.**
Polyvinyl chloride moulding powders, plasticized or
unplasticized, are produced for injection and compres-
sion moulding, and extrusion.
Examples of Uses: special-purpose hose and tubing;
cable covering; refrigerator parts; radio components.

(3) **Sheet.**
Polyvinyl chloride is produced as calendered sheet
(plasticized or unplasticized) in a range of widths and
thicknesses. All colours are available, and the surface
may be printed or embossed.
Examples of Uses: curtains; rainwear; luggage; hand-
bags; packaging; chemical tank linings; safety helmets;
display equipment; protective clothing.

(4) **Rod; tube; section.**
A wide range of diameters, in all thicknesses and pro-
files is produced.
Examples of Uses: Hose; industrial piping; handle
covering; beading.

**FIGURE 12:** Applications of PVC (years 1960s) [17].
FIGURE 13: Early machines used to process polyvinyl chloride [1].
Top-left: The "Iron Duke" calender made in 1849.
Top-right: The Willoughby Smith's apparatus for covering or insulating wire [1].
Bottom: A ram extruder used for making rigid PVC tube in Germany during the World War-II [1].
A.4) EARLY APPLICATIONS OF PVC

Representatives of the German Companies (Bitterfeld, Woflen and Ludwigshafen) jointly delineated most of the early applications of PVC on 1935 [23,1].

Interesting appears the classification of PVC applications made at that time by Ludwigshafen, which is hereafter reported [1]:

I) Without solvent

1.1) Without plasticisers
--- Moulded articles (combs, tooth brush-handles, spectacle frames, saucers, battery boxes, ecc.).
--- Surface lamination (paper, cork, wood) with thin films (cards, washable curtains, ecc.).
--- Blow articles (bowls, spectacle cases, brush backs, ecc.).
--- Blow articles (figures, dolls, ecc.).
--- Insulating films (electro-technology).

1.2) With plasticisers
--- Artificial leather (at the time in the experimental stage);
--- Cable (low and high tension cable using tricresyl phosphate and electrically superior plasticiser respectively);
--- Soft rubber (tubes and soft rubber articles).

II) With solvents

--- Adhesives;
--- Lacquer binders.

The following other applications were added to the above list by the Troisdorf Company:
--- Battery box separators;
--- Records;
--- Cap peaks;
--- Pipes for warm water transportation.

Application of PVC in the field of cable insulation were accounted for by its water and ageing resistance.
Uses of PVC as battery boxes were preferred because of its resistance to sulphuric acid.
Its ageing resistance accounted for the substitution of leather and rubber by PVC.
The good electrical properties of PVC together with its resistance against cold water explained its use as insulation film.
The application of PVC as adhesive films for wood was accounted for by the higher softening point and waterproof characteristics.
The substitution of celluloid films by PVC films in the field of wood and paper coating was mainly due to the better toughness and waterproof shown by the latter materials [1].
Interesting to note as in 1938-39 of the 110 tons per month of PVC (trade name Vinidur) produced by the I. G. Farbenindustrie at Ellensbarg (German) about 20 tons were used for making batteries and 10 for gramophone records [1].
The photo-reproductions of objects in PVC produced at the beginning of the industrial history of such a material are shown in the figures 14-21.

**FIGURE 14-left**: Extruded gaskets, permanently flexible, in polyvinyl chloride, which substituted rubber in many applications [24].

**FIGURE 14-Right**: *This 1935 Hawley Tropper had a thermoformed vinyl film on the surface* [24].

**FIGURE 15-Left**: *Following World war II, the plastisols were used to make realistic dolls* [24].

**FIGURE 15-Right**: Artefacts moulded of polyvinyl chloride, early 1940s [8].
FIGURE 16: the Carbide and Carbon Chemicals Corporation first introduced vinyl phonograph records in 1933 at the Chicago world’s fair, “A Century of Progress”.
< Vinyl records were introduced and marketed as the unbreakable record, unlike its shellac counterpart of days gone by, that would break at the drop of a hat and becomes more brittle over time > [25].

FIGURE 17: Exemplary of toy, manufactured in soft and coloured polyvinyl chloride [26].
FIGURE 18-Left: Blow moulded bottles in rigid polyvinyl chloride [4].
FIGURE 18-Right: Sandals produced by injection moulding of plasticized polyvinyl chloride [4].

FIGURE 19-Left: Army raincoat waterproofed with polyvinyl chloride plastic paste (produced, in the 1940s by the B. F. Goodrich Company, Chemical Division) [24].
FIGURE 19-Right: Protecting overall in polyvinyl chloride plasticized [4].
FIGURE 20: Top-left - A stack of pipes in rigid polyvinyl chloride in preparation for a canalisation project.  
Top-right – An industrial filter in rigid polyvinyl chloride used for chemical operations [4].  
Bottom-left – A pipe in plasticized polyvinyl chloride reinforced with a nylon fabric for outdoor watering applications [4].  
Bottom-right – Flippers obtained by injection moulding of plasticized polyvinyl chloride suitable for under-water fishing [4].
A.5) POLYVINYL CHLORIDE TODAY APPLICATIONS, DEMAND AND CONSUMPTION AND PROCESSING

At present about 25 million tons per year of PVC is worldwide used. Such a performance is accounted for by considering factors as cost efficiency, durability, self-extinguishing properties, processability, lightweight, toughness and resources saving features presented by this polymer. <This breakthrough material was brought about to substitute for metals, glass, wood, natural fibers, papers and fabrics... Owing to its safe, healthy, convenient and aesthetical advantages, PVC products support daily life in a wide variety of fields including urban infrastructures, electronic products, and consumer goods> [27].

Now a days about 70% of world consumption of rigid PVC is for the construction market (pipe, fittings, siding, windows, fencing, etc.). PVC since long times has more and more <used as a replacement for traditional construction materials such as wood and metals, so its growth has been above that experienced by the overall construction industry> [28].
As far as flexible PVC is concerned (essentially used for film and sheet, wire and cable insulation, floor coverings, synthetic leather products, coatings and many other consumer goods) it can be observed that its demand <has declined in the industrialized world, but continues to rise in certain countries such as China and India> [28].

The distribution per country of world consumption of PVC is shown through the diagram reported in figure 22, while the pie charts in figure 23 show world consumption of flexible PVC and rigid PVC by end use (year 2008) [28].

**FIGURE 22:** Distribution by country of the World consumption of PVC (year 2008) [28].

**FIGURE 23:** World consumption of flexible PVC (right) and rigid PVC (left) by end use (year 2008) [28].
In the year 2008 rigid applications (pipe, fittings, film, sheet, windows, and siding) accounted for about 65% of total consumption of PVC. As shown in figure 23, flexible PVC today is mostly used for the manufacture of film and sheet, wire and cable insulation, floor coverings, synthetic leather, etc. [28].

Most of the success of PVC is attributed also to its versatility in being processed and manufactured according to various modalities. The today most up to date processing techniques of PVC, are hereafter listed and briefly described.

--- Extrusion process
PVC pellets, are fed into a heated barrel inside which there is one or more rotating screws suitable to compact melt and homogenize the PVC while conveying the material, softened by both friction and heat, continuously forward. The softened plastic is then forced out through a die designed to give the desired shape to the final product (finished or semi-finished) [29,30,31]. The product of the extrusion goes directly into cool water where it solidifies. Finally it is conveyed onwards into the take-off rollers [29,30,31]. The basic principles of extrusion are schematically represented in figure 24 [30].

![Diagram of Extrusion Process](image)

**FIGURE 24:** Extrusion is a process by which a molten plastic is forced to flow through a shape-forming die. When it emerges out of the die it inherits the shape of the die. Using extrusion, a wide range of shapes can be produced [30].

A process known as “Profile Extrusion” is used to produces PVC pipes. Such a process is described in figure 25 [31].
**FIGURE 25:** Design of a tubing die, component part of a process known as "Profile Extrusion" used to produce PVC pipes.

The die is a metal plate placed at the end of the extruder with a section cut out of its interior, this cut out, and the speed of the take-off rollers, determines the cross-section of the product being manufactured. A simple way to understand this concept is to consider squeezing a toothpaste tube; the product comes out in a solid rod because of the opening at the end of the tube, if that opening had a different cross-section than the product produced would take on that new cross-section [31].

---

**Calendering**

As extrusion it is a continuous process consisting of feeding PVC, pre-gelatinised and then kneaded to form a viscous material, to heated cylinders of a calender. Modern calender has four rolls of different sizes that turn in slightly different speeds to form laminates or films. *These laminates can be treated mechanically or may be oriented by stretching for the manufacture of rigid or plasticized sheets* [29], see figure 26 [32].

---

**Spread coating**

It is a process that consists of depositing one or more layers of plastisols on a support such as natural or synthetic fibers, blankets or paper. Afterwards, the deposited layer is gelled in ovens. This technique allows for the manufacturing of a broad range of finished products, such as synthetic leather for segments that include clothing, footwear, purses furniture, waterproof tablecloths, tarpaulins, conveyor belts, wallpapers, floor mats, etc.
FIGURE 26: Exemplary of a modern calender machine for foil and sheet and for laminated PVC [32].

--- Dip [29].
By dipping processes it is possible to produce hollow items in PVC as well as to coat fabric previously set in determined shapes (gloves), flasks and domestic utensils. The various types of dipping processes are below described.

i) Dip molding
Pre-heated mold (in metal, ceramic or glass) are dipped in PVC plastisols for a short period allowing the layer of paste deposited in its surface to solidify.

ii) Hot dip coating
With this method it is possible the coating of various items (soap dish, drip rack, tweezers, hooks, glass flasks), to protect them against corrosion or to improve appearance. Before dipping the items must be pre-heated.

iii) Cold dip coating
<It is used mainly for glove manufacturing with or without fabric support. The glove with fabric is put in a cold mould with the shape of a hand, and afterwards is dipped in plastisol. After the paste excess has dripped off, the mould is introduced in a gelation oven. This process is specifically the most adaptable to PVC resins for plastisols (obtained by emulsion and micro-suspension polymerization process) > [29].

A scheme describing the several phases of a Hot dip coating process is shown in figure 27 [33].
**FIGURE 27:** Schematic representation of the various steps (dipping a solid mold; gelling, fusing and stripping the hollow part) of a *Dip molding* process used for the manufacturing of hollows objects in PVC as that, of artistic value reproduced in figure 28 [33].

![Diagram showing the steps of a Dip molding process.]

**FIGURE 28:** *Designed by Robert Bronwasser and his Dutch design company – Smool, the Dip Vase is a functional and logical product. This cool form of interconnected cylinders looks like it is made of porcelain but is actually a soft unbreakable vinyl which has been formed with a dip-molding technique* [34].

![Image of a Dip Vase with flowers.]

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--- **Molding**

By this technology it is possible to apply a number of coloured layers in a pre-designed model (mould) (it includes labelling manufacture, automotive carpets, ecc..) \(< A \text{ layer of plastisol in a } \text{ determined colour is applied to the mould and taken to the oven for pre-gelation. Then, consecutive } \text{ layers of different colours are applied to the corresponding cavities, and are pre-gelated before } \text{ application of the following layer} > \) [29].

--- **Blown or Extruded Film**

**Blown Film**

By this technology it is possible to produce a wide range of PVC films by using one or more extruders.

PVC \(< \text{ pellets are fed to the hopper of the extruder, which use a rotary screw in a long steel } \text{ cylinder (the barrel) to transform the solid pellets to a molten form under high pressure} \) ... The molten plastic is forced under high pressure through a die in the shape of a horizontal ring. With conventional air ring systems, the plastic from the ring is drawn upward and expands outward a number of times to produce a film of less than .001" to .1". As the plastic is pulled vertically (known as the bubble), forced air surrounds the plastic. A high-pressure blower supplies the air ring. The plastic goes from the molten state to a solid material \(> \) [35]. The scheme of the process is shown in figure 29 [36].

![Diagram of Blown Film Process](image)

**FIGURE 29:** Basic blown film line [36].

---

**Extruded Film (Flat Die Extrusion)**

In such a case the film forming die is flat. \(< \text{ This film is led to a cooling cylinder and is readily coiled. Usually, it presents the same optical properties as a blown film and can be manufactured at faster speed} > \) [29], see figure 30 [36].
--- Injection Molding
Such a process, used for producing items from both thermoplastic and thermosetting plastics, is essentially based upon the following procedure (see scheme in figure 31):
- PVC is fed into a heated barrel, mixed, and forced into a mold metal (steel or aluminum) cavity where it cools and hardens to the configuration of the mold cavity.
- The halves of the molds are opened and the final article is taken off.
<Injection molding may produce more complex articles than extrusion, but it is not a continuous process. The products obtained are in their final shape and may be rigid or flexible, compact or expanded> [29] (see example in figure 32) [37].

--- Injection Blow Molding
<During a blow molding process, a melted PVC compound in shape of a vertical tube (parison) is extruded between two halves of a mould. This tube is inflated with air so it acquires the shape of the mould. The tube is cooled and when the recipient is totally formed, it is de-molded> [29].

--- Spray-Up
This technology is essentially adopted in automotive industry and is finalized at protecting the <lower part of the body and assure good sealing of joints. In both cases, plastisols are applied with the help of a spray nozzle> [29].
**FIGURE 31:** Scheme of the injection moulding process used also for polyvinyl chloride.

**FIGURE 32:** Boots made by injection moulding of polyvinyl chloride [37].

--- *Rotational molding*

This process, which uses fluid plastisols, is extensively applied in the production of hollow objects (toys, balls and garden furniture).

Plastisols are introduced in the mould. The mould is closed, put in an oven and turned vertically and horizontally. The mould that is kept spinning, distributes nearly melting plastisol over its walls by centrifugation, forming a film. After a determined period of time, the mould is taken out of the oven and carefully cooled to prevent shrinkage or torsion [29].
--- **Slush Molding**

It is a process that also involves the application of plastisol to a mould, but in this case the piece is gelated in hot bath, temperature around 200-230 °C..... The piece is finally de-molded. Applications for this process include automotive pieces and PVC masks > [29].

--- **Thermoforming**

Thermoforming is essentially a manufacturing process for thermoplastic sheet or film. As matter of fact this process forms objects from flat sheets, with the assistance of pressure and temperature. Thermoforming is widely used for the packaging of various types of products (food, cosmetics, hardware, toys, medicine, etc.). Thermoformed PVC blister packs are shown in figure 33 [38]. Thermoformed processes also manufacture thermoformed door panels in rigid PVC (see figure 34) [39].

**FIGURE 33-left:** Strong, reusable blister packs with easy opening and closing, having fully usable interior and excellent transparency > [38].

**FIGURE 34-right:** dedicated special thermoformed processes also manufacture thermoformed door panels in rigid PVC [39].
The tremendous success of PVC as demonstrated by the wide range of applications, and in so many different fields, may be accounted for by the peculiar properties and characteristics, which this polymer is capable to exhibit in relation also to nasty environmental operative conditions (mechanical toughness, resistance to weather, water and many chemicals, including strong mineral acids, intrinsic fire retardancy, electrical insulating properties, colourability, foaming, etc.).

PVC, due to its versatility can be transformed to give either rigid products of significant strength and hardness or flexible articles if compounded with suitable plasticisers. Moreover by using various additives its mechanical, physical and chemical intrinsic properties may be improved and tailored in relation of the final use requested.

The chemical stability and inertness of PVC, especially against acids, bases and most of solvents and liquids, together with its behavior in relation to gases and vapors represent another aspect that contributed to its success in many application fields, including those in which <the direct contact with food, drugs and with the human body, during medical practices is requested> [29].

Polyvinyl chloride based plastics exhibit, as proved by application in many and different fields (coatings, cables, pipes for water and sewer systems, windows, etc.), a rather unusual long use life. Thus it may be concluded that versatility, stability and longevity account for the success of PVC.

It must also be remembered the disadvantages, some which hereafter listed, presented by PVC:

--- Predisposition to decompose following exposure to light or heat;
--- Emission of toxic vapours following chemical degradation decomposition;
--- Tendency to behave as a brittle material, sensitive to impact at low temperatures, in the case of formulations having an inadequate content of plasticiser;
--- Migration of additives toward the surface which may cause deleterious effects to objects present in proximity (PVC behaves as a malignant plastics);
--- The need of using additives to mitigate some of the above-mentioned undesired effects determines the rise of processing and manufacturing costs.
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33) http://www.loven-sp.co.uk/how%20do%20we%20do%20it.htm, (2010).
CHAPTER-SEVENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (VINYL CHLORIDE)

B) USE OF ADDITIVES FOR PLASTICIZATION, STABILISATION AND TO IMPROVE PROCESSING AND PERFORMANCE CHARACTERISTICS

Since the early attempts finalized at find out possible applications of polyvinyl chloride (PVC) it was recognized the need of using suitable additives as "on its own it (PVC) was an useless material" [1].
The necessity of additives immediately rose following the observations:
1) That in the course of PVC processing, on heating "choking and corrosive clouds of hydrochloric acid were evolved" [1];
2) That artefacts in pure PVC were practically useless due to their fragility at RT [1].
3) The instability of the polymer material against environmental factors of degradation (especially light and oxygen) [1,2,3,4,5,6,7,8].

Thus all objects made in PVC have been (are) manufactured from formulations obtained by compounding the virgin polymer with various additives capable to aid the processability and to improve the final properties of such a material. Consequently the first step in the PVC technology consists, usually, in the preparation of compounds tailored to the processing and to the final applications (end uses) of the manufactured items.

"A wide variety of applications for PVC exist because one can tailor the properties by proper selection of additives" [2].
As matter of fact PVC by a proper combination with suitable additives (fillers, stabilisers, lubricants, plasticisers, pigments or flame retardant) may be processed to various types of finished products with a wide range of properties and then field of applications (for example: flexible and rigid medical devices; electrical cable insulation and sheathing, rigid and flexible pipes; foam and window profiles).
"As such, PVC is one of the most versatile and industrially important plastic materials around today" [3].

Many and different compounding processes, have been developed during the years finalized at mixing the PVC with additives (stabilisers, lubricants, fillers and pigments) and to produce a homogeneous dry multi-component formulation where all components are strongly bonded to the polymer particles.
The scheme of compounding process, called "Optimum Mixing Sequence", used for highly filled PVC formulations, is schematically described in figure 1 [9].
Hereafter some of the most common additives used for PVC, together with their chemical structure and function, are described.
FIGURE 1: The scheme showing the various steps of the so called “Optimum Mixing Sequence”, compounding process, used for highly filled PVC formulations [9].
B.1) STABILIZERS

It is well known that PVC is susceptible to degradation when exposed to the action of heat and light and oxygen. Those processes cause embrittlement, discoloration and ultimately a loss of physical properties (mechanical, electrical and optical properties) (see details in the next chapter).

Above 70°C loss of HCl occurs; conjugated double bonds are generated along the chains, and this explains the change of colour produced in the polymer mass. Most of processing methods part of manufacturing line of PVC, including compounding, embossing, extrusion, moulding, thermoforming, laminating, occur at temperatures (in the range of 160 to 200°C) where degradation by dehydrochlorination reaction is significantly active. To mitigate such an effect stabilisers additives are used. Stabilisers are also added to alleviate photo-oxidation degradation caused by the exposition of PVC artefacts to light in presence of oxygen (see details later).

The main functions of a stabiliser in the case of PVC processing are summarized as follows in reference [4]:

*The job of the stabilizer is to delay heat degradation so that the compound can be formed into a product before it degrades. The stabilizer does this job by absorption of hydrogen chloride, displacement of active chloride atoms, free radical scavenging, disruption of double bond formation, deactivation of degradation by products, peroxide decomposition and ultraviolet energy absorption > [4].

Quite often in the PVC compounds heat stabilizers are combined with other additives such as titanium dioxide to mitigate the long-term degradation effects following weathering [3].

The importance that was given to the stabilization of PVC, as a relevant problem to be solved to make this polymer as usable plastics, is demonstrated by the significant number of patents issued on this topic in the period 1928-1940. The corresponding various products suggested as suitable stabilizers for PVC are listed in table 1 [1].

F. Chevassus and R. Broutelle in their monograph “The Stabilization of PVC”, published in 1963, classified PVC stabilisers according to the following families:

--- Salts of mineral acids;
--- Salts of carboxylic acids;
--- Organo-metallic compounds (largely tin);
--- Other organic compounds of metals and metalloids;
--- Epoxies;
--- Amines of all types;
--- Esters (mainly organic phosphites);
--- Organic acids, alcohols and phenols [5].

Very recently a list including the most common today used stabilisers for rigid PVC, with some interesting comments, was published in reference [4]. This list is hereafter reported:

< 1) Lead Salts: Mainly organic lead compounds like sulphates, silicates, phosphites, stearates, phthalates and maleates. They are inexpensive and provide good heat stability, excellent electrical properties and low water absorption.
2) Calcium-Zinc systems: Used in food contact applications like blow molded PVC bottles, film
and sheet. PVC so stabilized can meet FDA requirements. The stabilization power of calcium-zinc in PVC is weak and, therefore, scrap rework capability is poor. They can provide compounds with crystal clarity and low odour properties.

ii) Barium-Cadmium systems—Plate-out tendencies, toxicity of cadmium and poor melt viscosity are characteristic of these stabilizers in PVC. They provide good early colour, light stability and heat stability.

iv) Tin Mercaptides—Most commonly used to stabilize rigid PVC in the U.S. They give good heat, light and colour stability, and promote fusion and reduce melt viscosity. The main type of tin mercaptides in use is methyl tins and butyl tins. These are used in pipe, pipe fittings, siding profiles, cellular vinyl and some bottles.

<table>
<thead>
<tr>
<th>TABLE 1: PVC Stabilisers as suggested by patents applied for between the two Wars (1928-1940)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amines</td>
</tr>
<tr>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>Lead salts</td>
</tr>
<tr>
<td>Removal of low molecular weight polymers</td>
</tr>
<tr>
<td>Cadmium laurate and other soaps</td>
</tr>
<tr>
<td>Phenol derivatives</td>
</tr>
<tr>
<td>Amino acids</td>
</tr>
<tr>
<td>Methyl and ethyl acrylate</td>
</tr>
<tr>
<td>Sodium salts of acrylic acids</td>
</tr>
<tr>
<td>Lead oxide</td>
</tr>
<tr>
<td>Aryl esters of benzoic acid</td>
</tr>
<tr>
<td>Alkyl or aryl tin or lead</td>
</tr>
<tr>
<td>Lead salts of phenol</td>
</tr>
<tr>
<td>Alkaline-earth alcoholates</td>
</tr>
<tr>
<td>α-pyroazyl ethylenes</td>
</tr>
<tr>
<td>Various mercaptides</td>
</tr>
<tr>
<td>Leads salts of 2,4-dihydroxyquinoline</td>
</tr>
<tr>
<td>Sodium salts of acrylic acids</td>
</tr>
<tr>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>Alkali treatment of polymer</td>
</tr>
<tr>
<td>Removal of low molecular weight polymer</td>
</tr>
<tr>
<td>Lead or silver oxides or hydroxides</td>
</tr>
<tr>
<td>Sodium and calcium</td>
</tr>
<tr>
<td>Product of lead salt with alkali metal salt</td>
</tr>
<tr>
<td>Metallic lead, tin and aluminium present during polymerisation</td>
</tr>
<tr>
<td>Amines</td>
</tr>
<tr>
<td>Morpholine, sulphydryl, xanthate</td>
</tr>
<tr>
<td>Cadmium laurate and ether salts</td>
</tr>
<tr>
<td>Organic bases</td>
</tr>
<tr>
<td>Inert metallic oxides</td>
</tr>
</tbody>
</table>
One type of tin mercaptide, di-n-octyltin, and methyl tin are FDA acceptable for food contact applications with PVC. Some of the newer tin mercaptides have external lubrication capability and this must be considered in compounding [4].

It can be observed that lead stabilisers in particular lead sulphate and lead phosphite are mainly used in pipes, profiles and cables, while cadmium-based stabilisers are essentially used for producing window frames. Compounds containing as stabilisers mixtures of mono- and di-organotin are used mostly in the manufacturing of rigid packaging film, bottles, roofing, and clear rigid construction sheeting [6].

Some more details concerning the molecular structure as well as efficiency of some of the most used stabilisers for PVC are below reported.

**FIGURE 2**: Effect of various cadmium and barium stearates on the degree of dehydrochlorination of PVC:
- (1) hydrogen chloride loss in absence of stearates;
- (2) hydrogen chloride evolved as gas in presence of stearates;
- (3) hydrogen chloride lost from PVC in presence of stearates;
- (4) hydrogen chloride absorbed by stearates;
- (5) hydrogen chloride absorbed by barium stearate;
- (6) cadmium stearate.
Dotted line indicates points at which stearates are theoretically fully converted to chloride [8].
**Cadmium/Barium-based Stabilisers**

In this systems, available since many years, cadmium (Cd) and barium (Ba) are present as stearate or laurate. Usually Ca/Ba stabilisers are also combined with lead stabiliser.

*Barium/cadmium stabilisers do impart excellent heat stability and outstanding weatherability to PVC compounds. They were used in semi-rigid and flexible foil for products such as roofing membranes and in rigid applications for outdoor use such as window profiles. In Europe, they have been replaced by barium/zinc stabilizers in foils > [10].*

Due to safety, health and environmental problems the use of Cadmium/Barium-based stabilisers is declining.

The efficiency of some cadmium/barium-based stabilisers (stearates), in use in the 1960s years, upon the degree of PVC dehydrochlorination is shown in figure 2 [8].

**Organotin-based Stabilisers**

This systems, based on tetravalent tin, considered as high performance stabilizers in the PVC-processing industry (all organotin stabilisers are very effective, and thus can be used at quite low dosages) are mono- and/or di-alkylts having the following general chemical formula:

\[
\begin{align*}
R & \quad \text{MonoAlkyl} \\
R' & \quad \text{Dialkyl}
\end{align*}
\]

Where the alkyl group R can be: Methyl, Butyl, Octyl or Dodecyl, and the ligand Y can be: Mercaptoester (e.g., thioglycolate), Carboxylate (e.g., maleate) or Sulfide [11].

The physical and chemical properties of organotin-based Stabilisers depend on the nature and ratio of the chemical groups linked to the tin atom. The organic groups can be linked to the central tin through a carbon atom (alkyl tin or, of butyl and octyl tin derivatives).

Alternatively other organic groups are bound to the tin through sulphur (organotin mercaptides) or oxygen (organotin carboxylates) atoms. It's important to point out that *this part of the molecule is the one effectively responsible for the mechanism of PVC stabilisation and determines the behaviour of the stabiliser itself during processing and its subsequent activity in the service life of the finished products.* [12].

According to the today nomenclature organotin stabilisers with at least one tin-sulphur bond in their molecule are generally called organotin mercaptides or sulphur-containing tin stabilizers or thiotins.

Organotin stabilisers, which are derivatives of carboxylic acids, mainly maleic acids or semi-esters of maleic acids are usually named as organotin carboxylates or sulphur-free tin stabilizers.

Some useful stabilizers are produced by reaction of mono- and di-alkyltinchlorides (see their molecular structure in figure 3) with mercaptioesters [11].

It has been observed that organotin mercaptides impart excellent early colour and colour hold in the most difficult processing of plasticized and rigid PVC [12].

Certain organotin-based stabilisers *are firmly bound in the plastic matrix and, consequently,*
migration or leaching from rigid PVC is insignificant. Because of this, and owing to their low mammalian toxicity, certain methyl-, octyl-, and dodecyl tin stabilizers are approved for use in food packaging materials [11].

It has been found that octyl tin derivates, have a very low toxicity and good migration resistance in rigid PVC, making them suitable and sanctioned by most national legislations as stabilisers for PVC in food contact applications or for potable water pipes and fittings [12]. Moreover organotin stabilisers allow a high degree of transparency in PVC articles, which is of particular interest in packaging and in some building applications [12].

![Figure 3](image-url)  
**FIGURE 3:** Chemical structure of mono- and di-alkyltinchlorides, which reacting with mercaptoesters form efficient stabilisers for PVC [11].

![Figure 4](image-url)  
**FIGURE 4:** Molecular structure of some organotin-based Stabilisers for PVC (mercaptide and organic tin sulfides and organic tin carboxylate and maleate) [13].
Finally it is interesting to note as *the sulphur-free organotin carboxylates, and in particular tin maleates, confer excellent light stability to finished goods intended for outdoor applications. They are however less efficient as heat stabilisers than the sulphur containing organotin mercaptides* [12].

The molecular structures of some organic tin heat stabilizer ( mercaptide and organic tin sulfides and organic tin carboxylate and maleate) are represented through the scheme reported in figure 4 [13]

**Lead-based Stabilisers**

Lead salts systems are between PVC stabilisers those used since the years 1930s that is at the beginning of the industrialization history of this polymer ( see table 1 ).

According to reference [14] *Lead compounds are the most cost-effective and common form of stabiliser used for PVC. Their stabilising effects are excellent and used for PVC products with long service life and required to endure longer fabrication ( heating ) hours. Although use has been decreasing, they still represent nearly 50% of total stabilizers used in PVC applications* [14].

**TABLE 2:** List of the most common used lead-based stabilisers for PVC [14].

<table>
<thead>
<tr>
<th>Type</th>
<th>Lead Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra-basic lead sulphate</td>
<td>85%</td>
</tr>
<tr>
<td>Tri-basic lead sulphate</td>
<td>82%</td>
</tr>
<tr>
<td>Di-basic lead phosphite</td>
<td>82%</td>
</tr>
<tr>
<td>Di-basic lead phthalate</td>
<td>75%</td>
</tr>
<tr>
<td>Di-basic lead stearate</td>
<td>51%</td>
</tr>
<tr>
<td>Normal lead stearate</td>
<td>28%</td>
</tr>
</tbody>
</table>
A wide large number of lead-based stabilisers, differing for chemical and molecular structure and performances have been used throughout the years. The most commonly used are listed in table 2 [14]. Some of the properties of PVC formulations containing lead-salts as stabilisers are hereafter listed:

--- Excellent heat and light stability.
--- Good electrical properties.
--- Excellent short and long-term mechanical properties.
--- Low water absorption.
--- Wide processing range.
--- Good cost/performance ratio [14].

More recently, following concerns about possible adverse effects of lead on health and the environment, the use of lead-based stabilisers will be reduced in stages and ended by 2015 [14]. The most used stabiliser systems for PVC in the 1960s, as it emerges as from literature data, are listed in table 3 [15].

**TABLE 3:** Some of the most used stabilisers for PVC in the years 1960s [15].

<table>
<thead>
<tr>
<th>Type</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead salts</td>
<td>Lead carbonate</td>
</tr>
<tr>
<td></td>
<td>Lead maleate</td>
</tr>
<tr>
<td></td>
<td>Lead phthalate</td>
</tr>
<tr>
<td></td>
<td>Lead stearate</td>
</tr>
<tr>
<td></td>
<td>Lead sulfate</td>
</tr>
<tr>
<td>Barium-cadmium synergistic systems</td>
<td>Laurate naphthenate</td>
</tr>
<tr>
<td></td>
<td>Octoate phenate stearate</td>
</tr>
<tr>
<td></td>
<td>Epoxidized soybean oil</td>
</tr>
<tr>
<td></td>
<td>Organic phosphite esters</td>
</tr>
<tr>
<td>Organotins</td>
<td>Dibutyl tin dilaurate</td>
</tr>
<tr>
<td></td>
<td>Dibutyl tin dimaleate</td>
</tr>
<tr>
<td></td>
<td>Dibutyl tin mercaptoates</td>
</tr>
<tr>
<td></td>
<td>Dioctyl tin analogs</td>
</tr>
</tbody>
</table>

As already written, the capacity to absorb hydrochloric acid (HCl) represents the most important function of heat stabilisers. As matter of fact it is well known that PVC at higher temperatures and in presence of oxygen tends to lose HCl molecules following an autocatalytic process whose main reacting steps are schematically described in figure 5 [15]. The mechanism of thermal degradation of PVC is based on the fact that once a molecule of HCl is released a double bond is formed, which is capable to destabilise the adjacent repeat unit. The reaction proceeds along the macromolecule, and at the end of the process a conjugated polyene macromolecule is obtained (see figure 5).
Stabilisers by absorbing HCl prevent both the formation of metal halides, following the reaction of HCl and the metal parts of the equipments used for the processing of PVC and the damaging effects, which released HCl may cause to surrounding objects sensitive to the acid degradation.

From all above reported it arises as the typology of stabiliser used for PVC changed in the course of the time; this may cause problems when conservation of PVC items have to be undertaken as the knowledge of the composition of the used formulation is an essential task to be preliminary afforded.

B.2) LUBRICANTS

The main functions of lubricants in polymer technology are summarized as follows in reference [17]:

--- Assist flow in calendering, moulding and extrusion by lubricating the metal surfaces in contact with the polymer compound;
--- Assist in knitting and wetting of the resin in mixing and milling operations;
--- Impart lubricity to finished products > [17].

Lubricants, according to their effects, characteristics and functions usually may be divided in external, internal, and external/internal.

External Lubricants
Usually are non-polar molecules or alkanes (paraffin waxes, mineral oils or polyethylene). Their
function is that of realising good release from metal surfaces and lubricate between the individual PVC particles and the metal surface [4].

**Internal Lubricants**
They are polar molecules very compatible with PVC macromolecules (the most used are fatty acids, fatty acid esters or metal esters of fatty acids). They are used to implement lubrication at the molecular level and between resin particles. Moreover, they have to reduce the melt viscosity [4].

**External/Internal Lubricants**
These materials provide both external and internal lubrication depending on the combination of chemical groups contained. The characteristics and the properties and the functions of such systems are depicted in reference [4] as hereafter reported:

<...they have chemical groups (polar and non-polar) of both lubricant types. In general, they have long hydrocarbon chains, along with amide, alcohol, acids and ester groups. Common types used in PVC are fatty acid amides and oxidized polyethylenes. Some of these materials will lubricate as an external lubricant before melting and as internal lubricants after melting. Others will do the reverse> [4].

B.3 **FILLERS**

Are relatively inert, non-fibrous, substances which are mixed to polymers essentially to implement physical and mechanical properties (especially, stiffness, hardness and impact strength) [17]. Fillers are also used to lower the raw material cost of the finished compounds. The most common fillers used in PVC-based formulations belong to the following families:

--- metal carbonates and silicates, gypsum, clay, alum, barites and saw dust.

<...The most common (fillers) are metal carbonates, mainly calcium carbonate (which is usually in the form of ground limestone) and coated with stearic acid. The coating reduces the abrasiveness of the calcium carbonate...... As a general rule, the finer the calcium carbonate, the better the impact strength of the finished product...... Normally, increasing calcium carbonate content reduces tensile strength and increases tensile modulus> [4].

B.4 **PIGMENTS**

Generally, the addition of pigments to polymer systems since the birth of the plastic industry is a very useful procedure to implement the resistance of plastics to photo-degradation processes.

In the case of PVC technology pigments are essentially used to:

--- Accomplish opacity in non-weatherable products;
--- Protect weatherable compounds from UV degradation effects;
--- Produce permanently coloured compounds [4].

In the case of rigid PVC compounds Titanium dioxide (TiO₂) is the most used pigments.

Other pigments in combination with TiO₂ are used in small amounts to realize the required colour.

As shown by figure 6 PVC coloured formulations are capable to be processed in finished products with a wide range of permanent and stable colorations [18].
FIGURE 6: PVC tile components <Manufactured from rugged and resilient PVC> used for <a modular replacement floor system that quickly restores and enhances surface appearance hiding unsightly stains and minor cracks in concrete floors> [18].

B.5) PROCESSING AIDS

Such an additives have the functions of:
--- Reducing or increasing melts viscosity;
--- Increasing frictional heat;
--- Reducing uneven die flow;
--- Lowering extruder temperatures;
--- Giving the melt hot strength for string-up and draw down [4].

The most common processing aids used with PVC are acrylic polymers. Alpha methyl styrene has also been used [4].

B.6) IMPACT MODIFIERS

Impact modifiers in general are additives capable not only to absorb the energy generated by impact events, but also to dissipate such energy via non-destructive processes [2].
The use of impact modifiers is of particular relevance in case of products to be used in special applications where higher impact strength than PVC are requested.
From the technical literature it emerges that polymer-based systems have been (are) normally used to modify the impact strength of PVC [4]. The major impact modifiers additives used in the case of rigid PVC are listed in table 4 [2].
In reference [4], concerning the effects of such additives it is pointed out as:
<All impact modifiers reduce the weathering, chemical resistance, tensile strength and stress rupture of PVC compounds. If these properties are desired, the lowest possible level needed to achieve the desired impact should be used> [4].
**TABLE 4:** The major impact modifiers
Additives used in the case of rigid PVC [2].

- MBS (methacrylate butadiene styrene)
- MABS (methacrylate/acylonitrile-butadiene-styrene)
- ABS (acylonitrile-butadiene-styrene)
- CPE (chlorinated polyethylene)
- EVA (ethylene vinyl acetate)
- PMMA (polymethylmethacrylate)
- EPDM (ethylene propylene diene monomer)
- EPR (ethylene propylene rubber)

---

**B.7) PLASTICISERS FOR FLEXIBLE PVC COMPOUNDS**

According to “The International Union of Pure and applied Chemistry” (IUPAC), plasticisers are defined as *< a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability or distensibility >* [19].

In a previous chapter of this book it was previously recognized as the development of suitable plasticisers systems, following the fundamental researches of Waldo Semon represented one of the most relevant landmarks in PVC technology.

As shown by the data in table 5, where the patents dealing with PVC plasticization issued in the period 1929-1938, are listed, already in 1929 two patents were granted to Du Pont concerning the use of diethyl phthalate or aryl ester of a poly alcohol as plasticiser for PVC.

The large number of patents deposited between the two Wars indicates the importance given to the topic by the chemical industry of the sector all around the world, and especially in USA and German.

From technical literature it comes out that in the year 1935 and several years later the additives based on tricresyl phosphate and dibutyl phthalate (see molecular structure and properties in figure 7 and 8 and in table 6 and 7 respectively) were widely used as plasticisers for PVC [1,20].

Plasticisers are usually divided, according to their grade of compatibility with PVC in:

--- Primary (compatibility ratio to 1/1);
--- Secondary (compatibility ratio to 1/3) [22].
TABLE 5: Patents dealing with PVC plasticization. In table are reported the application date of the early patents (1929-1938) as well as the system suggested [1].

<table>
<thead>
<tr>
<th>Application date</th>
<th>Plasticiser</th>
<th>Application date</th>
<th>Plasticiser</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.11.29</td>
<td>Diethyl phthalate</td>
<td>25.5.35</td>
<td>Benzoic acid derivs. of long chain aliphatic alcohols</td>
</tr>
<tr>
<td>21.11.29</td>
<td>Aryl ester of a polyalcohol</td>
<td>10.8.36</td>
<td>Esters of monaryl ethers of polyhydric alcohols</td>
</tr>
<tr>
<td>30.7.29</td>
<td>TCP and TTP</td>
<td>27.6.35</td>
<td>Wick’s discovery of pvc plasticisation</td>
</tr>
<tr>
<td>30.6.39</td>
<td>TCP and DBP among others</td>
<td>24.7.36</td>
<td>Subst. products of tetrahydronaphthalene</td>
</tr>
<tr>
<td>15.12.30</td>
<td>DBP and other phthalates</td>
<td>26.10.35</td>
<td>Alkyl or aryl polynuclear aromatic derivatives</td>
</tr>
<tr>
<td>17.9.32</td>
<td>Key patent on plasticisation of pvc</td>
<td>16.6.36</td>
<td>Diethylene glycol benzoate, etc.</td>
</tr>
<tr>
<td>6.11.31</td>
<td>DBP, TCP, glycol or glycerol esters</td>
<td>18.5.36</td>
<td>Benzyil stearate, palmitate olate, etc.</td>
</tr>
<tr>
<td>12.6.33</td>
<td>Phthalates esters, tributyl phosphate, etc.</td>
<td>30.4.37</td>
<td>Ester of polymerised acid</td>
</tr>
<tr>
<td>27.6.33</td>
<td>Softeners</td>
<td>26.3.34</td>
<td>TCP—main example for paste polymers</td>
</tr>
<tr>
<td>19.10.33</td>
<td>TCP, tributyl phosphate, DBP</td>
<td>9.8.37</td>
<td>Aromatic sulphides or polysulphides</td>
</tr>
<tr>
<td>26.3.34</td>
<td>Long chain esters of polyhydric alcohols</td>
<td>31.2.36</td>
<td>Phenoxy propene oxide etc.</td>
</tr>
<tr>
<td>20.11.33</td>
<td>TCP, DMP, triacetin, etc.</td>
<td>12.4.38</td>
<td></td>
</tr>
<tr>
<td>15.3.35</td>
<td>TCP</td>
<td>27.4.35</td>
<td>Esters of benzophenone carboxylic acids</td>
</tr>
<tr>
<td>12.4.38</td>
<td>Dibenzyl sebacate, etc.</td>
<td>8.5.36</td>
<td>Aromatic carboxylic acid esters</td>
</tr>
<tr>
<td>14.4.22</td>
<td>Diethyl phthalate</td>
<td>8.5.36</td>
<td>Benzoic acid esters</td>
</tr>
<tr>
<td>12.5.33</td>
<td>Acetate, succinate phthalates, di-2 ethyl butyl phthalate</td>
<td>25.3.35</td>
<td>Naphthalene or diphenyl derivatives</td>
</tr>
<tr>
<td>1.10.32</td>
<td>Phthalates</td>
<td>18.3.37</td>
<td>TCP</td>
</tr>
<tr>
<td>20.1.32</td>
<td>O-nitro diphenyl ether, DBP, TCP</td>
<td>26.7.35</td>
<td>Complex aromatic alicyclic plasticiser</td>
</tr>
<tr>
<td>30.7.36</td>
<td>Chlorinated diphenyl</td>
<td>18.3.37</td>
<td>Nitrate aromatic ethers</td>
</tr>
<tr>
<td>30.12.33</td>
<td>TCP, DBP, etc.</td>
<td>1.9.37</td>
<td>Sebacates, etc.</td>
</tr>
<tr>
<td>5.8.35</td>
<td>Triaryl phosphate</td>
<td>12.4.38</td>
<td>Dibenzyl sebacate</td>
</tr>
<tr>
<td>7.7.34</td>
<td>Long chain alkoxy-alkanol esters</td>
<td>2.8.38</td>
<td>Naphthalene or aryl derivatives</td>
</tr>
<tr>
<td>25.6.37</td>
<td>Organic sulphones</td>
<td>9.7.36</td>
<td></td>
</tr>
</tbody>
</table>
**FIGURE 7:** Chemical structure of the three isomers of tricresyl phosphate (CAS chemical name: phosphoric acid, tritolyl ester; relative molecular mass: 368.4). **Top**- 2.1.2 Tri-o-cresyl phosphate. **Bottom-left**- 2.1.3 Tri-m-cresyl phosphate. **Bottom-right**- 2.1.4 Tri-p-cresyl phosphate [20].

**FIGURE 8:** Molecular structure of dibutyl phthalate.
**TABLE 7:** Some physical properties of tricresyl phosphate and isomers [20].

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Tricresyl phosphate mixtures of isomers</th>
<th>Tri-o-cresyl phosphate</th>
<th>Tri-m-cresyl phosphate</th>
<th>Tri-p-cresyl phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting or freezing point (°C)</td>
<td>33</td>
<td>11</td>
<td>25.6</td>
<td>77-78</td>
</tr>
<tr>
<td>Physical state</td>
<td>liquid</td>
<td>liquid</td>
<td>half-solid</td>
<td>solid crystalline</td>
</tr>
<tr>
<td>Boiling point or range (°C)</td>
<td>241-255 (4 mmHg) 190-200 (0.5-10 mmHg)</td>
<td>410 (760 mmHg)</td>
<td>260 (15 mmHg)</td>
<td>244 (3.5 mmHg)</td>
</tr>
</tbody>
</table>

**TABLE 8:** Some of the properties of dibutyl phthalate [21].

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>C₁₂H₂₄O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>278.34 g mol⁻¹</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless oily liquid</td>
</tr>
<tr>
<td>Density</td>
<td>1.05 g/cm³ at 20 °C</td>
</tr>
<tr>
<td>Melting point</td>
<td>-35°C, 238 K, -31°F</td>
</tr>
<tr>
<td>Boiling point</td>
<td>340°C, 613 K, 644 °F</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>0.013 g/L</td>
</tr>
<tr>
<td>log P</td>
<td>4.72</td>
</tr>
</tbody>
</table>

*Primary plasticizers* are low volatility liquids whose polarity and other characteristics are such that they are sufficiently compatible with PVC not to be readily squeezed out of plasticized PVC by moderate pressure ≥[23].

*Secondary plasticizers* are low volatility liquids whose compatibility with PVC is such that they can be used along with primary plasticizers as part of the plasticizer system, but which exude if used as sole plasticizer ≥ [23].
In some special circumstances polymers, compatible with PVC are used as flexibilizer agents. Such "solid flexibilizer" include: nitrile rubbers, polyurethanes, polyesters, ethylene-carbon monoxide-vinyl acetate terpolymers, and some poly-acrylates [23].

Some of the most common effects of plasticisers on PVC properties are hereafter listed:
--- Decrease the melt viscosity;
--- Lower the glass transition temperature (Tg), see examples in figure 9 and 10;
--- Reduce the elastic modulus and tensile strength;
--- Increase the toughness;
--- Implement the processability [23].

A doing well plasticizer for PVC, has to be characterized by the following properties:
--- Cost-effectiveness;
--- Stability and colorless;
--- Miscibility with PVC and readily dispersible in the polymer matrix;
--- Low in volatility, odor and toxicity;
--- Good permanence in matrix;
--- No unfavorable interaction with other compounding components to avoid negative effects on the end-use properties of the product [23].

According to what reported in reference [23] the most common primary plasticizers used for the formulation of flexible PVC products may be divided in the following chemical families:
--- Dialkyl orthophthalates;
--- Alkyl benzyl phthalates;
--- Dialkyl tere-phthalates;
--- Epoxides;
--- Aliphatic carboxylic diesters;
--- Polyesters;
--- Phosphate esters;
--- Trimellitate esters,
--- Benzate and dibenzoate esters;
--- Alkyl sulphonic esters of phenol and cresol;
--- Miscellaneous types.

Dialkyl ortho-phthalate esters, whose general chemical formula is below described, are the most commonly used plasticizers in flexible PVC compounds.
In such a substances the <alcohols range from hexyl (C6) to tridecyl (C13), and may be linear or branched. Increasing the degree of branching in the alcohol gives a plasticizer with higher volatility, greater susceptibility to oxidation, poorer low temperature brittleness in PVC, and higher volume resistivity in formulated PVC> [23].

It is well known that plasticisers lowers the glass transition temperature (Tg) of rigid PVC (the presence of a small amount of plasticiser can lower the Tg of PVC from the value of ≈ 83 °C even to −40 °C).
The Tg of a polymer material, from a practical point of view, may be defined as follows:
< The temperature below which an amorphous polymer (or an amorphous region of a crystalline polymer) is rigid and brittle (glassy) and above which it is rubbery or fluid like > [24].

The industry of PVC made profit of this effect of plasticization on PVC as it was capable of producing both rigid (unplasticized) and flexible (plasticized) compounds for tailored, and different fields of applications (flexible pipes for garden hose; rigid pipe for domestic hot water transportation, see exemplary in figure 9).

**FIGURE 9:** Bitterfeld pipe samples in rigid PVC, production 1935-1940 [25].

**FIGURE 10:** Modulus against temperature for plasticized and unplasticized PVC compounds [24].
The shape of modulus-temperature curves, as shown in figure 10, for rigid and flexible PVC accounts for both the different mechanical behaviour as well as the range of use temperature of these materials and evidences also the drastic reduction in the value of the modulus at Tg.

The effectiveness of a given plasticiser may be also related to its capacity in reducing the value of the Tg of PVC. Differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA), as can be seen by the trend of the curves reported in figure 11 and 12 in case of samples of unplasticised PVC and of compounds containing the 10 and 20% of dioctyl phthalate (DOP) as plasticiser turn to be suitable techniques in assessing the variation of the Tg of PVC compounds with additive type and content [26].

**Figure 11:** DSC thermograms (10°C/min heating rate in aluminium open container), left, and TMA curves (an expansion/compression probe was used, load 3g), right, of samples of unplasticised PVC and of compounds containing the 10 and 20% of dioctyl phthalate (DOP) as plasticiser [26].

In the DSC traces (figure 11-left) the shift of the base line, accompanying the glass transition, for each of the samples can be easily detected. Moreover it can be seen as the values of Tg decrease with the increase of DOP content [Tg of PVC = 76°C; Tg of PVC (10% DOP) = 51°C; Tg of PVC (20% DOP) = 31°C]. At Tg the TMA curves present a change point of the expansion ratio. The variations of Tg are qualitatively in agreement with those coming from DSC [26]. The dependence of the Tg of PVC, compounded with two different plasticisers, namely dioctyl phthalate (DOP) and dioctyl adipate (DOA), upon the weight fraction of the plasticisers is shown in figure 12 [27]. It can be seen as both DOP and DOA determine a drastic reduction in Tg whose entity depends on the plasticiser content, and as well as on the molecular structure of the low-molecular weight component.
FIGURE 12: Dependence of glass transition temperature of PVC as function of plasticiser content and type (open circles refer to experimental data).

**Left:** PVC compounded with diocetyl phthalate (DOP).  
**Right:** PVC compounded with diocetyl adipate (DOA)

In both figures the curves refer to different mathematical model [27].

The comparison of the trends of the curves, Tg against % content, may give a qualitatively estimation of the relative efficiency of different type of plasticisers for PVC. For example from the diagrams shown in figure 13 one may establish that for the same content the DOP plasticiser is more effective than the other two plasticisers tested, namely DOP-SH and **DOP-SH** whose molecular structures are shown in figure 14 [28]. Thus it can be concluded that the molecular structure and functionality strongly influence the efficiency of plasticisers. Such aspect is commented as follows in reference [28]:

<For both functionalised additives, the glass temperature is progressively reduced with the grafted amount of plasticisers. Although the plasticizing efficiency in these systems is worse than that of conventional PVC-DOP mixtures... Another interesting aspect is the difference in the plasticiser efficiency between both isomers. In both cases, the lowest glass temperature was lower than room temperature. However, the PVC/DOP-SH series has lower Tgs than that of PVC**DOP-SH. This is probably due to the relative position of the ester groups in the aromatic ring. However, it should also be possible to explain this fact with the increase of generated free volume of DOP-SH with respect to **DOP-SH>> [28].
FIGURE 13: Variation of the glass transition temperature of PVC with the content of different types of plasticisers DOP, DOP-SH, and isDOP-SH (see the molecular structure in figure 14) [28].

FIGURE 14: Chemical structures of the plasticisers used for the experiments described in figure 13 [28].
It well known that plasticisers tend to migrate to the surface of an article manufactured in plasticized PVC. This causes serious problems, especially in the case of items used for biomedical applications, packaging purposes and toys for children, as additives migrated to the surface may produce poisonous and undesirable effects to person and animals. Moreover the migration of additives determines the progressive loss of the mechanical properties of the constituent material [28].

\textit{In many studies it is described that DOP is liable of producing toxic and adverse effects, especially in animal or human tissues such as the pituitary gland, liver, or testicles. For this reason DOP is one of several phthalate plasticisers that has been recently (February 10, 2009) banned by the U.S. Consumer Product Safety Commission (CPSC) for the manufacture of child care articles and toys containing phthalates} [28].

Many approaches were developed during the years to reduce the process of migration of plasticisers from flexible PVC objects and then their release to the environments. The principles of some of the procedures tried are hereafter briefly summarized.

1) Cross-linking of the article surface in order to create a barrier to leaving go of the additives. Such an approach has been based essentially upon the following measures [28]:
--- Surface modification of articles with peroxides, azides, sulphides or acrylates;
--- Physical treatments of the surface with γ-radiation or plasma exposure.

2) Substitution of the conventional plasticisers with oligomeric biocompatible substances as: functionalized poly ethylene oxide (PEO) or poly(ε-caprolactone) or their combinations.

3) The linkage through covalent bonds of the additive molecules to the PVC chains.

Usually the migration tendency of the plasticisers is assessed by extraction experiments using heptane as solvent at room temperature. The method, applied for PVC compounds containing the plasticisers mentioned in figure 14, is described as follows in reference [28]:

\textit{In order to quantify the amount of migrated plasticizer, strips of the plasticized films were placed in a flask containing heptane and a small amount of 1,6-hexamethylene diisocyanate as internal reference. From time to time aliquots of the solution were extracted and the amount of plasticiser determined by IR spectroscopy} [28].

As shown by figure 15 in the case of the system PVC/DOP almost all amount of plasticiser is lost after less than 3 hrs. On the contrary, the loss of plasticiser in PVC mixed with thiol-functionalized DOP is practically zero. This behaviour is accounted for by assuming that the DOP-SH plasticiser is covalently linked to the polymer chains [28].

From the above cited study it comes out that it is possible by tailoring the chemical structure of additives to realize plasticisers able to guarantee plasticization of PVC and at the same time, being covalently linked to PVC macromolecules, not capable to migrate to the surface of the related artefacts.
**FIGURE 15:** Extraction of plasticized PVC sheets with heptane at room temperature.
*Top curve* - PVC plasticized with conventional DOP.
*Bottom curve* - PVC plasticized with a functionalised additive, DOP-SH (see text) [28].

**B.8) ULTRAVIOLET LIGHT STABILIZERS**

Light Stabilizers are used in the case of PVC to minimize or mitigate:

1) **Change of appearances:**
   - Milkiness
   - Chalking
   - Darkening
   - Fading
   - Loss of gloss [29].

2) **Change of Mechanical properties:**
   - Elongation
   - Tensile strength
   - Impact strength
   - E-modulus
   - Hardness [29].
Light Stabilizers are especially requested when PVC is used as main material in the following applications:
- Roofing
- Glazing
- Sidings
- Profiles
- Decorative foils
- Floorings and more [29].

Both titanium dioxide (TiO₂) and carbon black, being capable to absorb the ultraviolet light, have demonstrated their effectiveness as light stabilizers for PVC.

From the technical literature it comes out that "the carbon black is a stronger absorber than titanium dioxide and can therefore be used at lower levels in PVC for protection" [30].

In special applications in transparent and also pigmented PVC, various derivatives of benzotriazole are used such as, 2-[2'-hydroxy-3',5'-(di-t-butyl)phenyl] benzotriazole.
Moreover in case of formulations containing tin carboxylate as stabilizers then hindered amine light stabilizers, with ultraviolet absorbers, seem to be effective [30].

The effect of recent light stabilizers developed by Ciba, in flexible PVC, measured by the variation of the Yellow Index (YI) with exposure time, is described by the diagrams shown in figure 16 [29].

![Diagram](image)

**FIGURA 16:** The effect of light stabilizers in flexible PVC, may be assessed by measuring the variation of the Yellow Index (YI) with exposure time. In figure are shown the performances of some light stabilisers developed by Ciba [29].

It can be noticed as the effectiveness depends both on type and % of stabilisers used in the compound.
B.9) **BIOCIDES AND FLAME RETARDANTS**

**Biocides**
Rigid PVC compounds are resistant against the attack by micro-organisms. On the contrary, plasticized PVC, in specific applications such as flashing and sealing boots on roofs, shower curtains, and swimming pools, may need protection. Many biocides, often containing arsenic compounds, are available for a balance of stability, compatibility, weatherability, and biocide effectiveness > [30].

**Flame retardants**
Due to the presence along the chains of chlorine atoms PVC is inherently flame retardant. Nevertheless, when PVC is diluted with combustible materials, the compound combustibility is also increased. For example, plasticized PVC with > 30% plasticiser, may require a flame retardant such as antimony oxide, a phosphate type plasticiser, or chlorinated or brominated Hydrocarbons > [30].

In the conservation of artefacts manufactured in PVC the knowledge of the type and content of the additives contained in the compounds used play an important role, as these substances may be the cause of several degradation processes. Moreover the conservation actions to be undertaken must be tailored according to nature and functionality of the additives present as components in the object to be preserved.
REFERENCES

CHAPTER-EIGHTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY ( VINYL CHLORIDE )

C ) METHODOLOGIES AND TESTS FOR THE IDENTIFICATION OF PVC AND ADDITIVES IN ARTEFACTS

Polyvinyl chloride ( PVC ), due to its relatively low cost, good performance and versatility, is used in many applications, and in various different sectors ( see figure 1 ) [1]. Moreover, and quite often, PVC in most of those applications results to be in competition with other polymers.

![CURRENT WORLDWIDE USES OF PVC](image)

**FIGURE 1:** Current worldwide uses of PVC. Distribution of PVC uses by application sector [1].

The identification of PVC as plastic component in artefacts, especially those which are part of private and public collections, may be complicated by the large number of additives contained in the starting compound ( fillers, plasticisers, stabilizers, colorants, etc. ).

Some of the laboratory tests, which make profit of the physical and chemical characteristics of polymers, as well as instrumental analysis methodologies, both suitable for the identification of PVC are hereafter described.

C.1 ) Laboratory tests for the identification of PVC

--- Water and Copper wire test

The water test is especially useful for recognize PVC from the other most common plastics used ( Polyethylene terephthalate ( PETE ), High density Polyethylene ( HDPE ), Polypropylene ( PP ) and Polystyrene ( PS ), see flow chart shown in figure 2 ) [2].
It takes advantage of the fact that, as shown in Table 1, both PVC and PETE have values of the density higher that that of water. Thus samples of these two polymers sink in water, while those of the other polymers listed in Table 1 float.

The samples are saved for the “Copper Wire Test” (also named as “Beilstein test”) which is described as follows in reference [2]:

"Obtain a piece of copper wire about 5 cm long. Push one end of the wire into a small cork. (The cork is used as a handle so you are not touching a hot wire.) Place one pellet or plastic sample near your Bunsen burner. This is the sample you will be testing. Hold the free end of the copper wire in the burner flame until it is red-hot and the flame no longer has a green colour. Remove the wire from the flame and touch the hot wire to the plastic pellet or sample you will be testing. A small amount of the plastic should melt onto the wire......

Place the end of the wire, with the small amount of plastic on it, into the flame. You should see a slight flash of a luminous flame (a yellow-orange colour). If the flame turns green in colour, then the sample contains chlorine > [2]."

It is interesting to point out as < rubber-like PVCs may be confused with rubber hydrochlorides. When in doubt, a carbon tetrachloride solubility test can be performed — rubber hydrochlorides are soluble in carbon tetrachloride while PVCs are not. The Beilstein test cannot be used for mineral chlorides. In addition, certain flame-retardants can produce false positives. When in doubt, measure the pH of the combustion vapour in the pipette — PVC vapour is very acid (pH < 1 ) > [3].

--- Test based on the pH of the combustion vapour

The procedure and the utility of this test are described in reference [3] as follows:

"The pH of the combustion vapour is a useful way of identifying plastics. A pH indicator strip is inserted in the tubular end of the pipette...... Before inserting them in the pipette, the strips must be wetted. The tubular end of the pipette is then sealed with modelling dough. The sample in the capillary end of the pipette is then heated. Since the combustion vapour is heavier than air, the pipette is laid flat on the work surface for a few seconds or minutes, depending on the size of the sample, so that the vapour can come into contact with the pH strip. The colour of the strip in the pipette is then compared to the pH reference scale provided with the strips. Refer to tables 2 and 3... for the pH values of the combustion vapours of most common plastics > [3]."

From the data reported in Table 2 and 3 it can be seen as PVC samples are characterized by pH values of vapours released from sheet materials during heating comprised between 0.0 and 0.5 [3].

--- C.2 Instrumental analytical methodologies for the identification of PVC

--- Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy

A typical Fourier Transform Infrared spectrum of un-plasticized PVC (ATR mode) is reported in figure 3, while the corresponding characteristics of the various peaks (wave number, type of vibration and corresponding group assignment) are shown in Table 4 [4].
**TABLE 1**: Densities of water and polymers (*) [2].

<table>
<thead>
<tr>
<th>Substance</th>
<th>Density g/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.0</td>
</tr>
<tr>
<td>PETE</td>
<td>1.38-1.39</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.95-0.97</td>
</tr>
<tr>
<td>PVC</td>
<td>1.16-1.35</td>
</tr>
<tr>
<td>LDPE</td>
<td>0.92-0.94</td>
</tr>
<tr>
<td>PP</td>
<td>0.90-0.91</td>
</tr>
<tr>
<td>PS</td>
<td>1.05-1.07</td>
</tr>
</tbody>
</table>

(*) To note that the density of plasticized PVC (1.19-1.35) is lower than that of rigid PVC (1.38-1.41).

**FIGURE 2**: Flow chart indicating the various tests used for recognizing one of the polymers between those listed in table 1 including PVC [2].
### TABLE 2: pH values of vapours released from sheet materials during heating [3].

<table>
<thead>
<tr>
<th>Material</th>
<th>Approximate pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC/PVDC</td>
<td>0.0–0.5</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>2.5</td>
</tr>
<tr>
<td>Polyethylene/Polypropylene</td>
<td>3.0–4.0</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>4.0</td>
</tr>
<tr>
<td>(Mylar)</td>
<td>4.5–5.5</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>5.5</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>9.0–10.00</td>
</tr>
</tbody>
</table>

### TABLE 3: Litmus and pH tests for combustion vapours of plastics [3].

<table>
<thead>
<tr>
<th>Litmus Paper</th>
<th>Red</th>
<th>pH Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5–4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0–5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0–9.5</td>
</tr>
</tbody>
</table>

- **Red**: Polyolefins, Polyvinyl alcohol, Polyvinyl acetals, Polyvinyl ethers, Styrene polymers (including styrene-acrylonitrile copolymers)**, Polymethacrylates, Polyoxymethylene, Polycarbonates, Linear polyurethanes, Silicones, Phenolic resins, Epoxy resins, Cross-linked polyurethanes.
- **Blue**: Polyamides, ABS polymers, Polycrylonitrile, Phenolic and cresol resins, Amino resins (aniline-, melamine-, and urea-formaldehyde resins).

* Slowly heated in a pyrolysis tube.
** Some samples show slightly alkaline behavior.
**FIGURE 3:** Fourier Transform Infrared spectrum of un-plasticized PVC (ATR mode) [4].

**TABLE 4:** Characteristics peaks for un-plasticized PVC, see figure 2 [4].

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Type of vibration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000–2840</td>
<td>stretching</td>
<td>CH(_2) and CH</td>
</tr>
<tr>
<td>1426</td>
<td>in-plane deformation</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>1332</td>
<td>wagging vibration</td>
<td>CH</td>
</tr>
<tr>
<td>1252</td>
<td>in-plane deformation</td>
<td>CH</td>
</tr>
<tr>
<td>958</td>
<td>stretching</td>
<td>C—C</td>
</tr>
<tr>
<td>876</td>
<td>rocking vibration</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>615</td>
<td>stretching</td>
<td>C—Cl</td>
</tr>
</tbody>
</table>
Raman and Infrared spectroscopy turn to be useful not only for the identification of PVC polymer as component in a given object, but also for detecting the presence of additives in the starting compound. Example of such application is given in figure 4 where the IR and FT-Raman spectra of pure PVC and PVC compounded with unknown plasticisers are compared [5].

![FT-Raman and IR spectra](image)

**FIGURE 4:** FT-Raman (left) and IR (right) spectra of pure PVC and PVC package (compound containing a plasticiser) [5].

The band at 1729 cm⁻¹, observed only in the spectrum of PVC package, and assigned to the C=O stretching is in agreement with the presence as plasticiser of diisooctyl phthalate (DOP) and/or of DOA (dioctyl adipate) whose molecular structures are depicted in figure 5.

![Molecular structures of DOP and DOA](image)

**FIGURE 5:** Molecular structure of two plasticisers containing in the molecule C=O groups [5].

To define the nature of the plasticiser present in the PVC-compound the following procedure was followed by the Authors of the study cited in reference [5]:

--- The plasticiser was first extracted from the mass by using tetrahydrofuran (THF) as solvent, and then it was precipitated out by addition of ethanol and finally recovered by filtration;
--- The FT-Raman (left) and IR (right) spectra of common used plasticizers DOP and DOA and the spectrum of the plasticiser extracted from PVC package were compared (see figure 6).
From the comparison of the spectra it can be concluded that <the spectrum of plasticiser extracted is similar to the spectrum of DOA (dioctyl adipate). The absence of the bond at 3071 cm\(^{-1}\) assigned to benzene ring mode in the FT-Raman spectrum of plasticiser extracted confirms that this compound is not DOP> [5].

--- Solid state 13C CP/MAS NMR

B. Garnaik and S. Sivaram, demonstrated that solid state \(^{13}\)C CP/MAS NMR is a powerful tool for the study of the interactions, at molecular level, between PVC macromolecules and plasticisers. Moreover such a technique results to be also very effective in recognizing both polymer and nature of additives in plastic objects based on PVC compounds [6].

The \(^{13}\)C CP/MAS spectra of solid sample of PVC and of PVC in solution with nitrobenzene-\(d_5\) are shown in figure 7-a and figure 7-b respectively. From such a spectra the specific chemical shifts of the polymer have been obtained and reported in Table 5 [6].

<The peaks appearing at 57.9, 56.9, and 55.9 ppm in the solution spectra (Figure 7-b) are assigned to syndiotactic, heterotactic, and isotactic placement of CHCl groups. Similarly, the peaks due to the CH\(_2\) groups of PVC appeared at 45.8 and 46.8 ppm, for which no assignment as to sequence configuration could be made. The solid state spectrum of the same sample (Figure 7-a) shows only two broad peaks at 56.7 and 46.2 ppm corresponding to the CHCl and CH\(_2\) groups, respectively> [6].
FIGURE 7: $^{13}$C CP/MAS NMR spectra of (a) PVC; (b) solution spectra of PVC in nitrobenzene-$d_5$ at 25 °C. Spectra labelled as c, d, e and refer to PVC-DOP compounds with different plasticiser content (wt%).

[ (c, 4.8% DOP); (d, 16.7% DOP); (e, 28.6% DOP); (f, 33.3% DOP) ] [6].
TABLE 5: $^{13}$C NMR Chemical Shifts of pure PVC (P1), of PVC-DOP compounds with different plasticiser content (wt%) 
[P2, 4.8% DOP; (P3, 16.7% DOP); (P4, 28.6% DOP); (P5, 33.3% DOP)]. In table are also indicated the Chemical Shifts of pure DOP [6].

<table>
<thead>
<tr>
<th>$^{13}$C atoms</th>
<th>$^{13}$C NMR chemical shifts, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DOP</td>
</tr>
<tr>
<td>C=O (ester)</td>
<td>167.2</td>
</tr>
<tr>
<td>aromatic</td>
<td>128.4</td>
</tr>
<tr>
<td></td>
<td>132.2</td>
</tr>
<tr>
<td>C1</td>
<td>67.6</td>
</tr>
<tr>
<td>C2</td>
<td>38.5</td>
</tr>
<tr>
<td>C3'</td>
<td>28.6</td>
</tr>
<tr>
<td>C5</td>
<td>22.6</td>
</tr>
<tr>
<td>C3</td>
<td>30.0</td>
</tr>
<tr>
<td>C4</td>
<td>23.5</td>
</tr>
<tr>
<td>C6</td>
<td>13.6</td>
</tr>
<tr>
<td>C4'</td>
<td>10.6</td>
</tr>
<tr>
<td>CHCl of PVC</td>
<td>56.7</td>
</tr>
<tr>
<td>CH$_2$ of PVC</td>
<td>46.2</td>
</tr>
</tbody>
</table>

B. Garnaiik and S. Sivaram applied the solid state $^{13}$C CP/MAS also to compounds obtained by mixing PVC with various amount of a plasticiser, namely the bis (2-ethylhexyl) phthalate (DOP), whose the molecular structure is described in figure 5. The plasticized PVC samples used for analysis were obtained as cast films from tetrahydrofuran (THF).

As shown in figure 7 and table 5 the $^{13}$C CP/MAS NMR spectra of PVC-DOP compounds show values of chemical shifts depending on the molecular structure of DOP as well as on plasticiser content. Such a results indicate that the technique may be effective in assessing the composition of PVC-based compounds.

From the study cited above it was also possible to reach the following conclusions:

$^{<13}$C NMR spectra, spin-lattice relaxation time $T1(C)$ and spin-spin relaxation time $T2(C)$ were obtained for various PVC-DOP samples. Line widths of CH$_2$Cl show a sharp increase due to the strong hydrogen-bonding interaction between the CDO (ester) group of DOP and CHCl of PVC with various concentrations of DOP. The spin-lattice relaxation time $T1(C)$ also confirms the presence of a strong interaction due to hydrogen bonding $> [6]$. In figure 8 is reproduced the $^{13}$C NMR spectra of pure DOP in CDCl$_3$ at 25°C. The chemical shifts assignments are correlated with the carbon atoms as indicated in the molecule of DOP [6].

For above it emerges the potentiality of the $^{13}$C NMR technique in recognizing additives following migration from PVC artefacts (see later).
FIGURE 8: The $^{13}$C NMR spectra of pure DOP in CDCl₃ at 25°C. The structure of Bis(2-ethylhexyl) Phthalate (DOP) is on the top side. The chemical shifts assignments are correlated with the carbon atoms as indicated in the molecule of DOP [6].

Very recently the Perkin Elmer announced the results of a research where it was explored the potential of Raman spectroscopy with a fiber-optic probe for in situ, non-destructive investigation of polymers used for the restoration of artefacts. The innovative system developed was described, and its applications commented, as follows in reference [7].

< Until recently the use of micro Raman (removing a sample from the object of study and placing it under the microscope) has been the most common technique used for examination of works of art. Some research groups have adapted fiber-optics to their microscopes but this method has never been used as a conservation tool to work within a building and/or with large objects, such as the stained glass windows in cathedrals. Nor is the presence in the market in recent years of a portable, low resolution system a solution to the problem; the resolution and performance are insufficient.

This application note reports the successful characterization of polymers, pigments and techniques used from past glass conservation treatments by means of Raman spectroscopy with a fiber-optic
probe using the high performance PerkinElmer® RamanFlex™ 400F instrument (see figure 9). This high resolution instrument can be fitted with a fiber-optic probe up to a hundred meters which makes it a useful tool for such applications > [7].

![Figure 9: PerkinElmer RamanFlex 400F with fiber optic probe for in situ analysis of artefacts composition including objects made in PVC [7].](image)

Equipments as that described in figure 9 may be also used for the identification of PVC and additives in plastics artefacts [7].

The basic parts of a portable Raman spectrometer are described in the scheme shown in figure 10 [8].

The <Transportation and mounting are easy, and the equipment is ready for use in ~10 min. The only required facility is an electric plug > [8].

![Figure 10: The scheme of a portable Raman spectrometer. The excitation source and scattered beam are collected by the optic fibre of the probe [8].](image)
With the development of portable and remotely operated spectroscopy systems suitable for 
*in situ* chemical analysis two main objectives are fulfilled:
1) The investigation of objects occurs in their storage environment or in the place where the object
is still in use (see for example the case in figure 11);
2) The analyses are non-destructive and non-intrusive.

Some of the advantages of Raman spectroscopy by using portable instruments are hereafter listed

--- Non-destructive and non-intrusive, no sample preparation is required;
--- The Raman phenomenon depends on molecular structure and physical form; identification of
chemical species and bonding interactions are possible;
--- Spectra are generally well resolved and with high information content;
--- Samples can be solids, liquids and gases, transparent or opaque;
--- In situ real-time and in-air measurement [8].

Fourier Transform Infrared Spectra (FTIR), as will be later discussed, is not only very effective in
identifying PVC in unknown objects but it results to be also very useful in following and assessing
active degradation processes.

**FIGURE 11:** Window frames in rigid PVC [9].
X-Ray Fluorescence Spectroscopy (XRF) and Energy Dispersive X-Ray Fluorescence (EDXRF)

The X-Ray Fluorescence Spectroscopy (XRF) and the Energy Dispersive X-Ray Fluorescence (EDXRF) technique are useful in to determine the types and quantities of certain additives in PVC being capable to detect many chemical elements of practical interest (Va, Cl, Br, Sb, Ti, Pb, Cd, Zn, Si, S, P, Ca and Fe) which are frequently found as components of many additives (pigments, stabilisers, plasticisers, flame retardant, etc.) [10].

In reference [10] is reported an application of the XRF technique to analyse the composition of a blue plastic used in automotive instrument panels and door panels [10]. The XRF Spectra obtained for the above unknown sample using conditions A (lighter elements) and B (heavier elements) are shown in figure 12. The characteristics of these spectra are commented as follows by the Authors.

<There is a large amount of Cl and smaller amounts of Ca, Ti, Fe, Ni, Cu, Zn and Pb. The amount of Cl is quantified using instruments from four participating manufacturers. The average amount of Cl measured by the four instruments is 27±4%. Fundamental parameters calculations on three of the instruments give an average Cl concentration of 24±1%. Results from inductively coupled plasma spectrometry (ICP) measurements give a Cl concentration of 19.0%. Such a concentration for Cl indicates that the material is likely a blend of ABS and PVC > [10].

**FIGURE 12:** XRF Spectra of blue automobile interior trim. Tests were conducted using an instrument with a pin diode detector and an Rh target. Condition A utilized an X-ray tube voltage of 10 kV, a current of 50 μA and a Kapton filter. Condition B utilized an X-ray tube voltage of 25 kV, a current of 40 μA and a silver filter. Peaks at 2.7 and 3.0 keV due to the Rh target and Ar are hidden by the Cl peak at 2.6 keV > [10].
The advantages of the X-Ray Fluorescence Spectrometry are hereafter summarized:
--- Non-destructive;
--- Minimal (or no) sample preparation;
--- It is a tool for detecting the presence of most elements heavier than Mg;
--- Results are quickly obtained;

For the results in reference [10] it comes out as:
< The techniques allow for relatively quick qualitative and quantitative analysis of certain elements that are common in ...plastics. The previous examples have demonstrated the use of XRF to look for PVC (Cl), flame retardants (Br, Sb and P), or regulated heavy metals (Pb, Hg and Cd) > [10].
REFERENCES

CHAPTER NINTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (VINYL CHLORIDE)

D) DEGRADATION PHENOMENA IN POLYVINYLCHLORIDE ARTEFACTS

Polyvinyl chloride (PVC), one of the first synthetic thermoplastic polymer, has become worldwide, over its more than 70 year history, one of the most largely used thermoplastics. In previous chapters we have seen as the processing and the use of PVC, necessitate compounding with several types of additives to realize the best combination of chemical, physical properties and cost effectiveness. By using suitable additives properties such as: flexibility, weatherability, surface hardness, colourability, density, impact behaviour, service temperature, and ecc. may be improved.

By tailoring the composition of the compounds (PVC + additives) it is possible to produce materials (can be either rigid or flexible) having different kind of functions and a wide array of final application uses [1].

The possibility of inducing deep modifications in the processing and properties of PVC by controlling the composition of the shaping formulations explains why PVC is used in countless applicative sectors (toys, pipes, constructions, automobiles, graphic art, ecc.).

**TABLE 1: A typical PVC-based formulation for manufacturing flexible items [1].**

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl Chloride Polymer</td>
<td>30 – 80%</td>
</tr>
<tr>
<td>Inert Fillers</td>
<td>0 – 40%</td>
</tr>
<tr>
<td>Heat Stabilizer</td>
<td>1 – 3%</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>0 – 60%</td>
</tr>
<tr>
<td>Colorant</td>
<td>0 – 40%</td>
</tr>
</tbody>
</table>

The complexity of the PVC formulations used for the production of objects (an example of a PVC formulation for flexible items is indicated in table 1) strongly influences the mechanisms of degradation as the additives may actively take part to those processes, and in some cases, with their behaviour, they may directly be the cause of deep phenomena of deterioration (an electron scanning micrograph showing the multi phased structure of a PVC-based compound is reproduced in figure 1 [2]). In such a latest contest it was already mentioned as in the case of PVC for flexible applications, phthalates, which can account for 15 to 60% of the weight of a product, are commonly used as plasticisers, and since those molecules are not chemically linked to PVC macromolecules, they can leach out producing negative effects to the polymer matrix. Moreover those molecules may come into contact with other artefacts stored in proximity giving rise to undesired chemical reactions (malignant effect) [3].
FIGURE 1: Scanning electron micrograph of the surface of a PVC-based compound. The distribution of additives is visible through the white dots dispersed in the PVC matrix; Surface shown about 0.2x0.2mm [2].

PVC may undergo degradation following three different processes. The first occurs essentially through Chemical degradation of the macromolecules, while the second and third are basically related to Physical degradation and Mechanical degradation respectively [4,5]. The mechanisms and the factors more effective in determining these events will be hereafter described and discussed in some details as the knowledge of their mechanisms and effects on the stability of material components of the artefacts in PVC are essential to put into action suitable conservation measures.

D.1) CHEMICAL DEGRADATION OF PVC

It is well known that when un-stabilized PVC is processed at high temperature it undergoes deep phenomena of chemical degradation. Chemical degradation in PVC occurs mainly through the rupture of covalent bonds determined by the effects of heat and light in presence of oxygen and also of other environmental chemical active factors. The chemical degradation process of PVC is quite frequently initiated by dehydrochlorination with loss of chlorine in the form of hydrogen chloride (HCl). This leads to the formation along the chains of a system of conjugated double bonds. Such an event is often followed by oxidation, cleavage of the macromolecular backbones and cross-links formation [1-5].
The reaction is autocatalytic in nature that is

< A type of degradation in which the breakdown products produced in the initial phase of degradation accelerated the rate at which subsequent degradation proceeds > [6].
Thus in the case of PVC, degraded following light exposure in air, the process of deterioration is accelerated by contact with gaseous HCl evolved from the breakdown of the polymer chains [4].

The most significant symptoms, which characterize chemically degraded PVC artefacts, generally are:

- Evolution of HCl in a gaseous form;
- Yellowing, darkening and discoloration caused by the formation of conjugated polyene sequences of 5 to 30 double bonds;
- Chain scission and cross-linking of macromolecules;
- Changes in physical and chemical properties of the resin [4,5,7].

The prevailing mechanisms concerning the chemical degradation processes in PVC (Thermal and Thermal Oxidative Degradation, Oxidation and Photo-oxidation, and Radiation induced degradation) are hereafter described.

D.1.1) THERMAL DEGRADATION OF PVC IN ABSENCE OF AIR (PRIMARY DEGRADATION)

PVC even in absence of oxygen when processed at high temperature undergoes dehydrochlorination: an Intrinsic-Specific Primary Chemical Process due to the occurrence along the macromolecular backbone of a long succession of alternating CHCl and CH₂ groups, which allows a series of multiple consecutive eliminations [7].

The presence of chemical defects along the PVC chains such as tertiary or allylic chlorine atoms seems to increase the degradation rates. Nevertheless it was noted that even in PVC free of structural irregularities thermal degradation is effective. Such a finding indicates that the process is an intrinsic property of this polymer [7].

Quite recently a mechanism, which seems to account for most of experimental literature data, was proposed for the dehydrochlorination process of PVC in the absence of air (so called "primary degradation") [7].

The various steps of this mechanism, looking at figure 2, a), b) and c), are described as follows in reference [7]:

--- < The first step is slow formation of a double bond randomly along the polymer chain via a 1,2-unimolecular elimination of HCl through a four-center transition state (see figure 2-a) or a six-center transition state in the catalytic presence of HCl or metal chloride like ZnCl₂ (see scheme in figure 2-b). Structural irregularities such as allylic or tertiary chlorine atoms eliminate much faster than do normal secondary chlorines in the chain.
--- < The second and third steps (see figure 2-a) of the processes constitute the chain elimination, regardless of the initiation site. In the second step, an HCl molecule is eliminated from a cis-alkyl-allyl chlorine through a six-center transition state, generating a conjugated diene or polyene.

Next is an HCl-catalyzed, 1,3 chlorine rearrangement, generating a new cis-alkyl-allyl chlorine from the conjugated polyene. The second and third processes may continue as long as HCl is still present in the system. Elimination of HCl stops the 1,3-rearrangement of chlorine and consequently, the reaction chain. This explains the very important role of HCl in PVC degradation [7].
FIGURE 2: The various steps of the mechanism proposed for the thermal dehydrochlorination of PVC in the absence of air (see text) [7].
In the thermal degradation of PVC in absence of oxygen it has been observed that following an induction time, the degradation rate, for high conversions, increases with time. Such a finding is in agreement with an autocatalytic process. *Hydrogen chloride formed in the degradation increases both the degradation rate and the mean number of double bonds in the polyene sequence, and consequently plays an essential catalytic role in PVC degradation* [7].

The final product of the thermal degradation of PVC is a relatively stable trans conjugated polyene (see figure 2-a) at bottom side.

**D.1.2) THERMAL DEGRADATION OF PVC IN PRESENCE OF OXYGEN: THERMO-OXIDATIVE PROCESS (PRIMARY DEGRADATION)**

During the common methods of processing PVC suffers effects of degradation deriving from the combined actions of factors such as:

--- The high temperatures;
--- The oxidative action of the oxygen;
--- The mechanical stresses, which may induce chain scission.

When the thermal degradation occurs in presence of oxygen then the process is usually named as thermo-oxidative degradation.

In reference [7] the overall process of degradation occurring in the course of the industrial transformation of PVC, looking at the scheme in figure 3, is described as hereafter reported:

*The most significant damage during the commercial processing of PVC occurs as a result of mechano-chemical reactions in the presence of entrapped oxygen. The shear forces cause chain scission, generating radicals. Thermally-initiated HCl loss is followed by radical oxidation of polyenes to form peroxy radicals and hydroperoxides. Hydroperoxides decompose to generate alkoxy and hydroxy radicals that accelerate the oxidation process and form ketones and acid chlorides. Ketoallylic chlorides initiate the thermal dehydrochlorination process,...... it is clear that thermo-oxidative degradation does not differ in any essential way from thermal degradation. Dehydrochlorination, the most important process, has the same mechanism in both types of degradations.* [7].

**D.1.3) SECONDARY PROCESSES IN PVC DEGRADATION**

--- Cross linking

In the case of PVC samples exposed to thermal degradation in absence of oxygen an increase in molecular weight accompanied by a widening of the molecular weight distribution with the maximum shifting toward higher values was observed. Contemporaneously the melt viscosity of the polymer mass increases [7]. These results were accounted for by assuming that at some stage of the degradation cross linking processes catalyzed by HCl occur.

From literature data it comes out that *the most important cross linking reaction is the Diels-Alder condensation* whose reaction scheme is shown in figure 4 [7].
FIGURE 3: The scheme of the thermo-oxidative and mechano-chemical reactions occurring in the course of the industrial transformation of PVC in the presence of oxygen (see text) [7].
According to this scheme <Benzene is formed in very small amounts even at temperatures as low as 160 to 170 °C by an intra-molecular process. At higher temperatures, substituted benzenes and condensed aromatic hydrocarbons are formed by radical scission of Diels-Alder condensation products and radical cyclization of polyenes >[7].

The same reactions take place also in the presence of oxygen, but under these conditions oxidative scission of the chain predominates, thus a decrease in the molecular weight of the polymer is usually observed.

**FIGURE 4:** the cross-linking reaction occurring during in the case of PVC samples exposed to thermal degradation in absence of oxygen (see text) [7].

In order to mitigate and control the series of degradation reactions occurring during PVC processing at elevated temperatures, as already written, stabilizers need to be added to the polymer mass aiming at preventing the dehydrochlorination reaction that is the primary process in thermal induced degradation.

The effectiveness of stabilizers may be assessed by studying the kinetics of the thermal decomposition of PVC by measuring, as shown by figure 5, the amount of HCl released by samples heated in closed ampoules at constant temperature values (180°C) for different times [8]. Alternatively the process may be followed through measurements of the yellow index (YI) of PVC samples compounded with different heat-stabilizers as a function of milling time (t) in the dynamic heat stability test on a two-roll mill at 200 °C (see example in figure 6) [7].

M. Beneš and others have demonstrated that techniques such as, thermogravimetry (TG/DTG) coupled with evolved gas analysis (MS detection) of volatiles and simultaneous TG/FTIR are effective for the study of the chemical processes active during the thermal degradation of PVC. The study was performed on samples taken from commercial PVC insulation cable (containing di-octyl phthalate (DOP) as plasticiser) heated in nitrogen and air from 20–800°C [9].
FIGURE 5: Influence of cadmium salts on the rate of the thermal decomposition of PVC at 180\degree\text{C} and of PVC with additives (concentrations of additives in mole/g of PVC) in closed ampoules:
1) 1.5x10^{-4} cadmium stearate (l) + 2x10^{-4} stearic or lauric acid; 2) 1.5-2.0x10^{-4} (l); 3) 1.5x10^{-4} (l) + 1.0x10^{-4} monochloroacetic or 2.0x10^{-4} succinic acid; 4) 1.25x10^{-4} (l); 5) 1.0x10^{-4} (l); 6) 0.75x10^{-4} (l); 7) PVC without additives in sealed ampoules; 8) 0.5x10^{-4} (l); 9) 1.0x10^{-4} cadmium sebacate and azelaate [8].

FIGURE 6: yellowness Index (YI) of PVC samples compounded with different heat-stabilisers as a function of milling time (t) in the dynamic heat stability test on a two-roll mill at 200\degree\text{C}.
a: dioctyltin-bis(isoocetylthioglycolate);
b: monoocytln-tris(isoocetylthioglycolate);
c: 80\% dioctyltin-bis(isoocetylthioglycolate) and 20\% monoocytln-tris(isoocetylthioglycolate) [7].
FIGURE 7: Results of TG/DTG, and EGA (MS detection) obtained during heating of PVC cable insulation sample in air.

a – thermogravimetry results are represented by curve 1 (TG) and curve 2 (DTG).

b – mass spectrometry results of the evolved gases HCl, \( m/z =38 \), \( \text{H}_2\text{O} \) \( m/z =18 \) and \( \text{CO}_2 \) \( m/z =44 \).

c – mass spectrometry results of the evolved benzene \( m/z =78 \) [9].

From the diagrams of TG, DTG and evolved gas analysis, EGA (MS detection), obtained during the heating of PVC cable insulation samples in nitrogen and air (see figure 7) the following conclusions were drawn:
--- A mass loss of 45.6% was observed in the range 200–340 °C on heating in both nitrogen and air;
--- From DTG curves it was possible to assess that the temperature of the maximal rate of this process occurs at 275°C;
--- This mass loss was accompanied by the evolution of HCl (m/z=36), due to dehydrochlorination of PVC;
--- Besides HCl, the release of benzene (m/z=78) and other organic compounds, like di-n-octyl phthalate DOP (m/z=149), used as plasticiser in the PVC sample was also detected in the temperature range of 200–340°C [9].

**FIGURE 8:** TG/FTIR results demonstrating the release of volatile products (phthalates, CO, CO₂, HCl) during the heating of PVC sample in air [9].
Thus it was possible to state <besides the dehydrochlorination and evaporation of some additives (e.g. plasticiser) the PVC backbone degradation took partially place in the first degradation step, i.e. in the range 200–340°C (maximal rate 275°C) both on heating in nitrogen and air> [9].

Moreover it was observed that the degradation of the PVC backbone, started in the range 200–340°C, is accompanied by the release of HCl, H₂O, CO₂ and benzene. The release of volatile products during heating of PVC sample in air (phthalates, CO, CO₂, HCl) was clearly assessed, as shown by the trend of the diagrams in figure 8, by using the TG/FTIR technique [9]. K. P. J. Williams and D. L. Gerrard established that also the FT-Raman spectroscopy could be a useful tool for studying the thermal degradation of PVC artefacts. In particular the samples analysed were taken from two types of PVC clad steel coupon used in roof applications.

**FIGURE 9-left:** FT-Raman spectra obtained from: (a) the white PVC; (b) the yellow PVC clad steel coupon, both prior to degradation; (c) sample of PVC resin as a reference [10].

**FIGURE 10-right:** FT-Raman spectra obtained from the yellow PVC clad steel coupon: (a) after thermal degradation at 140 °C for 3 hr; (b) prior to treatment; (c) difference spectrum (a)-(b) [10].
FIGURE 11: FT-Raman spectra obtained from the white PVC clad steel coupon: (a) after thermal degradation at 140°C for 3 hr; (b) prior to degradation; (c) difference spectrum (a)-(b) [10].

< One sample was white PVC containing titanium dioxide filler; the second sample was aztec yellow and contained an aromatic dye > [10].
The two samples were both exposed, in air, to thermal degradation at 140°C for between 3 and 6 hr.
The FT-Raman spectra of the two PVC clad steel coupons, preceding thermal exposure, together with that obtained from a sample of a commercial PVC resin, are shown in figure 9. It can be seen that the three spectra are substantially different. The Raman characters, which are supplementary to those observed in the case of commercial PVC resin can be attributed to the plasticiser (a phthalate), figure 9-a) and to the yellow dye, figure 9-b) [10].
The FT-Raman spectra obtained from the yellow PVC clad steel coupon and from the white PVC clad steel coupon, before and after thermal treatment, are shown in figure 10 and 11 respectively [10].
The yellow PVC clad steel after 3hrs of heating at 140°C showed some additional discoulouration. Moreover it was observed that the < spectral subtraction [Fig. 10(c)] shows distinct additional features at 1118 and 1492cm⁻¹ >, which are assigned to a (C–C) and (C=O) stretching vibration of a polyene sequence, respectively [10].

In the case the white PVC clad steel coupon it was observed that after thermal degradation at 140°C for 3 hr the FT-Raman spectral subtraction, as shown by figure 11-c), < apart from a general increase in the fluorescence level, no additional Raman features are observed.>
This indicates that the level of polylene formation is not as great in the white PVC clad coupon as for the yellow sample after similar thermal treatment. Indeed, polylene formation from the thermally degraded white coupon was apparent only after 8 hr at 140°C; after that time, significant plasticiser loss was also noted [10].

The above findings gave clear evidence about the following topics:

--- The thermal degradation of PVC is not only a function of the polymer but also of the additives [10];
--- PVC compounds even stabilized may undergo thermal degradation if heated at relatively high temperatures.

Moreover the results of the above-cited studies are a further demonstration of the necessity of using thermal stabilisers during the production of PVC artefacts. Of these later substances, as essential components of PVC products, conservators have to take concern in establishing a plane action finalised to the conservation of artefacts in PVC.

**THERMAL INDUCED BIO-DEGRADATION**

Studies, carried out by A. de Campos and S. M. Martins Franchetti, showed that PVC films, with 30µm thickness, pre-heated at 130°C become less resistant to biodegradation [11]. It was observed that these films, colourless and transparent, following thermal treatment changed to a pink colour suggesting degradation. This was revealed by UV-Vis spectra which shown the presence of polynes in the range of 450 - 650 nm (see figure 12) [11].

The UV-Vis spectra of PVC films exposed to the action of *P. chrysosporium* and *A. fumigatus* fungi showed only an increase of the absorbance intensity, because the film became opaque (see figure 13), while in the spectra of PVC film previously thermally degraded and then exposed to bio-treatments an increase of the absorbance intensity in the range of 450-650 nm, attributed to the absorption of polynes sequences on PVC matrix was observed (see figure 14). Such results indicated that the bio-degradation was effective only after the thermal treatment of the samples [11].
FIGURE 12-top: UV-Vis Absorption spectra of PVC film without treatment and heat pre-heated at 130°C [11].

FIGURE 13-center: Left: UV-Vis Absorption spectra of PVC film without treatment and of film bio-treated with P. chrysosporium/ A. fumigatus

D.1.4) PHOTO-OXIDATIVE DEGRADATION OF PVC ARTEFACTS [12-17]

Sunlight, generally, affects negatively many of the properties of materials. In absence of oxygen the process is named “Photochemical degradation”. The process of deterioration occurring as consequence of the combined action of UV radiation and atmospheric oxygen is defined as “Photo-oxidation”.

When pure PVC is exposed to ultraviolet ( UV ) or solar radiation it discolours becoming yellow/brown and brittle. It has been widely demonstrated that this discoloration, following photo-oxidation, is due to the formation of long conjugated polyene sequences in the polymer chains as a result of dehydrochlorination according to the below oversimplified scheme:

At first an isolated double bond is formed in the backbone chain. Afterwards this double bond acts as the preferred site for subsequent elimination of HCl which occurs increasingly rapidly via the so-called ‘unzipping’ reaction to form a conjugated polyene > [16].

It is interesting to point out that as dehydrochlorination proceeds at a certain critical level, due to the high reactivity of the long conjugated polyenes formed, cross-linking occurs via the type of free radical mechanism illustrated below [16].

According to the above mechanism two long polyenes combine to form four shorter polyenes [16].
The process described is significant, in terms of the physical and mechanical properties of the polymer, as *the cross-linking process leads to incompatibility between the PVC and its plasticiser causing the latter to be forced out onto the surface of the polymer* [16].

The rate and level of discolouration are strictly connected to the quantity of radiation absorbed. It is interesting to underline that even at atmospheric temperatures between 25 to 35°C, PVC artefacts exposed to direct sunlight can present, depending on the colour and time of exposition, buckling phenomena (see example in figure 15) [12].

![Figure 15: Photo-oxidation, together with moderate surface high temperatures, produces buckling effect on PVC pyramid roof lights [12].](image_url)

To mitigate the effects of light, oxygen and heat, especially when the items in PVC are to be used for exterior applications, generally stabilisers, tailored for the specific functions and application condition, are used. Special care is requested with coloured products for outdoor use with respect to light fastness. In the case of coloured PVC foam sheet it was found that:

*Short-term exposure should not cause noticeable changes to colour but consideration should be given to the choice of colour. Wherever possible do not use dark colours* [13].

The enhancement of PVC-based formulation stabilised against photo-oxidative processes, by using suitable additives, and thus capable to resist degradation over long periods of sunlight exposure, led to the production of compounds with a high weatherability. These achievements increased the utilization of PVC in many exterior applications, especially in building, as window profiles, cladding structure and siding [14].

To make sure of the weatherability of stabilised PVC-compounds usually they are exposed to accelerated weathering, in laboratory, test methods [14]. The resistance to photo-oxidation is then assessed by studying the chemical transformations induced in post treated samples by usual analytical instrumental analysis (FTIR, NMR, Raman Spectroscopy, ecc.), while the change in the average molecular weight values may be followed by viscosimetry.
**FIGURE 16:** The molecular structure of the photo-stabilizers used in the study reported in reference [14]:

--- (ON), 2-(4-nitro phenyl)-5-[4-(4-nitro benzoyloxy)-phenyl]-1,3,4-oxadiazole;
--- (OE), 2-(4-methoxy phenyl)-5-[4-(4-methoxy benzoyloxy)-phenyl]-1,3,4-oxadiazole;
--- (OC), 2-(2-chloro phenyl)-5-[4-(2-chloro benzoyloxy)-phenyl]-1,3,4-oxadiazole;
--- (OP) 2-(phenyl)-5-[4-(benzoyloxy)-phenyl]-1,3,4-oxadiazole [14].

**FIGURE 17:** Change in FTIR spectrum, in the range 4000-400 cm\(^{-1}\), of PVC film (control) (30 \(\mu m\)) at zero and after 250 hours (see text) [14].
An interesting example of the above approach is described in reference [14] were the weatherability of non stabilised PVC polymer films (30 μm thickness) is compared to those produced from PVC-compounds stabilised with UV absorber additives, all belonging to the family of the 2-(aryl)-5-[4-(aryloxy)-phenyl]-1,3,4-oxadiazole (see molecular structure and name in figure 16) [14].

As shown by figure 17, by comparing the FTIR spectrum of pure untreated PVC film with that exposed to artificial weathering for 250 hours it is possible to put in evidence the chemical modifications induced at molecular level [14].

It can be seen that the irradiation with light of wavelength, λ = 313nm gives rise to bands at 1772 cm⁻¹ and 1724 cm⁻¹, which are attributed to the formation of carbonyl groups belonging to chloroketone and aliphatic ketones respectively. Moreover it was also observed the appearance of a band at 1604 cm⁻¹ related to polyene groups.

The variation of the FTIR carbonyl and polyene index with irradiation time, for films of pure PVC and for films containing the 0.5% of the additives listed in figure 16 are described through the diagrams shown in figure 18 and 19 respectively [14].

It can be seen that in PVC film, manufactured from the compounds containing additives, the growth rate of the carbonyl index with irradiation time is systematically lower than that of pure PVC film. Moreover it can be noticed as the entity of mitigation depends upon the molecular structure of the additive used and as well from its concentration in the formulation. Also the growth rate of polyene index results to be lower for PVC-compounds. Nevertheless the influence of the chemical structure seems to be negligible, at least under the experimental conditions investigated [14].

To assess the influence of artificial aging on the average molecular mass of PVC the Mark-Houwink equation [η] = KM^α, which relates the intrinsic viscosity [η] with the viscosity average molecular weight M, was used. In the equation K, α are constants whose values, at a given temperature, depend upon the polymer-solvent system.

It is well known that <the relative change in viscosity average molecular weight M has been shown to provide a versatile test for random chain scission> [14].

As expected the viscosity average molecular weight Mw, both for pure PVC and stabilised compounds, decreases with the time of artificial aging. Moreover, as shown by trends of the curves shown in figure 20, the degree of degradation seems to be, for the same irradiation time, larger in the case of pure PVC. Such a result indicates that the investigated stabilisers are effective in mitigating chain rupture processes [14].

The Photo-stabilization of PVC by the 2-(Aryl)-5-[4-(Aryloxy)-Phenyl]-1,3,4-Oxadiazole molecules is attributed essentially to the ring of 1,3,4-oxadiazole, which is capable to act as UV absorber according to the scheme in figure 21-top.

< The UV light absorption by these additives containing 1,3,4-oxadiazole dissipates the UV energy to harmless heat energy (see scheme in figure 21-top). Furthermore this ring play a role in resonating structures conjugation of radical in peroxide decomposer, which support these compounds as photo-stabilizer> [14].

The attraction between the stabilizer and PVC macromolecules is accounted for, as depicted by the scheme in figure 21-bottom, taking into consideration that in the additive molecules are present nitrogen and oxygen atoms with different electo-negativity.
FIGURE 18: The relationship between the carbonyl index and irradiation time for films of pure PVC and for films containing the 0.5% of the additives listed in figure 16 [14].

FIGURE 19: The relationship between the polyene index and irradiation time for films of pure PVC and for films containing the 0.5% of the additives listed in figure 16 [14].
FIGURE 20: Changes in the viscosity average molecular weight Mw during irradiation of PVC films (30μm) (control) and with 0.5 wt% of the various additives whose molecular structure is described in figure 16 [14].

P. V. C. Rao, V. K. Kaushik and I. S. Bhardwaj studied the photo-oxidation degradation of PVC samples by the combined use of $^{13}$C and $^1$H NMR spectroscopy. The samples were characterized by determining tacticity and the length of isotactic and syndiotactic indexes [15]. Photo-degradation experiments were performed by using a photochemical reactor equipped with a fluorescent lamp emitting radiations in the wavelength range of 300-450nm. The pure PVC and UV degraded samples (finely powdered) exposed to 2, 3 and 4 hr of UV dosages were labelled as PU$_1$, PU$_2$, PU$_3$, and PU$_4$, respectively. The $^{13}$C and $^1$H NMR spectra (methylene and methine regions) of plain PVC and PVC exposed to different dosages of UV irradiations are shown in Figs 22 and 23 respectively [15].

From the variations induced by photo-oxidation in the lines of the NMR spectra was possible to the Authors to draw the following conclusions:

< (1) The rate of dehydrochlorination and the polyene distribution increase while the length of the isotactic index L, decreases with the increase in UV-irradiation time.

< The polarity of the compound explains the attraction between the stabilizer and PVC (see scheme in figure 21-bottom). This mechanism can lead to the conclusion that cross-linking take place upon UV irradiation, which may be correct for all compounds prepared > [14].
**FIGURE 21-top:** Suggested mechanism of photo-stabilization of 1,3,4-oxadiazole carboxylates compounds as UV absorber, see text [14].

**FIGURE 21-bottom:** The suggested mechanism of photostabilization of PVC through the interaction between PVC and oxadiazole additives [14].

( li ) The degradation changes are clearly seen in the proton NMR spectra especially in the methylene proton region wherein the peaks corresponding to isotactic and syndiotactic sequences are not discernible in the spectra of UV-degraded samples. Also there is a decrease in the intensity of methylene protons on UV-degradation which supports the dehydrochlorination process >[15].

From the above reported data it can be concluded that the processes connected to weathering (photo-oxidation) of PVC < are very complex as they follow various steps and pathways leading to cross-linking, chain scission and by-product formation > [16]. These reactions affect not only the physical properties of the polymer but also drastically modify the chemical and molecular characteristics of the material [16].

< Investigations concerning the photo-oxidative processes in PVC indicated that traces of peroxides and carbonyl impurities are responsible for initiating photo-reactions. Such reactions result in eventual degradation of the polymer through chain scission and cross-linking. This is a slow process and follows the formation of unsaturated polymers through dehydrochlorination > [16].

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**FIGURE 22-left:** $^1$C NMR spectra of UV virgin PVC [(a) PU$_0$] and photo-degraded PVC samples [(b) PU$_2$; (c) PU$_4$], see text [15].

**FIGURE 23-right:** $^1$H NMR spectra of UV virgin PVC [(a) PU$_0$] and photo-degraded PVC samples [(b) PU$_2$; (c) PU$_4$], see text (the lines in the up field correspond to methylene protons ($\beta$-protons) and the one at down field corresponding to methine protons ($\alpha$-protons). Five distinct peaks are seen in the case of the methylene proton region whereas a single broad peak appeared for a methine proton) [15].
According to A. Faucitano and others the most relevant reactions occurring during the photo-oxidation process of PVC, schematically described through the scheme in figure 24, may be summarized as follows [17,5]:

--- Sensitization due to polyenic structures seems to play an important role as far as the initiation step is concerned.
--- Peroxides and ketones, formed in the course of processing, may be also relevant for the initiation step.
--- The polyenic products are capable to transfer excitation energy to the allylic C-Cl bonds. This produces alkyl radicals and Cl atoms.
--- The formed radicals by abstracting the H atoms located on the secondary and tertiary C-H bonds produce peroxyradicals.
--- The most important products of photo-oxidation are: tertiary and primary hydroperoxides, ketones [-CH(Cl)(=O)CH(Cl)-], acyl chlorides [-CH₂C(=O)Cl], carboxylic acid [-CH₂C(=O)OH], and alcohols.

![Diagram]

**FIGURE 24:** Scheme reporting the most effective reactions in the photo-oxidation process of polyvinylchloride (see text) [17,5].

The formation of polyene, carbonyl, chloroketone and aliphatic ketones products in films of PVC exposed to the action of light with $\lambda = 313\text{nm}$ is in agreement with the change observed in the FTIR spectrum, in the range 4000-400 cm$^{-1}$, as shown by the diagrams reported in figure 17 [14].
D.1.5 ) RADIATION INDUCED DEGRADATION OF PVC: EFFECTS OF IONISING GAMMA RADIATION ON PVC

The degradation induced to samples of PVC by ionising gamma (γ) radiation (highly penetrating electromagnetic radiation, emitted by radioactive isotopes with high energy, much higher than ordinary X-rays), from a 60Co source, was investigated in reference [18]. The major effects observed are hereafter summarised:

• Change in molecular weight and distribution of polymer chain lengths;
• Formation of conjugated C=C systems;
• Oxidation and production of observable C=O chromophores;
• Formation of, long term survival, free radicals;
• Radiation-induced HCl production;
• Discolouration whose extent depends on applied dose, irradiation environment and post-irradiation time [18].

The off gassing of corrosive HCl, as shown by the curves exhibited in figure 25, increases with the amount of dose and seems to be function of the molecular mass of PVC [18].

![Graph showing Cl emission from PVC exposed to gamma radiation as function of dose amount and molecular mass.](image)

**FIGURE 25:** Cl emission from PVC exposed to gamma radiation as function of dose amount and molecular mass [18].
**FIGURE 26:** Overall free-radical mechanism concerning the HCl evolution from PVC macromolecules exposed to radiations [18].

\[
\begin{align*}
\text{Cl}^- & \rightarrow R-\dot{\text{C}}\text{H}-\text{CHCl}-R + \text{HCl} \\
R-\dot{\text{C}}\text{H}-\text{CHCl}-R & \rightarrow R-\text{C}\text{H}=\text{C}H-R + \text{Cl}^- \\
R-\text{CH}_2-\dot{\text{C}}\text{H}-R & \rightarrow R-\text{C}\text{H}=\text{C}H-R + \text{H}^+
\end{align*}
\]

**FIGURE 27:** Initiation reaction of radiation induced C-Cl scission in PVC. In figure is reported the scheme of the radical reactions of the propagation step [18].

**FIGURE 28:** Radiation induced C-Cl scission in PVC. In figure is reported the scheme of the radical termination reactions [18].
The overall free-radical mechanism leading to the evolution of HCl from PVC exposed to radiation is schematically described in figure 26, while the reactions concerning the propagation and the termination steps ( \( \text{R}^* + \text{R}^* \rightarrow \text{R}-\text{R} \) ) are described in figure 27 and 28 respectively [18]. The effects of dose amount on the discoloration induced by radiation on PVC powders is evidenced through the images reported in figure 29 [18].

![Figure 29](image)

**FIGURE 29:** The effects of dose amount on the discoloration induced by radiation on PVC powders. Left: blank; Center: 20 kGy; Right: 100 kGy [18].

### D.1.6) CHEMICAL RESISTANCE

Being the backbone chain of PVC constituted by single bonds of carbon atoms, the polymer is characterized by good chemical resistance against many organic solvents, salts, acids and alkalis (see the chart showing the chemical resistance of PVC in comparison with other plastics in table 2) [13-b)].

According to what reported in reference [13-a]) the resistance of PVC against chemical agents can be summarised as follows:

--- Resistant to salt solutions;
--- Resistant to most alkali solutions;
--- Resistant to most acid solutions;
--- Resistant to most alcohols, petrol, oils, fats [13-a].

On the contrary PVC undergoes degradation, in varying degrees, when exposed to the action of:

--- Organic chemicals containing nitro and chlorine groups;
--- Aromatic hydrocarbons, ketones, some ethers;
--- Aromatic amino compounds [13-a].
### Table 2: Chemical resistance of various plastics and relative indexes [13-b)].

<table>
<thead>
<tr>
<th>PLASTIC</th>
<th>ORGANIC SOLVENTS</th>
<th>SALTS</th>
<th>ALKALIS</th>
<th>ACIDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-66</td>
<td>7</td>
<td>10</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>Polyester chemical resistant</td>
<td>6</td>
<td>10</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>6</td>
<td>10</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Polyfluorocarbon</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>4</td>
<td>10</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>8</td>
<td>10</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>PVC-flexible</td>
<td>4</td>
<td>10</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>PVC-rigid</td>
<td>6</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>ABS</td>
<td>4</td>
<td>10</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>6</td>
<td>10</td>
<td>7</td>
<td>9</td>
</tr>
</tbody>
</table>

**Note:** The 1-10 scale has been set by empirical means. Higher value shows higher effectiveness.

### D.1.7) Physical Aging and Mechanical Degradation of PVC Compounds

It is generally recognised that the mechanical properties of polymer materials are dependent upon the physical interactions among PVC macromolecules at the use temperatures. In many thermoplastic polymers, processed above the value of the glass transition temperature (Tg) and used below Tg, that is while in a glass-like status, negative changes with time such as stiffening, crack growing and embrittlement, are often observed. This process is known as “Physical Aging” [19].

The physical aging phenomenon in PVC is described in reference [20] as follows: <The PVC chains show motion during the processing at high temperatures,... Besides PVC chains, additives among which stabilizers are mixed during processing. This high temperature conformation is frozen in when the PVC product is cooled below its transition glass temperature. During the cooling from the Tg down to the storage and the operation temperature, a slow process occurs, in which the PVC chains re-orientate to reach a more dense state > [20].

It well known that the degree of physical aging, a slowly developing process which can be accelerated by exposure at elevated temperatures, depends on the rate at which the artefact is cooled after shaping.

Mechanical degradation occurs when under the service conditions internal or external stresses determine the initiation and the growth of crazes, cracks, flaws and other microscopic damages till critical degree after that macroscopic failures develop. Of course the presence of impurities...
favours the formation of cracks and their growth (see examples in figure 30). [20].
The modalities of processing, especially in the case of rigid PVC compounds, as well as factors, such as design, installation, improper use <directly affect the key properties that relate to a product’s ability to withstand stress during use as well as environmental assaults. Often, design and materials are good, but manufacturing is inadequate, which can lead to failures> [21].

FIGURE 30: Top-left, multiple internal cracks on a PVC pipe in operation. Top-right, internal crack on a PVC pipe that failed prior to installation. Bottom-left, axial cracks throughout a PVC pipe that failed during operation [21]. Bottom-right, Crack growth starting from inhomogeneities in PVC pipe walls [20].

The deterioration observed in many properties of polymer materials, deriving from the migration of solid or liquid additives, especially plasticisers, is usually considered as a physical degradation processes. It is well established that in the case of flexible artefacts, manufactured from plasticized PVC compounds, the migration of the plasticisers towards the surfaces induces negative effects on many of their use functions.
The loss of plasticiser produces the decline of the physico-chemical properties and frost resistance of the material and increases its cracking tendency [22]. B. I. Lirova and others quantified the migration tendency of different plasticisers from PVC films by measuring, at constant temperature, the weight loss, $\Delta m$, as function of the time [22]. PVC films plasticized with di-(2-ethylhexyl)-$o$-phthalate (DOP) or dibutoxyethyladipate (DBEA) or dibutyl sebacate (DBS) (or their mixtures) were investigated (100/45, PVC/plasticiser weight ratios) [22].

As shown by the trends of the curves reported in figure 31 the rate of migration strongly depends upon the chemical nature of the plasticisers used [22].

**FIGURE 31:** Weight loss $\Delta m$ in air at 90°C and atmospheric pressure vs. time of PVC films containing:
(1) DOP, (2) DOP + DBEA, (3) DBEA, (4, 5) DOP+DBS, and (6) DBS, see text [22].

In particular it was observed that:

< in the samples plasticised with individual compounds, the weight loss changes in the following order DOP < DBEA << DBS. The samples containing mixtures of plasticisers occupy the intermediate positions > [22].

From the trends of the IR spectra shown in figure 32 it was possible to conclude that the amount of volatile compounds (DOP, DBEA, and DBS), released and properly recovered from the surfaces of PVC samples, grows with increasing time.

< The spectroscopic results were presented as time dependences of the optical density of the absorption band of the plasticiser (~1720, ~1130, and ~1175 cm$^{-1}$ for DOP, DBEA, and DBS, respectively).... > [22].
The above results indicated that FTIR is suitable to assess the migration tendency of plasticisers from PVC-based artefacts.

**FIGURE 32:** IR spectra of the volatile compounds released from the film containing DOP. (T) Transmission and (v) wave number. (1) Absorption of KBr windows, (2) spectrum recorded 7 min after the beginning of the experiment, and (3) spectrum recorded 245 min after the beginning of the experiment. The arrow indicates the order of recording of the spectra [22].

Now a day the correlation between the rate and extent of degradation of plasticized PVC objects and the migration of plasticisers may be qualitatively as well as quantitatively established by using suitable analytical diagnostic techniques. In reference [23] about this last topics is reported that

< a non-destructive analytical technique was developed using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy to quantify the concentration of DEHP (a common used plasticiser) at the surfaces of samples. Weight loss was used to quantify total loss of plasticiser. Changes in the distribution of DEHP were mapped using Low Vacuum Scanning Electron Microscopy (LV-SEM). Densitometry was used to quantify darkening of the PVC component of samples > [23].
The resistance to natural aging of PVC-based materials, and their related artefacts (see exemplars in figure 33), strongly depends upon the:
--- Molecular weight of the base resin and its distribution;
--- Irregularities along the polymer chains (carbonyl groups and cross linking of the polymer chains hinder the thermal dehydrochlorination of PVC and the disintegration of PVC, while weak peroxy linkages (which make easy degradation processes) and conjugated double bonds reduce the temperature of decay);
--- Morphology of the PVC matrix and of the compounds containing additives;
--- Type and function of additives, especially plasticisers and stabilisers;
--- Entity of migration of plasticisers towards the surfaces;
--- Degree of de-chlorination and of chain cleavage, and chemical nature of by-products formed and active inside the mass or at the surface;
--- Internal stresses cumulated during the processing;
--- Functional properties and use temperature and the interaction with degrading chemicals during the lifetime.

**FIGURE 33:** Artefacts in PVC.
*Left:* *PVC simulates not other materials but living matter. Made in Hong Kong in the 70s and again today PVC Grapes, 1970s* [24].
*Right:* *A standard wide-hole 7” vinyl record from 1978 on its respective sleeve. The majority of non-78 rpm records are pressed on black vinyl. The colouring material used to blacken the transparent PVC plastic mix is carbon black, which increases the strength of the disc and makes it opaque* [25].

The possibility of interventions suitable to prolong the lifetime of PVC-based objects will be discussed in detail in the next chapter.
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CHAPTER TENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (VINYL CHLORIDE):

E) THE CONSERVATION AND CARING OF ARTEFACTS IN POLY VINYL CHLORIDE

As previously described PVC is used, due to its extraordinary ratio of cost to performance, in various sectors going from essential services (water supply, sewage, supply of electric power, etc.), housing, transportation, consumer products, and electronics, to medical devices. For sake of simplicity the applications of PVC are usually divided on the basis of the stiffness of products, e.g., rigid or flexible [1-a].

As shown by the diagram reported in figure 1), the durability of PVC artefacts depends upon the composition of the formulation used for the manufacturing. PVC formulations may lead to outstandingly durable materials, as those used for example in water supply and sewage pipes, which can be used for over 50 years. *Most of PVC products are used in durable applications. More than half of all PVC products are long life products with service lives of over 15 years* [1-a].

![Diagram of plastic durability](image)

**FIGURE 1:** Durability of plastics according to their composition and molecular characteristics [1-a].
**FIGURE 2-left:** PVC inflatable furniture, very fine Italian design, 1960s-1970s [1-b].

**FIGURE 3-right:** Waterproof jacket in PVC [2].

**FIGURE 4:** Airship model in PVC, 1970, Panamarenko, SMAK, Gent Belgium. On the bottom right it is shown an area where clear symptoms of degradation (discoloration, sticky, loss of flexibility) are observed [3].
FIGURE 6-right: PVC figurine by Jun Planning. Nightmare Before Christmas Band [5].

Many artefacts made from flexible or rigid PVC (toys and dolls, waterproof and protecting clothes, records, electrical insulation devices, photograph pockets, plastic furniture, inflatable furniture, garden hoses, medical devices, modern sculptures and objects with very fine design, etc.) nowadays, find place in collections located in private or public museums (see examples in figures 2-6).

The extensive use of PVC in so many industrial and commercial sectors is accounted for by the possibility to tailor material formulations, containing several types of additives (plasticisers, stabilizers, etc.), capable to impart many different use functions.

It must be remarked that the increase in research efforts led in the course of the years to the development of more sophisticated types of PVC. This allowed the use of PVC-based formulations, as occurred also for many other plastics, <for modernist design projects, several of which straddled the applied/fine art divide, for example the inflatable chair designed by William H. Miller (c. 1944; New York, Museum of Modern Art)..... By the 1960s various types of plastic were being used in the emerging Pop art. Claes Oldenburg (b. 1929) began using flexible polyvinyl chloride (PVC) materials to make sculptures filled with kapok as he began to explore the ideas of soft art..... ... In the 1960s designers began to use the recent advances in plastics technology to develop new shapes in product design and furniture, in particular chairs. More importantly, plastics began to be used for their own intrinsic qualities rather than as substitutes for other materials. Polyurethane, ABS (acrylonitrile butadiene styrene), acrylic and polyvinyl chloride (PVC) were used in the design of foam shapes, glossy ‘wet look’ products, including clothes and jewellery.....and inflatable furniture > (see examples in figure 7)[6].

As already written the chemical and mechanical properties of PVC-based materials, as well as their resistance to degradation during processing and in relation to the exposure to external factors of aging, are strongly dependent upon the processing conditions, molecular characteristics and structure of the base PVC, the nature, function and content of additives present in the formulation and to the mutual chemical/physical interactions between polymer chains and additives.
**FIGURE 7:** Examples of application of PVC in the manufacturing of objects valuable for their artistic and design content.


*Bottom:* Giuseppe Celi, *mixed technology*, prints on PVC [6-d].

In the case of PVC-based artefact, as described in details in previous chapters, the most relevant processes of degradation are essentially related to:

1) *De-chlorination*

2) *Migration and loss of plasticisers*
The exposure to heat, light, chemicals and mechanical damages may facilitate the initiation or the acceleration of both types of degradation processes. De-chlorination is catalysed by the presence of metal part in contact with plastic components (see for example the case of PVC insulated wiring).

For the conservation of plastic objects two types of treatments may be followed, which are generally divided in:

--- *inhibitive/preventive measures* (with the intend of controlling the environment to hamper or mitigate the degradation processes);

--- *interventive measures* (they include the cleaning and repair of artefacts).

To choose the right conservation procedure for PVC-based artefacts it is necessary to identify first, by using proper, and hopefully non-destructive, diagnostic techniques:

--- The chemical structure of the polymer component (molecular weight and its distribution and the occurrence of chain scissions or cross-links);
--- The most evident signs of deterioration (smells, yellowing, crazing, cracking, crumbling, embrittlement, shrinking, warping, weeping, blistering, blooming, tackiness of the surface, ecc.);
--- The presence at the surfaces of traces of hydrochloric acid or plasticiser beads [6,7,8].

Interventive approaches, being generally based on invasive treatments (adhering, deacidifying, washing, ecc.), due to the chemical characteristics of the polymer and additives components are very difficult to be carried out in the case of PVC items.

Even cleaning, apparently the simplest interventive treatment may be not easily to be executed in the case of PVC artefacts since many common solvents with the exception of alcohols dissolve the polymer. Thus proper cleaning agents are not easily found for such objects.

Not properly done mechanical cleaning may cause on the surface of the artefacts scratches and change in surface gloss (see figure 8) [2].

In reference [9] concerning cleaning treatments for the surface of plastic objects the following general recommendations, valid also for PVC artefacts, are given:

--- Apply only when absolutely necessary;
--- Use a dry lint free, soft cloth;
--- If further cleaning is necessary:
  - Do not use cleaning agents;
  - Avoid solvents;
  - Use water with caution;
  - No water on items with gelatine, film, sequins;
  - Avoid degraded areas;
  - If in doubt don’t [9].

In general interventive or restoration treatments of conservation involving degraded plastic objects should be limited especially when damages are caused by chemical reactions.

*Mechanically damaged objects may present more possibilities but will depend on the object, its construction and circumstances* [9].
Figure 8: Not appropriate mechanical cleaning may cause scratches on the surface of the plastic artefacts and change in surface gloss [2].

In the case of the conservation of plastic artefacts, usually the curators prefer to assume inhibitive/preventive actions, which aim essentially at the reduction of the rate of degradation by a suitable control of the chemical composition, light and temperature of the surrounding environment. This requires the adoption of proper conditions of storage/display.

The effect of an inhibitive intervention on the degradation rate of plastics, as measured by a property (colour, pH, weight, etc.) variation with time, is schematically described in figure 9 [2,10]. It must be pointed out that in the case of PVC and other plastics once chemical degradation starts, its effects are generally irreversible; thus the inhibitive conservation may only slow down the rate of the degradation processes [2,10].

Mitigation measures suitable to minimise loss of plasticiser from flexible PVC have been developed; some of them include the storage of the objects in enclosures made by non-adsorbent material such as glass, containing non-agitated air. Optimal storage for PVC objects is a closed glass container at lowered temperatures, avoiding freezing [11].

< Enclosing plasticised PVC objects, whatever their level of deterioration, is inexpensive to implement, of low practical complexity and allows public accessibility to plastics objects > [11].

On the contrary in the case of objects made by plasticized PVC, the following maintaining conditions, which may cause high losses of plasticisers, should be avoided:
--- The storage in environments with circulating air (for example: open glass shelf);
--- The wrapping in an adsorbent packaging material (for example: polyethylene), or with adsorbents to control air quality [11].

The loss of plasticisers in many cases determines, in PVC-based artefacts, the formation and growth of cracks deriving< from stresses that built up as the plastic shrinks and become more rigid > [12].
**FIGURE 9:** Generic curve describing the effect of inhibitive conservation actions on the degradation rate of plastics as measured by a property (colour, pH, weight, etc.) variation (on the ordinate) with time [2,10].

**FIGURE 10:** Cockling, shrinking and distortions in PVC-based artefacts due to loss of plasticisers.  

In some other cases, as shown by figure 10, the migration of plasticisers produces cockles and distortions [11]. In others the surface becomes tacky while discolouration effects are also observed (see figure 11) [9].
FIGURE 11: Camera case with a sticky surface causing it to tear and lose areas where it has been stuck to and then removed from surrounding items [9].

FIGURE 12: Doll manufactured from plasticized PVC (years 1950-1960) showing on its face clear symptoms of degradation due to the migration of the plasticiser at the surface, see text [13].
The so called "doll disease" is a process of degradation connected with plasticiser migration observed in many vintage dolls and toys made, in the 1950s and 1960s, by using compounds based on plasticized PVC.

<What happens is that in certain (not all) formulations of the plastic used to make these old dolls and toys, the plasticiser has separated from the plastic mix and has begun to ooze out of the toy, see the doll pictured, in figure above (figure 12), who suffers from this condition-the doll's face has a shiny look.> [13].

Other symptoms, observed on some Barbie dolls have been so described in reference [14]: <The skin develops green spots and they weep tears. It can't be stopped or cured...> [14].

The origin and the damage caused by the "doll disease" are described as follows in reference [15]:

<...The plasticiser traditionally added is dibutyl phthalate, a pale liquid with a boiling point of 340°C. Dibutyl phthalate does not vaporise at room temperature, but starts to migrate slowly out of the PVC soon after manufacture. Migration causes the formation of sticky 'tears' on the surface of objects, making the damaged PVC unsafe to touch. This usually takes place within ten years of manufacture. Dibutyl phthalate is toxic to humans through contact with skin and by ingestion. Losing plasticiser leaves the PVC itself highly vulnerable to deterioration. Hydrogen chloride, a corrosive, acidic gas, is produced by deteriorating PVC. If not rapidly removed from the surface of the plastic, degradation progresses three times faster than before......... Deterioration of plastics cannot be stopped under the usual indoor climate conditions comfortable for people. Active preservation treatments such as applying protective coatings and paints are complex for technical and ethical reasons. Any coating which adheres successfully to a plastics surface must also soften the surface, thereby increasing the damage and altering the original appearance. This is unacceptable for museum objects.> [15].

As already written the control of the environment surrounding the object is the only reasonable action to be undertaken to reduce the rate of deterioration of PVC based items, especially those manufactured by flexible materials.

The control of the environment may be accomplished by:
--- <limiting the factors causing deterioration or
--- ensuring that, if it occurs, the concentration of acidic degradation products is as low as possible>

Moreover taking into consideration that <the major causes of deterioration of PVC are heat and light. In general the rate of a chemical reaction doubles if the temperature is raised by 15°C. By keeping PVC as cool as possible, and in the dark, deterioration would be slowed dramatically>

Y. Shashoua, concerning the conservations of PVC-flexible artefacts, and especially dolls in reference [15], recently suggested:
--- <A domestic freezer operating around -20°C is a possibility.....Transparent windows could be incorporated into the freezer design to facilitate inspection of objects>
--- Once the deterioration process has begun, the concentration of hydrogen chloride produced can be minimised by removing it from the environment surrounding the PVC object. One simple, clean technique is to trap the hydrogen chloride molecules so that they are no longer sufficiently mobile to make contact with the PVC surface and attack "healthy" objects.
--- Zeolites are crystalline silicates of calcium and aluminium, which are strongly suitable to remove water. The heating process opens up spaces in the silicate structure into which small molecules>
such as hydrogen chloride can flow and be trapped firmly.
--- Zeolites are readily available as small pellets, ..., which are inexpensive, occupy little space, and offer no hazard to the health of people or that of other materials. They are commercially available as Molecular sieve, Type 4A >[15].

It was widely demonstrated that zeolites < are effective at slowing the rate of deterioration of PVC even when simply introduced into a museum showcase, contained in a small glass dish or wrapped in pure cellulose filter paper, and placed close to the object. For more sophisticated systems, zeolites could be incorporated into a filter for the outgoing gases where the air was re-circulated in a storage room or showcase >[15].

The presence of metal components in PVC objects, see the case of dolls wearing earrings, gives rise to a damaging process deriving from the reaction between the hydrogen chloride produced and the metal elements. In case of copper components, green copper chloride is formed, which, as shown by figure 13, stains the surface [15].

![Figure 13](image)

**FIGURE 13:** < Barbie often wears earrings, and, as hydrogen chloride is produced by her cheeks it reacts to form green copper chloride which stains her skin >[15].

The environmental toxicity of some of the most common used plasticisers for PVC (see the case of DOP) have led to their substitution with more safe additives as diisononyl adipate (DINA) and other substitutes such as diisononyl phthalate (DINP) (see below for their molecular structures) [15,16].

Artefacts in flexible PVC, due to the migration of plasticisers and/or the release of hydrochloric acid, must be stored far away from other objects made by materials, which are chemically sensitive to those reactive species. This especially includes items made on textiles, paper and metals [6].
PVC plasticisers may also attack some plastics such as polystyrene for which it is a solvent, and where PVC is in contact with such materials, marks or more serious damages may occur. Damage to polystyrene camera bodies by contact with PVC wrist straps was sometime observed. For the same reason, PVC should not be packed in polystyrene foam . . . . . > [17].

\[
\begin{array}{c}
\text{diisononyl adipate (DINA)} \\
\text{diisononyl phthalate (DINP)}
\end{array}
\]

PVC artefacts containing lead based stabilisers should be stored far away from objects in rubber or vulcanite as sulphurous fumes emitted by this latter materials are capable to interact with lead stabilisers migrated on the surfaces of PVC items determining darkening effects [17].

**TABLE 1:** Plasticized PVC, predicted time (days) to lose 10% of weight at 20°C [2].

<table>
<thead>
<tr>
<th><strong>ENVIRONMENT</strong></th>
<th><strong>DAYS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Enclosed in LDPE bags</td>
<td>256</td>
</tr>
<tr>
<td>Glass plate</td>
<td>256</td>
</tr>
<tr>
<td>Enclosed with activated carbon</td>
<td>320</td>
</tr>
<tr>
<td>Enclosed with silica gel</td>
<td>576</td>
</tr>
<tr>
<td>Enclosed with Ageless oxygen absorbers</td>
<td>2112</td>
</tr>
<tr>
<td>Freezer, enclosed in glass, high relative humidity</td>
<td>&gt; 4160</td>
</tr>
</tbody>
</table>

The efficiency of various environmental conditions upon the stability of items manufactured in plasticized PVC was established by comparing the values of the predicted time to lose 10% of their weight at 20°C. From the results of this analysis as reported in table 1, it may be concluded that the best environmental conditions are those already mentioned: Freezer, enclosed in glass, with high relative humidity [2].
In some cases PVC-based objects are so badly and irreversibly deteriorated that the curators of collection are forced to submit request to de-accession. This was the case reported by J. Holt concerning two pairs of PVC of women’s galoshes (see figure 14).

"Both pairs of these women’s galoshes are suffering degradation of the PVC. The chemical breakdown has caused yellowing as well as surface tackiness that is leaving behind an oily residue. The breakdown is irreversible and the galoshes will continue to deteriorate. In order to prevent any damage to other artefacts, it is necessary to remove them from the collection." [17]

**FIGURE 14:** Two pairs of women’s galoshes, in PVC, badly and irreversibly deteriorated.
In order to prevent any damage to other artefacts, it was necessary to remove them from the collection [17]

For the above behaviour PVC, as celluloid, is included in the families of plastics defined as “Malignant”. Thus artefacts in PVC as general rule have to be isolated from other materials to prevent their deterioration.
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CHAPTER-ELEVENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (METHYL METHACRYLATE)

A) HISTORY, SYNTHESIS, PROCESSING, PROPERTIES AND APPLICATIONS

A.1) HISTORY

Poly (methylmethacrylate) (PMMA), IUPAC name, Poly( methyl 2-methylpropenoate), commercialised as Perspex, Plexiglas, Lucite, Duralon, is a thermoplastic polymer belonging to the broad family of acrylic resins. PMMA is obtained by free radical vinyl polymerization of the monomer (methyl methacrylate, MMA). The molecular structures of both MMA and PMMA, including that of the corresponding repetitive unit of the polymer chains, are schematically depicted in figure 1.

![Molecular structure of PMMA](image)

**FIGURE 1** Left, molecular structure of methylmethacrylate monomer (MMA). Center, molecular structure of polymethylmethacrylate (PMMA). The repetitive unit is in brackets. Right, PMMA stick and ball chain model (oxygen atoms are in full-black; carbon in grey and hydrogen in light-black or charged-grey).

The most relevant technical and scientific achievements that led to the industrialization of PMMA are hereafter summarized.

--- 1873- Casperly and Tollens prepared for the first time various esters of acrylic acid.
--- 1890- Kahlbaum polymerised methyl acrylates
--- 1901- Otto Rhom (see figure 2) awarded doctorate, in Germany, for his thesis on acrylates polymers <and the title of the well-known firm of Rhom and Haas, engaged in making and selling plastics in Germany and the United States, is a constant reminder of his work> [1].

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--- 1907-1909- The Rohm and Haas Company was established, first in Germany (1907) and then in Philadelphia (1909).
--- 1928- The first PMMA industrial productive plant was established in Darmstadt, Germany.
--- 1931-1932- W. Bauer, in Germany, and R. Hill, in England, discovered that PMMA was a beautiful clear glass-like substance [1]. The Rohm and Haas Company first manufactured in German, transparent methyl methacrylate resins, named Plexiglas, used for coating and safety glass. More or less at the same time PMMA was introduced in England under the trade name “Perspex” [1,2,3].
--- 1933- J. W. C. Crawford invented a new chemical synthesis for MMA that utilized cheap raw materials, acetone and hydro-cyanic acid. With this method was possible to produce Perspex, in England, on a more convenient commercial scale [1].

![FIGURE 2: Dr. Otto Röhm who did his original research on acrylic acid and its derivatives in the course of his Ph.D. thesis [2].](image)

--- 1934- The ICI Company built, in UK, the first industrial plant for the manufacture of PMMA sheets. In that year a limited amount of moulding powders and aqueous dispersion of PMMA were also produced [1]. A plant for the production of PMMA was built in France by the Alshorn Company, in Colombes (Paris).
--- 1936-1937- Transparent sheets in PMMA were manufactured in USA.
Du Pont entered in the field of acrylic resins and soon, under the responsibility of Daniel E. Strain, developed a technology to produce, under the trade name “Lucite”, transparent sheets and also powders for moulding suitable to be shaped as thermoplastics materials [3].
The first casting process for making sheets involved working in a room at 40°C......The sheets

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were made then, as now, by pouring a syrup mixture of monomer and polymer into glass cells, and one of the tricky operation was to take up evenly the twenty per cent shrinkage on polymerization [1].

In Italy the first plant for the production of PMMA was built on 1937 c/o the “Vetrocoke” in Porto Marghera (Venice) [4].

--- 1938- The Röhm and Haas established in Berlin a second production plant for PMMA.
--- 1939-1945- (war time)- Transparent sheets in PMMA, all over the industrialised world, were essentially produced for aircraft applications (windows and enclosures, cockpit canopies, gunner's turrets, etc.) (see example in figure 3) [1,2,3].
PMMA substituted materials such as vulcanite or hard rubber in the manufacturing of dentures [1,3]. In England < Dr S. A. Leader of Portland Plastics was largely instrumental in devising methods for producing suitable polymer and a process for making the dentures > [1].
--- 1946- The H. D. Justi Company set up, in USA, a line of acrylic replacement teeth [3].

**FIGURE 3:** A Hurricane military aircraft of World War-II with its PMMA (Perspex) cockpit-hood [1].

**FIGURE 4:** < This 1937 Kem plastics playing card box was compression moulded of Lucite (PMMA) in beryllium copper moulds. This package pioneered three-dimensional lettering in clear plastics and sparked the production of many automobile horn buttons and decorative insignia > [3].
Decorative objects in PMMA were designed and produced in USA by Dave Swedlow who recognized acrylic’s true novelty, that it could be softened with heat and twisted into compound curves...... Swedlow created bowls and trays by folding and crumpling sheets of acrylics into shapes varying from the representational to the vaguely biomorphic to the abstract. Loop-the-loop candle holders shared space in his catalogue with stylised barely-twist lamps, all transparent and marked by the sharp brilliance of their transmitted light. An item of high fashion at the end of the decade (1940) > [5]. Examples of items in PMMA designed and produced by Dave Swedlow are reproduced in figure 5 [5].

**FIGURE 5:** decorative artefacts manufactured by transparent polymethyl methacrylate (1940) [5].

*FIGURE 6:* <The transparent acrylic plastics dome is a beacon for business, especially at night when the dome is brightly illuminated. (Courtesy Rhom & Haas Co.) > [6].
Clear sheets of PMMA were also used, as shown by figure 6, to build up transparent plastics dome for large show room [6].

A.2) SYNTHESIS AND PROCESSING OF PMMA

The synthesis on industrial scale, of the methyl methacrylate (MMA) is based on the hereafter described two-step process (see figure 7).

First step: acetone [CH₃-CO-CH₃] and hydrogen cyanide [HCN] are reacted to form acetone cyanohydrin [CH₂-C(CN)-CH₃].

Second step: cyanohydrin, in presence of sulphuric acid, reacts with methanol giving rise to the formation of the methyl methacrylate ester [4, 7].

Some of the most relevant properties of MMA are reported in the below table. MMA at RT is a clear colourless liquid, soluble in water and in organic solvents [8].

<table>
<thead>
<tr>
<th>Properties of MMA</th>
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<tbody>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Solubility in water</td>
</tr>
<tr>
<td>In organic solvents</td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>Boiling point</td>
</tr>
<tr>
<td>Basicity (pKₐ)</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
</tbody>
</table>

**Figure 7**: A old plant used, about 1950, for the production of the MMA monomer [4].
PMMA, a transparent thermoplastic polymer, as all acrylates resins, is obtained by free radical polymerization initiated by peroxide or azo catalysts. It may be also obtained by means of a so called "redox polymerization" [7]. Essentially PMMA is produced according to one of the following four different processes:
--- Bulk or Mass
--- Suspension
--- Emulsion
--- Solution [7].

Usually PMMA is produced in the form of sheets, tubes or rods <which can be machined, bonded, and formed into a variety of form, which can be conventionally processed via extrusion or injection moulding.> [9].

Some of the most common methods used to obtain PMMA sheets are below described.

--- Cell Casting- It is a batch process in which first the MMA monomer, after the addition of the suitable catalyst, is allowed to polymerised in a stirred vessel to form a viscous syrup liquid (a pre-polymer with a relatively low molecular weight). At this point then the stirring is stopped and the viscous liquid pre-polymer is poured into moulds were the polymerization reaction is allowed to continue until a like-glass hardened mass is obtained. Usually such an operation is performed by heating the syrup <between two sheets of polished glass held together by spring clips to respond to the contraction of the acrylic material during cure> [7], see figure 8 [9].

![Figure 8](image.png)

**FIGURE 8:** Schematic representation of the casting process used to produce PMMA sheets (left) and shaped objects (right) [9].

--- Continuous casting- The bulk polymerization of PMMA occurs between polished stainless steel moving belts [7].
According to reference [7]:
*Cell cast material has better optical quality and a smoother surface, whereas continuous casting provides sheets of more uniform thickness and less thickness variation.* [7]

Generally PMMA with very high molecular weight are produced with the mass polymerization processes. Thus such a method is not suitable for producing injection molding grade resins [10]. Bulk or solution polymerization is used to produce PMMA in the form of pellets, suitable to be used for extrusion or calendaring processes. Alternatively methods consisting on the continuous polymerization of PMMA in extruders were also used [7].
PMMA for typical melt processing (with a lower molecular weight) is usually produced by suspension polymerization. Such a technique is described as follows in reference [10].
*In this process, MMA is suspended in water to which the peroxide is added along with emulsifying/suspension agents, protective colloids, lubricants, and chain transfer agents to aid in molecular weight control. The resultant bead can then be dried and is ready for injection molding, or it can be further compounded with any desired colorants, plasticizers, rubber-modifier, as required.* [10]

Examples of sheets (also colored), tubes and rods in PMMA are photographically reproduced in figure 9 whereas crack-resistant, and transparent small tables, manufactured in batch dyed PMMA, are shown in figure 10.

**FIGURE 9:** Examples of sheets, tubes and rods in PMMA [11,12].
**FIGURE 10:** Crack-resistant small tables in transparent or batch dyed PMMA [13].

**FIGURE 11:** Simplified schemes of the shaping methods used to transform PMMA sheets in curved non-planar objects. 
*Top,* Vacuum forming, *Center,* Press forming, *Bottom,* Sheet blowing (see text for details) [9].

Sheets of PMMA, when warmed above the Tg of the polymer (≈105°C) became soft. Thus they can be pressed and molded, by simple shaping techniques (vacuum forming, sheet blowing and press forming, see the schemes in figure 11), and then easily transformed in nonplanar or curved objects.
such as domes, lighting fittings of street lamps, screens, etc [9].

The procedures followed for shaping PMMA sheets by vacuum forming, sheet blowing and press forming, with reference to the schemes in figure 11, have been described as follows in reference [9].

**Vacuum forming (figure 11, top):** A sheet of PMMA is warmed to soften it, and then placed on the top of a hollow mould fitted with a pipe through which air can be drawn. The sheet is clamped over the mould, and the air is drawn out the pipe. A vacuum forms under the sheet, which is drawn down and held in the shape of the mould. When it cools, the plastic hardens and retains the shape of the mould.

**Press forming (figure 11, center):** A sheet of thermoplastic is warmed to soften it, and then clamped on the top of a hollow mould. A former is then forced down onto the plastic, which is pressed into the hollow of the mould. When it cools, the plastic hardens and retains the shape of the mould [9].

**Sheet blowing (figure 11, bottom):** A sheet of thermoplastic is softened by warming and placed on a table in which there is an air inlet pipe. A collar is clamped onto the plastic, and air is blown into the space between plastic and table-top. The plastic forms a large bubble with its base conforming to the shape of the collar. As it cools in the blown shape, the plastic may be also blown in this way into a mould, the bubble of plastic then taking up the shape of the mould [9].

The most interesting properties of PMMA sheets are:

--- Transparency;
--- Weather resistance;
--- Mechanical processability;
--- Light, safe in use;
--- Non-toxic;
--- Easy to process.

PMMA sheets are widely used in engraving, advertisement sheet, instrument, parts of instrument, lamps, decoration, airplane, automobile fittings, medical appliances, work of art, insulation material for electrical appliances, specimen, sign board and various articles for light industry, culture and education, livelihood, etc. [14].

The main characteristics of PMMA in various form and grade have been summarized in reference [9] through the data panel reproduced in table 1 whereas typical properties of commercial grade PMMA are reported in table 2 [15].

The values of some more interesting quantities of PMMA are listed in table 3.

As already written in many applications PMMA substituted glass. Such an interesting process, according to reference [16], is accounted for by comparing some of the properties that characterize the two materials.

1) Glass is more heavy than PMMA;
2) PMMA does not shatter;
3) PMMA is easily shaped around its glass transition temperature (≈105°C);
4) PMMA transmits 92% of visible light, more than glass;
5) PMMA, contrary to glass, does not filter UV light (<Some manufacturers coat their PMMA with UV films to add this property> [16]);
TABLE 1: POLYMETHYL METHACRYLATE- DATA PANEL

4) CHARACTERISTICS

Colour: Excellent clarity and high transparency. Will pipe light and transmit it round curves.

Texture: Warm and pleasant to the touch.

General Physical Properties:
Odourless, tasteless and non-toxic.
Strong and rigid.
Good resistance to sharp blows.
Surface scratches easily, and contact with grit and other harsh scouring agents should be avoided.
Easily moulded and machined.
Slightly heavier than water (S.G. 1.18).

Water: Negligible absorption. Dimensional stability and electrical properties remain good under humid conditions.

Heat: Thermoplastic. Loses shape in boiling water.
(Some cast acrylic compositions will withstand boiling water, and heat-resisting moulding compositions remain undistorted up to 200° F.)
Cannot be steam sterilized.
Decomposes on heating strongly and burns slowly but does not flash-ignite. (Contd. p. 120.)

Does not become brittle at low temperatures.

Solvents and chemicals:
Unaffected by most household chemicals such as weak and strong alkalies, bleaching compounds and window-cleaning solutions, salt, vinegar, animal and mineral oils, waxes and common foodstuffs.
Attacked by perfume, petrol (gasoline), cleaning fluids, acetone, chloroform, and strong solutions of oxidizing acids.

Light: Effect negligible.
Age: Weathering does not affect transparency, dimensional stability or electrical properties.

Electrical: Excellent insulation and arc-resistance.

Continue
TABLE 1: POLYMETHYL METHACRYLATE - DATA PANEL

B) APPLICATIONS

(1) Solutions; emulsions.
Solutions and emulsions of polymethyl methacrylate are produced for use as surface coatings, adhesives, finishes, etc.

(2) Sheet.
Polymethyl methacrylate is available in sheets of various thicknesses and in many sizes. There is a complete range of colours and transparencies ranging from clear transparent to black, opaque. They are also made in patterned and corrugated surfaces.
Examples of Uses: Aircraft glazing; building panels; advertising display; lighting fittings, baths; sinks; protective shields; dials; ornamental ware, roof lighting (corrugated sheet).

(3) Rods and tubes.
A range of diameters and thicknesses is available.
Examples of Uses: Electric lighting; fancy goods; advertising displays; dental and medical illuminating equipment.

(4) Moulding materials.
Moulding powders are produced in a range of clear and coloured grades, for compression and injection moulding, extrusion, etc.
Examples of Uses: Lenses; dentures; toilet articles; handles and knobs; telephones.

6) PMMA allows infrared light of up to 2800 nm wavelength to pass. IR of longer wavelengths, up to 25,000 nm, is essentially blocked [16].

7) PMMA can be joined using cyanoacrylate cement (so-called "Superglue"), or by using liquid di-or-trichloromethane to dissolve the plastic at the joint which then fuses and sets, forming an almost invisible weld [16].

8) PMMA can also be easily polished to restore cut edges to full transparency [16].

A typical light transmission curve of a 2mm thick Plexiglas (PMMA) sheet in air is shown in figure 12 [17].
Artifacts, where glass was substituted by PMMA, obtained by cast thermoforming techniques, are shown in figure 13 [18,19].
PMMA is also used in the manufacturing of lenses of automobile running-lights.
TABLE 2: typical properties of commercial grade PMMA [15].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, g/cm³</td>
<td>1.17–1.20</td>
</tr>
<tr>
<td>Refractive index, ( n_D^{25} )</td>
<td>1.49</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>7000–11,000</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>2–10</td>
</tr>
<tr>
<td>Tensile modulus, ( 10^8 ) psi</td>
<td>4.5</td>
</tr>
<tr>
<td>Impact strength, ft-lb/ in. of notch</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Heat-deflection temp., °F, 264 psi</td>
<td>155–210</td>
</tr>
<tr>
<td>Dielectric constant, 1000 cycles</td>
<td>3.0–3.6</td>
</tr>
<tr>
<td>Dielectric loss, 1000 cycles</td>
<td>0.03–0.05</td>
</tr>
<tr>
<td>Water absorption, 1/4 in. bar, 24 hr, %</td>
<td>0.3–0.4</td>
</tr>
<tr>
<td>Burning rate</td>
<td>Slow</td>
</tr>
<tr>
<td>Effect of sunlight</td>
<td>None</td>
</tr>
<tr>
<td>Effect of strong acids or bases</td>
<td>Attacked</td>
</tr>
<tr>
<td>Effect of organic solvents</td>
<td>Soluble</td>
</tr>
<tr>
<td>Clarity</td>
<td>Transparent</td>
</tr>
</tbody>
</table>

TABLE 3: The values of some more interesting quantities of PMMA.

- Glass transition temperature (\( T_g \)) = 105°C
- Crystalline PMMA: Density = 1.23 g/cm³;
  \( T_m = 170-200°C \)
- Thermal linear expansivity (\( 10^{-3} \) K⁻¹) = 4.5
- Specific heat capacity (KJ Kg⁻¹ K⁻¹) = 1.39
- Thermal conductivity (W m⁻¹ K⁻¹) = 0.19
- Solubility parameter (\( \delta \)) (cal¹/² cm⁻³) = 9.2
  (the resin is soluble in acetone and toluene).
- Upper service temperature (continuous use) = 80°C
- Heat enthalpy of combustion (KJ g⁻¹) = 26.2
- In the presence of air, PMMA ignites at 460°C and burns completely to form only carbon dioxide and water.
**FIGURE 12:** Light transmission curve of a 2mm thick Plexiglass (PMMA) sheet in air. At wavelength above 400nm, the transmission is constrained by the Fresnel losses which amount to approx. 8%. Below 400nm the bulk absorption becomes predominant. The sample doesn’t transmit any light below 360nm [17].

**FIGURE 13:** Artifacts in PMMA, obtained by cast thermoforming techniques.  
*Left:* Double bubble screens produced by Fabbri  *< It is made of 3mm thick PMMA cast thermoformed acrylic for maximum strength and flexibility......The double bubble design gives the rider improved aerodynamics and improved visibility of the bike, instruments whilst offering Italian styling and top quality > [18].*  
*Right:* Billion Lighting PMMA outdoor lamp & lamp shade.  
*< Billion LED has a big advantage in safe, energy saving, luminance and life time, and is new high technical green products which is widely used in streets, bridges, factories, living areas... > [19].*
For some special applications, where higher impact performance needed, the impact strength of PMMA may be implemented by rubber toughening procedures based on the formulation of suitable compatible blends with rubber-like polymers.

PMMA resins, because of their interesting combination of properties, and especially for their high optical clarity and exceptional weatherability now a days, find use in a wide variety of applications ( glazing, signs and displays, lighting fixtures, automotive (mainly taillights) and sanitary ware applications ). In many of these uses, PMMA resins compete directly with polycarbonate, < which has similar optical properties and better impact resistance but is more susceptible to UV degradation and is more expensive than acrylics. Other competing materials in selected applications include styrene-acrylonitrile (SAN), thermoplastic copolymers (i.e., PETG and PCTG, which are glycol-modified PET resins), polystyrene, polyvinyl chloride ( particularly for extruded sheet ) and polycarbonate > [20].

The relevant role of PMMA, and more in general of the acrylic resins, in the market of plastic materials emerges by the pie charts, showings the world consumption of MMA and of acrylic resins and related plastics, reported in figure 14 [20,21].

**FIGURE 14:** World consumption per country and geographic Regions. Left- Methyl methacrylate monomer (MMA), 2008. Right- polymethylmethacrylate (PMMA) and acrylic resins, 2006 [20,21].

Quite recently the synthesis conditions of MMA have been innovated to produce tailor made products. As example the case of the "Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization" procedure may cited in the above context.
Most of the advantages of RAFT polymerization as described in reference [22] include:

- The ability to control polymerization of most monomers polymerizable by radical polymerization. These include (meth)acrylates, (meth)acrylamides, acrylonitrile, styrenes, dienes and vinyl monomers.
- Tolerance of unprotected functionality in monomer and solvent (e.g., OH, NR₂, COOH, CONR₂, SO₂H). Polymerizations can be carried out in aqueous or protic media.
- Compatibility with reaction conditions (e.g., bulk, organic or aqueous solution, emulsion, mini-emulsion, suspension).
- Ease of implementation and inexpensive relative to competitive technologies.

The molecular structures of some typical RAFT agents for controlled radical polymerization, and of radical initiators, especially suited for the polymerization of MMA, are described in the figures 15 and 16 respectively [22].

**Figure 15:** The molecular structures of RAFT agents effective in controlling the radical polymerization of MMA, see text [22].
<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1'-Azobis(cyclohexanecarbonitrile), ACHN</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>2,2'-Azobis(2-methylpropanamidine) dihydrochloride, AAPH</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>2,2'-Azobis(2-methylpropanitrile), AlBN</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>4,4'-Azobis(4-cyanovaleric acid), ACVA</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
</tbody>
</table>

**FIGURE 16**: The molecular structures of some radical initiators, used for the polymerization of MMA [22].

**FIGURE 17**: Molecular weight distributions of PMMA formed by high conversion RAFT polymerization of MMA (6.55 M in benzene) with 1,1'-azobis(1-cyclohexanecarbonitrile) (0.0018 M) as initiator and various concentration of RAFT agent 5 for 6h at 90°C [22].
From figure 17 it can be seen as by playing with the chemical nature of the RAFT agent, with its concentration and with the nature of initiator, as well as with many other physical chemical parameters it is possible to obtain PMMA polymers with a sharp distribution of the molecular mass but also with a wide range of tailored molecular weight [22]. This means that now day it is possible to produce PMMA with properties adjusted to the final use [23].

It must be underlined that a limitation to the optical performances of PMMA is related to the relatively poor abrasion resistance compared to glasses even if effort have been developed to improve this properties by using additives and polymers with tailored molecular characteristics.
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17) C. Joram, <Transmission curves of plexiglass (PMMA) and optical grease>, 26 October 2009, pdf (2010).
CHAPTER – TWELFTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (METHYLMETHACRYLATE )

B ) METHODOLOGIES AND TESTS FOR THE IDENTIFICATION OF PMMA IN ARTEFACTS

In previous chapter it has been seen as PMMA is generally obtained by a free radical polymerization, according to the hereafter reported scheme.

\[
\text{methyl methacrylate} \xrightarrow{\text{free radical vinyl polymerization}} \text{poly(methyl methacrylate)}
\]

As shown by the data reported in the tables 1, 2 and 3 the mechanical, thermal, rheological and optical properties, as well as density, of PMMA are strongly influenced by:
--- Synthesis method; additives used and processing conditions [1,2,3].

For example it can be seen as it is possible to produce impact-modified moulding compounds based on PMMA characterized ( see table 3 ) by:
--- High break resistance and impact strength;
--- Improved crazing resistance;
--- Brilliant optics;
--- High surface hardness and abrasion resistance [3].

The Properties of the Plexiglass-7M Moulding Compound from EVONIK Industries are shown in table 1 [1]. In the catalogue such a compound is recommended for the following characteristics:
--- Excellent light transmission and brilliance;
--- Excellent weatherability;
--- High mechanical strength, surface hardness and abrasion resistance [1].

This Plexiglass-7M PMMA is suitable for extruding profiles and panels for use in lighting engineering.
**TABLE 1:** Properties of the Plexiglass-7M Moulding Compound from EVONIK Industries [1].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Standard</th>
<th>PLEXIGLAS® 7M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>1 mm/min</td>
<td>MPa</td>
<td>ISO 527</td>
</tr>
<tr>
<td>Stress @ Break</td>
<td>5 mm/min</td>
<td>MPa</td>
<td>ISO 527</td>
</tr>
<tr>
<td>Strain @ Break</td>
<td>5 mm/min</td>
<td>%</td>
<td>ISO 527</td>
</tr>
<tr>
<td>Charpy Impact Strength</td>
<td>23°C</td>
<td>kJ/m²</td>
<td>ISO 179/1eU</td>
</tr>
<tr>
<td><strong>Thermal Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicat Softening Temperature</td>
<td>8 / 50</td>
<td>°C</td>
<td>ISO 306</td>
</tr>
<tr>
<td>Glass Transition Temperature</td>
<td></td>
<td>°C</td>
<td>IEC 10006</td>
</tr>
<tr>
<td>Coeff. of Linear Therm. Expansion</td>
<td>0 - 50°C</td>
<td>E-5 /°K</td>
<td>ISO 11359</td>
</tr>
<tr>
<td>Flammability UL 94</td>
<td>1.6 mm</td>
<td>Class</td>
<td>IEC 707</td>
</tr>
<tr>
<td><strong>Rheological Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Volume Rate, MVR</td>
<td>230°C / 3.8kg cm³/10min</td>
<td>ISO 1133</td>
<td>2.9</td>
</tr>
<tr>
<td><strong>Optical Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Luminous transmittance</td>
<td>D65</td>
<td>%</td>
<td>ISO 13468-2</td>
</tr>
<tr>
<td>Refractive Index</td>
<td></td>
<td></td>
<td>ISO 489</td>
</tr>
<tr>
<td><strong>Other Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>g/cm³</td>
<td>ISO 1183</td>
</tr>
</tbody>
</table>

**TABLE 2:** Properties of the Plexiglass-7H Moulding Compound from EVONIK Industries [2].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Standard</th>
<th>PLEXIGLAS® 7H</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Properties</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>1 mm/min</td>
<td>MPa</td>
<td>ISO 527</td>
</tr>
<tr>
<td>Stress @ Break</td>
<td>5 mm/min</td>
<td>MPa</td>
<td>ISO 527</td>
</tr>
<tr>
<td>Strain @ Break</td>
<td>5 mm/min</td>
<td>%</td>
<td>ISO 527</td>
</tr>
<tr>
<td>Charpy Impact Strength</td>
<td>23°C</td>
<td>kJ/m²</td>
<td>ISO 179/1eU</td>
</tr>
<tr>
<td><strong>Thermal Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicat Softening Temperature</td>
<td>8 / 50</td>
<td>°C</td>
<td>ISO 306</td>
</tr>
<tr>
<td>Glass Transition Temperature</td>
<td></td>
<td>°C</td>
<td>IEC 10006</td>
</tr>
<tr>
<td>Temp. of Deflection under Load</td>
<td>0.45 MPa</td>
<td>°C</td>
<td>ISO 75</td>
</tr>
<tr>
<td>Temp. of Deflection under Load</td>
<td>1.8 MPa</td>
<td>°C</td>
<td>ISO 75</td>
</tr>
<tr>
<td>Coeff. of Linear Therm. Expansion</td>
<td>0 - 50°C</td>
<td>E-5 /°K</td>
<td>ISO 11359</td>
</tr>
<tr>
<td>Fire Rating</td>
<td></td>
<td></td>
<td>DIN 4102</td>
</tr>
<tr>
<td>Flammability UL 94</td>
<td>1.6 mm</td>
<td>Class</td>
<td>IEC 707</td>
</tr>
<tr>
<td><strong>Rheological Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Volume Rate, MVR</td>
<td>230°C / 3.8kg cm³/10min</td>
<td>ISO 1133</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>Optical Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Luminous transmittance</td>
<td>D65</td>
<td>%</td>
<td>ISO 13468-2</td>
</tr>
<tr>
<td>Haze</td>
<td></td>
<td></td>
<td>ASTM D1003</td>
</tr>
<tr>
<td>Refractive Index</td>
<td></td>
<td></td>
<td>ISO 489</td>
</tr>
<tr>
<td><strong>Other Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>g/cm³</td>
<td>ISO 1183</td>
</tr>
</tbody>
</table>

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TABLE 3: Properties of the Plexiglas zk4(5.6)BR; Rohm Moulding Compound [3].

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Unit</th>
<th>Standard</th>
<th>PLEXIGLAS®zk4BR</th>
<th>PLEXIGLAS®zk5BR</th>
<th>PLEXIGLAS®zk6BR</th>
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<tbody>
<tr>
<td>Tensile modulus (1 mm/min)</td>
<td>MPa</td>
<td>ISO 527</td>
<td>2800</td>
<td>2400</td>
<td>1800</td>
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<tr>
<td>Yield stress (50 mm/min)</td>
<td>MPa</td>
<td>ISO 527</td>
<td>71</td>
<td>62</td>
<td>45</td>
</tr>
<tr>
<td>Yield strain (50 mm/min)</td>
<td>%</td>
<td>ISO 527</td>
<td>4.5</td>
<td>4.5</td>
<td>5</td>
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<tr>
<td>Nominal strain at break</td>
<td>%</td>
<td>ISO 627</td>
<td>19</td>
<td>27</td>
<td>54</td>
</tr>
<tr>
<td>Charpy impact strength (23°C)</td>
<td>kJ/m²</td>
<td>ISO 179</td>
<td>25</td>
<td>50</td>
<td>80</td>
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<tr>
<td>Thermal properties</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Vical softening temperature (B/50)</td>
<td>°C</td>
<td>ISO 306</td>
<td>102</td>
<td>100</td>
<td>95</td>
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<tr>
<td>Glass transition temperature</td>
<td>°C</td>
<td>IEC 10000</td>
<td>108</td>
<td>109</td>
<td>109</td>
</tr>
<tr>
<td>Temp. of deflection under load (0.45 MPa)</td>
<td>°C</td>
<td>ISO 75</td>
<td>95</td>
<td>88</td>
<td>83</td>
</tr>
<tr>
<td>Temp. of deflection under load (1.8 MPa)</td>
<td>°C</td>
<td>ISO 75</td>
<td>95</td>
<td>93</td>
<td>88</td>
</tr>
<tr>
<td>Coeff. of linear therm. expansion (0-50°C)</td>
<td>10⁻¹⁰K⁻¹</td>
<td>ASTM E831</td>
<td>11</td>
<td>9</td>
<td>11</td>
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<td>Flammability UL 94 (at nom. 1.6 mm)</td>
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<td>IEC 707</td>
<td>HB</td>
<td>HB</td>
<td>HB</td>
</tr>
<tr>
<td>Rheological properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt volume rate, MVR (230/3.5)</td>
<td>cm³/10min</td>
<td>ISO 1133</td>
<td>4.5</td>
<td>3.3</td>
<td>1.6</td>
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<tr>
<td>Optical properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transmission factor, fₚₚₛ</td>
<td>%</td>
<td>DIN 6036</td>
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<td>92</td>
<td>91</td>
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<tr>
<td>Haze</td>
<td>%</td>
<td>ASTM D1003</td>
<td>&lt; 1.5</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Refractive index</td>
<td></td>
<td>ISO 489</td>
<td>1.49</td>
<td>1.49</td>
<td>1.49</td>
</tr>
<tr>
<td>Other properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>ISO 1183</td>
<td>1.18</td>
<td>1.17</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Some of the most used techniques used for the characterization of PMMA samples are below discussed.

**Infrared and Raman spectroscopy**

FT-IR Spectroscopy represents an effective technique for the recognizing of PMMA in plastic made objects. As matter of fact as shown by figure 1, specific features characterize the Infrared spectrum of PMMA, which allows the easy identification of this polymer.

In particular it can be seen that the FTIR spectrum of PMMA shows (see figure 1):

--- A sharp intense peak at 1731 cm⁻¹, which can be attributed to the presence of C=O stretching vibrations;
--- A broad peak ranging from 1260 to 1000 cm⁻¹ that is due to C-O (ester bond) stretching vibrations;
--- A broad band from 950 to 650 cm⁻¹ related to the C-H bending;
--- A broad peak from 3000 to 2900 cm⁻¹ due to the presence of C-H stretching vibrations [4].

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Lycra fabrics are largely used in the production of exercise clothing, leggings, bathing suits and socks. It is more often used in women's clothing for its form-fitting nature. Most commonly used for cycling clothes, dance costumes or any activity that requires stretch fabric. The thinnest type of Lycra is used in hosiery [32].

**FIGURE 15:** Electron micrograph showing PU-Spandex fibers. It can be seen that each fiber consists of several filaments [31].

**FIGURE 16:** Modern PU industries are capable to offer Lycra fabrics in a wide range of colors [32].
Very useful data for the identification of PMMA are also obtained by Raman spectroscopy as can be observed by the Raman spectrum of a sample of PMMA shown in figure 2 [5].

**FIGURE 2:** Raman spectrum of PMMA [5].

**FIGURE 3:** the $^1$H-FTNMR proton Fourier transform nuclear magnetic resonance spectrum of PMMA (in deuterated chloroform as solvent) [4].
FIGURE 4: the $^{13}\text{C}$-FT-NMR proton Fourier transform nuclear magnetic resonance spectra of PMMA (in deuterated chloroform as solvent) [4].

FIGURE 5: The NMR-$^1\text{H}$ spectra registered in solutions of o-dichlorobenzene-$d_8$ of samples of PMMA: a) isotactic; b) syndiotactic, and c) atactic [6].
**Liquid state $^{13}$C- and $^1$H-NMR Nuclear Magnetic Resonance Spectroscopy**

These techniques turn to be also useful in the identification of PMMA. As matter of fact, the $^1$H-FTNMR and the $^{13}$C-FT-NMR proton Fourier transform nuclear magnetic resonance spectra of PMMA shown in the figures 3 and 4 respectively, shown clear features characteristic of the molecular structure of the polymer [4].

The peaks related to the methoxy carbon (OCH－) are clearly observed in the $^1$H-FTNMR spectrum of PMMA (figure 3).

The main features of the $^{13}$C-FT-NMR spectra of PMMA (see figure 4) are the peaks corresponding to the methyl carbon (CH$_3$－) at $\delta = 17$–21 ppm, the methoxy carbon (CH$_3$O－) at $\delta = 51.27$ ppm, the quaternary carbon (C$_4$) at $\delta = 44$–45 ppm, the methylene carbon (–C$_2$H$_2$－) at $\delta = 52$–54 ppm and the carbonyl carbon (–C=O) at $\delta = 176.9$ ppm [4].

The technique of the Nuclear Magnetic Resonance Spectroscopy (1H NMR), as can be deduced by the spectra shown in the figure 5, is suitable also in differentiating between PMMA polymers having a different molecular stereo-structure (isotactic; syndiotactic, and isotactic) [6].

**Solid state NMR Nuclear Magnetic Resonance Spectroscopy**

Such a technique is interesting not only for the kind of data capable to gives and for its non-destructive nature, but also because, with suitable devices, may be applied in “situ” that is directly in the room where the objects are stored.

A well resolved solid state CP/MAS $^{13}$C-NMR spectrum of PMMA is shown in figure 6 [7].

It can be seen that PMMA presents signals at 16.7, 45.2, 52.2 and 178.1 ppm,

![FIGURE 6: CP/MAS 13C NMR spectra of a sample of PMMA (in figure the spectrum of PMMA is shown at the bottom)](image-url) [7].
The assignment of CP/MAS 13CNMR Chemical Shifts of PMMA, led to the results hereafter reported [7].

\[ \text{\textgreater{}C\textless{}O ( 178.1 \)} \text{-CH}_2\text{ ( 52.2 )} \text{-OCH}_3\text{ ( 52.2 )} \text{\textgreater{}C\textless{} ( 45.2 \)} \text{-CH}_3\text{ ( 16.7 )} \]

From the CP/MAS 13CNMR study ( the experiments were performed at ambient probe temperature ) it was also possible to conclude that the polymer presents an heterogeneous morphology, having rigid as well as mobile regions [7].

To recognize PMMA the following tests may be also of utility [8]:

--- \textbf{Litmus and pH Tests for Combustion Vapours of Plastics}. In the case of PMMA the colour is essentially unchanged and the pH of the paper results to be between 5.0–5.5.

--- \textbf{Specific Gravity measurements}. For Poly(methyl methacrylate) the values are 1.16–1.20.

--- \textbf{Specific Gravities in Relation to Standard Saturated Solutions}. Suitable data, attesting the suitability of this test, are shown in figure 7 [8].

--- \textbf{Burning Identification Test}: Yellow flame; yellow top; drippings may burn.

--- \textbf{Odour after extinguishing the flame}: Fruity [9].
**FIGURE 7**: Specific gravities of selected plastics in relation of standard saturated solutions [8].
REFERENCES

9) F. Rémillard, 200Identification of Plastics and Elastomers, Miniaturized Tests 7, Centre de Conservation du Quebec, pdf.
CHAPETER—THIRTEENTH
THE EARLY SYNTHETIC THERMOPLASTICS
POLY (METHYLMETHACRYLATE)

C) DEGRADATION PHENOMENA IN PMMA ARTEFACTS

Polymethylmethacrylate (PMMA) like any other polymer exposed, especially in outdoor conditions, to solar or ultraviolet light, temperature fluctuations, oxygen, humidity, acid rains, snow, wind, and air-borne biological and to various chemical agents undergoes degradation. Hereafter the most relevant mechanisms of degradation, together with their effects, are described according to the nature of the generating factors.

C.1) Thermal degradation and thermo-oxidative processes

ThermoGravimetry (TGA), Differential Thermogravimetry (DTGA), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC) are very effective techniques in studying the thermal and thermo-oxidative degradation of PMMA. PMMA is a low burning material, with flammability and ignition characteristics quite similar to wood; for such a reasons the thermal and flammability of PMMA have been also widely investigated [1].

**FIGURE 1:** Thermogravimetry (TGA), diagram (a), Differential thermogravimetry DTGA, curve (b) and Differential thermal thermogram DTA, curve (c) of PMMA, under nitrogen atmosphere (heating rate 10°C/min) [1].

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Typical TGA, DTGA and DTA thermograms of samples of PMMA (average Mn = 292,000), under nitrogen atmosphere are shown in figure 1 [1].

From the figure 1-(a) it can be seen that the TGA diagram presents two main reaction stages, which are clearly evidenced by the two corresponding peaks in the DTGA curve, figure 1-(b).

Moreover it also emerges that the thermal decomposition of PMMA is accompanied by a process of heat absorption as shown by the endothermic peak observed at its decomposition temperature, figure 1-(c) [1].

In reference [1] the thermal data presented in figure 1 are accounted for by assuming that:

<--- The first reaction stage (240-310°C) and second reaction stage (310-430°C) were caused by end initiated and random scission respectively.
--- The second part of the degradation shows two peaks (351 and 376°C) in the DTA curve; the former degradation may be due to the de-polymerization of saturated end group product of disproportion.
--- PMMA is destroyed virtually completely at 433°C.
--- A lower tendency to form char...... is related to the de-polymerization which yields only monomer....> [1].

The thermal degradation of PMMA, also in presence of oxygen (thermo-oxidative process) was investigated in reference [2].

From the DSC thermogram shown in figure 2 (curve 1), performed in inert gas, helium, with only a small % of O2, the following information have been obtained:

--- The thermal degradation of PMMA begins at about 320°C.
--- The temperature of the onset of intensive degradation of the polymer, T5, in inert atmosphere, is between 290-315°C.
--- The DSC thermogram shows well-defined peaks corresponding to the degradation process of the polymer [2-a].

According to literature data <at elevated temperatures, the thermal degradation of PMMA is the chain radical reaction of de-polymerization > [2-a]. The chemical reactions involved the initiation, propagation and termination stages of this process are described, with reference to the schemes shown in figure 3, as follows in reference [2-a]:

< At 300-400°C, initiation of the PMMA depolymerization proceeds via random scission of backbone C-C bonds with formation of two free macro-radicals (Eq. (1) in figure 3). The main volatile product of the degradation process, methyl methacrylate, (≈ 100%) forms in de-propagation of macro-radicals (Eqs. (2) and (3) in figure 3)...... Reactions (1)-(3) are endothermic and reactions (4) and (5) are exothermal. The overall process of the thermal degradation of PMMA is endothermic > [2-a].

In agreement also with other literature data it may be concluded that the thermal degradation of PMMA in absence of oxygen is essentially based on a mechanism of depolymerization that starting from a chain end or other weak points along the macromolecules, successive monomer units are lost to yield as final product essentially only MMA units (see figure 3) [2-a,b]. It is important to note that this mechanism of degradation produces a rapid volatilisation with small change in PMMA molecular weight [2-b].

The DSC thermogram of PMMA in dynamic oxygen is shown in figure 4. In presence of oxygen the thermal stability of PMMA decreases significantly. As matter of fact it is found that the value of T5 diminishes by 45°C (T5 = 275°C) in comparison with the value observed for PMMA heated in
the inert gas containing only a small amounts of oxygen (compare figure 2 and 4) [2-a]. It is interesting to note that $T_b = 290$-$315^\circ\text{C}$ in inert atmosphere.

The thermo-oxidative processes of degradation as reported in reference [2-a], may be described according to the scheme of chemical reactions depicted in figure 5. It has been demonstrated that reactions (10), (11), and (13)-(17) are endothermic while reactions (12), (18) and (19) are exothermal. The overall thermo-oxidative process results to be exothermal [2-a].

![DSC thermogram of PMMA in dynamic helium containing 0.06% of oxygen](image)

**FIGURE 2:** DSC thermogram of PMMA in dynamic helium containing 0.06% of oxygen [2-a].

The mechanism of thermo-oxidative degradation at higher temperatures, is dominated by the fact that 

"oxygen enhances random main-chain scission: thermal oxidation reduces the degree of polymerization much faster than thermal degradation under nitrogen" [2-a].

The monomer MMA is the major low molecular weight product of the PMMA thermo-oxidative process (>90%). Nevertheless the presence of methyl-oxirane carboxylic acid methyl ester, methyl pyruvate, dimethyl itaconate and acetaldehyde was also observed [2-a].

In conclusion it can be affirmed that the thermo-oxidation of PMMA at high temperatures is a very complex process "which includes the stages of the purely thermal (Eqs. (1)-(5) in figure 3) and oxidative (Eqs. (10)-(19) in figure 5) degradation"> [2-a].

In figure 6 the thermal stability of PMMA as determined by TGA in nitrogen is compared with those of other polymers. The data shown in figure 6 are commented as follows in reference [3]:

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< Polyvinylchloride (PVC) first loses HCl; later, the mixture of unsaturated carbon-carbon backbone and unchanged PVC partly chars and partly degrades to small fragments. PMMA, linear polyethylene (HPPE) and polytetrafluoroethylene (PTFE) degrade completely to volatile fragments, while a polyimide (PI) partly decomposes, forming a char above 800°C > [3].

**FIGURE 3:** Chemical reactions involved in the Initiation (1), Depropagation (2), (3) and Termination (4) stages of the process of thermal degradation of PMMA at elevated temperatures (see text) [2]. In the figure: $K_{int}$, $k_d$, and $k_t$ are the rate constants and $R_{m}^*$ and $R_{n}^*$ are macro-radicals; $M$ is a polymer molecule [2-a].
It has been demonstrated that PMMA have the tendency, at elevated temperatures, to degrade via an unzipping mechanism that leads to the production of essentially MMA monomers. To mitigate such a disadvantage, especially in the course of processing, many procedures have been developed to improve the stability of PMMA against heat and oxygen. Most of them forecast the use of proper and tailor-made additives capable to inhibit the thermal and thermo-oxidative degradation processes [4]. Some of them, recently investigated, are hereafter briefly described.

--- Use of silica nanoparticles as filler for PMMA

The effect of the presence of silica nanoparticles (SiO₂) on thermo-oxidative behaviour of PMMA was investigated by TGA in reference [5]. It was found that as can be seen by the thermograms reported in figure 7, the dispersed SiO₂ may mitigate, using relatively low amount of filler, the thermo-oxidative degradation of PMMA.

From their study Zou and Yoshida were able to demonstrate that:

< The improvement efficiency on thermal stability depended on the dispersion state of SiO₂ nano-particles and the size of SiO₂ particles. The degradation improvement increased with increasing the specific surface area of SiO₂ particles due to the decrease in PMMA molecules free from the trapping on SiO₂ particle surface > [5].
\[
\begin{align*}
\text{RH} + \text{O}_2 &\rightarrow \text{R}^* + \text{HO}_2^* \quad (10) \\
2\text{RH} + \text{O}_2 &\rightarrow 2\text{R}^* + \text{H}_2\text{O}_2 \quad (11) \\
\text{R}^* + \text{O}_2 &\rightarrow \text{RO}_2^* \quad (12) \\
\text{RO}_2^* + \text{RH} &\rightarrow \text{ROOH} + \text{R}^* \quad (13) \\
\text{ROOH} &\rightarrow \text{RO}^* + \text{HO}^* \quad (14) \\
\text{ROOH} + \text{RH} &\rightarrow \text{RO}^* + \text{H}_2\text{O} + \text{R}^* \quad (15) \\
\text{RH} + \cdot\text{OH} &\rightarrow \text{R}^* + \text{H}_2\text{O} \quad (16) \\
\text{RH} + \text{RO}^* &\rightarrow \text{ROH} + \text{R}^* \quad (17) \\
\text{R}^* + \text{RO}_2^* &\rightarrow \text{ROOR} \quad (18) \\
\text{RO}_2^* + \text{RO}_2^* &\rightarrow \text{ROH} + \text{O}_2 + \text{R}=\text{O} \\
&\rightarrow \text{ROOR} + \text{O}_2 \quad (19)
\end{align*}
\]

**FIGURE 5:** Main reactions in the thermo-oxidative process of degradation of PMMA [2-a].

**FIGURE 6:** Comparison of thermal stability of various polymers (see text) [3].
Concerning the values of the thermal degradation temperature (Td) the following was demonstrated:
1) For the composite of 23 nm (diameter) SiO$_2$–PMMA (6.1 wt%) Td is 13.5 °C higher than that of PMMA.
2) The Td of 17 nm SiO$_2$–PMMA (3.2 wt%) and 13 nm SiO$_2$–PMMA (4.8 wt%) resulted to be 21 and 23 °C higher than that of PMMA without SiO$_2$ respectively [5].

--- Antimony oxide (Sb$_2$O$_3$) particles as thermal stabilizer of PMMA

The influence of the presence of Sb$_2$O$_3$ particles dispersed as filler in PMMA matrices upon the thermal stability behaviour and the flammability properties of the polymer was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), cone calorimetry and limiting oxygen index (LOI) measurements by Laachachi and others as function of Sb$_2$O$_3$ amounts: 5, 10 and 20 wt% [6].
The TGA and DTGA thermograms (in air) of the plain PMMA and of the composites containing different amount of \( \text{Sb}_2\text{O}_3 \) (5, 10 and 20 wt\%) are shown in figure 8 [6]. It can be seen that the first DTGA peak shifts from 325°C for plain PMMA to 366°C for the composite containing the 20 wt\% \( \text{Sb}_2\text{O}_3 \). Such a finding indicates an increase of the thermal stability of about 40°C. Moreover the results of the investigation showed also an enhancement of the fire retardant properties of PMMA, which increases with the content of \( \text{Sb}_2\text{O}_3 \) [6].
--- *Inhibition of thermo-oxidative degradation of poly(methylmethacrylate) by Fullerene \( \text{C}_{60} \)*

The effects of \( \text{C}_{60} \) (see molecular structure in figure 9) on the thermo-oxidative degradation of PMMA was investigated by Troitskii and others by TGA and DSC. The samples were kept under oxygen at 282°C, at initial pressure of 200 mm, and the weight loss (%), as function of time, of plain PMMA was compared with that of a sample containing the 0.2 mol% of fullerene.

**FIGURE 9:** Molecular structure of fullerene \( \text{C}_{60} \).

**FIGURE 10:** Dependence of weight loss (%) on time in the thermo-oxidative degradation of PMMA under oxygen at initial pressure of 200 mm at 282°C. Curve-1: without additives. Curve-2: with addition of 0.2 mol% of fullerene \( \text{C}_{60} \) [2-α].
From the trends of the curves in figure 10 it can be concluded that the presence of C_{60} retards the degradation of PMMA. As matter of fact the induction period, as can be seen by the curves of dependence of weight loss of polymers on time of degradation, rises significantly in the case of the mixture (PMMA + C_{60}) [2-a].

By DSC Troitskii and Others also found that fullerene significantly increases the temperatures of the beginning of polymers degradation.

The effectiveness of C_{60} in mitigating, at high temperature the thermo-oxidative degradation process is accounted for by the interaction between C_{60} and oxygen-containing radicals with formation of less active compounds [2-a].

In the conservation of PMMA artefacts attention has to be paid to the presence of stabilisers used in the formulation as they may play some role both in degradation as well as in the maintenance effectiveness of conservative procedures. This requires the knowledge of the chemical nature and reactivity of the stabilisers most used in the past for the processing of thermoplastic polymers [4].

C.2) Photo and photo-oxidation of PMMA

Osawa and Fukuda studied the photo and the photo-oxidation of PMMA films by infrared spectroscopy [7]. Samples of the polymer films were exposed to the action of light emitted by high pressure mercury lamp (300 W), (main emission at 254, 290 and 365 nm), in air or nitrogen atmosphere.

The IR spectra of PMMA films before and after exposure are compared in figure 11. Following irradiation significant changes in IR spectra are observed at \(\approx 3400 \text{ cm}^{-1}\) due to hydroxyl groups and at 1641 cm\(^{-1}\) due to carbon-carbon double bonds.

**FIGURE 11:** Change in IR spectrum and difference spectra of PMMA during photo-irradiation. IR spectra: before exposure, full line; after 10 hrs exposure, dashed line [7].
The chemical changes induced by the photo-degradation (Photolysis) in PMMA are attributed essentially to the three major, concurrently occurring, reactions, whose schemes are described in figure 12:

--- Random homolytic scission of main-chain carbon—carbon bonds;
--- Photolysis of the ester side-groups;
--- Photo-dissociation of the methyl side-groups [8].

The formation of monomer, observed in the course of the light exposure is attributable to a process of chain depolymerization caused by the photolytic scission of main chains [8].
**FIGURE 13:** Infrared changes in the absorbance at 1641 cm$^{-1}$ during photo-irradiation in air of PMMA films as function of the time exposure [7].

**FIGURE 14:** Changes in number of chain scissions during photo-irradiation in air of PMMA homo-polymer films [7].
The photo-oxidation of PMMA was quantitatively followed by plotting the changes in absorbance at 1641 cm⁻¹ (the carbon-carbon double bonds absorption) as function of time exposure to irradiation in air. As shown by figure 13, due to formation of double bonds, the absorbance at 1641 cm⁻¹ largely increases with the ongoing of the photo-oxidation process of degradation. By suitable and consolidate procedures Osawa and Fukuda were capable to determine the variation in molecular mass induced by irradiation by measuring the number of chain scissions in the PMMA homo-polymer following photo-oxidation. The results, reported in figure 14, indicate that chain scission is a relevant process, and the number of chain scissions increases almost linearly with time [7].

Interesting to point out that under nitrogen, obviously, photo-degradation of PMMA films proceeded similarly but the rate was fairly slow [7].

The photo-oxidation of PMMA films, together with its effects on some polymer properties, was also studied by Caykara and Guven [8]. The samples were degraded in air by using as an irradiation source a high-pressure mercury lamp, 250 W and 259 nm wavelength, situated 10 cm away from the samples. The FTIR and UV-VIS absorption spectra of untreated and irradiated films of PMMA are shown in figure 15 and 16 respectively. In order to better point out the changes induced by the photo-oxidation processes the difference diagrams are also reported [8].

In the case of FTIR it may easily seen, especially from the difference spectrum, as the irradiation produces a strong increase in the intensity of the following bands:

\[ C=O \ (1735 \text{ cm}^{-1} \text{ stretching}), \]
\[ C\equiv O \ (1192 \text{ cm}^{-1} \text{ antisymmetric stretching}), \]
\[ C\equiv O \ (1149 \text{ cm}^{-1} \text{ symmetric stretching}), \]
\[ \text{and } C\equiv O \ (733 \text{ cm}^{-1} \text{ bending}) \] [8].

From the examination of the UV-VIS absorption spectra shown in figure 16 it emerges that the intensity of the \( C\equiv C \) bands at 235 nm following irradiation increases. Such finding was accounted for by scission of ester side-groups and formation of olefin insaturations [8].

From literature it comes out that the dominant mechanism of the photo-degradation of PMMA is the decomposition of ester groups followed by the scission of the backbone chains. The main products of photo and photo-oxidation result to be: methyl formate, methanol, methyl methacrylate, methane, carbon monoxide, and carbon dioxide [8,9].

The scheme of the main reactions occurring during the photo-degradation of PMMA in vacuum, following irradiation at RT with light having a wavelength of 254 nm, is depicted in figure 17 [9].

In general it is well established that the photo-oxidation of polymers is a radical process initiated by photo-active functional groups presents along the macromolecular chains or by impurities and chemical defects capable to absorb radiations with \( \lambda > 295 \) nm (this includes peroxides, carbonyls, insaturations and catalyst residues) [10,11].

According to Faucitano and Others [11] the process of photo-oxidation, following exposition to sunlight or to artificial radiations between 295 and 330 nm, in agreement with what above reported, is essentially based on the

<direct photolysis of the ester groups, with scission of the \( C\equiv C \) or \( C\equiv O \) bonds leading to the>
predominant formation of tertiary-carbon-centred chain radicals, acyloxy and acyl radicals. In the presence of oxygen, these species act as initiators of the oxidative degradation propagated by peroxy and alkoxy radicals [11].

**FIGURE 15:** FTIR absorption spectra of PMMA films. (a), after UV irradiation at room temperature. (b), before UV irradiation. (c), difference spectrum [(a)-(b)] [8].
FIGURE 16: UV-VIS absorption spectra of PMMA films. (a) after UV irradiation, (b) before UV irradiation, (c) (a)-(b) difference spectrum [8].

TABLE 1: Comparison between some of mechanical properties of irradiated and non-irradiated samples of PMMA films [8].

<table>
<thead>
<tr>
<th></th>
<th>Non-irradiated</th>
<th>Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile strength (MPa)</td>
<td>Elongation at break (%)</td>
</tr>
<tr>
<td></td>
<td>69.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

According to literature data it was found that in samples of PMMA films exposed to photodegradation no cross-links of the polymer are observed, scissions occur randomly, and the rate of photo-degradation results to be proportional to the light intensity.

The tensile mechanical properties of PMMA samples, before and after UV irradiation are compared in table 1 [8]. From the reported data it results that after UV irradiation both tensile strength and elongation at break of PMMA films decrease. Such a finding was attributed to chain scissions that, as demonstrated by the comparison of the Gel Permeation Chromatography curves shown in figure 18, lead to a considerable decrease in the molecular weight of PMMA (before irradiation, Mn = 284,000; after the irradiation, Mn = 67,000) [8].
FIGURE 17: Main reaction occurring during the photo-degradation of PMMA in vacuum. The final products of the degradation are indicated [9].

FIGURE 18: GPC chromatograms of PMMA: (a) before UV irradiation, and (b) after UV irradiation [8].
PMMA is one of the most stable polymers. Nevertheless especially in the case of out door applications and as well as in the case of products containing dyes it needs to be stabilised against photo-oxidation [4,11].

The effectiveness of some photo-stabilizers commonly used around the years 1970, was assessed by Shlyapintokh and Goldenberg [12]. The Authors investigated about the action of photo-stabilizers on the rate of macromolecule scission for PMMA films exposed in air or in inert gas to the action of light with a wave length of 253.7 nm. It was found that the effectiveness of the photo-stabilizers, whose name and chemical structure are shown in table 2, is determined solely by their absorbing capacity. Photo-conversion of PMMA is accelerated by addition of monomer or of some antioxidants. Simultaneous acceleration of the accumulation of free radicals, photo-degradation and scission of CH₂ groups is also observed. The initiating additives possess a lower photochemical activity relative to PMMA. The acceleration is due to stronger light absorption by these additives, compared to the polymer > [12].

The effectiveness of each of the photo-stabilisers listed in table 2 on the photo-degradation of PMMA was given by the ratio $W_o/W$ (where W and Wo are the degradation rates with and without additives, respectively) [12].

\[ \text{TABLE 2: The effect of additives on the rate of molecular weight decrease in the photolysis of PMMA films at room temperature in air [12].} \]

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Additive (%)</th>
<th>$W_o/W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salol</td>
<td>2</td>
<td>1.45</td>
</tr>
<tr>
<td>DSR</td>
<td>1</td>
<td>1.45</td>
</tr>
<tr>
<td>Tinuvin P</td>
<td>2</td>
<td>1.45</td>
</tr>
<tr>
<td>Tinuvin P</td>
<td>3</td>
<td>1.70</td>
</tr>
<tr>
<td>PTBPS</td>
<td>1.5</td>
<td>1.35</td>
</tr>
<tr>
<td>UV-9</td>
<td>1</td>
<td>1.20</td>
</tr>
<tr>
<td>PESA</td>
<td>2</td>
<td>1.45</td>
</tr>
<tr>
<td>A 63'99</td>
<td>4</td>
<td>1.15</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1</td>
<td>1.15</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2</td>
<td>1.50</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1</td>
<td>1.40</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>0.5</td>
<td>1.20</td>
</tr>
</tbody>
</table>

DSR-disalicylatresorine; Tinuvin P-2 (2'-hydroxy-5'-methylphenyl)-benzotriazole; PTBPS-paratertbutylphenylsalicylate; UV-9-2-hydroxy-4-methoxybenzophenone; PESA-phenyl ester of 3,5-dichlorosalicylic acid;

\[ \text{OR} \]
In investigating about the degradation and conservation of PMMA artefacts the presence of the above-mentioned additives has to be taken into consideration.

The outstanding stability of PMMA toward sunlight is due primarily to its weak absorption in the region of the UV light reaching the Earth (see figure 30 ahead). Nevertheless, it was found from molecular weight measurements that the photo-oxidation degradation of PMMA increases steadily when exposed to light with $\lambda < 330$ nm. According to reference [12-b] the photolysis of PMMA may be best explained by the assumption of light absorption by the carbonyl chromophore groups. The excited states formed this way lead to a loss of ester side groups at random with formation of free radicals. The resulting macro-radicals may either lead to chain scission directly or, in the presence of oxygen, induce oxidation processes that also cause chain scission > [12-b].

From the viewpoint of photo-stability, PMMA is classified as highly photo-stable polymers; consequently it could be used without any photo-stabilizer added. It has been found that in presence of not severe conditions of aging PMMA objects may have an outdoor life of many years [12-b].

C.3) Weathering and physical degradation of PMMA

*Weathering* is a generic term used to indicate physical and chemical degradation of materials caused on exposure to atmospheric factors (solar light, temperature, oxygen, humidity, rain, snow, wind, and air-borne biological and chemical agents) [13].

Polymer materials, including PMMA, when used for outdoors applications suffer chemical and physical damages due not only to UV radiations, which as above described produces a reduction in molecular weight and a lowering in mechanical properties, but also to other factors such as:

--- Extremes of temperatures;
--- Temperature cycling;
--- Temperature gradient (it occurs when one surface of the component is exposed to sunlight while the other is in shadow or in contact with a heat sink);
--- Erosion by rain or by wind-transported particles;
--- Chemical modifications induced by the presence of chemically reactive pollutants [14].

The weathering that drastically reduces the performance of many polymers, is, as a result, a very complex process whose mechanisms are not easy to be understood.

By following the change of some specific properties, which result to be particularly influenced by weathering, it is possible to assess the sensitivity of a polymer to the combined actions of environmental factors.

It has been found that resistance to fracture in the case of many polymers noticeably change on weathering.

< Many polymers become very brittle after exposure to natural outdoor weathering, showing a marked reduction in strength and an even greater reduction in toughness > [14].

In the case of transparent artefacts weathering may reduce the transparency inducing surface opacity while in the case of pigmented objects discoloration was quite often observed.
Suitable tests have been developed capable, by monitoring these properties; to assess the degree of damage induced by weathering on PMMA artefacts. Techniques as infrared spectroscopy and gel permeation chromatography (GPC) are very effective in following alteration of the chemical structure of PMMA, as for any other polymer, induced by weathering. As already reported by FTIR it is possible to measure an increase in the concentration of carbonyl or C=C groups resulting from photo-oxidation, while the GPC is useful in assessing the level of scission and/or cross-linking developed.

< Breaking of molecular chains will necessarily lead to a reduction in strength and toughness, and cross linking will often lead to embrittlement, hence the popularity of the GPC method of characterization in weathering studies > [14].

The results of the investigation by Qayyum and White [14] as an example of application of the above mentioned techniques to study the weathering effects on samples of PMMA taken from injection-moulded specimens are hereafter summarized.

Natural weathering experiments were performed by exposing for various periods of time, polymer specimens in the very extreme climate experienced in Jeddah, Saudi Arabia. The samples, as described in reference [14], were characterized as below reported:

< ---Samples with different exposures were tested to failure using monotonic uniaxial tension and three-point bend tests. Some Charpy impact tests were also conducted.
--- The fracture surfaces obtained in these tests were inspected in the SEM. In addition, the moulded surfaces were examined in the SEM to see whether surface markings developed on weathering.
--- Material cut from exposed samples was subjected to GPC molecular weight distribution analysis and to thermal analysis.
--- In addition, the residual stress distribution was measured for samples with different exposures > [14].

From the GPC data shown in table 3 it results that following natural environmental ageing the molecular weight of PMMA samples decreases [14]. Correspondingly reduction in some mechanical properties ( tensile strength and extension to break; flexural strength and Charpy impact strength ) were observed as demonstrated by the trend of the curves in figures 19, 20 and 21 [14].

**TABLE 3:** The results of the measurements of molecular weight by GPC in the case of PMMA exposed for various times to weathering. The corresponding Tg values are also reported [14].

<table>
<thead>
<tr>
<th>Weeks exposed</th>
<th>$M_w \times 10^{-3}$</th>
<th>$M_n \times 10^{-3}$</th>
<th>$M_w/M_n$</th>
<th>$T_g(\degree C)$ (by DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>87</td>
<td>44</td>
<td>2.0</td>
<td>101</td>
</tr>
<tr>
<td>8</td>
<td>82</td>
<td>40</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>62</td>
<td>32</td>
<td>1.9</td>
<td>97.5</td>
</tr>
</tbody>
</table>
From table 3 it can be also observed as the Tg of PMMA samples, measured from DSC thermograms (see the example shown in figure 22), following weathering is lowered of about 3-4°C.

The morphology and structure of the uniaxial tension fracture surfaces and of the Charpy impact fracture surfaces of unexposed and weathered 52 weeks specimens were investigated by Scanning
**FIGURE 22:** Typical DSC thermogram of PMMA samples from which Tg values can be easily measured from the deflection point of the curve [elaboration of the Author from data in reference 15].

**FIGURE 23:** Uniaxial tensile fracture surfaces from PMMA (a) unexposed, (b) weathered for 52 weeks [14].

**FIGURE 24:** PMMA Charpy impact fracture surfaces (a) unexposed, (b) weathered 52 weeks [14].
Electron Microscopy (SEM). From the analysis accomplished, with reference to the electron micrographs shown in figures 23 and 24 no marked differences were found indicating that weathering does not significantly affect the mode of deformation and rupture of the samples. Nevertheless the authors emphasise the fact that <weathering may cause a significant change in the residual stress distribution within a moulded bar. This can cause distortion but may also have an important influence over the fracture properties of the moulding> Moreover they pointed out <that it is necessary to know about physical changes that are promoted by weathering as well as chemical changes in order that long term serviceability may be predicted> [14].

Finally they concluded that molecular weight reduction together with changes in the residual stress distribution must be considered as the main processes in determining degradation during weathering of polymer materials [14]. The influence of temperature of service upon mechanical tensile properties is clearly evidenced by the dependence of the shape of the stress-strain curves from this factor. As shown by figure 25 it can be seen as below Tg the shape of the curve are typical of a glassy polymer, while above Tg they show features of a plastic (rubber)-like polymer material [16].

![Figure 25: Tensile stress-strain behaviour of PMMA at several temperatures][16]

Some defects in PMMA artefacts (i.e. crazes) may also be related to the well-known process of assessment of internal residual stresses accumulated during processing at high temperatures (for example injection moulding). Stress release occurs in samples of PMMA, first maintained at a temperature well above Tg, and then rapidly quenched to RT. Under such conditions <the density of the polymer will be lower than if it is slowly cooled. The rapidly quenched structure apparently freezes in some empty space in the form of holes of atomic dimension. Stress relaxation is very much more rapid in these quick-frozen samples than in slowly annealed samples> [17].
It was observed that stress relaxation in glassy polymers might produce the formation of crazes also as consequence of post cooling shrinkage. In some other samples due to the presence of residual orientation, induced by processing, typical patterns that negatively affect material properties are also observed.

**FIGURE 26:** Application of the ethanol test to verify the presence in PMMA sheets of residual stresses or orientation that may develop crazes and other defects.
- **Top-left:** Item, after the ethanol treatment, apparently showing no defects with good quality.
- **Top-right:** Sample after the ethanol test showing crazes following the relaxation of high residual stresses.
- **Bottom-right:** Sample, after the ethanol test presenting the features of the effects of the presence of both residual stresses and orientation (crazes and opacity).
- **Bottom-left:** Sample, following ethanol test showing effects caused by the presence of orientation phenomena [18].
It may happen that residual stresses relax only when the object in PMMA is already in service giving rise to the above-described negative symptoms.

The presence of residual stresses in a PMMA sample, apparently free of physical defects (crazes, opacity) may be easily evidenced by using the ethanol test. Such a test is described as follows in reference [18].

< Ethanol will reveal any residual stress. Strong surface orientation is seen as a white film on the surface of stress concentration area. Stresses which exceed the critical values give rise to crazing. The test involves immersing the cooled part in 90% ethanol at 25°C (± 1°C) for 15 minutes and then drying it as quickly as possible with compressed air. The temperature of the ethanol is important since it determines the rate at which crazing forms. >

The results of the ethanol test on samples of PMMA appearing free of defects but with stress accumulation, are clearly visible through the sequence of photo shown in figure 26 [18].

The injection moulding generally gives rise to moulded parts with accumulation of surface and internal stresses whose effects may be mitigated by annealing as reported in reference [18].

< The purpose of annealing is to redistribute both surface and internal stresses more uniformly and also to reduce their magnitude. Annealing is simply insurance of optimum quality for a well-moulded part: it cannot overcome the defects of a poor item. Properly annealed parts are more resistant to crazing by solvents which may be present in adhesives, lacquers, paints or cleaning and polishing agents. Annealing produces a substantial improvement in the strength of cemented joint.

No single combination of annealing time and temperature is satisfactory for annealing…. all items...An annealing cycle which is good for one part may have no annealing effect whatsoever on another part. Although annealing is often omitted, it is an important operation and the benefit should be evaluated wherever possible, especially where moulded parts are to be machined or bonded or decorated > [18].

FIGURE 27: defects (from left to right: orientation lines, transparent bubbles; white stains) observed in samples of PMMA, and caused by non-proper processing [18].
The above considerations are prominent in order to establish procedures capable to extend the service time of objects in PMMA and also in the choice of the best practices for the conservation of PMMA items.

Other typology of defects induced by factors such as, orientation, shrinkage and partial depolymerization, following inadequate processing, are evidenced in the photographs shown in figure 27 [18].

Physical aging, related to stress accumulation and stress relaxation, may be also studied by correlating annealing temperature ($T_a$), time of annealing ($t_a$) and values of the refractive index ($n$) of PMMA samples measured using light with a pre-fixed wave length ($\lambda$) (the values on $n$ for PMMA changes with $\lambda$ according to the optical dispersion curve in figure 28) [19].

![Optical dispersion curve for a dry PMMA cast sheet at 20°C](image1)

**FIGURE 28:** Optical dispersion curve for a dry PMMA cast sheet at 20°C [19].

![Refractive index ($n$) at 633nm plotted against the aging time ($t_a$) at various annealing temperatures in the case of PMMA samples in the glassy state](image2)

**FIGURE 29:** Refractive index ($n$) at 633nm plotted against the aging time ($t_a$) at various annealing temperatures in the case of PMMA samples in the glassy state [20].
As shown by figure 29, at temperatures < $T_g$, $n$ increases with the time of annealing. This behaviour is accounted for by assuming that by annealing a densification process occurs due to the annihilation of microvoids produced in PMMA material during manufacturing [20].

Interesting to point out that the $n$ values of PMMA (1.4893 to 1.4899) are close to those of glass for windows ($n=1.51$).

The wave length used in the experiments of figure 29 is equal to 633nm that is in the visible region of the electromagnetic spectra (see figure 30).

![Figure 30: The electromagnetic and visible spectra.](image)

C.4) **Factors influencing transparency and optical properties of PMMA sheets, and thermal stability.**

As previously underlined one of the most prominent property of PMMA is its transparency to visible light. This means that sheets of this material allow the observation of objects through or beyond the specimen. Transparency can be measured as that fraction of the normal incident light which is transmitted without deviation from the primary beam direction of more than $0.1^\circ$ [3].

Transparency of PMMA objects depends essentially by the optical homogeneity, both in the bulk and at the surface.

Abrasion, especially in the case of outdoor applications, may represent one of the main factors in reducing transparency in PMMA.

The abrasion resistance, defined as the ability of a surface to resist wearing following the contact with another surface moving to respect to it [21], is usually quantified by means of abrasion tests by the weighing of a material sample before and after subjecting it to a known abrasive stress throughout a known period time, or by reflectance or surface finish or by dimensional comparison [21].

It is well known that PMMA in many applications, where transparency is requested (i.e. engraving, advertisement sheet, instrument, parts of instrument, lamps, decoration, airplane, automobile fittings, medical appliances, work of art, insulation material for electrical appliances, specimen, sign board and various articles for light industry, culture and education, livelihood), has to compete with glasses and polycarbonate. The success of PMMA in such competition depends by
a combination of many properties, some of which are hereafter listed:

1. Very good transparency
2. Good weather resistance
3. Wear resistance
4. Good mechanical processability
5. Light, safe in use
6. Non-toxic
7. Easy to process.

A comparison between some relevant characteristics PMMA and glass is hereafter reported [21-b]:
-- The processing temperatures of PMMA (around 240-250 °C) are lower than those usually used for glasses.
-- The density of PMMA (1150 to 1190 kg/m³) is lower than that of glass (2400 to 2800 kg/m³).
-- The impact strength of PMMA is higher. Moreover PMMA sheet does not break, dangerously and suddenly, into small pieces.
-- Glass, being harder at RT, results to be more resistant to be scratched than PMMA (in some PMMA applications scratch-resistant coatings are used).
-- PMMA sheets transmit up to 93% of visible light. Glass may be manufactured with optical transmittances from 0% to about 100%.
-- PMMA is unable to filter UV light, contrary to glass. For this reason, and for some applications special coatings have been developed to make UV-absorbing PMMA sheets.
-- PMMA sheets are essentially transparent to IR-light up to 2800nm. Special PMMA coloured compounds, for application in the field of heat sensors, are tailored to block visible light while allowing specific IR wavelengths to pass through [21-b].

Against polycarbonate it must be underlined as PMMA is characterised by a greater UV stability.

Due to its optical properties PMMA find applications in the:
-- Construction of aquariums;
-- Manufacturing of lenses of exterior lights of automobiles;
-- Spectator protection in stadiums;
-- Motorcycle helmets visors;
-- Aircraft windows;
-- Greenhouse windows;
-- Cockpit canopies;
-- Screen protectors or cell phone screens;
-- Etc.

An example of use of PMMA thin sheets in a very sophisticated field of application as that of screen protectors or cell phone screens is shown in figure 31 [22].

The presence of impurities or of other components added to implement same of the PMMA characteristics might have the effect of reducing transparency.

In some special application fields such as optical fibers, optical disk, lenses, etc. where high strength and thermal stability, together with good transparency, are requested hybrid materials obtained by the suitable combination of PMMA with inorganic particles such as SiO₂, TiO₂ or zirconium oxide (ZrO₂) at the nanometer level have been prepared [23].

To maintain optical transparency the dispersed phase must have dimensions in the order of tens of nanometers, far less than the wavelength of visible and ultraviolet light. As matter of fact only
under such conditions light is not lost due to scattering. Larger particles of TiO$_2$ or ZrO$_2$ with a high refractive index, result in optical scattering and material opacity, thus limiting the optical applications of these hybrid materials. Recently Otsuka and Chuj demonstrated that was possible to synthesise (PMMA)-based hybrid materials with reactive zirconium oxide nano-crystals.

![Figure 31](image)

**Figure 31:** Ultra pure PLEXIGLASS® Super Clear guarantees maximum transparency and excellent surface quality. It shows no haze or light absorption, and has an extremely smooth surface. The transparent grey or completely colourless material is therefore eminently suited for use as screen protectors or cell phone screens [22].

< PMMA/ZrO$_2$ nanocrystal (ZrO$_2$-NC) hybrids with a coupling agent, 3- (methacryloxy) propyltrimethoxysilane (MPTS), grafted onto the surface of ZrO$_2$-NCs by zirconium hydroxide groups. The ZrO$_2$-NCs functionalised with MPTS were used as macro-monomers in the polymerization of methyl methacrylate (MMA) [23].

The authors playing with synthesis conditions and composition were able to produce hybrid materials with dispersed domains in the order of a nanometer in size homogeneously dispersed in the matrix (see figure 32) showing still good transparency as well as excellent thermal stability. According to the Authors this PMMA-based hybrid materials are susceptible to be applied in optical functional materials and coatings [23]. A dispersed phase, especially when its dimensions exceed the level of nano-dimensions (10$^\text{9}$ meters), as shown by the curves in figure 33, produces a reduction in the optical transparency of PMMA sheets [23].

It is interesting to note, as the degree of opacity induced is also function of the wavelength of the incident light.
FIGURE 32: Transmission electron microscopy of PMMA-based hybrid materials with reactive zirconium oxide nanocrystals (methyl methacrylate (MMA)/3-(methacryloxy) propyl-trimethoxysilane (MPTS)-zirconium oxide (ZrO$_2$), molar ratio of 10:1) showing the homogeneous distribution of a very tiny dispersed phase [23].

FIGURE 33: The optical transmittance of plain PMMA sheet (curve e) is compared with those of various PMMA-based hybrid materials with reactive zirconium oxide nano-crystals [23].
Very recently special PMMA sheets have been commercialised under the trade name “Altuglas” characterized, as can be seen by the data reported in figures 34, 35 and 36, by a high resistance to the environmental factors of degradation [24]. Moreover it also emerges as the PMMA sheets behave better that sheets of polycarbonate (PC) and poly vinyl chloride (PVC). As matter of fact Altuglas materials, after many years of exposure to weathering, show almost no variation of the transparency, of yellowing index, and a relatively low increase in the value of the haze (haze measures the cloudy or turbid aspect of appearance of an otherwise transparent sample; is given by the % of transmitted light which, in passing though the specimen, deviates from the incident beam) [24].

**FIGURE 34:** Variation of transparency ( % of light transmitted ), on the ordinate, as function of the weathering time ( years ) for PMMA sheets (Altuglas-grade). In figure the data are compared with those of PC and PVC sheets [24].

**FIGURE 35:** Yellowing index ( % ), on the ordinate, as function of the weathering time ( years ) for PMMA sheets (Altuglas-grade). In figure the data are compared with those of PC and PVC sheets [24].
The possibility of implementation of the thermal stability of PMMA by adding suitable nano-phases is exemplified in figures 37 and 38 where the DSC and TGA thermograms of the plain polymer with those of the nano-composites are compared [23].

From the DSC experiments it results as the Tg of PMMA-hybrid materials is higher that that of plain PMMA (see figure 37).

<These results indicate that ZrO$_2$-NCs serve as an effective inhibitor for segmental mobility of PMMA.> [23].

From TGA studies it emerged that the weight loss observed in the PMMA/ZrO$_2$-NCs hybrid was shifted to a higher temperature compared with that of the PMMA homo-polymer (see figure 38).

Very recently C. Y. Zhi and others developed boron nitride nano-tubes (BNNTs)/PMMA composite films showing significant enhancements, in comparison with PMMA films, of the following properties:
--- The elastic modulus, improved up to 19%;
--- The coefficient of thermal expansion, reduced (see thermo-mechanical curves in figure 39);
--- Thermal conductivity, improved;
--- The Tg, increased (see figure 40) [25].

Thus according to the Author by using this procedure it is possible to realize PMMA innovative materials presenting a very attractive combination of properties such as: thermal conductivity; mechanical properties and electrical insulation [25].

The results attained confirm that by using special compounding procedures it is possible to realize PMMA-based materials with tailored thermal, physical and mechanical properties. Moreover it was demonstrated that the thermal properties of PMMA may be improved by creating a homogeneously and compatible dispersed nano-phase.
**FIGURE 37:** Differential scanning calorimetry (DSC) thermograms of plain PMMA homo polymer (a) and (b), (c) and (d) of various types of PMMA-Hybrid Composites [23].

**FIGURE 38:** Thermogravimetric analysis (TGA) traces of PMMA homo polymer (a) and (b), (c) and (d) of various types of PMMA-Hybrid Composites [23].

When the conservation of PMMA artefacts is to be afforded it must be clear in mind that quite often the starting material is not only plain PMMA but in many cases it is a compound with sophisticated composition. To this all conservators or curators of collection of PMMA-based objects have to pay attention before the selection of a proper conservation and maintaining plan [26].
**FIGURE 39:** Thermo mechanical (TMA) analysis of film samples of a blank PMMA and of Boron nitride nano-tubes (BNNTs)/PMMA composite. In figure is shown the value of the thermal coefficient of expansion (α) that results significantly reduced after adding BNNTs [25].

**FIGURE 40:** DSC of a blank PMMA and BNNTs/PMMA composites, which indicates that the glass transition temperature is modified (see text) [25].
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CHAPTER – FOURTEENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (METHYL METHACRYLATE)

D) CONSERVATION, PROTECTION AND MAINTENANCE OF PMMA ARTEFACTS

Materials based on PMMA, due to the high value of the performance to cost ratio, since the early appearance on the market (early years of 1930 decade), as already stated in previous chapters, found wide applications in many sectors. Most of the advantages presented by PMMA, half as heavy as glass but more expensive than glass, and considered to be the impact resistant substitute for many of glass applications are below summarized [1]:

- High hardness, rigidity (the modulus of elasticity, at RT, lies between 2300 and 3300 Mpa) and strength.
- Impact strength better than that of glass or polystyrene, but lower than that of polycarbonate (rubber toughening has been used to increase the strength of PMMA owing to its brittle behavior in response to applied loads).
- High surface quality (high shine, scratch resistance, possibility of glazing).
- Excellent optical properties, in particular high transparency.

<PMMA is colorless, limpid and absorbs nearly none of visible light spectrum. The light permeability is 92 % and the refractive index is 1.491. It is the most light-permeable plastic. The permeability can be preserved even when PMMA is additionally colored with transparent dyes. The surface glaze is excellent, too. The PMMA panels absorb UV light. Panel of only 2 mm of thickness can absorb all of the UV light> [1]. As shown by figures 1 and 2 it is possible to produce PMMA sheets, UV-block, suitable to be used even for the protection of artifacts of cultural value stored in museums, having the capability to absorb almost all UV radiation whose λ is between 200-370nm. Sheets able to filter the white radiations with λ in the range of 250-570 nm have been also commercialized [2]. The transmission curves of the two types of sheets are shown in figure 1 and 2 respectively [2].

- Good thermal stability.

<PMMA glass transition temperature is 106 °C and up to 115 °C for cast intermediates. The Vicat B softening point depends on the value of mean molar weight and lies between 84 and 111 °C. This implies that PMMA belongs to thermoplastics with good thermal resistance. In a long term, the products can be permanently used up to temperatures of 70 - 100 °C> [1].

- Good electric and dielectric characteristics.
- High resistance against weak acids and alkalis, non-polar solvents, fats, oils, salty solutions aliphatic hydrocarbons and detergents.
- Resistance against water, high relative humidity and moisture fluctuations.
- High resistance against weathering.
- High Resistance against exposure to light and UVA radiations.
- Excellent environmental stability compared to other plastics such as polycarbonate, and is therefore often the material of choice for outdoors applications.

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- Easy processing and machining. It is interesting to note that laser cutting may be used to form intricate designs from PMMA sheets. PMMA vaporizes to gaseous compounds (including its monomers) upon laser cutting, so a very clean cut is made, and cutting is performed very easily. In this respect PMMA has an advantage over competing polymers such as polystyrene and polycarbonate, which require higher laser powers and give messier and charred laser cuts [1-b]. Moreover it must be also reminded that PMMA can also be sawed, whereas glass must be scored. In addition it must be also considered the capability of PMMA to be easily shaped. There are also no seams in acrylic structures, as chemical welding at the molecular level actually "melts" seams into one piece of solid material. Seams that are welded and polished are invisible [1-b].

It must be added as advantage even the non malignant behavior of PMMA. As matter of fact on degrading it results to be not dangerous for neighboring stored materials been unable to produce stains, corrosion, stickiness and harmful gases [3].

**FIGURE 1:** Curve of light transmission for PMMA UV block sheets. In ordinate is the % light transmittance, in abscissa the wavelength of the incident light. The % transmittance is measured at 3, 5 and 10 mm from the surface of the sheet [2].

**FIGURE 2:** Curve of light transmission for PMMA sheets, capable to inhibit the transmission of white light. In ordinate is the % light transmittance, in abscissa is wavelength of the incident light [2].
In comparison to other polymers PMMA shows the following weaknesses [1,2,4]:

--- Poor resistance to some solvents, as it swells and dissolves easily as well as poor resistance to some reactive chemicals capable to hydrolyze the ester groups present along the macromolecular chains.
--- Flammability ( PMMA is very easily combustible. <It burns with lucent flame even after the flame source has been removed. Combustion-produced gases have typically sweetish smell. Self-ignition point is between 400-465 °C > [1].
--- Fragility at RT with relatively low impact resistance below Tg.
--- Mechanical properties highly dependent upon temperature ( as shown by the trend of the curves in figures 3, 4 and 5, the modulus of elasticity, the elongation to break as well as the tensile strength decrease with increasing temperature ).
--- Environmental stress cracking, swelling phenomena and degradation produced by chemical pollutants and solvents ( strong acids and alkalis, benzene, polar solvents, ketones, esters, ethers, aromatic hydrocarbons and chlorohydrocarbons ).
--- Capability to become brittle following a creep process at relatively low value of the stress with formation of crazes.
--- Mechanical resistance may be drastically affected when the PMMA is in contact with specific substance as alcohols, silicon oil, ecc.
--- Under tension and in contact with solvents PMMA suffers degradation. <This decreases its usability at higher temperatures or when in long-term contact with solvents > [1].
--- When internal stresses are present, to avoid the formation of crazes ( see figure 6, [5] ) the raw materials needed to be annealed before manufacturing and shaping objects in PMMA.

![Graph](image)

**FIGURE 3:** Tensile mechanical properties of PMMA as function of the temperature.
*Left*- Stress-strain curves at various indicated temperatures.
*Right*- dependence of the modulus upon the temperature. It can be seen that at Tg the modulus suddenly drops [3].

PMMA artifacts, due to the combined action of stress, strain and the contact of some specific liquid chemicals, suffer environmental stress cracking ( ESC ), a phenomenon that causes premature cracking and embrittlement [6]. According to reference [6] ESC is a process that can be generally described as:

<the formation of cracks in a plastic material caused by low tensile stress and environmental conditions. This failure is caused when plastic materials, in contact with surface active substances>
(stress cracking agents), start to become brittle at or about room temperature due to concurrent external and/or internal stress and strain action. Stress cracking agents include fluids such as alcohols, soaps, dyes and agents containing moisture [7].

**FIGURE 4-left:** Elongation to break, on ordinate, in tensile experiments, as function of the temperature (°C), on abscissa, for PMMA sheets [2].

**FIGURE 5-right:** Tensile strength, in ordinate, as function of the temperature (°C), on abscissa, for PMMA sheets [2].

**FIGURE 6:** Crazes developed in PMMA labels following the release of internal stresses [5].
Adhesives, lacquers, cleaning agents, anti-rust agents as well as vegetable oils, inks points, lubricants, aerosol sprays, leak detection fluids, fruit essences, plasticizers, etc. may act as stress cracking agents for polymers [6].

The resistance of PMMA to ESC results to be dependent on molecular factors such as molecular weight and molecular weight distribution. Moreover it was demonstrated as the presence in the material of frozen-in stresses from processing as well as of polyaxial stress and strain-induced orientation facilitates the process of ESC [8]. The rate of ESC depends also upon the chemical nature, concentration and reactivity of the liquid stress cracking agents as well as on the temperature and the strain rate [9].

Crazes produced by ESC in PMMA drinking beaker are evidenced by the photo-reproduction shown in figure 7 [9].

The effectiveness of a liquid chemical in determining ESC in polymer materials may be assessed by tests based on creep experiments [6].

The “Tensile Creep Rupture” and the “Tensile Creep” tests are described as follows in reference [6].

![Figure 7: Crazes produced by environmental stress cracking (ESC) in PMMA drinking beaker](image)

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**Tensile Creep Rupture test** - This is the most direct method of quantifying the effect of a fluid on the durability of a plastic material. It involves the application of a tensile stress and recording the time to rupture. In air, the time to rupture increases gently as the applied stress decreases. A safe allowable stress would be one half the stress required to cause rupture at the expected service life. A stress cracking fluid may have little or no effect at high stresses and short rupture times. However, in the medium to longer term there will be a massive reduction in strength and therefore a massive impairment of durability (the effect of a stress cracking agent is shown on figure 8) [6].

**Tensile Creep test** – The tensile strain of a material in air and contact with a stress cracking fluid is monitored prior to creep rupture. The departure in creep response occurs typically at one tenth of the time for departure in the creep rupture response. The increase in creep rate coincides with crack/craze initiation and as such can be taken as a non-subjective criterion for safe application (allowable stress and allowable service life) (see figure 9) [6].

**FIGURE 8:** The “Tensile Creep Rupture” test used to assess the ESC effectiveness of a liquid chemical. In figure is reported the stress against the time to failure. Upper curve in air. Lower curve in presence of a liquid stress cracking agents (see text) [6].
FIGURE 9: Creep strain against time for generic polymer materials. For a given stress the curves refers to experiments performed in air and in presence of a stress cracking agent. It can be seen that in presence of the stress cracking agent, grey lines, the rupture occurs at shorter times (see text) [6].

From above it may be concluded that when PMMA is stressed or strained in air below its yield point, stress cracking usually may occur only after a relatively long period of time. When samples of PMMA suffer to the action of internal or external stresses (or a combination of both), while in contact with a chemical agent then a dramatic shortening of the time to failure is quite often observed [10].

The results of an ESC test performed on PMMA and PC samples by H.T. Wang and Others, are reported in table 1. From the data it can be seen <that the cracking time changed dramatically with the change of strain. Moreover, only at a strain of 0.017, PC and PMMA both have cracking time of a few minutes and a small change in the strain will cause cracking too slowly or too quickly to observe. Therefore, in the experiments of ESC the appropriate selection of the value of strain is necessary> [10]. It can be also noted as the ESC behavior strongly depends upon the chemical nature of the stress cracking agent.

J.G. Williams and Others performed a series of tests on unnotched PMMA samples in which the central sections were completely immersed in various chemicals <The specimens were then loaded at a fixed rate (0.5 cm min -1) in an Instron testing machine and the load at which crazes were first observed was noted> [11].

The liquid used for the experiments, together with the value of the solubility parameter, viscosity and of the initiation stress σ, are reported in table 2 [11]. The data show that <there are two distinct types of behavior. The first three liquids in Table 2, namely acetic acid, methanol, and ethanol, give significantly lower values of σ, than the rest listed> [11].
TABLE 1: The cracking time of PMMA at different strain, and in contact with different chemical mediums [10].

<table>
<thead>
<tr>
<th>Chemical medium</th>
<th>Strain</th>
<th>0</th>
<th>0.017</th>
<th>0.073</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>Uncracked</td>
<td>98 min</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>Uncracked</td>
<td>dissoluble</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Uncracked</td>
<td>3 min</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>Uncracked</td>
<td>dissoluble</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>Uncracked</td>
<td>6 min</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>Uncracked</td>
<td>8 min</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>Uncracked</td>
<td>6 min</td>
<td>at once</td>
<td></td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>Uncracked</td>
<td>4 min</td>
<td>at once</td>
<td></td>
</tr>
</tbody>
</table>

The tendency of a polymer materials to ESC can be connected to the values of the solubility parameters (SP) of the stress cracking agent and of the polymers. Such an hypothesis was confirmed, in the case of PMMA, by the data in figure 10 where the values of stress at which crazes are first observed (initiation stress $\sigma_i$) are reported against the values of the SP of the various liquids used [11].

TABLE 2: The liquid used for the ESC experiments performed in reference [11] on PMMA samples. In table are given, for each of the agents, the values of the solubility parameter, viscosity and of the stress at which crazes are first observed (initiation stress $\sigma_i$) see text [11].

<table>
<thead>
<tr>
<th>Environment</th>
<th>Solubility parameter (cal cm$^{-3})^{1/2}$</th>
<th>Viscosity (cP)</th>
<th>$\sigma_i$ (MN m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>10.1</td>
<td>1.3</td>
<td>17.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>14.5</td>
<td>0.59</td>
<td>21.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.7</td>
<td>1.22</td>
<td>21.5</td>
</tr>
<tr>
<td>Butanol</td>
<td>11.4</td>
<td>2.95</td>
<td>28.3</td>
</tr>
<tr>
<td>Hexane</td>
<td>7.3</td>
<td>3.33</td>
<td>31.0</td>
</tr>
<tr>
<td>Heptane</td>
<td>7.4</td>
<td>0.41</td>
<td>38.0</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>12.2</td>
<td>3.3</td>
<td>38.3</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.6</td>
<td>0.97</td>
<td>40.0</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>14.6</td>
<td>19.7</td>
<td>40.3</td>
</tr>
<tr>
<td>Paraffin</td>
<td>7.8</td>
<td>1.16</td>
<td>47.0</td>
</tr>
<tr>
<td>Water</td>
<td>23.5</td>
<td>1.0</td>
<td>52.4</td>
</tr>
<tr>
<td>White spirit</td>
<td>$\sim$ 6.9</td>
<td>0.87</td>
<td>59.6</td>
</tr>
<tr>
<td>Adinol (detergent)</td>
<td>350.0</td>
<td>64.3</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>0.018</td>
<td>67.8</td>
<td></td>
</tr>
</tbody>
</table>
The curve shown in figure 10 presents a distinct minimum in $\sigma_i < where there is a close match of solubility parameter between the fluid and the polymer [SP for PMMA = 11 (cal/cm$^3$)${^{1/2}}$]. This simply means that good solubility of liquid and polymer results in preferential craze growth but while this is a necessary condition it is not sufficient. This is illustrated by ethylene glycol which has a good solubility match but exhibits a high crazing stress. This may be attributed to the very high viscosity of ethylene glycol which inhibits craze growth even though there is high solubility [11].

It is interesting to note that also the mechanism of craze formation in PMMA appears to be strongly dependent upon the chemical nature of the stress cracking agent. Such observation, as shown in figure 11, found support by the morphological analysis performed by optical and electron microscopy on PMMA samples exposed to ESC in presence of two different liquid, methanol and n-heptane ( an effective and a less efficient stress cracking agent respectively ) [11]. In the case of PMMA samples methanol-exposed a few well developed craze-system is observed ( figure 11-a ) while specimens treated with n-heptane exhibit a pattern with a large number of small crazes ( see figure 11-b ) [11].

The effect of the value of the applied stress upon the ESC effectiveness of a given liquid is shown by the curves reported in figure 12. It can be seen that the growth rate of the crazes, till fracture occurs, increases steadily with the stress applied [11].

![Figure 10: Craze stresses as a function of solubility parameter. The values of stress at which crazes are first observed (initiation stress $\sigma_i$), in the case of PMMA samples are plotted against the values of the SP of the various liquids used (see text) [11].](image-url)
PMMA may be attacked by a number of chemical substances having various reactivities and functionalities, which may produce also irreversible chemical changes and structural modifications. Some of the most effective, from chemical point of view, are listed in table 3 [10]. The knowledge of chemicals capable to act as stress cracking and as degrading agents represents an important issue when conservation and especially cleaning procedures have to be applied to PMMA artifacts.

**FIGURE 11:** PMMA exposed to the action of stress cracking agents. Micrographs show how the types of craze pattern depend upon the molecular structure of the liquid used (see text) [11]:

a) methanol;

b) n-heptane.
From the above reported data it emerges that is strongly recommended to perform suitable ESC and solubility tests to select the most right cleaning and bonding agents for PMMA objects. Of course chemicals as those reported in table 1, 2 and 3 should be always avoided in any conservation procedure for PMMA artifacts.

**FIGURE 12:** Craze growth in PMMA samples exposed to methanol. In figure is plotted the craze length as function of time at various value of the applied stress [11].

**FIGURE 13:** Chemical probe calibration curve for determining residual stresses in polymer preforms, see text [13].
**TABLE 3:** Chemicals most effective in reacting and degrading PMMA materials [12].

<table>
<thead>
<tr>
<th>CATEGORY</th>
<th>EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ACIDS</strong></td>
<td>Acetic acid - 100%; Concentrated butyric acid;</td>
</tr>
<tr>
<td></td>
<td>Chromic acid, concentrated solution;</td>
</tr>
<tr>
<td></td>
<td>Formic acid - 90% solution; Hydrofluoric acid;</td>
</tr>
<tr>
<td></td>
<td>Nitric acid, concentrated solution</td>
</tr>
<tr>
<td></td>
<td>Sulphuric acid - 90% solution</td>
</tr>
<tr>
<td><strong>ALCOHOLS</strong></td>
<td>Amyl alcohol-pure; Benzyl alcohol-pure;</td>
</tr>
<tr>
<td></td>
<td>Butyl alcohol-pure; Ethyl alcohol-pure</td>
</tr>
<tr>
<td></td>
<td>Ethyl alcohol-pure, Methyl alcohol-pure</td>
</tr>
<tr>
<td></td>
<td>Propyl alcohol-50% solution</td>
</tr>
<tr>
<td><strong>ALKALIS</strong></td>
<td>Potassium hydroxide, Sodium hydroxide</td>
</tr>
<tr>
<td><strong>GASES</strong></td>
<td>Sulphuric anhydride</td>
</tr>
<tr>
<td><strong>PHENOLS</strong></td>
<td>Cresol, Methacresol, Phenol</td>
</tr>
<tr>
<td><strong>CLEANING AND DISINFECTANT PRODUCTS</strong></td>
<td>Ammonia-concentrated solution, Chlorine water-48%Cl; Hydrogen peroxide-90 volumes; Iodine tincture</td>
</tr>
<tr>
<td><strong>MINERAL SALTS IN SOLUTION</strong></td>
<td>Copper sulphate; Iron per-chloride; Mercuric chloride</td>
</tr>
<tr>
<td><strong>VARIOUS SOLVENTS</strong></td>
<td>Acetic aldehyde; Acetone; Aniline; Benzene;</td>
</tr>
<tr>
<td></td>
<td>Benzoic aldehyde; Butyl acetate; Carbon sulphide; Chloroform; Cyclohexane;</td>
</tr>
<tr>
<td></td>
<td>Dichloroethane; Ethylamine</td>
</tr>
<tr>
<td></td>
<td>Ethyl acetate; Ethyl chloride; Ethyl ether</td>
</tr>
<tr>
<td></td>
<td>Ethyl sulphate; Freon; Methylenechloride;</td>
</tr>
<tr>
<td></td>
<td>Green petrol; Toluene; Trichloroethylene;</td>
</tr>
<tr>
<td></td>
<td>Trichloroethylene; Xylene</td>
</tr>
</tbody>
</table>
In some circumstances it can be useful to apply an annealing treatment in order to release the amount of internal residual stresses accumulated in the PMMA-made objects. As matter of fact as can be seen by the plot in figure 13 in the case of annealed sample the failure occurs at higher values of the applied pressure in comparison with the unannealed sample [13]. According to the Author this difference gives a measure of the internal tensions present in the sample. Annealing should be performed at temperatures below that of softening of PMMA ( 70-100°C ).
An object made by PMMA, with evidences of stress whitening pattern, symptoms of crazes formation, is shown in figure 14 [14].

![Figure 14: Evidences of stress cracking (see the stress-whitening pattern) in a PMMA artefact [14].](image)

PMMA is usually resistant to abrasion, nevertheless due to improper use, especially following mechanical actions (rubbing, scraping, erosion, ecc.), in many artifacts the removal of material from the surface with formation of a scratched structure is often observed (see figure 15).

![Figure 15: Surface scratches observed on: Right - the surface of a lens manufactured in PMMA [15]. Left - the surface of a Perspex artefact [14].](image)
FIGURE 16: Examples of PMMA artifacts manufactured by using a scratch-free PMMA composition.

Left - The Dräger X-plore® 6300 full face breathing mask. The scratch-proof and distortion-free visor is made in PMMA Plexiglas with 180° wide-angle [16].

Right - Tanks aquariums in scratch-free PMMA sheets are lighter, stronger, and clearer [17].

Bottom – The “Marie Louise Lamp” with a highly sophisticated design.<This lamp is pretty and amazing. It will get our eyes in any environment. They have 8 colors including amber, yellow, orange, purple, blue, pink, red and green. The Marie Louise Lamp made of PMMA sheets are illuminated by a special fluorescent bulb > [18].

PMMA as transparent component is used in many applications (panels for household appliances, covers for vehicle dashboard instruments, display windows, ecc.), examples are given in figure 16 [16,17,18]. <Such parts can only stay perfectly transparent if the surface is not damaged by scratches or abrasion during use. This imposes very high demands on the optical quality, and mechanical and chemical resistance of the surface. PMMA has the greatest surface hardness and scratch resistance of all thermoplastics, yet even PMMA articles will not meet particularly high standards on scratches and other signs of wear unless they are coated > [19].
Some of the most effective scratch-resistant coatings for PMMA capable to induce to the surfaces also resistance to chemical attacks and as well to withstand high stresses are based on a traditional hard coat, which is a UV-or thermally cured acrylic polymer with dispersed colloidal silica particles [19].

A process for producing scratch-resistant coatings <.....comprise as binders one or more polyacrylate resins having a hydroxyl number of from 100 to 240, an acid number of from 0 to 35, and a number-average molecular weight of from 1500 to 10,000, and as cross linkers one or more free or blocked isocyanates and/or triazine-based components (see molecular structure below) which crosslink with the hydroxyl groups of the binder to form ether and/or ester structures> [20].

![Molecular structure](image)

Very recently a coating procedure (Scratch-Resistant in One Step) was developed that allows PMMA parts to be coated directly in the mould with a reactive system composed of multifunctional acrylates, which harden under the influence of heat and UV radiation [19]. The methods named “CoverForm” results to be, according to the Authors, cost effective alternative to the classic coating.

The effectiveness of the above procedure was tested by comparing the behavior of untreated PMMA objects with those treated with a one step coating coverform procedure and with a classic methodology.

It was observed that in the Taber abrasion test (see figure 17) the CoverForm parts in PMMA yield Haze values comparable to those of Plexiglas8N parts coated with acrylic based lacquers; of course the haze values are sensibly lower than that of the uncoated PMMA sample [19].

![Haze values](image)

**FIGURE 17:** In the Taber abrasion test, CoverForm parts yield values comparable to those for Plexiglas8N parts coated with traditional acrylic-based lacquers [19].
The scratch resistance was also established with the aid of the Erichsen test. The results are shown in figure 18 where the depth of penetration is reported, for coated and uncoated parts, as function of the contact force. It can be seen that CoverForm coated PMMA samples are characterized by a better performance if compared with the other ones [19].

![Contact force vs Depth of penetration graph](image)

**FIGURE 18**: The Erichsen scratch-hardness test applied to PMMA sample to assess the scratch-resistance of various coating procedures, see text [19].

Abrasion-resistant nano-composites based on PMMA as matrix and calcium carbonate (CaCO₃) nano-powder as filler have been prepared by an in situ polymerization process. The influence of nano-powders on the chemical physical properties of the polymeric matrix has been investigated by performing thermal, morphological, and mechanical analysis. The abrasion resistance has also been evaluated. The nanocomposites showed an average weight loss about half with respect to that of neat PMMA, by adding only 2% of nanoparticles [21].

The morphology (mode and state of distribution and size distribution of the CaCO₃ nano-particles) was assessed by scanning electron microscopy analysis (SEM), see as example the micrographs shown in figure 19 [21].

From the data shown in figure 20 and tables 4, and 5 it can be concluded that the PMMA/ CaCO₃ nano-composites present:
--- A better flexural modulus;
--- A higher value of the glass transition temperature;
--- A major abrasion resistance [21].

The above results were accounted for by the homogeneous and very fine dispersion of the CaCO₃ nano-particles and by the high adhesion between the matrix and the dispersed phases as demonstrated by the SEM micrographs in figure 19 [21].

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Scratch-resistant coatings effective in preventing reproduction of bacteria too, and characterized as well by good optical characteristics, excellent transmission and impact resistance have been also developed. From the above considerations it comes out that PMMA is softer and more easily scratched than glass, thus scratch-resistant coatings (which may also have other functions) are often added to PMMA.

Whenever active or passive actions of conservation are planned the curators have to pay attention to the fact that in some PMMA artifacts scratch-resistant components are present.
**FIGURE 20:** Flexural modulus of PMMA/ CaCO₃ nano-composites as function of CaCO₃ content[21].

**TABLE 4:** Glass transition temperature of neat PMMA and PMMA/ CaCO₃ nano-composites [21].

<table>
<thead>
<tr>
<th>CaCO₃ content (%)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>124</td>
</tr>
<tr>
<td>4</td>
<td>127</td>
</tr>
<tr>
<td>6</td>
<td>125</td>
</tr>
</tbody>
</table>

**TABLE 5:** Abrasion test results. Abrasion is measured from the surface weight loss material [21].

<table>
<thead>
<tr>
<th>CaCO₃ content (%)</th>
<th>weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>2.4</td>
</tr>
<tr>
<td>6</td>
<td>2.4</td>
</tr>
</tbody>
</table>
RECOMMENDATIONS FOR THE CONSERVATION OF ARTIFACTS IN PMMA

The conservation of artifacts in PMMA, due to the characteristics of this polymer, above widely discussed, consists, essentially, of treatments of active type such as:
--- Cleaning;
--- Polishing;
--- Bonding and joining.

Some of the recommended procedures are hereafter briefly described.

--- Cleaning

Cleaners are liquid formulations generally used to remove dirt, soil and impurities from the surface of artifacts.
First of all a cleaner has to be safe and non toxic both for the curators and for the environment. In addition a cleaner formulation has to be non-flammable.
A suitable cleaner is based on an emulsion of silicone oil and cationic detergent in water.
Some of the cleaners used today are chemically inert maintenance products whose anti-static properties require less frequent applications. Some others are tailored to leave also a protective film on the surface of the artifact [22].
Cleaners should be applied by wiping, without rubbing, by means of a soft, lint-free cloth. Normally cleaners should be never used before gluing or serigraphy operations [22].
As far as the cleaning of PMMA objects it is concerned it must be assumed as general precaution that dry cleaning, based on powders and abrasive products, are forbidden as well as the use of specific solvents (e.g., trichloroethylene).

--- Polish

According to reference [23] <polish is a powder, liquid or semi liquid used to give smoothness, surface protection, or decoration to finishes; for example, finely ground red oxide ( rouge ) is used to polish plate glass, mirror backs, and optical glass; solvent-wax liquids and pastes are used in protect and enhance leather and wood surfaces ....> [23].

Altuglas commercialises a “Polish 1” formulation for PMMA surfaces that consists of <a mixture of mineral abrasives and soaps in aliphatic hydrocarbons with an aromatics content of less than 5%> [24]. The seller claims that this formulation is capable, in the case of PMMA sheets, to <eliminates slight surface scratches and restores all the original shine and transparency> [24].
The Polish-1 turns to be effective especially in the case of windows, furniture, poster advertising panels, display stands and sanitary ware [24]. In using such a polish attention should be paid to the following aspects:
- -Polish 1 has a flash point of 61°C, which makes it inflammable. It is recommended, therefore, that the product be stored away from all sources of ignition.
- -Polish 1 can react dangerously with highly oxidizing agents, such as strong acids and halogens > [24].
The procedure to be followed is hereafter described:
<1) Prior to polishing cross-sections or grooves, roughness should be minimized with careful
sanding. Use a block equipped with “waterproof” abrasive paper. Keep paper damp as you increase grain from n° 600, 800 or 1000 depending on desired surface quality. Soak a cotton pad and rub the surface to be polished in a circular motion until the Altuglas Polish 1 is completely absorbed. A chamois cloth can be used to accelerate the operation. Complete the operation by wiping (suede-type soft cloth or cotton pad) > [24].

A liquid polish suitable to remove small scratches from the surfaces of PMMA objects, “Polish 2” was developed and commercialised also by Altuglas [25]. This product is a formulation consisting of a combination of mineral abrasives in a mixture of water and aliphatic hydrocarbons with an aromatics content of less than 5%. Altuglas suggests the use of Polish-2 as a finishing agent after polishing with Altuglas Polish 1 [25]. Polish 2 is recommended for components in PMMA including windows, furniture, poster advertising panels, display stands sanitary ware, etc. [25]. From toxicological and safety point it must be taken into account that Polish 2, having a flash point of 61°C, it is inflammable, then it must be stored away from all sources of ignition. Moreover the product is capable to react with highly oxidizing agents, such as strong acids and halogens > [25].

The procedure suggested for the application of Polish 2, a product that is chemically inert against PMMA components, is below summarized:
< The container must be well shaken before every use. Soak a cotton pad and rub the surface to be polished in a circular motion until the Altuglas Polish 2 is completely absorbed. A chamois cloth can be used to accelerate the operation. Complete the operation by wiping (suede-type soft or cotton pad). > [25].

--- Bonding and joining

Broken off parts of objects in PMMA can be easily re-joined by using proper adhesive or glue formulations.

The adhesives or glues that result to be consistent with the criteria of the modern view of active conservation of PMMA objects are those capable to create a PMMA joint between the parts being assembled. In such a contest the products developed are of different types.

**Type-I**- Are formulations based on solution of a preformed PMMA polymer whose solvent rapidly evaporates during the application or curing [26].

**Type-II**- Are formulations containing MMA monomer dissolved or not in suitable solvents. In such a case with the help of a proper catalyst the PMMA polymer is formed “in situ” following the evaporation of the solvent.

**Type-III**- The products are based on a solution between the MMA monomer and the PMMA polymer. In such a case a third component, the catalyst, is added to the mixture just before the application.

The suggested working procedure is described in reference [26] as follows:

< ....the first step is to apply either the volatile solvent-based glues, or the monomer solvent for polymerising glues, to both the faces to be bonded. However, before any bonding, it is essential to apply an annealing heat-treatment, to relieve any internal stresses left by machining or forming. It is also advisable, once the glue has dried and hardened at room temperature, to carry out another heat treatment for 2 to 3 hours at approx. 60°C, to improve the quality of the joint > [26].

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Altuglas® adhesive commercialises the following types of glues/adesives capable to bond PMMA parts:

--- Contact glues (Altuglas® Adhesive S)
< These are solutions of generally small quantities of PMMA in a solvent, or may even be pure solvent. The setting time is the time required for the solvent to evaporate, but complete evaporation seldom occurs > [26].

Polymerizing glues (Altuglas® Adhesive P)
< Catalysts are added to these fairly viscous solutions of polymethylmethacrylate and methylmethacrylate just before use, to polymerise the monomer. The material in the joint is therefore identical to PMMA. The setting time is the time required for the polymerization reaction to take place > [26].

From proper tensile tests, performed after the bonding treatment, was possible to assess the effectiveness of the treatment by measuring the “Glue strength”. From such measurements it was possible to reach the following conclusions:
< ...the strength ......is within the following range:
--- Contact glues: 25 to 35 % of the strength of the original adjacent material.
--- Polymerizing glues: 60 to 75 % of the strength of the original adjacent material > [26].

Some more details concerning the composition and the working procedures of commercial adhesives or glues, specific for bonding PMMA parts are hereafter reported.

- Transparent, viscous, solvent adhesive with one single component

Such products, based on the fact that the evaporation of the volatile solvent induces the adhesive to thicken, may be used for PMMA components in different types of bonding: ( e. g. edge-to-edge bonding ( casing, boxes ), angle bonding ( signs ), edge onto surface bonding ( raised sign lettering ), etc ) [27]. As general precaution when the parts to be bonded present a phenomenon of stress concentration they need to be annealed before the application in order to prevent the formation of crazes following the contact with the solvents contained in the adhesive.
The Altuglas adhesive S2003E, belonging to the class of transparent, viscous, solvent adhesive with one single component, is classified as highly flammable and as an irritant. It does not contain chlorinated solvent. It is recommended to not inhale the solvent vapors, to work in a ventilated area, and to avoid all contact with the skin and eyes [27].

Some of the working instructions for Altuglas adhesive S2003E, as suggested in reference [27], are hereafter reported:

< --- Speed is one of the key benefits of solvent-type adhesives... The surfaces to be glued must be completely dry and clean. Remove all traces of grease from the parts to be glued using petroleum spirit or a 50/50 mixture of water/methylated spirit.
--- Hardening varies according to the thickness, temperature and hygrometry. It is usually possible to handle glued objects after 60 to 90 minutes but a minimum period of 48 hours must be respected before any machining. Complete hardening is achieved after 15 to 20 days at a temperature of 20°C. If necessary, this can be accelerated by heating for several hours at 80°C ... > [27].
• Three component transparent, polymerisable adhesive

The adhesive, commercialized as “Altuglas® Adhesive P12”, belongs to this class. It is a viscous solution of PMMA in MMA monomer. A suitable catalyst, added at the time of application, determines the polymerization of the monomer to PMMA macromolecules [28]. This product is used for:

- Bonding PMMA in different applications, such as shop windows, aquariums, furniture, glove boxes, etc. This adhesive can also be used for bonding other plastic materials, such as polystyrene and ABS, after they have first been annealed as a precaution [28].

In the application of the Altuglas® Adhesive P12 the operators have to pay attention because MMA is highly flammable and its vapors can cause irritation to the skin, eyes and respiratory tracts. Consequently the application has to be performed in a very well ventilated area [28]. Moreover it must be taken into account also the fact that the methacrylic acid, presents in the formulation, being corrosive can cause burns.

Suggestions for the application of such adhesives are reported, as follows, in reference [28].

- Polymerisable adhesives originate from a deposit of material and can counterbalance the roughness of surfaces. Preferably roughen the surfaces of the joint face in order to improve the contact surface. Dry sand the chamfered edges and sand the smooth sides with sandpaper. The surfaces to be glued must be completely dry and clean. Remove all traces of grease from the parts to be glued using petroleum spirit or a 50/50 mixture of water/methylated spirit. If necessary, the areas adjacent to the area being glued can be protected by a special adhesive strip made from adhesive-resistant material (e.g. polypropylene). If necessary, pre-assemble the parts with the help of the same adhesive strips....

Polymerization of Altuglas® Adhesive P12 is accompanied by a reduction in volume of approximately 15%. The volume of adhesive to be applied must always be greater than the volume of the joint face cavity [28].

The objects glued with Altuglas® Adhesive P12 may be handled after 2 to 3 hours but a minimum period of 24 hours must be respected before any machining [28].

• Highly fluid, transparent, single-component glue based on a mixture of solvents

This kind of products, see for example that commercialized as Altuglas® Adhesive SPC, are used especially because of their powerful solvent properties that penetrate deep into the surfaces of the components to be bonded, ensuring firm joints that are excellent in appearance. Its high volatility makes the process very rapid and allows the assembly of multiple components in a very short space of time. Being highly fluid, Altuglas® Adhesive SPC is easy to apply to the surfaces to be bonded, either from a syringe or polyethylene container fitted with an applicator tip (tube, needle or sponge) [29]. These kinds of products are usually used to:

- Edge-to-surface joints (boxes, dividers, embossed lettering for signs);
- Edge-to-edge joints;
- Angled joints (display cabinets, boxes, containers);
- All kinds of joints on small components [29].
The sellers strongly recommend that before treatment the parts to be bonded < must be free from internal strains caused by various operations (machinging, bending, flame polishing, thermoforming or laser cutting). Such strains must therefore be released, otherwise cracking (crazing), by a precuring of the parts in an oven > [29].

Cyanogacylate adhesives "super glue"

Cyanocrylates instant adhesives, exhibiting an excellent adhesion profile, are one component, solvent free, very fast setting adhesives. These cyanocrylates polymerize within seconds due to the presence of a weak base, such as surface moisture, and will bond well to a wide range of substrates [30]. The main components of the cyanocrylate-based formulations are cyanocrylate monomers such as methyl-2-cyanoacrylate and ethyl-2-cyanoacrylate whose molecular structure are below represented.

Left: Methyl 2-cyanoacrylate. Right: Ethyl 2-cyanoacrylate

Those acrylate monomers are capable to polymerize (easily and rapidly, within seconds especially in the presence of a weak base, such as surface moisture water (hydroxy ions OH) giving rise to the formation of macromolecules efffective in creating strong bonds with substrates, and thus joining the bonded surfaces together [31]. The molecular structure of the repeat unit of the linear form of the poly methyl 2-cyanoacrylate is below represented.

\[
\begin{align*}
\text{C-CN} & \quad \text{C-CH}_{2} \\
\text{COOCH}_{3} & \quad \text{COOCH}_{3}
\end{align*}
\]

The scheme of the polymerization reaction is depicted in figure 21 [32].

Cyanocrylates are then capable to bond to large types of surfaces to give a very fast and strong linkage. They present as disadvantages:
--- Limited thermal stability;
--- Brittleness at RT;
--- Blooming effect due to the fact that they can leave a white residue at the interface.

It is interesting to note that < acetone, is a commonly available solvent capable of softening cured cyanocrylate. Nitromethane is also an excellent solvent > [32].
Welding (the term includes also heat sealing) is a technique where the joining of more pieces of plastics occurs essentially by applying heat at adjoining or nearby areas. The procedure may be effectuated either with or without the addition of other kind of plastics.

The welding, useful applied to PMMA parts (see example in figure 33 [33]), is described as follows in reference [26]:

< Welding involves placing the two parts to be joined in contact and then causing them to soften considerably in the contact area. ... many methods are available (hot gas, heating bars, induction, radiation, ultra-sonic)... the operation leaves high internal stress and an annealing heat-treatment is essential. Under optimum conditions, the strength of the welded joints varies from 10 to 40% of that of the original adjacent material > [26].
As schematically depicted in figure 34, acid base interactions and covalent bonds represent the most effective types of linkages in creating the best conditions for adhesion between parts of different plastic materials [33].
--- Finishing, Maintenance and Cleaning

Following any active treatment on PMMA objects finishing, maintenance and cleaning procedures are strongly recommended. Cleaning is applied to remove finger and handling marks. This improves the shine and reduces static, which slows down the accumulation of dust. However, if the parts have accidental scratch marks, they should first be polished using a soft cloth or polisher [26].

As far as maintenance is concerned it is suggested to wash with clean water and a soft cloth, chamois leather or sponge. Never rub the dry surface. The use of solvents such as methylated spirits, turpentine, white spirit or window cleaning products is to be discouraged [26].

--- Bonding with other plastics

PMMA, by using proper solvents and adhesive lacquers, and reactive and fusion adhesives, can easily be bonded with other plastics such as crystalline and tough polystyrene, polycarbonates, cellulose derivatives, ABS terpolymers or SAN copolymers [1].

To make unfailing joint, bonded surfaces must be perfectly clean with any dust and dirt removed. As a cleaning agent, use either water with detergents or alcohols [1].

An example of object in PMMA damaged because of mechanical failure, and easily repairable by suitable bonding techniques, is shown figure 35 [14].

![Figure 35: Mechanical failure of a PMMA construction [14]]
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CHAPTER – FIFTEENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLY (METHYL METHACRYLATE)

E ) EXAMPLES OF ARTEFACTS MADE IN PMMA VALUABLE FROM THEIR ARTISTIC AND DESIGN CONTENT

Polymethylmetacrylate, since the beginning of its industrial and commercial history, appealed many artists and designers for the peculiarity of its intrinsic properties and workability. PMMA for its characteristics was chosen by designers and artists for manufacturing precious objects, which now a days, being considered valuable as far as cultural heritage is concerned, are part of important private and public collections.

Some examples of those artistic artefacts, made in PMMA, are hereafter described and photographically documented.

1 ) “Construction in Space with Crystalline Centre” (1938-40)

This artistic piece (figure 1) was made by Gabo Naum (1890-1977), a Russian-born American sculptor who quite often used transparent plastics in works that attempt to define space rather than occupy it. Gabo Naum is well known <for his sculptural experiments with constructivism> [1,2].

**FIGURE 1: “Construction in Space with Crystalline Centre” (1938-40)** manufactured in PMMA and celluloid (324 x 470 x 220 mm) by Gabo Naum [2].
2) The transparent sculptures made by Bruce Beasley

**FIGURA 2:** The transparent sculptures in PMMA made by Bruce Beasley.

*Top:* Stamper’s Lighthouse, 1967.
*Bottom:* Apolymon, 1968-70 (2.74x4.57x1.82m)
Sacramento, State of California USA [3,4].
Bruce Beasley, born in Oakland (USA), realized the artefacts in PMMA, shown in figure 2, by using a sophisticated casting technique to avoid the formation of voids, stress concentration and shrinkage effects [3,4]. The Apolymon (figure 2-bottom) for its dimensions was at the time considered as a monumental outdoor sculpture.

3) Artefacts realized by carving PMMA preformed blocks or sheets.

Examples of this kind of objects made by carving preformed blocks or sheets of PMMA are shown in figures 3, 4 and 5 [5].

**FIGURA 3:** Left: The sculpture, *Lot’s Wife. The famous carving from “Perspex” acrylic block by Dr. A. Fleischmann, F. R. B. S. - I. C. I. Plastics Division* > [14].
Right: *Candlesticks designed by Sir Francis Rose, and sculptured in perspex by A. J. Lockley for the Gertrude Stein Memorial Room, in New York, (I. C. I., Plastics Division)* > [5].
**FIGURE 4:** The sculpture "Adam and Eva", designed and carved in thick Perspex sheet by Marcel Ronay, (I. C. I. Plastics Division) [5].

**FIGURE 5:** Marcello Morandini (Italy), recent sculptures in black and white PMMA [6].
4 ) *Artefacts realized by using various processing techniques.*

The high transparency, constant in time, the resistance to impact, the easy colourability and plasmability, and the exceptionally high resistance to weathering explain the success of PMMA in realizing artifacts where innovative design represented an added value in comparison to other materials. In such a contest interesting examples are visible in the figures 6, 7 and 8.

**FIGURE 6:** Decorative vases and flower pots made in colored PMMA [7].

**FIGURE 7:** Fountain pens made in PMMA characterized by a very fine design [8].
5) **PMMA as component in costume jewelry.**

PMMA became extremely popular, especially after the 1950s, as component for the manufacturing of very fine designed costume jewelry [10]. Some examples of this kind of application is shown in figure 9 and 10 [10,11].

**FIGURE 8:** Low lounge chairs created with a single piece of molded transparent PMMA plastic which spirals around itself to form a radically innovative seat. It is available in four different colors, which makes it a good choice for those who want to add a piece of elegance in their bedroom [9].

**FIGURE 9:** Application of PMMA in the field of custom jewelry.  
Left- Necklace made of zinc-alloy (chain) and acrylic stone.  
Right- Blue lucite lilies as Angels dress [10].
6) **PMMA as component in the manufacturing of purses, handbags and shoulder bags.**

Concerning such an application in reference [12] is written:

<The most expensive Lucite (a Du Pont’s trademark for a group of polycrystalline esters including PMMA) purses were made by Wilardy of New York and once they were showcased in major department stores throughout the country, as a cheaper alternative to leather handbags. Some of the best Lucite purse designers were Rialto, Llewelyn, Charles S. Kahn, Gilli Originals, Patricia of Miami, Evans, and Myles & Maxim. The most popular (and therefore pricey) color of vintage Lucite purses seems to be the tortoiseshell, followed closely by amber. Vintage Lucite purses come in many shapes too. There are square & rectangular “box” styles, ovals, trapezoid, cylinders, “kidney” shapes, “beehives,” scalloped shaped “kidney” clutches... Some vintage Lucite purses will have “lids” that open, others open up like “clams.” Most have Lucite handles, but some will have straps of chain or other material... > [12].

Examples of old fashion purses in PMMA of various colors and manufacture are shown in figure 11 [12].

The presence of metallic components in some of the purses made in PMMA may be the cause of mechanical and as well as of chemical damages.
FIGURE 11: Vintage purses in Lucite (PMMA) [12].
Top-left: Yellow pearlized confetti vintage lucite purse.
Top-right: Open vintage Myles lucite handbag showing black lining.
Bottom-left: Vintage clear carved lucite purse from Iwannas.
Bottom-center: Vintage tortoiseshell lucite purse.
Bottom-right: Vintage amber lucite purse.
From all the evidences previously reported it could be understood why now a day so many artefacts, in PMMA are more and more part of private and public collections. Consequently it emerges the necessity that great attention should be paid to the proper conservation of objects in PMMA to be considered valuables for their cultural, artistic, technical and historical point of view. In such a contest particular regards has to be devoted to artefacts exposed to external environmental factors of degradation.

Moreover the availability of analytical techniques based on instrumental diagnostic suitable not only for recognizing PMMA artefacts but also for identifying damages and defining their state of conservation is absolutely necessary in order to decide about the most appropriate active and passive actions (including maintenance) to be undertaken to prolong the life time of those precious objects [19,20,21].
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CHAPTER-SIXTEENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLYSTYRENE

A.) HISTORY, SYNTHESIS, PROCESSING, PROPERTIES AND APPLICATIONS

A.1 ) HISTORY

The most relevant landmarks in the history of discovery and technological and industrial development of polystyrene (PS), a thermoplastic polymer obtained from polymerization of the styrene (see figure 1), are hereafter, chronologically, delineated.

--- 1839- Eduard Simon, a Berliner German pharmacist, working on the basis of earlier investigations, prepared styrene by steam distillation of "Storax" (a balsam secreted within the trunk of the tree Liquidambar orientalis, see figure 2) and suggested the name "Sterol". He also observed that on standing for a prolonged period it was transformed from a mobile liquid to a viscous jelly-like, and subsequently solid, material. Mistakenly he thought that this was an oxidation process >[1].

FIGURE 1: Top- Schematic representation of the polymerization reaction of the styrene (monomer) that leads to the formation of polystyrene macromolecules. Bottom- molecular structure of the repeat unit of polystyrene.
At that time Eduard Simon was not in the condition to understand that the product obtained by the thickening of Styrol, named as styrol oxide (Styroloxyd), in effect was the result of the polymerization reaction of the styrol. Simon unintentionally, and without knowing what he had discovered, for the first time synthesised the polystyrene [1,2,3].

--- 1845- A. W. Hoffman (a German chemist born at Giessen on the 8th of April 1818, and died in Berlin on the 2-May- 1892, see figure 3-top-left) and J. Blyth, an English chemist, found that the <same transformation of styrol took place in the absence of oxygen. They called their substance meta-styrol. Analysis later showed that it was chemically identical to Styroloxyd> [2].

--- 1866- Pierre Eugene Marcelin Berthelot, famous French chemist (born in Paris on the 25th of October 1827, died on 1907, see figure 3-top-right) was able to demonstrate that was possible to obtain styrene from the combination of ethylene and benzene. The process involved the passage of the two substances, while in a gaseous state, through a red-hot tube [1]. Marcelin Berthelot suggested that the formation of meta-styrol from styrol was due to a polymerization process.

--- 1911- The British chemistry, Matthews, first recognized the potentiality of PS, and suggested to use this material as substitute of celluloid and other plastics [4].

--- 1922- Herman Staudinger, a German organic chemist (figure 3-bottom), <realized that Simon's discovery, comprised of long chains of styrene molecules, was a plastic polymer. In 1922, Hermann Staudinger published his theories on polymers, stating that natural rubbers were made up of long repetitive chains of monomers that gave rubber its elasticity. He went on to write that the materials manufactured by the thermal processing of styrene were similar to rubber. They were the high polymers including polystyrene> [5].

--- Late 1920s- Herman F. Mark, German I.G. Farben, and Iwan Ostromislensky, Naugatuck Chemical Division of US Rubber, were capable to synthesize in laboratory the PS [6].
--- 1927- A process for the production of toughened PS from the polymerization of styrene in a solution of rubber in styrene monomer was patented by Iwan Ostromislensky. This process was unsuccessful from industrial point of view.

**FIGURE 3:** Top-left- A. W. Hoffman.  
Top-right- Pierre Eugène Marcelin Berthelot.  
Bottom-left- Herman Staudinger (1881 - 1965), Nobel Prize winner on 1953.  
Bottom-right- Herman F. Mark (1895, Austria – 1992, USA ), see text.
--- 1930-1931- At the Badische Anilin & Soda-Fabrik Company ( BASF ), established in 1861, a process apparently suitable to commercially manufacture PS, was developed. <A company called I.G. Farben is often listed as the developer of polystyrene because BASF was under trust to I G. Farben in 1930. The I.G. Farben, a German Company began manufacturing polystyrene in Ludwigshafen > [5]. With the process developed, based on a reactor vessel capable to extrude PS through a heated tube and cutter, PS in pellet form was produced [5]. Injection moulding of PS started in Germany and at Du Pont [7].

Mark and Wulff set up a process from making styrene by means of a catalytic dehydrogenation of ethylbenzene.

--- 1933- The first PS was commercialised in USA by Naugatuck’s Victron. This product was sold < at a prohibitive price of more than 1.50 dollar a pound; the material also suffered because of impurities preventing the company from providing a “water-white” or fully colourless variety > [6]. The Norddeutschen Seekabelwerke EG patent on extruded polystyrene film [7].

--- 1934- R. R. Dreisbach ( figure 4 ), at Dow Chemical Company, gave a great contribution to the production of pure styrene and developed a process of polymerization potentially suitable to be used at an industrial scale [8].

--- 1936- PS was introduced commercially in German [7].

--- 1937- The Dow Chemical Company introduced its PS, named Styron, to the U.S. market. The product was sold at a relatively lower price ( sixty-eight cents of dollar for a pound ) [5,6].

--- 1938- Bakelite and Monsanto commercialised PS products [6]. PS was introduced commercially in USA [7].

--- Years just before the second World-War.

< Before the Second World War PS had become one of Germany’s most important plastic......

In Germany at that time polystyrene was occupying the place that cellulose acetate held in Britain and USA: it was used more than other plastic for injection moulding > [5].

--- FIGURE 4: Left- R. R. Dreisbach of the Dow Chemical Company ( see text ) [8]. Right- Fritz Stastny ( 1908-1985 ), chemical engineer at BASF, Germany; was the inventor of “Styropor” ( see text ) [9].

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Around the time of World War II (1939-1945) - Synthetic rubbers based on styrene copolymers (for example the family of the Styrene-Butadiene Rubbers) capable to substitute the natural rubber were developed in Germany and in USA.

Ray McIntire (Dow Chemical Company scientist) invented expandable or foamed polystyrene (EPS). Ray McIntire said his invention of foamed polystyrene was accidental. His invention came as he was trying to find a flexible electrical insulator. PS......, was a good insulator but too brittle. McIntire tried to make a new rubber-like polymer by combining styrene with isohexylene, a volatile liquid, under pressure. The result was a foam polystyrene with bubble, 30 times lighter than regular polystyrene [5].

1946 - The PS <commercial break through came in 1946 when styrene radio cabinets knocked out the thermosets> [8].

1947 - Dreisbach and Grebe, of the Dow Chemical Company, were given the Hyatt Award for their contribution to the production of pure styrene and its polymerization to PS [8].

1948 - PS in the form of oriented monofilaments was produced [8].

1949 (around) - Munson in Sweden invented polystyrene foam [8].

Fritz Stasny (chemical engineer at BASF) <developed pre-expanded PS beads by incorporating aliphatic hydrocarbons, such as pentane. These beads are the raw material for moulding parts or extruding sheets. BASF and Stasny applied for a patent which was issued in 1949> [10].

**FIGURE 5:** Transmission electron micrographs of a thin section of a high impact polystyrene sample showing the multiphase-structure (salami-like) of the material (see later for more details) [11].
--- Late 1940s-Early 1950s- Dow Chemical Company developed and commercialised a product of PS and a styrene butadiene copolymer (SBR) that was named for its properties “High Impact Polystyrene” (HIPS). The morphology and the phase structure of this product are shown through the electron micrograph in figure 5 [11].

![Figure 6: High resolution scanning electron microscope micrograph showing the cellular structure of the Neopor EPS, an innovative foamed PS produced by BASF [12].](image)

--- 1952- The moulding process of the pre-expanded PS beads, developed by Stasny was demonstrated at the Kunststoff Messe 1952 in Düsseldorf, Germany. These PS beads were also useful in producing foam cup. The EPS products were commercialised as “Styropor” [10].

--- 1954- The Dow Chemical Company introduced EPS products to the United State with the trademark “Styrofoam” [5].


--- Years late 1960s- Machineries suitable to be used to injection moulding of foamed PS were developed. This led to the expansion of the production of objects or parts for furniture.

--- 1966- Plastics Industries Incorporated produced furniture (items or components) in HIPS [8].

--- 1968 – An all plastic chair, manufactured in EPS, appeared in the market (see figure 7) [8].

--- 1970- The Koppers Company filed a patent for a plastic foam cup with walls that do not exceed twice the diameter of the foamed beads used to compose it. This foam had excellent insulation properties, and it was adopted as the material of choice for dispensing hot drinks > [10].

It is worthwhile at this point to underline how the so-called Styrene resins represent a very large family as they includes also a great number of copolymers and terpolymers (i.e. styrene/butadiene, styrene/acrylonitrile, styrene/butadiene/acrylonitrile, etc.), which, according to composition, may cover a wide range of properties and then applications.
A selection of early artefacts is PS or in styrene resins is shown through the figures 8, 9, 10, 11 and 12 with the main aim at demonstrating as these polymers, for their characteristics, very soon in many applications competed with other plastics, and also with more traditional materials (i.e. wood, glass, asbestos, etc.) [13,14].

**FIGURE 8:** PS substitutes shellac, a natural resin, in the production of photograph cases.  
*Left:* Photograph case in moulded shellac in the 1860 era.  
*Right:* Photograph case obtained by injection moulded PS (1960) [8].

**FIGURE 9:** *Left:* Telephone, first produced by using Bakelite, were then obtained by injection moulding of styrene/acylonitrile resins. The dial component is in polymethylmetacrylate [8].  
*Right:* Piano keys were first manufactured in ivory and then in celluloid. In early 1960s were produced by moulding of styrene/acylonitrile resins [8].
**FIGURE 10:** Components in PS (around 1958).
*Top:* Refrigerator with internal door in HIPS and with internal containers in normal PS.
*Bottom-left:* Dinner tray, salt and pepper containers and cutlery in PS.
*Bottom-right:* Containers for food and beverages in PS [15].
FIGURE 11: Clocks moulded of polystyrene (around mid 1950s) [6].

FIGURE 12: Left- Early application of foamed polystyrene in the field of safe shipping packaging [16].
There are three basic types of polystyrene resins: general-purpose (GPPS), high-impact (HIPS) and expandable polystyrene (EPS).

The general reaction scheme of the production of styrene monomer and then of PS, HIPS and EPS is represented in figure 13 [17].

**FIGURE 13:** Sequence of operations to produce different types of polystyrene, GPPS, HIPS, and EPS from crude oil and natural gas [17].
The methods of synthesis, the techniques of manufacturing, the properties, and the applications of GPPS, HIPS and EPS resins are hereafter described.

A 2.1 General-purpose Polystyrene ( GPPS )

As shown by figure 14 GPPS or PS belongs to the family of commodity amorphous thermo-plastics [18]. PS is produced through a free radical polymerization of the styrene (vinyl benzene), an aromatic hydrocarbon with the chemical formula C₈H₈CH=CH₂. This monomer, at RT, is an oily colourless liquid (boiling point = 145.2°C) that evaporates easily, and due to the presence of double bonds without difficulty polymerises to a transparent glass-like plastic.

![Diagram](image)

**FIGURE 14:** Diagram where plastics are ordered according to the values of price and performance and of volume demand. Commodity plastics are characterized by relatively low value of price and performance and by a high production volume. Polystyrene is a commodity plastic [18].

The free radical polymerization of polystyrene, in absence of any chain transfer reaction, occurs through the following steps:
--- Initiation;
--- Chain propagation;
--- Termination [19].

The step of initiation needs the presence of special substances capable to dissociate, under the action of light or heat, giving rise to the formation of primary reactive radical species.
Typical initiators include molecules like dialkyl peroxides, diacetyl peroxides, and azo compounds. As shown by the schemes in figure 15, for 2,2'-azo-bis-isobutyrilnitrile (AIBN) and benzoyl peroxide, they easily split forming molecular fragments having unpaired electron. Such types of molecules, highly reactive, called free radicals, are usually indicated as $R^\ast$ [20].

The various steps of the free radical polymerization of PS, excluding reactions of chain transfer, are hereafter schematically depicted [21]:

--- **INITIATION STEP**

$$I \xrightleftharpoons[k_d]{k_i} 2R^\ast$$

$$R^\ast + M \xrightarrow{k_i} P_1^\ast$$

Where $I$, $(R^\ast)$, $M$ and $P_i^\ast$ represent the molecule of the initiator, of the primary radical and of the monomer radical respectively.

--- **PROPAGATION STEP**

$$P_1^\ast + M \xrightarrow{k_p} P_2^\ast$$

$$P_2^\ast + M \xrightarrow{k_p} P_3^\ast$$

$$\ldots$$

$$P_n^\ast + M \xrightarrow{k_p} P_{n+1}^\ast$$

Where $P_1^\ast$, $P_2^\ast$, $P_n^\ast$, and $P_{n+1}^\ast$ represent the dimer radical, the trimer radical, the chain radical formed with $n$ unit and the chain radical with $n+1$ unit respectively.

--- **TERMINATION STEP**

$$P_n^\ast + P_m^\ast \xrightarrow{k_t} P_{n+m}^\ast$$

$$P_n^\ast + P_m^\ast \xrightarrow{k_t} P_n + P_m$$

Where dead polymers chains ( $P_{n+m}$ or $P_n$ and $P_m$ ) are produced through a combination ( above ) or a disproportionation ( below ) reactions. PS has been shown to terminate essentially by combination reaction [19].
Styrene can be polymerised according to the below described different types of methods.

A) Bulk Polymerization
The styrene monomer with catalyst added polymerises in suitable reactors under well-established conditions of temperature and time. Around the years 1950s the following conditions were followed [15]:
--- A pre-polymerization step at ≈ 80°C where the % of monomer converted to polymer was 33-35.
--- A polymerization step in a column at 150-210 °C where the polymerization is completed and the polymer reaches the desired molecular mass.
--- The polymer still fluid is transferred in an extruder line where it is transformed by spinning in ribbons or filaments finally these filaments are cut in pellets to be shipped for further processing and shaping operations.
The PS obtained is colourless and perfectly transparent. At high conversion a polymer with a rather broad distribution of molecular mass is produced.
The method presents as critical aspect the fact that being the polymerization reaction highly exothermic the heat developed and the temperature need to be carefully controlled (see figure 16).

B) Solution Polymerization
Styrene is dissolved in a suitable solvent (toluene, ethylbenzene, methanol, ethylmethylketone and others [15].
The advantages of such kind of polymerization may be summarized as follows [21]:
--- Easy control of heat and temperature of polymerization;
--- The solution may be directly usable.
FIGURE 16: Industrial production plants of polystyrene according to the bulk polymerization technique (1950s) [15].

Top-left: Plant for the pre-polymerization step. Top-right: Polymerization columns. Bottom-left: Extrusion of the polymer mass into filaments, subsequently cut into pellets [15]. Bottom-right: Schematic cross section through center of three longitudinal tanks showing Dow’s first commercial continuous melt process for PS. Styrene was thermally polymerized alternately in tanks 1 and 2, and devolatilized in the receiving tank which was always about half full [15-b].
The disadvantages are:
--- Possibilities of chain transfer reactions if improper solvents are selected [21];
--- Difficulties in the complete removal of the solvent from the polymer. As matter of fact such an operation requires long times and this make the technique not always convenient from industrial point of view.

C ) Suspension Polymerization
In such a technique the monomer is dispersed in an aqueous system. The initiator is dissolved in the monomer phase. The kinetics is practically the same of the polymerization in bulk.

The method is described as follows in reference [21].

*The dispersion of monomer in droplets, typically 0.01-0.5cm in diameter is maintained by a combination of agitation and the use of water soluble stabilizers.... The tendency to agglomerate may become critical when the polymerization has advanced to the point where polymer beads become sticky. At the completion of the reaction the polymer is freed of stabilizer by washing and is dried. For some applications the polymer beads can be used directly, whereas for others compaction is required* [21].

Usually a suspension stabilizer is used to prevent the coalescence of polymer droplets. The polymerization proceeds in presence of a suitable catalyst at a temperature of about 80-120°C that is sensibly higher than that used for emulsion polymerization.

At the end of the process the polymer in the form of solid pearls or beads is obtained. [4].

![Sodium Lauryl Sulfate](image_url)

**FIGURE 17:** Top- molecular structure of a single soap molecule. Bottom- at a critical value of concentration the soap molecules aggregate forming micelles where the hydrophilic heads are at the surfaces of the particles [22].
D) Emulsion Polymerization

An emulsion consists in a suspension where an immiscible liquid is dispersed, forming droplets, in another liquid. The system needs to be stabilised by the addition of a substance suitable to act as an emulsifier agent.

Fatty acid soaps, such as for example the sodium lauryl sulphate, whose structure is characterized by a non polar tail and a water soluble head (see molecular structure in figure 17), are typical surfactant or emulsifier agents [22].

The main steps of a generic emulsion polymerization are hereafter summarized.

I ) The system constituted by water and soap , is vigorously stirred until the critical micelle concentration is reached (see figure 17-bottom).

li ) The monomer and a water soluble free radical initiator (i.e. potassium persulphate) is added and the whole batch is stirred. The monomer forms separated particles, but part of it may find place inside micelles. The interior of the micelle provides the site necessary for the free radical polymerization.

lii ) Polymerization proceeds very rapidly due to the presence of catalyst at a temperature of about 60°C.

<Initiation takes place when an initiator fragment migrates into a micelle and reacts with a monomer molecule.....Polymer particles can grow to extremely high molecular weights, especially if the initiator concentration is low. That makes the radical concentration and the rate of termination low as well. Sometimes a chain transfer agent is added to the mix to keep the molecular weight from getting too high..... Monomer migrates from the large monomer droplets to the micelles to sustain polymerization. On average, there is one radical per micelle. Because of this, there isn't much competition for monomer between the growing chains in the particles, so they grow to nearly identical molecular weights and the polydispersity is very close to one. Practically all the monomer is consumed in emulsion polymerizations, meaning the latex can be used without purification...... Each micelle can be considered as a mini bulk polymerization. Unlike traditional bulk polymerizations there is no unreacted monomer leftover, and no thermal "hot spots" form. In bulk polymerizations (no solvent, just monomer and initiator), thermal hot spots cause degradation and discoloration and chain transfer broadens the molecular weight distribution > [22].

lv ) The protecting layer of the soap is neutralized allowing to the tiny droplets to coagulate together [4].

The diameter of the polymer particles produced is of the order of 0.1μm, much smaller than those obtained with suspension method [21].

With the emulsion polymerization it is possible to produce polymers, in comparison to bulk or suspension techniques, with higher molecular mass, and at higher rates [23].

In the common industrial practice the product of an emulsion polymerization is called as latex [22].

The most significant characteristics of PS and the main field of application, around the years 1960s, as taken from reference [4], are listed in the table 1 and 2 respectively.
### TABLE 1: Main characteristics of general purpose polystyrene [4].

<table>
<thead>
<tr>
<th>Colour:</th>
<th>Clear and colourless.</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Physical Properties:</td>
<td>Tastless and odourless.</td>
</tr>
<tr>
<td></td>
<td>Hard and rigid.</td>
</tr>
<tr>
<td></td>
<td>Good dimensional stability.</td>
</tr>
<tr>
<td></td>
<td>Moderate strength. Inclined to be brittle.</td>
</tr>
<tr>
<td></td>
<td>High surface gloss (copolymers are duller).</td>
</tr>
<tr>
<td></td>
<td>Lightweight plastic (S.G. 1.07).</td>
</tr>
<tr>
<td>Water:</td>
<td>Negligible effect.</td>
</tr>
<tr>
<td>Heat:</td>
<td>Thermoplastic. Softens in boiling water.</td>
</tr>
<tr>
<td></td>
<td>Retains properties at freezing temperatures.</td>
</tr>
<tr>
<td></td>
<td>Burns slowly.</td>
</tr>
<tr>
<td>Solvents and chemicals:</td>
<td>Good resistance to most foods, drinks, household acids,</td>
</tr>
<tr>
<td></td>
<td>oils, alcohol, vinegar.</td>
</tr>
<tr>
<td></td>
<td>Attacked by citrus fruit rind oil, cleansing fluids, gasoline (petrol), turpentine, nail polish and remover.</td>
</tr>
<tr>
<td>Light:</td>
<td>No effect. High transparency.</td>
</tr>
<tr>
<td>Age:</td>
<td>Little effect. Not suitable for continued exposure outdoors.</td>
</tr>
<tr>
<td>Electrical:</td>
<td>Excellent insulator, including high-frequency.</td>
</tr>
<tr>
<td></td>
<td>Not affected by humid conditions.</td>
</tr>
</tbody>
</table>
### TABLE 2: Application of polystyrene according to processing and manufacturing [4].

1. **Solutions: emulsions.**
   Polystyrene solutions and emulsions are used for the production of water paints, for surface coating, textile finishing, etc.

2. **Sheet.**
   Polystyrene sheet is available in a range of thicknesses and sizes.
   Examples of Uses: High-frequency electrical equipment, e.g. radio, television; instrument panels; refrigerator parts and containers.

3. **Film.**
   Extruded film is produced in a range of thicknesses.
   Examples of Uses: Electrical insulation.

4. **Rod; tube; sections.**
   Rod and tube are available in a range of diameters, wall thicknesses and profiles.
   Examples of Uses: High-frequency electrical equipment; tableware.

5. **Moulding Materials.**
   Moulding powders are produced in a wide range of colours; transparent, translucent and opaque. They are used primarily for injection moulding.
   Examples of Uses: Buttons, buckles; electrical and electronic equipment; refrigerator parts; radio cabinets; food containers; tiles; toys; picnic equipment.
A 2.2) **High Impact Polystyrene (HIPS)**

PS-homopolymer, a rigid, transparent thermoplastic with a glass transition temperature between 90-100°C, at RT shows a brittle behaviour, and exhibits low impact energy absorption. As matter of fact because the PS chain segments, below Tg, have no local mobility the material is unable to dissipate energy through the rearrangement of part of macromolecules. Thus the impact resistance, measured by the impact strength (the energy required to break a material using very rapid loading rates [23-b]) of PS is relatively low for many applications.

To overcome this disadvantage in the early 1950s a tougher rubber modified PS, was developed (High Impact Polystyrene (HIPS)), a more impact resistant and less crack-sensitive PS-based material.

The first step of any procedure that leads to HIPS by rubber modification of PS consists in the dissolution of a preformed polybutadiene (a rubbery polymer that at RT is above its glass transition temperature; Tg ≤ -40°C) in styrene monomer. Even if HIPS may be produced by an emulsion procedure, from industrial point of view the bulk polymerization was generally preferred.

In the bulk process of HIPS <the styrene monomer/rubber/additive mixture is fed through a series of reactors and reaches a conversion of 70-90%. The reaction can be carried thermally or by using initiators. The resin is then devolatilized under high vacuum to remove residual monomer, and pelleted for sale> [24].

The polymerisation of styrene in the presence of polybutadiene due to the immiscibility of polystyrene and polybutadiene gives rise essentially to a two-phase system where, at low rubber content, the PS is the continuous phase (matrix). As shown by figure 18 the dispersed phase is constituted by rubber particles containing a relatively small amount of PS included as dispersed phase.

The rubber particles in HIPS generally have a diameter of 0.5 – 10 micro-meter. They, therefore, scatter visible light. Thus, following rubber modification, the transparency of the PS moulding materials is lost.

It is well established that in the course of the HIPS synthesis grafting of polystyrene chains onto polybutadiene (PB) macromolecules occurs. The mechanism of formation of the PS-PB graft copolymer is schematically described in figure 19 [11].

It can be concluded that the improvements in the impact resistance of PS induced by the rubber modification approach has to be essentially attributed to:

--- The introduction of a flexible amorphous component in the brittle matrix of PS;
--- The degree of cross linking of polybutadiene (PB) segments;
--- The chemical interaction between PS and PB macromolecules, this includes the formation of PS-PB graft copolymers;
--- The interfacial adhesion between the phases PS-rubber;
--- The occlusion of fractions of the PS phase inside the rubber dispersed particles, which has the consequence of increasing the volume fraction of the latter [11].

In the common industrial practice of bulk process the amount of PB used for the production of HIPS, due to the high viscosity of the medium, is limited to 14% (w/w).

The tensile stress strain curves of PS and HIPS are schematically compared in figure 20 [26]. It can be seen as PS behaves as a brittle material while HIPS presents a typical tough-ductile behaviour. HIPS according to its impact resistance value is commercially sold in various grade (medium impact, high impact and very high impact).
FIGURE 18: Electron micrographs of rubber modified polystyrene (HIPS). The continuous phase (matrix) is constituted by PS, while the dispersed rubbery particles are constituted by particles of polybutadiene (domains are shown in black), which occlude particle of PS. The rubber modified sample contains about 6-7% of polybutadiene [25].

To prevent the rubber degradation antioxidants as well as flame retardants additives for specific applications are used.

HIPS owing to its ease of processing (it is transformed by injection moulding, extrusion and thermoforming), low cost and high performance is used in many sectors (packaging, disposable containers and cups, consumer electronics, razors, audio and video cassettes, TV cabinets, refrigeration liners, computer housings, and toys).

Some early applications of PS, HIPS and of PS-based copolymers as well as related processing procedures are shown in the figures 21, 22, 23 and 24, while in figure 25 is shown a more recent use of both PS and HIPS in the production of CD cases [29].

Typical properties of general purpose (GPPS) and of high impact (HIPS) polystyrene are shown in table 3 [30].
**FIGURE 19:** Mechanism of formation of PS-PB graft copolymers during the process of HIPS production, see text [11]. In figure: Cadeia is for Chain; Em crescimento is for chain growing and Copolimero grafitizado is for graft copolymer.

**FIGURE 20:** Tensile stress strain curves for PS and HIPS (schematic comparison) [26].
**FIGURE 21 (Top):** Polystyrene cage in form of radio cabinet (USA, 1940) [27].

**FIGURE 22 (Bottom):** Series of artefacts in Polystyrene where glass was substituted (USA, Italy, 1940-1950) [27].
**FIGURE 23:** Vacuum forming of Polystyrene sheets. Left - *A sheet of polystyrene has been heated and blown out into a “bubble” by air pressure. A mould is placed under the bubble, and the sheet drawn down over by application of vacuum (see right figure).* [4].

**FIGURE 24-a:** Early application of HIPS. Top - Refrigerator liners being vacuum formed from high impact PS [4]. Bottom, Left - Portable radio in high impact polystyrene [15]. Bottom, Right - Air grating in HIPS [15].
FIGURE 24-b): Floral Leaves Made of High Impact Polystyrene Soap Size [28].

FIGURE 25: Recent applications of transparent General Purpose Polystyrene (GPPS) and opaque High Impact Polystyrene (HIPS) in the production of CD case [29].
<table>
<thead>
<tr>
<th>Property</th>
<th>GP-PS</th>
<th>HI-PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (lb/in³) (g/cm³)</td>
<td>0.043</td>
<td>0.043</td>
</tr>
<tr>
<td>1.05</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>Water Absorption, 24 hrs (%)</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Tensile Strength (psi)</td>
<td>7,500</td>
<td>4,000</td>
</tr>
<tr>
<td>Tensile Modulus (psi)</td>
<td>450,000</td>
<td>260,000</td>
</tr>
<tr>
<td>Tensile Elongation at Break (%)</td>
<td>47</td>
<td>55</td>
</tr>
<tr>
<td>Flexural Strength (psi)</td>
<td>6,100</td>
<td>8,700</td>
</tr>
<tr>
<td>Flexural Modulus (psi)</td>
<td>475,000</td>
<td>280,000</td>
</tr>
<tr>
<td>Compressive Strength (psi)</td>
<td>14,500</td>
<td>7,500</td>
</tr>
<tr>
<td>Hardness, Rockwell</td>
<td>75M</td>
<td>56L</td>
</tr>
<tr>
<td>IZOD Impact Notched (ft-lb/in)</td>
<td>0.8</td>
<td>2</td>
</tr>
<tr>
<td>Coefficient of Linear Thermal Expansion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x 10⁻⁶ in./in./°F)</td>
<td>4.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Heat Deflection Temp (°F / °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 264 psi</td>
<td>200 / 95</td>
<td>195 / 92</td>
</tr>
<tr>
<td>Vicat Softening Temp (°F / °C)</td>
<td>224 / 107</td>
<td>214 / 102</td>
</tr>
<tr>
<td>Max Operating Temp (°F / °C)</td>
<td>150 / 65</td>
<td>140 / 60</td>
</tr>
<tr>
<td>Thermal Conductivity (BTU-in/ft²-hr-°F)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(x 10⁻⁸ cal/cm-sec-°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flammability Rating</td>
<td>H-B</td>
<td>H-B</td>
</tr>
<tr>
<td>Dielectric Strength (V/mil) short time, 1/8&quot; thick</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>Dielectric Constant at 1MHz</td>
<td>2.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Arc Resistance (sec)</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Volume Resistivity (ohm-cm) at 50% RH</td>
<td>&gt;10⁶</td>
<td>&gt;10⁶</td>
</tr>
</tbody>
</table>
A 2.3) Expandable Polystyrene or Polystyrene foams (EPS)

According to R. D. Deamin, a foamed plastic is actually a dispersion of gas in a solid polymeric matrix and derives properties from both phases. The polymeric structure contributes most of the mechanical and chemical properties, whereas the gas phase contributes most to thermal and electrical insulation [31].

Foamed plastics may have a closed or an open cell structure. In the case of a closed cell structure, the material is stiff and presents a higher resistance to compression stresses, while open cell foams are more soft and flexible [31].

Expandable polystyrene (EPS) is a generic term that includes PS and PS copolymers supplied as compounded with physical blowing agents and other additives, which can be processed into low density foamed articles. The most common form of this product is crystal PS (for crystal PS it is intended an amorphous transparent PS) beads containing pentane as blowing agent [32].

To produce beads of PS containing an expandable agent the suspension polymerization method is generally used. The various phases of the procedure are hereafter summarized:

1) A surge tank is charged with styrene, water, suspending agent (barium sulfate or copolymers of acrylic and methacrylic acid and their esters) initiator (such as benzoyl peroxide) and a blowing agent (propane, butane, pentane, methylene chloride, and the hydro chlorofluorocarbons (HCFCs)).
2) According to the initiator used the polymerization temperature cycle is between 80-150°C. The conversion of styrene to PS beads is almost total.
3) At the end of the reaction the product in the form of beads, which occlude the blowing agent, is cooled, washed, centrifuged, dried on a fluid bed and finally riddled.
4) Additives (antistatic, lubricants, etc.) are added in the dried state by dispersion methods.
5) The final product, usually named as expandable polystyrene (EPS) is then stocked in a refrigerated storehouse to reduce the loss of the expanding agent [33].

The EPS may be processed and then shaped in the final articles following two main steps.

I) The expansion step - The beads containing blowing agent are heated allowing the polymer to soften. Under such conditions the blowing agent may vaporize. As a result millions of cells in each particle are created and expanded. The amount of expansion, which determines the final density of the material, is controlled essentially by parameter such as temperature and time [33].
At the end of this expansion step the foamed beads are stored by allowing air to diffuse inside the newly produced cells.

II) The Manufacturing step-

II.1) Moulding
After aging, the beads are fed into a mold of the desired shape. Low-pressure steam is then injected into and between the beads, expanding them once more and fusing them together. The mold is then cooled, either by circulating water through it or by spraying water on the outside [34].
Figure 26: Photomicrographs of cross-sections of:
Left- extruded PS-foam, 10x.
Right- molded bead PS- foam, 10x [35].

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extruded Type</td>
<td>1.5-5.0</td>
<td>4.0-6.0</td>
<td>3.0-4.0</td>
<td>0.3-1.5</td>
<td>&lt;0.5</td>
<td>25-140 at 5% deflection</td>
<td>165-175</td>
</tr>
<tr>
<td>Moulded Bead Type</td>
<td>1.0-5.0</td>
<td>4.3-3.7</td>
<td>3.0-4.0</td>
<td>0.4-2.2</td>
<td>&lt;3.0</td>
<td>13-115</td>
<td>167-185</td>
</tr>
</tbody>
</table>
II.2) Extrusion

To produce this type of foam a molten polystyrene-based plastic compound containing a blowing agent is extruded at elevated temperature and under pressure through a slit orifice to the atmosphere; at this point the mass expands to about 40 times its pre-extrusion volume. It is extruded in board form with continuous surface skin or in large billets that can be cut into standard board or fabricated into other desired shapes. Woodworking tools (hand-operated or power-driven) are commonly used to convert foams into useful shapes...> [35].

As shown by the comparison of the micrographs reported in figure 26, < extruded foam has a simpler, more regular structure (Figure 26-left) than molded bead foam (Figure 26-right); and also has better strength properties and higher water resistance > [35].

EPS resin is generally classified as rigid closed-cell foams, which as can be seen by the data listed in table 4, may be processed according to a wide range of densities and properties [35]. The influence of density upon the EPS physical properties is clearly shown by the data reported in table 5 [36].

![Table 5: Physical properties of EPS samples as function of density](image)

Some of the main applications of EPS are hereafter listed:

--- In construction, principally as thermal insulation.
--- In low-temperature insulation and low temperature storage facilities.
--- As core material in exterior sandwich panels.
--- In the packaging sector (the major outlet for EPS), including protective packaging.
--- As an art medium or handicraft material and in the fabrication of consumer items such as chairs, tables, and lamp bases.

Many items in EPS, valuable from design and artistic point of view, and characterized by attractive and elegant appearance, now days are appealed for private and public collections.
The properties of EPS depend upon density, type and size of cells, and then by the method of production. They are thermoplastics, rather deformable, and resilient at low densities. EPS, usually, are resistant against the attacks of fungus or bacterial [35].

EPS generally have poor outdoor weathering resistance. < The plastic matrix deteriorates when exposed to direct sunlight for extended periods, as evidenced by a characteristic yellowing. To protect polystyrene foam against the effect of outdoor weathering and physical damage adequate coating should be applied on the surface....... Coatings containing aromatic or chlorinated hydrocarbons, ketones and esters dissolve polystyrene foam and should be avoided. Special grades of styrene-acrylonitrile copolymer foams are solvent resistant.......... EPS undergo slight deterioration in their mechanical properties (e.g., reduction in strength) when the temperature is raised to the heat distortion point (71 to 77°C).

Under small thermal and moisture gradients, polystyrene foams absorb relatively low amounts of water. Experimental evidence shows, however, that under larger fluctuating temperature and moisture gradients some polystyrene foam can absorb high proportions of water....... It cannot be expected to act as a continuous vapor barrier or as an air barrier> [35].

It must be pointed out that conventional EPS foams generally show a poor resistance to oil and gasoline. Now days innovative EPS resistant to these agents are under development, and some of them also commercially available.

Some EPS-based materials are requested for the hereafter reported advantages:

--- Remarkable durability and low maintenance
--- Impervious to pests
--- Cost effective
--- Lightweight and easy to install
--- Weather and fire resistant

Moreover by applying suitable coating techniques it is possible to match a specific texture like granite, stone, or wood. This makes EPS very useful in making paint sceneries for stage theatre and cinema set. Some of the items in EPS used in this field are collected in many famous museums dedicated to the history of the cinema and of the theatre.

Examples of typical EPS applications are shown in the figures 27, 28, 29 and 30 [37-43]. Since the beginning of 1960s EPS block moulding plants were established all around the world. Now days they are able to manufacture EPS in large and thick blocks, which can be cut ( generally with hot wires into any shape required ) [44].

According to modern procedures < manufacturing EPS does not involve the use of ozone depleting chlorofluorocarbons or hydro chlorofluorocarbons (CFCs or HCFCs). The final product is a moisture-resistant, closed-cell structure consisting of 90-percent air, yet can possess a compressive strength of up to 276 kPa (40 psi). It is available in varying densities, usually from 14.4 kg/m³ to 28.8 kg/m³ depending on the intended application.....

......From humble beginnings, EPS has grown into one of the most versatile insulating materials in construction today > [44].
FIGURE 27: **Left:** Hand crafted country living vintage Christmas shaped fabric ornament. The components are: 60% Styrofoam, 30% Polyester, 10% Other [37]. **Right:** Universal Studios' Islands of Adventure Park (Orlando, Florida). Figures were obtained by hand sculpting expanded polystyrene (EPS) foam to be applied over steel framing. *<is another perfect example of using plastic materials to achieve extraordinary aesthetics>* [38].

FIGURE 28: **Left:** Surfboard manufactured by using a core of expanded polystyrene and a surface protective layer in epoxy [39]. **Right:** A model of the famous Mini Interceptors toys manufactured by a high quality EPS foam. *<With an excellent paint finish, extremely smooth and well filled.>* [40].
FIGURE 29: Left- The “Chaise Longue” designed by Arthur Rotier.
< The furniture is made from EPS and polyether foam, with a solid coating on the white base and leather-like coating on the coloured cushions > [41].
Right- “Aero head bicycle racing helmet” designed by Jim Gentes. Manufactured in EPS (Expanded polystyrene) foam and Lycra (a Du Pont fiber) [42].

FIGURE 30: Massive sculpture made by Kordian Lewandowski entitled "Game Over", the piece was inspired by Michelangelo's famous sculpture "La Pietà" and formed of polystyrene foam which Lewandowski shaped entirely with a chainsaw [43].
FINAL CONSIDERATIONS ABOUT HISTORY AND DEVELOPMENT OF POLYSTYRENE

The great success of PS on the international markets started since the latest years of 1930s, especially when moulders became more confident with polystyrene and manufacturers more convinced of its durability, it appeared in transparent crisper drawers and other refrigerator parts [6].

PS around the mid-to-late 1950s became the favoured plastic for moulding cabinets for radio and then for television set. In such applications thermosets such as phenol and urea formaldehyde resins were substituted by PS, and this was possible because of the high-speed injection moulding procedures that could be followed with PS in comparison to the slow compression moulding techniques used in the case of thermo-set resins [6].

< Capable of flowing smoothly into sharply angled moulds, polystyrene facilitated a shift from bulbous streamlining to a flared look,... Once again plastic materials and processes contributed to an expressive visual style > [6] (see figure 31).

![Catalin Styrene](image)

**FIGURE 31:** Polystyrene television cabinet (1959), see text [6].

Polystyrene remained a major plastic for making toys (cars, ships, fighter planes, all with realistic details) all over the 1950s. Decorators and designers discovered the possibilities given by EPS as cheap material suitable for manufacturing, by easy carving, painting and coating, objects to be used in many different application fields.
The following figures give an idea of the success gained by PS from commercial point of view. In 1941 the production of PS in USA was around 2,000 tons per year, while in 1945 it reaches the value of about 6,800 tons [44]. In the period 1956-1967 the production of styrene-based resins is growth from 636 to 2,550 millions of pounds [7].

As can be seen by the diagram reported in figure 32 still today PS-based materials are worldwide used. < The regional markets for polystyrene with the highest growth potential over the forecast period include Asia, Central and Eastern Europe, and the Middle East. All of these regions will see increased capacities and rising demand for polystyrene. Specifically, within Asia polystyrene demand is projected to increase at a rate of almost 5% compounded annually; Central and Eastern Europe is expected to see growth of almost 6% per year and the Middle East is projected to increase on the order of about 5% annually during 2007–2012 > [45].

![World Consumption of Polystyrene—2007](image)

**FIGURE 32:** The regional markets for polystyrene (2007) [45].

From the diagram shown in figure 33 it comes out that, concerning the period 1990-2025, PS, EPS and ABS are the three largest styrene derivatives representing nearly 75% of styreneic demand. Moreover over time, EPS will become a more important part of the styrene-based resins demand [46]. The above data are in agreement with those of the pie chart reported in figure 34 showing the world consumption of styrene by end use [47].

< Global production and consumption of styrene in 2009 were each approximately 23 million metric tons. Global capacity utilization was 77% in 2009……… The largest end use of styrene is for production of polystyrene, which accounted for almost 60% of global styrene consumption in 2009; the second major use is ABS/SAN resins. Other applications for styrene include manufacture of SBR solid and latex, SB copolymer latex, unsaturated polyester resins, and styrene copolymers > [47].
FIGURE 33: Distribution of styrene consumption according to styrenic resins types [46].

FIGURE 34: World consumption of styrene according to polymer material types [47].

Since the years 1960s PS together with polyethylene, polyvinylchloride and polypropylene is one of the major used four mass thermoplastics.
The commercial PS-based products obtained from common industrial processes are amorphous materials. This is due to the fact that the polymerization processes used lead to macromolecules where the tertiary, asymmetric, carbon atoms linked to benzene rings are present along the chain axis with a random configuration (atactic structure; see macromolecule sketched in figure 35-right).

With the discovery of the stereo specific Ziegler-Natta catalysts (years 1950s) it was possible to synthesise PS products, which due to the ordered distribution of the tertiary atoms configuration, were capable to crystallize. According to the stereo specific nature of the catalysts used was possible to produce two ordered PS polymers named Isotactic or Syndiotactic (see molecular structures sketched in figure 35-center and left respectively) having different structural and physical characteristics.

![Molecular structures of the three possible stereo isomers of polystyrene. From left to right: syndiotactic, isotactic, and atactic.](image)

As shown by figure 35 the chains of both syndiotactic and isotactic PS are very ordered, with the phenyl groups falling on alternating sides of the chain or all on the same side in an ideal zigzag planar conformation of the chain backbones. These regular configurations determine the easily packing of the chains allowing the formation of ordered crystalline structures. On the contrary the atactic PS is amorphous due to the fact that the irregular chains can't pack together.

*The isotactic polymer will have the highest melting point due to its packing efficiency and high inter-chain forces. X-ray crystallography can be used to elucidate the structures and look for different degrees of crystallinity. $^1H$ or $^{13}$C NMR can be used to assign tacticity. Checking the melting point and density will verify which one is isotactic: the isotactic one will have both the highest melting point and the highest density > 48].*
FIGURE 36: Wide-angle X-ray diffractograms of amorphous polystyrene (top); crystalline-isotactic polystyrene (center) [49], and crystalline syndiotactic polystyrene (bottom) [50].
The technique based on the wide-angle diffraction of X-rays, as shown by the comparison of the
diffractograms reported in figure 36, is very useful in distinguish between amorphous and crystalline PS.
As consequence of its more compact structure crystalline PS have a higher value of the density as compared with the amorphous one (density of iso-PS = 1.111 g/cm³; of amorphous-PS = 0.854 g/cm³)
The tendency to crystallize of the stereo-regular isomers of PS is clearly demonstrated by the
electron micrographs in figure 37 where crystals or sheaf-like crystal aggregates are shown in the
case of melt crystallize samples of iso-PS [51].

**FIGURE 37:** Transmission electron micrographs of a sample of:
**Left:** isotactic polystyrene crystallized at 220°C for 81 min showing
(a) sheaf-like aggregates and (b) hexagonal lamellae.
**Right:** lower molecular mass isotactic polystyrene crystallized at
190°C for 10 min. Complex sheaf-like aggregate [51].
Quite recently a syn-PS-based resin obtained by using metallocene catalysts have been developed and commercialised under the trade name XAREC® as an engineering environmentally friendly plastic [52]. The most relevant properties of the above product, together with possible applications fields are summarized and compared with those of other polymers in table 6 [52].

**TABLE 6: Properties and applications of syndiotactic-polystyrene based resins [52].**

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance to</td>
<td>Compared to polyester- and polyamide-based resins, XAREC® offers a superior hydrolysis resistance,</td>
</tr>
<tr>
<td>hydrolysis</td>
<td>comparable to polyphenylene sulfide.</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>XAREC® is highly resistant to corrosion by various acids and alkalis, and can withstand automobile oils</td>
</tr>
<tr>
<td></td>
<td>and antifreeze.</td>
</tr>
<tr>
<td>Low specific</td>
<td>With one of the lowest specific gravities of all engineering plastics on the market, XAREC® reduces</td>
</tr>
<tr>
<td>gravity</td>
<td>the weight and cost of parts.</td>
</tr>
<tr>
<td>Heat resistance</td>
<td>With a long-term heat resistance of 130°C, a heat distortion temperature of 250°C and a melting point</td>
</tr>
<tr>
<td></td>
<td>of 270°C, XAREC® can be used for wave and reflow soldering. XAREC® is also moisture resistant, and</td>
</tr>
<tr>
<td></td>
<td>useful for surface mount chip parts and connectors.</td>
</tr>
<tr>
<td>Electrical properties</td>
<td>XAREC®s electrical properties, including its dissipation factor and dielectric constant, are similar</td>
</tr>
<tr>
<td></td>
<td>to those of fluororesins. Because it is electrically stable over a wide range of frequencies and</td>
</tr>
<tr>
<td></td>
<td>temperatures, XAREC® is suitable for high-frequency components.</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>Because the flow and transversal direction of the molten resin changes little during mold shrinkage,</td>
</tr>
<tr>
<td></td>
<td>XAREC® offers good dimensional performance when compared to other glass-fiber-reinforced crystalline</td>
</tr>
<tr>
<td></td>
<td>resins.</td>
</tr>
<tr>
<td>Processability</td>
<td>XAREC® can easily be molded on any standard specification injection molding machine. It possesses</td>
</tr>
<tr>
<td></td>
<td>high flow properties, close to those of liquid crystal plastic, and degradation due to heating is</td>
</tr>
<tr>
<td></td>
<td>minimal. It is also ground easily, making XAREC® easy to recycle.</td>
</tr>
</tbody>
</table>
XAREC®'s dielectric properties, including its low dissipation factor and dielectric constant, are close to those known for fluororesins, making XAREC® ideal for use in high-frequency components [52] (see example in figure 38).

**FIGURE 38:** Internal antenna of cellular telephone in syndiotactic polystyrene-based resin [52].

Besides the above reported uses of syn-PS it can be said that so far isotactic and syndiotactic PS, did find a rather limited number of applications, and only in some special and sophisticated sectors all characterized by a low volume of production.

Due essentially to the great amount of improvements developed in the field of polymer catalysis and polymer and copolymer synthesis several types of styrene-based resins where produced with a tailored combination of several properties such as transparency, impact strength, and chemical resistance.

As summarized by the diagram shown in figure 39 nowadays there is the possibility to find on the market the following PS-based plastics:

1) General Purpose Polystyrene (GPPS), an amorphous, colourless polymer of styrene as sole monomer;
2) High Impact Polystyrene (HIPS), a graft polymer in which synthetic rubber is chemically bonded to GPPS resulting in having impact strength;
3) Styrene Acrylonitrile copolymer (SAN), a copolymer of styrene and acrylonitrile resulting in having chemical resistance;
4) Acrylonitrile Butadiene Styrene Resin (ABS) that has both impact strength derived from polybutadiene rubber and chemical resistance derived from acrylonitrile [53].
FIGURE 39: Diagram showing how the modern chemistry allows the possibility to produce a wide range of styrene-based resins with tailored use properties (see text). GPPS: General Purpose Polystyrene. HIPS: High Impact Polystyrene. SAN: Styrene Acrylonitrile Copolymer. ABS: Acrylonitrile Butadiene Styrene Resin [53].
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CHAPTER-SEVENTEENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLYSTYRENE

B) PROPERTIES RELEVANT AS FAR AS DEGRADATION BEHAVIOUR AND CONSERVATION PRACTICES ARE CONCERNED: METHODOLOGIES AND TESTS FOR THE IDENTIFICATION OF POLYSTYRENES IN ARTEFACTS

As reported in the previous chapter plain polystyrene (PS) is a thermoplastic colourless, rigid material with some degree of flexibility, capable to be easily shaped into transparent or variously coloured objects with fine and elegant design (see figure 1). Because of the convenient value of its cost performance ratio PS is widely used for producing plastic model assembly kits, plastic cutlery, CD "jewel" cases, and many other objects where a fairly rigid, economical plastic of any of various colours is desired [1].

![Figure 1](image.jpg)

**FIGURE 1:** PS, according to process can be shaped in transparent sheets or in coloured objects.

PS is also widely commercialised as expanded foams (EPS). This material is suitable to produce light models to be used in architecture, movie sets, and airplane construction and in airspace [1]. EPS for its low thermal conductivity, low density, rather inexpensive processing and as well as for its capability to be easily formed into a variety of shapes is applied also in insulation applications and in protective packaging [2].

PS in its high impact version (HIPS), obtained by rubber modification, finds applications in sectors such as packaging and disposables, appliances, consumer electronics, toys and recreation, and building [3]. Some advanced, and special HIPS grade have been also used in more sophisticated market segments where innovative designs represent an added value.
In such a contest it is worthwhile to mention the fact that in the production of radio and television cabinets, audio and videocassettes, business machines, etc., specialty grade HIPS resins <have replaced more-costly engineering resins in many of these applications> [3].

**FIGURE 2**: "Corner Knot" by Daniel Arsham, 2008. EPS, plaster, paint, joint compound. 18 x 64 x 20 inches [4].

**FIGURE 3:**
**Left** - Benjamin Phelan pathways accumulator sign 2008 (polystyrene foam, epoxy, enamel spray paint).
**Center** - Terra nova device 2008 (polystyrene foam, wire, rock, melamine, wire loom).
**Right** - cool devices, nbc late night broadcast, date 02/15/2008 (polystyrene foam, wood putty, epoxy, enamel, bulbs, melamine) [5].
FIGURE 4: Artistic works by Aisling Hedgecock with parts in PS [6].

Left- Spelunker, Site-specific architectural intervention located in an air-vent at The British School at Rome. Polystyrene Beads, Glue, Pigment, Dimensions \( \approx 100\text{cm} \times 80\text{cm} \times 160\text{cm} \), 2006.


Right- Welcome To Hell, The Laocoön Revisited Polystyrene Beads, Dow Glue, Pigment, Cardboard Tube, \( \approx 200\text{cm} \times 180\text{cm} \times 170\text{cm} \), 2007.

Polystyrene-based plastics, for their intrinsic chemical/physical properties, for the versatility of shaping procedures of objects with fine details and elegant and artistic design, and also for their capability to be physically/chemically combined with other materials have been widely used by modern artists. Many of their artefacts are part of collections in several modern art museums. Some examples testifying the use of PS plastics in fine art are shown in the figures 2, 3 and 4 [4,5,6].

As for any other object, the conservation of artefacts in PS-based materials requires first of all the knowledge of the most reliable methods for recognizing the presence of these materials as component of the item or of part of it. Nevertheless it seems still a prerequisite for the conservation plan of PS-based artefacts the knowledge of the type of response of the component material to the action of stresses induced by physical and chemical factors.
B.1 ) Reactions of PS-based plastics to mechanical and thermal stresses

--- Mechanical Tests
The stress-strain behaviour, following uniaxial deformation at low rate, of general purpose -PS ( GPPS ) and high-impact polystyrene ( HIPS ), as shown by the trend of the diagrams reported in figure 5, results to be quite different.

--- GPSS presents a stress-strain curve with an almost linear trend, and with rupture occurring at relatively low values of the strain. The behaviour is typical of \textit{a rigid and dimensionally stable but relatively non-ductile material having a high tensile strength and low elongation at break} \cite{7}.

--- A HIPS displays a behaviour that is characteristic of ductile-tough materials. The rupture occurs at lower stresses but at much more higher strains. The toughness of HIPS increases with the growing of rubber content \cite{7}.

\textbf{FIGURE 5:} Left- Stress-Strain curves for general purpose-PS and for high impact-PS \cite{7}.
\textbf{FIGURE 6:} Right- Influence of temperature upon the shape of the HIPS stress-strain curve \cite{7}.

In general the stress-strain behaviour of PS materials, at constant rate of deformation, depends upon the temperature at which the test is performed.

In particular in the case of HIPS, as can be seen by the curves shown in figure 6 \textit{the elongation at break decreases as the temperature drops and as the deformation rate increases while the tensile strength displays the opposite relationship. The temperature effect is significantly greater than the influence of the deformation rate} \cite{7}.

Concurrently it is observed that the modulus of elasticity ( Young’s modulus ), that gives a measure of the rigidity of the materials, decreases with the increase of the test temperature \cite{7}.
The different response to mechanical stimuli of GPPS and HIPS clearly appears when samples are tested by torsion pendulum. Under such conditions instead of the modulus of elasticity, the shear modulus, to assess rigidity, can be measured as function of temperature (see figure 7) [7].

< The shear modulus of GPPS (polystyrol 168N in figure 8) is virtually constant over a wide temperature range. Only in the softening range of polystyrene does it drop sharply by several orders of magnitude. The logarithmic decrement of the mechanical damping displays a maximum at this juncture. HIPS (polystyrol 486M in figure 7) display an additional slight drop in the shear modulus or a secondary damping maximum at about -80 °C. This is explained by the glass transition temperature of the rubber component which lies in this region> [7].

**FIGURE 7: Left**- Shear modulus and mechanical damping curves as obtained by torsion pendulum tests for GPPS (polystyrol 168 N) and HIPS (polystyrol 486 M) as function of temperature [7].

**FIGURE 8: Right**- Creep experiments for GPPS sample. The failure boundary represents the limit beyond which crazes are formed before rupture [7].

In creep experiments it was observed that in the case of GPPS samples <crazing becomes visible before rupture and this indicates the limit to which damage can proceed before failure> [7]. As shown by figure 8 a failure boundary may be evidenced for the materials under investigation [7].

The effect of the presence of rubber in HIPS is usually assessed by means the Izod impact test whose basic principles are described through the scheme reported in figure 9 [8]. The improvement in the impact resistance induced by the rubber results from the following comparative data [9]:

Notched Izod Impact (ft-lb/in):

- **GPPS** – from 0.090 to 0.53
- **HIPS** – from 0.64 to 2.7
FIGURE 9: Schematic description of the basic principles of the Izod impact test
<... is a simple, quick test for a comparative material assessment... it is used to investigate the effect of changed formulation, compounding or injection molding conditions on the test specimen... The use of notched test specimen is necessary in order to produce a break in ductile materials. The test is possible within a temperature range from -60 °C to +23 °C > [8].

--- Thermal tests
The thermal behaviour of PS may be followed by means of differential scanning calorimetry (DSC). A typical thermogram is shown in figure 10 [10]. From the deflection point a value of the glass transition temperature of 98.3°C is measured [10]. The deflection observed at Tg is related to the fact that at this temperature an abrupt change in the value of the specific heat is produced following the transition from a glassy to a rubbery state (see figure 11) [7].

The value of Tg of PS rises constantly with the polymerization degree or molecular mass (M) [11]. This behaviour is consistent with the diagram shown in figure 12 where the dependence of the absolute temperature of the glassy transition Tg on the inverse of molecular weight (Mn) is reported [12].

Dynamic mechanical analysis (DMA) results to be also very effective in investigating transitions induced by heating in polymer materials. As can be seen by the generic curves reported in figure 13 Tg may be identified with the temperature of the onset of change in the slope of the storage modulus (E'), or with the maximum of the loss modulus (E'') or the maximum of the loss tangent (tanδ) [13].

380
**FIGURE 10:** DSC thermogram of PS showing the glass transition region [10].

**FIGURE 11:** The temperature dependence of the specific heat of PS showing the jump at $T_g$ (see text) [7].
FIGURE 12: The dependence of the absolute temperature of the glassy transition \( T_g \) on the inverse of the molecular weight \( M_n \) [12].

FIGURE 13: Dynamic Mechanical Analysis (DMA) is useful for the determination of the glass transition temperature (\( T_g \)) in polymer materials. In figure are shown the temperature dependence of the storage modulus (\( E' \)), of the loss modulus (\( E'' \)) and of the loss tangent (\( \tan \delta \)) for a generic amorphous polymer (see text) [13].
The heat resistance of GPPS, as for any other amorphous polymer, is usually estimated by the value of its Vicat Softening Point, which is defined as follows in reference [14]:

"The temperature at which a flat-ended needle of 1sq.mm circular or square cross section will penetrate a thermoplastic specimen to a depth of 1mm under a specified load using a uniform rate of temperature rise" (Test: ASTM D 1525-58T) [14].

The values of Vicat softening point (ISO-306) in the case of GPPS, as shown in table 1, are dependent upon the grade of the polymer, ranging, for the resins investigated in reference [15], from 88 to 101°C [15].

**TABLE 1:** Relationship between Vicat Softening Point and other properties for GPPS [15].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>High performance grade</th>
<th>Conventional grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt index (200°C, 5,000g)</td>
<td>(g/10min)</td>
<td>111--------2.1--------2.1</td>
<td>30------10--------4.2</td>
</tr>
<tr>
<td>Tensile Strength (Break)</td>
<td>(Mpa)</td>
<td>41--------54--------48</td>
<td>39--------46--------53</td>
</tr>
<tr>
<td>Charpy (Notched)</td>
<td>(KJ/m2)</td>
<td>1.5--------3--------3</td>
<td>1.5------1.5------2.5</td>
</tr>
<tr>
<td>Vicat Softening Point (49N)</td>
<td>(°C)</td>
<td>88--------101--------95</td>
<td>87--------96--------101</td>
</tr>
</tbody>
</table>

The heat distortion resistance of finished PS components in artefacts, measured by the deflection temperature <is> dependent on their shape, the production conditions, the type of heat source and the duration of heating and also on the Polystyrol grade in question. Parts produced without application of an external load and having low internal stresses can be heated for a short time to about 15°C below the Vicat softening temperature without undergoing distortion [8].

According to the ASTM D648 test the temperature at which a standard bar deflects 0.010 inches under a stated load measures the deflection temperature [14].

Value of the deflection temperature between 108-121°C (under a pressure of 1.82Mpa) have been estimated for some commercial PS resins [16].
B.2) **Reactions of PS-based plastics against chemicals**

The chemical resistance of PS, against chemicals of various type and functionality, can be derived by the data reported in table 2 [17]. In this table the chemical resistance of PS in opposition to a given chemical is classified on a scale from 1 to 4. As explained in reference [17]:

--- 1 = **Resistant** - The resin can be treated with the substance at room temperature for years without any influence on the physical, optical and chemical properties.
--- 2 = **Limited resistance** - Resin can be treated with the substance at room temperature over weeks without any influence on the physical, optical and chemical properties.
--- 3 = **Moderate resistance** - Can be treated with the substance at room temperature in short terms (minutes or 1 hour) without any effect on the physical, optical and chemical properties (mix and measure is possible).
--- 4 = **Not resistant** - Changes in the physical, optical, and chemical characteristics of the resin may occur within seconds when treated with the substance > [17].

From the data in table 2 it can be observed that PS-resins are resistant to water, alkalis and dilute mineral acids, as well as to aqueous solutions of most salts. Nevertheless, PS-based resins may swell in some organic solvents and be dissolved by others (see for example the case of aromatic and chlorinated hydrocarbons, ethers, esters and ketones).

It is interesting to point out as concentrated sulphuric acid and strong oxidizing agents, e.g. nitric acid, chlorine water, bromine water and sodium hypochlorite solution, also may attack polystyrene [18].

B.3) **Environmental stress cracking of PS-based plastics. Solubility parameter approach**

Some chemicals have the capability to initiate cracking processes in PS mouldings especially when the materials are exposed to the action of external or internal mechanical stresses. <**Cracking may be induced even by chemicals that normally do not attack or hardly attack unstressed mouldings**>

[18].

It was observed that heptane is very effective in generating environmental stress cracking in both GPPS and HIPS grades. A chemical < is said to initiate environmental stress cracking if its presence reduces the time-dependent load ability compared to the behaviour in a neutral environment. The tensile creep test is an example of a method which can be employed for such an evaluation > [18].

The environmental stress cracking behaviour of HIPS samples produced with the same process but exposed during the test to different chemicals is shown in figure 14. The environmental stress cracking behaviour of HIPS samples, obtained under different process conditions, in presence of the same chemical is schematically shown in figure 15 [18].

From the schematic trend observed in the above-mentioned figures it may be concluded that:

--- The environmental stress cracking resistance depends not only on the type of product in question but also on its condition after processing.
--- If damage by environmental stress cracking is to be avoided, it is therefore not sufficient to know the product properties but it is just as important to monitor the quality of the mouldings rigorously > [18].
**TABLE 2:** Chemical resistance of PS-resins against chemicals. For the meaning of the numbers, 1, 2, 3 and 4 see the text [17].

<table>
<thead>
<tr>
<th>Chemical</th>
<th>PS 20°C</th>
<th>PS 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid 10 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Acetic acid 50 %</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Acetic acid 90 %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Acetone</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Ammonia</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ammonia 25 %</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ammonia acetate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Amyl alcohol</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Boric acid 10 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Chloroform 100 %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Citric acid 10 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Detergents</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dimethyl acetamide</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Erucic acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol 50 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ethanol 96 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ether</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Formaldehyde 10 %</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Formaldehyde 40 %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Formamide</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Formic acid 50 %</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Glucose</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Glycerine</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Heptane</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Hexanol</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrochloric acid 20 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hydrochloric acid conc.</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Hydrogen peroxide 3 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Isopropyl acetate</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Isopropyl benzene</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical</th>
<th>PS 20°C</th>
<th>PS 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl propyl ketone</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Methyl phenyl ether 100 %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Methylamine 32 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Naphtalene</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitro benzene</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Oxone</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Phenol 10 %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Phenol 100 %</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Phosphoric acid 1-5 %</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Phosphoric acid 85 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Propanol</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sodium hydroxide 30 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sodium hydroxide 45 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sodium hydroxide 60 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sodium hypochlorite</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sodium permanganate</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Sodium thiosulphate</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Sulphuric acid 1-6 %</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulphuric acid 60 %</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sulphuric acid conc.</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Terpentine oil</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Toluene</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Urea</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Uric acid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Urine</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Xylene</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
A test suitable for the evaluation of the environmental stress cracking resistance (ESCR) of PS samples was developed by A.R. Sousa Et Al. (n-butanol was used as active fluid) [19].

< Experiments under stress were conducted in a......tensile testing machine. The injected bar was attached to the sample holder and a target load (100 - 700 N) was applied. During the application of the load the solvent was spread evenly over the......surface and the stress relaxation effects were monitored as a decay in load whereas the length of the sample remained constant. The rate of stress relaxation was taken as the ratio between the decay in load and the time of solvent application (fixed at 20 min) > [19]. The method used is summarized through the scheme of figure 15:

< After solvent application, the specimen was unloaded and immediately tested for tensile properties......Besides tensile testing, the samples were characterized by......optical and scanning electron microscopy > [19].
FIGURE 15: Procedure used in the stress relaxation test to evaluate environmental stress cracking resistance of polystyrene samples (n-butanol was used as active fluid), see details in the text [19].

FIGURE 16: Tensile strength of virgin PS bars under different conditions (see text and legend in figure) [19].
**FIGURE 17:** Aspect of PS bars after loading at 500 N then tensile tested until fracture. Left: loading without butanol; right: loading with butanol [19].

![Image of PS bars after loading](image_url)

**FIGURE 18:** Stress relaxation curves of PS bars under different conditions. Initial load set at 500 N. Upper curve unexposed to the butanol action. Lower curve in presence of butanol [19].

![Stress relaxation curve](image_url)

Fig. 7. Stress relaxation curves of PS under different conditions. Initial load set at 500 N.
From the trend of the diagrams reported in figure 16 it emerges that the variation of the tensile strength of PS bars with time strongly depends upon the previous treatments and experimental conditions. In particular it may be observed that:

--- Almost no change occurs when no external stress is applied.
--- Only a modest diminution in strength occurs when an external stress is applied in absence of butanol.
--- The concurrent effect of the external stress and the contact with butanol determines a large decline in tensile strength. Such a behaviour exemplifies the phenomenon of ESC as the consequence of the action of an active fluid that diffuses into stressed regions, causing local plasticization that leads to crazing and surface cracks [19].

The fact that butanol acts as a stress-cracking agent for polystyrene was confirmed by investigating by optical microscopy the structure of the surface of PS samples, which were exposed to the action of applied stress and butanol. As can be seen by the micrographs shown in figure 17 the cracks appeared over all the stressed areas and were perpendicular to the stress direction. Under stress and butanol the number of cracks became very large and deep, reducing the sample transparency [19].

The above results are summarised through the diagrams in figure 18 were the stress relaxation behaviour of PS samples is given in presence or in absence of butanol [19]. In the conservation of plastic artefacts, especially those made by amorphous polymers with a T_g higher than RT, then in a glassy state, the stress-cracking may be a relevant problem because it may occur, as a consequence of contact with cleaning agents, acids, alcohols, cosmetic creams, soaps, oils, grease, which unpredictably may act as stress cracking agents [19,20].

< That is the reason why stress cracking is considered to be a "silent killer" [21].

In cleaning operations of PS-based artefacts the choice of the less harmful liquid agent may be afforded by taking into consideration the values of its solubility parameters (\( \delta \)), and considering as general rule that the cleaning agent has to be a non-solvent for PS. The solubility parameter of PS results to be equal to 8.6 (cal/cm\(^3\))\(^{1/2}\). According to the solubility-parameter approach (valid, and in first approximation, in the absence of strong interactions between polymer and solvent molecules (i.e. hydrogen bonds)) polymer/liquid solubility will probably occur when the absolute value of the difference (\( |\delta_p - \delta_l| \)) between the \( \delta \) values of the solvent and that of the polymer is less than 1.7-2.0 [22]. This means that of the solvents listed with their \( \delta \) value in table 3 only methanol will have no possibility to be solvent for PS materials, while the others, in suitable conditions, may be capable to dissolve PS or at least to be able of acting as swelling agent.

B.4) Permeability to gases and water vapour of PS-based plastics

PS-based plastics are permeable to some gases and vapours. As shown by the data reported in table 4, the permeability of water vapour and gases depends by the type of PS taken under consideration. From table 4 it can be noticed as the values of the permeability, for a given agent, increases going from GPPS to HIPS and to EPS materials. It must be also observed as the permeability increases with the rising of the temperature [23].

From degradation and conservation point of view major concern has to be reserved to oxygen
permeation in PS artefacts considering that:
<the risk of changes caused by gases permeating in is particularly great in the case of atmospheric oxygen which can lead to oxidative degradation of constituents or give rise to microbiological processes > [22].

**TABLE 3:** Solubility parameter \( \delta \) for some common solvent [22].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta_1 ), (cal/cm(^3))(^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>7.24</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.58</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>9.04</td>
</tr>
<tr>
<td>Benzene</td>
<td>9.15</td>
</tr>
<tr>
<td>Chloroform</td>
<td>9.24</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.71</td>
</tr>
<tr>
<td>Methanol</td>
<td>14.5</td>
</tr>
</tbody>
</table>

**TABLE 4:** Permeability to water vapour, oxygen, nitrogen and carbon dioxide of general purpose, impact resistant and foamed (Styrolux) polystyrene. The values were measured at 23°C on 100μm thick samples [23].

<table>
<thead>
<tr>
<th>Material</th>
<th>Water vapor(^b)</th>
<th>Oxygen</th>
<th>Nitrogen</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>General-purpose Polystyrene</td>
<td>12</td>
<td>1000</td>
<td>250</td>
<td>5200</td>
</tr>
<tr>
<td>Impact-resistant Polystyrene</td>
<td>13</td>
<td>1600</td>
<td>400</td>
<td>10000</td>
</tr>
<tr>
<td>Styrolux(^b)</td>
<td>14</td>
<td>2600</td>
<td>700</td>
<td>15000</td>
</tr>
</tbody>
</table>

\(^b\) DIN 53 122; moisture gradient from 85% to 0% relative atmospheric humidity.

B.5) **Methodologies and tests for the recognition of Polystyrenes in artefacts.**

--- **The FT-IR Infrared Spectroscopy**
The infra-red spectroscopy is a very effective analytical instrumental methodology for the identification of PS-based materials as components of objects. As matter of facts in the FTIR spectrum of PS are present bands of absorbance whose corresponding wave numbers are strictly related to the types of vibration and deformation of the functional groups, which are the main constituents of the polymer chains.
The FTIR diagram of a sample of GPPS is shown in figure 19 [24]; the main peaks observed, with reference also to table 5 [20], may be assigned as hereafter reported:
- C-H aromatic tension 3081.2 cm$^{-1}$, 3001.1 cm$^{-1}$;
- 2923.91 cm$^{-1}$ and 2850.40 cm$^{-1}$ CH$_2$ asymmetric and symmetric tension;
- 1943.19 -1728.23 cm$^{-1}$ aromatic ring mono-substitution;
- 1452.28 cm$^{-1}$ deformation CH$_2$ C=C of the aromatic ring;
- 1069.65 cm$^{-1}$ flexion C-H in the plane [25].

**FIGURE 19:** Infrared spectrum of general purpose polystyrene [24].

**TABLE 6:** Wave number, type of vibration and chemical assignment of the main peaks present in a FTIR spectrum of GPPS [20].

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Type of vibration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3150-3000</td>
<td>stretching</td>
<td>=CH</td>
</tr>
<tr>
<td>3000-2850</td>
<td>asymmetric and symmetric stretching</td>
<td>CH$_2$</td>
</tr>
<tr>
<td>1600-1372</td>
<td>stretching</td>
<td>benzene ring</td>
</tr>
<tr>
<td>1181</td>
<td>in-plane deformation</td>
<td>=CH</td>
</tr>
<tr>
<td>1154</td>
<td>in-plane deformation</td>
<td>=CH</td>
</tr>
<tr>
<td>1089</td>
<td>in-plane deformation</td>
<td>=CH</td>
</tr>
<tr>
<td>1028</td>
<td>in-plane deformation</td>
<td>=CH</td>
</tr>
<tr>
<td>906</td>
<td>out-of-plane deformation</td>
<td>=CH</td>
</tr>
<tr>
<td>841</td>
<td>out-of-plane deformation</td>
<td>=CH</td>
</tr>
<tr>
<td>749</td>
<td>out-of-plane deformation</td>
<td>=CH</td>
</tr>
</tbody>
</table>
It is worthwhile to underline that infrared spectroscopy is also effective in distinguishing between different types of PS, namely between GPPS, HIPS and acrylonitrile-butadiene-styrene copolymers (ABS) [26]. Such a possibility appears by the comparison of the IR spectra shown in figure 20 from which it can be seen as the HIPS has a distinctive absorption at 965 cm\(^{-1}\), attributable to the butadiene units, and the ABS a sharp peak at 2240 cm\(^{-1}\) characteristic of the acrylonitrile units. Of course these peaks are not present in the IR-spectrum of the unmodified GPPS [26].

**FIGURE 20:** Infrared spectra of, from top to bottom, HIPS, GPPS and ABS [26].
--- The Raman Spectroscopy

The Raman spectroscopy, a diagnostic analytical chemical technique that is complementary to infrared absorption spectroscopy, can be used for both qualitative and quantitative analysis. The spectra are very specific, and chemical identifications can be performed by using search algorithms against digital databases. As in infrared spectroscopy, band areas are proportional to concentration, making Raman amenable to quantitative analysis. In fact, because Raman bands are inherently sharper than their infrared counterparts, isolated bands are often present in the spectrum for more straightforward quantitative analysis [27].

**FIGURE 21:** A commercial example of a portable high performance Raman Analyzer that is ideal for condensed material identification and process control [29].

**FIGURE 22:** Comparison of the Infrared absorption (top-side) and Raman spectra (bottom-side) of GP-polystyrene [27].
The possibility of using fiber optical probe components (up to 100's of meters in length) and of building portable and small systems make Raman spectroscopy a very versatile tool for remote non-invasive analyses to be performed on almost any sample in-situ (see figure 21) [28,29,30]. A comparison between the Infrared absorption and Raman spectra of GP-polystyrene is shown in figure 22. It is interesting to outline the complementary nature of the two data sets [27]. Raman spectroscopy is effective, as shown by the diagrams reported in figure 23, also in distinguishing between GPPS and HIPS materials [29].

**FIGURE 23:** Raman spectra of sheets of polystyrene and styrene-butadiene copolymer (HIPS), (bottom to top) [29].

A typical application in situ of the Raman spectroscopy is exemplified in figure 24 where is shown the effectiveness of this methodology in assessing the degree of conservation and the nature of pigments used in the case of an ancient wall painting [31].

**FIGURE 24:** In situ Raman spectroscopy to investigate about the nature of pigments used in the case of an ancient wall painting [31].
B.6) Other properties and tests suitable to recognize Polystyrenes in artefacts

The tests and properties hereafter listed may be useful in recognizing PS materials in objects.

--- The pH values of vapors released during heating of PS is between 9.0–10.00.
--- The Litmus and pH tests for combustion vapors of PS leads to the following conclusions:
  - pH paper between 5.0–5.5
  - Color-essentially unchanged (some samples show slightly alkaline behavior) [32].

Moreover PS demonstrates the following characteristics:
--- Specific Gravity in the range of 1040–1080 kg / m$^3$ (foamed polystyrene has a density between 20 (building insulation) and 90 kg / m$^3$).
--- Chemically attacked by hydrocarbon solvents, oils, ketones, esters, inorganic acids (EPS decomposes, following a contact with little acetone, ethyl acetate or toluene).
--- Resistant to organic acids, alkalis, alcohols, and it shrinks in boiling water.
--- Burns with luminous smoky flame giving faint odor of marigolds.
--- Glass transition temperature of about 100°C. The commercial atactic form is amorphous then shows no melting temperature, while the isotactic and syndiotactic crystalline forms present a fusion temperature of 240 and 270°C respectively.
--- Burns with a bright yellow, heavily russo flame and a flowery, sweetish odour of styrene.
--- Degrades in UV light.
--- It creates a brittle, almost glassy sound when tapping (butter dishes). When bending or breaking it smells distinctly of styrene.
--- Tends to stress cracking.
--- It can be etched by dichloromethane and almost seamlessly welded [33,34].
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34) 1-PS-SUp/PS%20polystyrene%20-%20is%20a%20transparent,%2, (2010).
CHAPTER-EIGHTEENTH
THE EARLY SYNTHETIC THERMOPLASTICS

POLYSTYRENE

C. ) THE PROCESSES OF DEGRADATION OF POLYSTYRENE-BASED PLASTICS
INDUCED BY VARIOUS PHYSICAL AND CHEMICAL FACTORS (ENVIRONMENTAL
AGEING)

C.1 ) Thermal and Thermo-oxidative degradation of PS

It is well known that the thermal degradation of PS leads to the formation of monomers (major
degradation product) and to a mixture of saturated and unsaturated compounds, including dimers
and trimers. To explain the presence also of these later products the molecular chain scission
mechanism illustrated in figure 1, was proposed [1]:

In the scheme of figure 1 monomers and dimers are produced but analogous scission reactions
would generate the formation of monomers and trimers as well. Grassie and Scott [2] demonstrated that the 40% monomer, with decreasing amounts of dimer,
trimer, tetramer, and pentamer are the products of the thermal degradation of PS. The mechanism
they proposed (below shown) assumes that

< ....... thermal scission produces two primary radical species. The reaction continues by
producing a dimer via an intra-molecular radical transfer reaction > [1].
FIGURE 2: A mechanism proposed to explain the chain scission that occurs during the thermal degradation of PS leading to the formation of a dimer [2].

The mechanisms illustrated by figure 1 and 2 are both based essentially on transfer reactions, which are generally named as "unbutoning", while de-polymerization reactions that produce only monomers are usually called as "unzipping". According to many authors the degradation of PS macromolecules initiates at weak links generated in the course of the synthesis <that is carried out in the presence of oxygen, which gives rise to peroxyl and hydroperoxy structures. Once all of the weak-link sites have given way to initiation, the major mass loss of polymer occurs due to the random scission process described earlier> [1].

From the thermo-gravimetric diagram reproduced in figure 3 it can be concluded that PS, in nitrogen, degrades in a single step beginning at 250°C and ending at 500°C. Such a result is in agreement with the shape of the DSC thermogram, in nitrogen, illustrated in figure 4 that shows a well-defined endothermic peak at ≈430 °C that is in the vicinity of the temperature where the maximum mass loss in the TGA occurs. These findings are consistent with the de-polymerization mechanisms illustrated above [1]. Thus it can be concluded that the thermal degradation of PS proceeds by both end-chain scission and random scission (appearing to be the predominant mechanism) followed by intermolecular transfer. According to the comprehensive scheme of figure 5 styrene monomer and oligomers as well as benzene and toluene are produced [3].

The investigation of thermo-oxidative degradation of PS is of great relevance as it can provide useful information on how artifacts behave under more practical and use conditions [4]. It is generally assumed that the mechanism of the thermo-oxidative degradation of vinyl polymers at moderate temperatures involve the formation of hydro peroxide radicals in the propagation step of the process [5].
**FIGURE 3-left:** TGA curves for the thermal decomposition of PS in nitrogen (dashed line) and air (solid line). [1].

**FIGURE 4-right:** DSC scans of measured heat flow for degradation of PS in nitrogen (dashed line) and air (solid line). [1].

**FIGURE 5:** The main reactions occurring during the thermal degradation of polystyrene, see text [3].
It is well known that the initiation step of the thermo-oxidative degradation of PS, which may be caused by physical (e.g., temperature, UV radiation, mechanical stresses) and/or chemical factors (e.g., traces of peroxides and hydro peroxides used in the course of polymer synthesis) consists in a reaction where radical precursors are formed (see equation (1) [1,3,4].

\[ \text{Initiation: } RH + R^* + H^* \quad (1) \]

The propagation step begins with the reaction of oxygen with the formed chain radicals \( R^* \). Reactive \( ROO^* \) peroxy radical intermediate are formed (equation (2)). This peroxy radical is capable to abstracts a labile hydrogen from another polymer chain forming hydro peroxide species (\( ROOH \)) together with another chain radical \( R^* \) through which the degradation further proceeds (see equation (3)) [1,4,5,6].

\[ \text{Propagation: } R^* + O_2 \rightarrow ROO^* \quad (2) \]

\[ ROO^* + RH \rightarrow ROOH + R^* \quad (3) \]

Following the below reported reactions alkoxyl radicals (\( RO^* \)) are also produced:

\[ \begin{align*}
& ROOH + RO^* + OH^* \quad (4) \\
& ROOH + RH \rightarrow RO^* + R^* + HOH \quad (5)
\end{align*} \]

The alkoxyl radical, \( RO^* \) through the hereafter scheme are able to abstract hydrogen from the remaining polymer chains:

\[ RH + RO^* \rightarrow ROH + R^* \quad (6) \]

This last reaction contributes at increasing the concentration of the radical species involved in the propagation step thus accelerating the oxidative degradation [1,3,4,5].

From the shape of the TGA diagram of PS in air it can be seen as under such conditions PS degrades at a lower temperature than it does in nitrogen (see figure 3). According to reference [1] such a behavior is the <result of switching the limiting step from random scission to decomposition of the hydro peroxy radical, which occurs with a lower activation energy>.

The DSC thermograms of figure 4 show that the whole process of degradation of PS in air is less endothermic. This is accounted by the exothermicity of the reactions related to the polymer oxidation [1].

The small exotherm at about 575°C is consistent with the tiny step of the mass loss as observed in the TGA thermogram of figure 3 <that occurs as a result of a complex process involving oxygen and PS degradation products as well as various carbon oxide species, which originate from thermo-oxidative degradation> [1].

The analysis of the TGA and DSC data from a kinetic point of view suggests that the step concerning the decomposition of peroxides represents a limiting step of degradation. <On the other hand, since the overall degradation remains endothermic under air; this suggests that the slow step of decomposition of the peroxoradical is followed by fast unzipping. This mechanism has been shown to occur using Fourier transform infrared spectroscopy> [1].
FTIR measurements were used by G. Botelho and others to examine the changes in the chemical structure associated with the thermo-oxidative degradation of PS samples kept at 150°C in oxygen atmosphere [7]. Following thermal treatment in presence of oxygen two weak bands at 3540 and 3450 cm⁻¹ attributable to alcohols and hydro-peroxides respectively were observed. Moreover the spectra of PS showed an increasing band at 1688 cm⁻¹ due to the presence of the carbonyl group of an aromatic end chain ketone or to acetoephone [7].

The thermal stability of PS may be enhanced by using proper stabilizers/ antioxidants. Hindered phenols and amines, which effectively act as scavengers of the oxidative reactivity of peroxo radicals are commonly used [8].

The effectiveness of two additives, namely CdS particles and Fullerene (C₆₀) molecules, is evidenced through the data shown in figures 6, 7 and 8 [9,10].

![Figure 6: The thermograms of the pure PS (a) and the PS–CdS filled polymers with 1.4 (b), 2.9 (c) and 5.2 vol% (d) of inorganic phase, obtained under an atmosphere of nitrogen [9].](image)

From the TGA diagrams reported in figure 6 it can be seen as it is possible to improve the thermal stability of the PS matrix for about 50 K by adding CdS as filler [9]. The thermo-oxidative stability of PS at elevated temperature in dynamic oxygen, as demonstrated by the DSC thermograms in figure 7, is enhanced following addition of fullerene [10]. Such finding is in agreement with the trend of the kinetic curves of PS degradation under oxygen at 238°C as obtained from TGA analysis (figure 8) [10].

*<It is seen that C₆₀ inhibits the weight loss of PS. In the thermo-oxidative degradation of PS alone, there is an induction period equal to ≈10 min. Fullerene increases the induction period up to ≈40 min. After the induction period, the rate of PS degradation in the presence of C₆₀ is less than in degradation of the polymer without addition of fullerene (compare curves 1 and 2 in figure 8). The inhibiting influence of C₆₀ on the PS thermo-oxidative aging at elevated temperatures is supposed to be mainly due to its interaction with oxygen-containing radicals with formation of more stable compounds> [10].*
**FIGURE 7:** DSC curves in dynamic oxygen for (1) PS, and (2) with addition of 0.134 mol% of fullerene (C_{60}) [10].

**FIGURE 8:** Dependence of weight loss (%) on time in the thermo-oxidative degradation of PS at initial pressure of 200mm at 238°C: (1) without additives and (2) with addition of 0.04mol% of C_{60} [10].

For certain applications flame retardant (FR) additives are used to provide PS materials with improved fire resistance. FR additives may induce fire resistance in polymers following the hereafter listed different mechanisms:
--- By raising the ignition temperature;
--- By reducing the rate of burning;
--- By reducing flame spread;
Substances like hexabromocyclododecane and triphenyl phosphate are examples of FR additives for PS [11].

C.2) Photo-oxidative degradation of PS

Samples of plain PS following exposure to sunlight undergo photo-oxidative degradation due essentially to the UV light component. This process of environmental ageing gives rise to damages evidenced by several types of symptoms: yellowing, brittleness, loss of surface gloss and decrease in the mechanical strength.

![Graphs showing loss of Mw and weight loss vs. irradiation time](image)

**FIGURE 9-top-left:** Films of polystyrene. Loss of Mw versus time of irradiation of films in accelerated weathering tester [12].

**FIGURE 10-top-right:** Polystyrene foam sheet, Mw versus time of irradiation in an accelerated weathering tester [12].

**FIGURE 11-bottom:** Polystyrene foam sheet irradiated for 0, 1, 2, and 4 days. % weight loss during tumbling [12].
According to literature data this photo-oxidative degradation is caused by the presence of chromophores, which are mostly created during the processing of the polymer. For the above reasons PS, to be suitable for artefacts which should be used outdoors for a prolonged period, needs to be always stabilized through the addition of UV stabilizers.

K. Sikkema and others [12] investigated the photo-oxidative degradation of samples of PS and of PS-foams following accelerated artificial ageing. The films and foams were irradiated with light in a QUV accelerated weathering tester. The samples were held 5 cm from UV-340A fluorescent light bulbs having a 290 nm cut-off at 340 nm. The black panel temperature was 50°C. [12].

The degradation was followed by measuring the loss of molecular weight as function of the irradiation time as produced in the accelerated weathering tests [12]. The results are summarized by the trend of the plots illustrated in figures 9 and 10 for PS and PS-foam respectively.

The weight-average molecular weight (M_w) before and after irradiation was measured by Gel Permeation Chromatography (GPC) [12].

Irradiated samples of PS-foam sheets were tumbled with wood blocks in a box. The weight loss during the tumbling was also used as the measure of degradation (see figure 11) [12].

The data in the figures 9 and 10 show that following irradiation the PS samples undergo reduction in molecular mass. Such a finding indicates that in the chains some of the backbone intra-molecular carbon-carbon bonds are broken. It is interesting to note as in the case of PS-foam irradiated samples a reduction in weight, following tumbling is also observed [12].

The degradation effects derived from the exposure to UV light on PS was investigated by H. Kaczmarek et others by means of IR spectroscopy. Because the competitive photo-processes take place simultaneously in the samples studied, spectral subtraction was used for better visualization of UV effect [13].

**FIGURE 12:** FT-IR spectra of unexposed PS [13].
As already discussed in the IR spectrum of PS, in the 3700–400 cm⁻¹ region (see figure 12), the following main bands are observed:

--- Five peaks at 2800–3100 cm⁻¹ attributed to C–H stretching vibrations in the main chain and in aromatic rings;
--- Six peaks at 1601, 1492, 1451, 1029, 757, 698 cm⁻¹ due to deformation and skeletal vibrations of C–H [13].

**FIGURE 13:** Subtracted FT-IR spectra of PS (spectrum of 8 h-irradiated PS minus spectrum of non-irradiated PS) in whole IR range (a) and in 1300–2100 cm⁻¹ range (b) [13].

Form the analysis of the bands appearing in the subtracted FT-IR spectra of PS (spectrum of 8 h-irradiated PS minus spectrum of non-irradiated PS), shown in figure 13, assuming that the changes observed in the carbonyl and hydroxyl regions are evidence of photo-oxidation, it was concluded that:

*The increase of absorbance in the analyzed ranges is attributed to the formation of aromatic and aliphatic ketones of the acetophenone type and OH/OOH groups in the main chain. According to literature data carboxylic acids, esters, anhydrides and cyclic structures (lactone type) are other PS
photoproducts. Moreover, low-molecular weight compounds such as benzoic acid, acetophenone, benzaldehyde, methyl benzoate, formic acid, acetic acid, styrene and benzene were identified in UV-irradiated PS in various conditions >[13].

A quantitative estimation of the PS photo-oxidation process was performed by plotting < the relative changes of the total amount of carbonyl and hydroxyl groups (calculated as an integral intensity of absorption band i.e. as surface area of peaks) versus irradiation time >. The results are illustrated through the figures 14 and 15 [13].

![Graphs showing relative changes of carbonyl and hydroxyl groups in PS](image)

**FIGURE 14-left:** The relative changes of carbonyl groups in PS during UV irradiation (measured as an integral intensity of carbonyl band at 1641–1826 cm⁻¹ range) (see figure 13) [13].

**FIGURE 15-right:** The relative changes of OH/OOH groups in PS during UV irradiation (measured as an integral intensity of hydroxyl band at 3126–3546 cm⁻¹ range) (see figure 13) [13].

The main paths of the photo-oxidation of PS were described as follows by H. Kaemzmarek et others in their cited paper [13]:

< PS photodegradation is a result of excitation of phenyl rings after quantum absorption. The main primary reaction is elimination of hydrogen atom from the backbone, mainly from carbon at a position to benzene ring, but random chain scission also occurs. Macroradicals react with oxygen from the atmosphere and formed peroxy radicals are able to further react with macromolecules. The other initiation sites in PS are unsaturated chain ends, internal impurities and structural defects (hydroperoxides, ketones) The intermediate products (e.g. alkoxy and hydroxyl radicals) participate in subsequent decomposition. The complex mixture of photoproducts contains macromolecules with hydroxyl, acetophenone (CH₃-CO-Ph⁻), benzophenone (Ph-CO-Ph⁻), diketone, α-unsaturated ketone, peracid, peroxy ester and ketolactone moieties. Photo oxidative degradation of polymers containing carbonyl groups occurs by Norrish I (α cleavage) and Norrish type II (scission through a six-member cyclic intermediate) mechanisms yielding a number of photooxidation products. Thus volatile, low-molecular weight products and insoluble cross linked macromolecules are simultaneously formed in irradiated polymeric samples > [13].
Photochemical changes in PS films were followed also by UV-visible absorption spectroscopy on degraded films [13]. It was found that following the exposure to UV-rays PS films present an increase of absorbance in the 200–600 nm range. This result indicates that absorbing photoproducts, chromophores (e.g. conjugated double bonds) have been produced [13]. Such a process as shown in figure 16 may be monitored by plotting the intensity of the absorbance of the bands at 262, 300 and 400 nm against the irradiation time. The results indicate that the number of chromophores produced increases rapidly at the beginning of the degradation process [13].

The yellowing phenomenon observed on PS samples, which underwent photo-oxidation is explained as follows in reference [13]:

< ...PS absorption below 300 nm arises from the presence of various degradation products of the type of acetophenone, benzaldehyde or benzoic acid. The species absorbing above 300 nm are macromolecules containing conjugated double bonds and unsaturated bonds neighboring carbonyl groups. These chromophores cause sample color (mainly yellowing) > [13].

**FIGURE 16:** Kinetics of chromophore formation in UV-irradiated PS on the basis of absorbance at 262, 300 and 400 nm as assessed by UV-visible spectroscopy [13].

The most relevant aspects of photo-oxidation of PS were summarized by A. Faucitano and others in reference [14].
The main assumptions, findings and conclusions, in agreement with the above reported issues, are thereafter pointed out:
1) The photo-oxygenation of PS is initiated essentially by aromatic ketones (i.e. acetophenone-type) produced in the course of the high temperature processing of the polymer.
2) Triplet-state ketones are capable to abstract benzyl hydrogen and decompose the hydroperoxides by energy transfer.
3) The foremost propagation path is the hydroperoxideation based on the H abstraction at the carbon adjacent to the aromatic ring, forming tertiary hydroperoxides, tertiary alcohols and acetophenone residues [14].

G. Geuske and others demonstrated by chemical analysis and infra-red and ultraviolet spectroscopy that hydroperoxide and acetophenone groups are produced when PS is processed at 160°C in a half full chamber of a Brabender Plastograph in contact with the air oxygen. Under such a condition the hot polymer undergoes extensive oxidation, which was easily detected following well established chemical methodologies of analysis [15].

FIGURE 17: Hydroperoxide concentration (mol/kg) in polystyrene processed at 160°C in the open chamber of a Plastograph Brabender in contact with the air oxygen [15].

The hydroperoxide concentration (mol/kg) detected in PS processed at 160°C in the open chamber of a Plastograph Brabender, as function of time, is plotted in figure 17 [15]. From the shape of the curve it is possible to conclude that the concentration of hydroperoxide first rapidly increases, then after a maximum starts to decline as usually observed in the thermal oxidation of polymers [15]. The presence of acetophenone groups was assessed by measuring the intensity of the band in the infra-red spectrogram at 1685 cm⁻¹. It was found that

<their concentration increases linearly with time. It is about 2 × 10⁻¹ M after 10 min and reaches a value of about 10⁻² M after 60 min. These are undoubtedly the most important light absorbing groups in oxidized polystyrene since their absorption coefficient is 60 M⁻¹ cm⁻¹ at 310 nm compared with 0.3 M⁻¹ cm⁻¹ for hydroperoxide groups at the same wavelength > [15].
The thermo-oxidative degradation of PS, as shown by the data reported in table 1, determines a decrease in the values of the ultimate tensile strength of samples processed in the presence of air. After 60 minutes of processing, the polymer is so brittle that no specimen could be prepared for tensile strength measurement [15].

The above cited results clearly demonstrated that in the open chamber of the Brabender Plastograph extensive oxidation occurs, resulting in chain scission and formation of acetophenone groups [15].

**TABLE 1:** Processing of Polystyrene at 160 °C in an open chamber in contact with the air oxygen.

Values of ultimate strength with and without additive stabilizers.

The antioxidant labeled as AO is the bis [2,2’-methylene-bis (4-methyl-6-t-butylphenol)]terephthalate, HPM 12 (SFOS). The HALS light stabiliser, is the Tinuvin 770 (bis[2,2,6,6-tetramethyl-piperidinyl-4] Sebacate) [15].

<table>
<thead>
<tr>
<th>Processing period (Min)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>0-5% AO</th>
<th>0-5% HALS</th>
<th>0-25% AO</th>
<th>0-25% HALS</th>
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<tbody>
<tr>
<td></td>
<td>No additive (Initial value 34 MPa)</td>
<td></td>
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<td>10</td>
<td>31</td>
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<td>20</td>
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<td>31</td>
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</tbody>
</table>

*Sample too brittle, measurement not possible.

**FIGURE 18:** Decrease in the ultimate tensile strength of polystyrene as function of irradiation time in the solar UV range, after processing at 160°C in presence of air. A-no processed sample. B-10 min processing. C-20 min processing [15].
For the formation of acetophenone groups the following mechanism was proposed [15]:

\[
\begin{align*}
\text{OOH} & \quad \text{CH}_2-\text{CH}_2- & \quad \text{O}^\cdot \quad \text{OH}^- & \quad \text{CH}_2-\text{CH}_2- \\
\text{CH}_2-\text{CH}_2- & \quad \text{CH}_3 \quad \text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

As can be deduced by the diagrams represented in figure 18 the photo-oxidative stability of PS, processed in presence of air, results to be significantly lowered if compared with that of a non-processed sample [15]. *The rate of decrease of the ultimate tensile strength on exposure to ultraviolet light increases by a factor of four after 10 minutes of processing in the presence of air. Moreover, it seems to be proportional to the processing period* [15].

The results shown by figure 18 are accounted for by assuming that in the initial stage of the photo-oxidation acetophenone groups are largely in charge for the absorption of light. Nevertheless, following literature data these groups can transfer their electronic energy to nearby hydro peroxides which decompose according to the hereafter reported scheme [15]:

It is interesting to point out as according to the above scheme chain scission and the formation of acetophenone groups occur concurrently.

It must be noticed that as the degradation induced by photo-oxidation proceeds, due to the formation of sequences of conjugated double bonds, PS samples gradually yellow [15]. The stability of PS against the thermal and photo-oxidation is strongly influenced by additives. As can be seen by the data in table 1 *the addition of a phenolic antioxidant, results in very good retention of the mechanical properties of the polymer* [15].

The trends of the diagrams shown in figure 19 demonstrate as PS samples, previously degraded following processing in contact with air for 20 min at 160 °C, once exposed to UV radiation, suffer a drastic reduction in the values of the ultimate strength due to the induced photo-oxidation degradation processes [15].

From the curves presented in figure 19 it can be also seen that the resistance against photo-oxidation may be enhanced by the use of proper antioxidant and light stabilizer additives (see for example the case of curve D) [15].

The above mentioned data show that the photo stabilization of PS-based plastics may be conveniently accomplished by using a combination of different stabilizers including:

--- Benzotriazole-type UV Absorbers;
--- Hindered Amine Light Stabilizers (HALS) [14].
FIGURE 19: Decrease in the ultimate tensile strength of polystyrene on irradiation in the solar UV range, after processing for 20 min at 160 °C in contact with air.
A-no additive.
B-0.5 weight % phenolic antioxidant (HPM 12). C-0.5 weight % hindered amine light stabiliser (Tinuvin 770).
D-0.25 weight % phenolic antioxidant + 0.25 weight % hindered amine light stabilizer [15].

FIGURE 20: Decrease in the ultimate tensile strength of polystyrene on irradiation in the solar UV range. The data points refers to different time of processing at 160°C in the closed chamber of the Plastograph of the samples [15].
**Mechanical degradation** usually occurs when polymers are processed under shearing forces in absence of air. The molecular mass reduction observed is of course less than in the case of processing in air. Nevertheless, as can be seen by the diagram in figure 20, partially mechanically degraded PS samples exposed to the effects of UV-rays suffer photo-oxidation. Consequently a decrease in the ultimate tensile strength is observed [15].

In reference [15] was underlined that < *since thermal oxidation in these conditions is practically negligible, no new chromophores are produced and therefore the period of processing has no influence on the photo-oxidative stability of the samples* > (see data in figure 20).[15]

The most relevant aspects of **photo-degradation and photo-oxidation of PS**, comprehensively revised by B. Ranby and J. Lucki [16], are hereafter summarized.

1) When polystyrene is exposed in air to UV rays, it undergoes a rapid yellowing and discoloration accompanied with a gradual embrittlement. This environmental ageing represents a serious disadvantage especially for exposure outdoors.

2) The main reactions induced in PS by the photo-oxidation are bond scission, chain cross-linking and oxidative degradation. It is generally accepted that photo-oxidation, based on a free radical mechanism that involves peroxy group formation, proceeds according to the following main steps: initiation, propagation, radical chain branching and termination.

*Initiation Step*

In the initiation step following the absorption of a quantum of light by a macromolecule or by an impurity present in the polymer, polymer free radicals (P*) are formed:

\[ \text{PH} \rightarrow \text{P}^* + \text{H}^* \] (1)

The various reactions leading to the initiation of photo-chemical degradation of PS are hereafter reported:

--- **Absorption of light by Pure PS Units.** It occurs when PS is exposed to radiation with \( \lambda < 280 \text{ nm} \). Under such conditions quanta absorbed by the phenyl groups determine the excitation of benzene rings to singlet and triplet states. This process is then followed by reactions giving rise to the formation of free radical by bond scission [16].

--- **Absorption of light by charge-transfer complexes (CTC).** This CTC, as shown by the below scheme, may results from intra- or intermolecular charge transfer between electron donating and electron accepting groups, e.g. molecular oxygen and phenyl groups in polystyrene [16].
The CTC so formed is capable to absorb radiation with $\lambda > 300$ nm.

--- **Initiation by Singlet Oxygen**. Singlet oxygen $^1O_2$ may arise from different kind of reactions:
- The energy transfer from the excited triplet state of phenyl groups in polystyrene to molecular oxygen;
- By energy transfer from a CT complex to molecular oxygen;
- by energy transfer to molecular oxygen from excited internal impurities (modified groups);
- External impurities (added compounds) present in commercial polystyrene > [16].

--- **Initiation by free radicals formed from excitation of carbonyl groups**. Carbonyl groups absorb in the near UV region ($\lambda$ between 290 to 400 nm). This process determines the formation of carbonyl bi-radicals according to the following reactions:

$$\text{C}=\text{O} + h\nu \rightarrow ^1(\text{C}=\text{O})$$
$$^1(\text{C}=\text{O}) \rightarrow ^3(\text{C}=\text{O}) \rightarrow (\text{C}=\text{O})$$

These bi-radicals are capable to abstract hydrogen from the same or neighboring macromolecules (HP), see below scheme:

$$\text{C}=\text{O} + \text{HP} \rightarrow \text{C}=\text{OH} + \text{P}^*$$

--- **Initiation by photodecomposition of hydro-peroxide groups on the PS chains**. Hydro-peroxide groups (R - OOH), present on the PS chains (R) may decompose thermally or photo-chemically forming various types of radical species as below depicted [16].

$$\text{R} - \text{OOH} \rightarrow \text{RO}^* + \text{OH}^* \quad \text{R}^* + \text{HO}_2^*$$

**Propagation Step**
It includes the formation of PS-peroxy radicals (ROO*) deriving from the reaction of PS-alkyl radicals (R*) produced in the initiation step with molecular oxygen (triplet state), see below scheme:

$$\text{R}^* + O_2 \rightarrow \text{ROO}^*$$

The peroxy radicals by abstracting hydrogen (preferentially tertiary bonded) from other PS macromolecules (R H) form hydro-peroxides and new PS-alkyl radicals (R') according to the hereafter described reaction:

$$\text{ROO}^* + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'^*$$
In the course of the propagation several types of reactions occur leading to the formation of various functionalities and quite often to reactive species or groups. Some of these processes are hereafter briefly described.

--- The formation of hydroxyl groups

The decomposition of polymer hydro-peroxides into free radicals (see above reactions) may induce the formation of hydroxyl and carbonyl group on PS macromolecules. As reported in the below scheme the hydroxyl groups along the backbone chain may form following the reaction between alkoxy-PS radicals and other PS macromolecules:

![Chemical structure](image)

The formation of hydroxyl groups, in ortho position of phenyl groups in degraded PS, according to reference [16], can occur through the below depicted molecular mechanisms:

![Chemical mechanism](image)

--- The formation of acetophenone groups

It has been firmly established that during the photo-oxidation of PS carbonyl groups belonging to molecules of the acetophenone family are formed. Some of the possible reactions leading to the production of such compounds are delineated in the scheme described in figure 21 [16].
**Ring opening reactions.**

Such reactions, occurring without polymer chain scission, take place by a five-member ring mechanism between an alkyl peroxy radical and an adjacent excited phenyl group, and lead to aldehyde and ketone groups (see scheme in figure 22) [16]. Noteworthy to note that these new formed side groups are yellow colored because of the conjugated double bonds.

**FIGURE 21:** Reactions occurring during the photo-oxidation of PS with formation of carbonyls belonging to acetophenone-based compounds [16].
**FIGURE 22:** Some of the possible ring opening reactions occurring during the PS photo-oxidation leading to the formation of ketone and aldehyde groups [16].

--- *Olefin double bonds formation*

The double bonds along the backbone of a PS are probably formed as a result of a peroxy radical reaction via an intermediate six-member ring mechanism (see below scheme) [16].

--- *Termination Step*

The termination of PS chain radicals occurs through mutual combination reactions that lead to the formation cross-linked inactive products. *<The new bonds are peroxides at high oxygen pressure, e.g. in air, and ether or C-C bonds at low oxygen pressure, e.g. in vacuum or inert atmosphere. All these reactions lead to cross-linking of polymer chains. If the polymer peroxy radicals are in neighboring positions on a chain, they can probably also recombine to form stable cyclic peroxides or epoxies (see below scheme of reactions).>***
Scission and cross-linking may occur simultaneously in the same polymer sample. Scission may degrade a solid polymer into a thin liquid and cross-linking may create a brittle polymer network [16].

C.3) **Photo-oxidative degradation of high impact polystyrene (HIPS)**

The effect of natural weathering on the mechanical, morphological and thermal properties of HIPS was investigated by T. Sahin, T. Smmazcelik and S. Sahin [17].

<After natural weathering period of 8760 h, under known meteorological parameters, the changes in mechanical properties are investigated by using tensile, instrumented impact and hardness tests. Thermo-mechanical properties are characterized by using thermo-mechanical analysis (TMA) and melt flow index (MFI). Fractured surfaces of the materials are investigated by scanning electron microscope (SEM) ... The natural weathering experiment was performed in Izmit/Turkey. Half of the samples were placed on the roof of our research building and was exposed to natural weathering for 8760 h (365 days) > [17].

![Graph showing changes in properties over time.](image)

**FIGURE 23:** The yield strength ($\sigma_y$), the fracture strength ($\sigma_f$), the yield displacement ($\varepsilon_y$) and the fracture displacement ($\varepsilon_f$) of weathered HIPS [17].

From the diagrams shown in figure 23 it can be seen as, at the end of the time period of natural ageing, both yield strength ($\sigma_y$) and the fracture displacement ($\varepsilon_f$) values were significantly decreases as 53.59% and 94.53%, respectively compared to original sample [17]. Moreover from the $\sigma$–$\varepsilon$ diagrams in figure 24 it was possible to conclude that the degraded samples present a dramatic reduction in the strain at break as well as a remarkable change in strength and toughness values [17].
**FIGURE 24:** The $\sigma$-$\varepsilon$ curves of the original HIPS and of the weathered HIPS (8760 hrs) [17].

**FIGURE 25:** Charpy impact tests on original and 8760 hrs weathered HIPS samples. The force-time curves for the two kind of materials are shown [17].
As can be deduced from the impact curves in figure 25 the natural ageing affects the impact resistance of the HIPS. It was found that after 8760 hrs of natural weathering, decreasing in maximum impact force is reached to 40.2% and the degraded samples are fractured with remarkable lower Fmax and Emax values.

In charpy tests <Upon impact of the pendulum, the force rises sharply to a maximum value (Fmax) and then gradually decays to zero due to catastrophic failure. Total area under the force-time curve gives the impact energy for the system (Emax). These curves can be divided into two regions. The first region is the crack initiation and the second is the crack propagation regions. The areas under each region give the energy for these processes, which are defined as energy for crack initiation (Ei) and energy for crack propagation (Ep) > [17].

![Graph showing MFI values over time]

**FIGURE 26:** The results of MFI investigations of weathered HIPS samples.

Following ageing the melt flow index values of HIPS samples rapidly increases, especially during the first 4320 hrs of exposure, then it keeps almost constant (see curve in figure 26) [17].

The above finding indicates that natural degradation induces a reduction of the average molecular weight of polymer components [17].

Infra-red spectroscopy was used by F. Parres and others to have information about the chemical modifications produced in HIPS following exposure to solar radiation [18]. In particular the attenuated total reflectance Fourier transform-infrared spectroscopy (ATR-FTIR) technique demonstrated to be suitable to obtain the infrared spectrum of the surface of the HIPS sheet before and after direct exposure to solar radiation.

The ATR-FTIR spectra belonging to the unexposed and exposed HIPS samples are compared in figure 27 [18]. From the analysis of the two spectrograms it clearly emerges that the intensity of the peak corresponding to carbonyl groups with absorption bands around 1735 cm\(^{-1}\) increases in the case of exposed sample [18]. The formation of such groups is the result of the reaction of radicals in the presence of O\(_2\). According to literature butadiene units seems to be the origin for the activation steps of the photo-oxidation processes caused by UV radiation in HIPS [18].

< The exposure of styrene butadiene to solar radiation results in the rupture of chains and the formation of smaller compounds as the exposure time increases, and the butadiene phase is more susceptible to this type of radiation..... the UV energy and the presence of oxygen facilitate the reaction between different elements resulting in the formation of new compounds > [18].

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FIGURE 27: The ATR-FTIR spectra (n range, between 1500 and 2000 cm⁻¹) of two HIPS sample sheets: Top: following exposure to solar radiation for 6 weeks; Bottom: no solar exposure [18].

By using atomic force microscopy (AFM) it was possible to study the effects of photo-degradation upon the surface topography and roughness of the aged HIPS samples. It was demonstrated by F. Parres and others that solar radiation causes significant changes in the materials surface, in such a way that the external layers of HIPS sheets are altered, thereby modifying the surface topography. These variations cause an increase in roughness, which results in the appearance of micro-cracks over long exposure periods (see results in table 2 and figure 28) [18].

TABLE 2: Superficial characteristics of the HIPS sheets with different exposure time to solar radiation as resulted from atomic force microscopy (AFM) [18].

<table>
<thead>
<tr>
<th></th>
<th>No exposure</th>
<th>6 weeks of solar exposure</th>
<th>12 weeks of solar exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness (nm)</td>
<td>83.35</td>
<td>155.50</td>
<td>227.35</td>
</tr>
<tr>
<td>Average height (nm)</td>
<td>243.26</td>
<td>352.80</td>
<td>505.48</td>
</tr>
<tr>
<td>Maximum height (nm)</td>
<td>539.52</td>
<td>1063.81</td>
<td>1157.23</td>
</tr>
</tbody>
</table>
The roughness observed on the surface of HIPS degraded samples may act as concentrators of tensions which, in turn, contribute to the loss of mechanical properties of those materials [18].

**FIGURE 28:** AFM 3D topographic images and different roughness profiles for HIPS sheets with different exposure time to solar radiation (see text and table 2) [18].
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CHAPTER - NINETEENTH

THE EARLY SYNTHETIC THERMOPLASTICS

POLYSTYRENE

D) CONSERVATION OF PS ARTEFACTS VALUABLE FOR THEIR HISTORICAL, ARTISTIC AND DESIGN CONTENT.

In previous chapters it was seen as commercial General Purpose Polystyrene (GPPS), a transparent amorphous thermoplastics, whose mass production started in the early years of 1930s, because of its chemical inertness, particularly when stabilized against environmental agents (especially heat, oxygen and light) was/is the base material for the fabrication of objects used in many sectors of everyday life (containers for chemicals, solvents, and foods, radio and TV cabinets, CD case, jewel box, hair combs, transparent films, sheets and plates, etc.). Expandable PS (EPS) also cover a wide range of applications (as shock-absorbing packing material, for insulating buildings against soil and heat, in making models and scenery, ceiling tiles, protective packaging, disposable cups for hot drinks, insulating food containers, blister packaging, etc.). High impact PS (HIPS) due to its ease of processing, mechanical performance, and low cost is extensively applied in markets, which include packaging and disposable (for example: flatware, closures, safety razors, and pens), appliances, consumer electronics, electrical engineering (switches, coil formers and cases), automotive interior trim applications, toys, etc.[1,2,3,4].

Artefacts in PS are in exhibition in many private and public museums all around the world. Some of these objects, because of their innovative design and function, testify the evolution of material science and technology, market demands and plastic industry. Other types of PS-based artefacts are pieces of modern art, especially sculptures, which rightfully, now a day, are valuable for their artistic content.

The selection of items made in PS, shown through the figures hereafter reproduced, together with those already earlier shown, gives clear evidences of how wide is the range of uses that could be covered by PS-based resins.

The objects shown in figure 2, a toy car and a toy space racer testify the fact that cheap toys from the 1950s and 60s were generally made of injected polystyrene plastic, a cheap material ideal for mass production that reached the markets in large volumes after WWII. This brittle plastic made toys short-lived and it is great to find some in great shape like this serviceable car > [9, 10].

Figures 1 and 3 demonstrate that PS substituted other materials (wood, ceramics and also plastics) in many application fields. Such an event was the cause of interesting and important change in the market-industrial world, and this occurred especially in the years just after the Second World War. The figures 4, 5, 6, 7 and 8 represent a further witness, see also examples shown in previous chapters, of how largely PS-based materials found/found application in the realization of modern art pieces.
FIGURE 1: **Left**- Streamlined "Ice Water Pitcher", c. 1963, originally designed in 1948 by Clarence M. Burroughs and made by the Burroughs Co., Los Angeles, USA. molded of Burrite, their trade name for polystyrene plastic. This one is a copy, made in Brazil circa 1963 in Eltex [7].
**Right**- Two color injection molded polystyrene Wedgewood Pottery, 1950s, made in England, by "Dialene Better-Maid" [8].

FIGURE 2: **Left**- Toy Car in PS, early 1950s [9].
**Right**- Space Razer Ray Gun, 1960s.< *This Space Racer (friction powered!) releases sparkles in the transparent nose when triggered.* >[10].
FIGURE 3: Left—Emerson radio model 646 B. Made in 1947 in USA, with the case molded of polystyrene plastic, it is a mains or battery radio [11]. Right—Injection moulded polystyrene toothbrush beaker. Made in Germany [12].

**FIGURE 5:** Left- "Untitled, 2000" by Tom Friedman, polystyrene insulation construction. Created in 2000, this unique work measures 15 1/2 by 16 by 16 inches. [15].
Right- Pendant lights designed by Elise Fouin made from recyclable polystyrene [16].

**FIGURE 6:** Left- Kate McGwire, Rile, 2009, Pigeon feathers, felt, glue, polystyrene, 180 x 60 x 60 cm [17].
Right- Echolalia (2010) by Franz West, <Is a work comprised of seven painted totems, made from papier-mâché, polystyrene, cardboard and other objects. Each form is presented as a stacked structure, rising alternately from trash cans or ready-made pedestals. The sculptures appear to struggle for balance and equilibrium. They can be viewed from sofas which West has situated within their midst, in order to explore them from various angles, and at a leisurely pace> [18].
FIGURE 7: Left: “Equinox pants” by Jean Dubuffet (French, 1901 - 85). Painted expanded polystyrene 43 1/2" (1973). <This sculpture belongs to the series of drawings and sculptures Dubuffet called L’hourloupe, a term he coined to suggest “something rumbling and threatening with tragic overtones.” The series originated from doodles in red and blue ballpoint pen, some of which the artist eventually translated into three-dimensional forms like this one. Dubuffet regarded the strange objects in this series as apparitions or emissaries from another world—hence the mysterious title of this object, “equinox pants.” All of them include organic and abstract shapes, meandering lines and stripes, commercial inks, and artificial materials> [19].


It is interesting to underline as the sculpture of Gino de Dominicis, "Calamita cosmica" shown in figure 8 was manufactured just for outdoor exhibition. Thus to prevent possible degradation due to environmental factors a highly stabilized PS was most probably used by the Italian artist.
FIGURE 8: The sculpture of the Italian artist Gino de Dominicis, "Calamita cosmica" that represents a giant size human skeleton (24 meters long) realised in stabilised polystyrene, iron and resin while is in outdoor display at the “Piazzetta Reale” right in the centre of the Italian city of Milan [20].

SOME CONSIDERATIONS ABOUT THE CONSERVATION OF ARTEFACTS IN POLYSTYRENE-BASED MATERIALS

From the examples reported above and also in previous chapters it comes out that generally the conservation of artistic pieces in PS may be difficult because they are quite often manufactured by assembling parts constituted by different materials (other plastics, metals, wood, etc.), and this in addition with the fact that usually the plastic formulations are, on its own, very complex multi-component systems containing several additives and fillers. This entire make not always simple the knowledge of the deleterious chemical and physical interactions between the various material components. Moreover in some cases also the determination of the overall chemical composition of the artefacts may be not easily to be established.

For the above reasons the proper conservation (it includes procedures such as: cleaning, direct restoration, inhibitive or protective and maintenance actions) of artistic pieces may be, quite often, hard to be accomplished [21].

The above critical issues were commented as follows by J. D. Portell and others:

"The chemical analysis of polymeric materials used by an artist is difficult because the artist often experiments to achieve a desired visual effect and because performing the analysis should not alter the art. Non destructive tests are preferred. Many traditional polymer analysis methods require removal of a small sample and dissolving, heating or decomposing it to get data for identification or characterization of the polymer. Though many tests need only a small sample, any removal of
material is undesirable. Moreover the artists may create compositional gradients or combine immiscible polymers to achieve an internal refraction. Dyes and pigments add colour and aesthetic impact. The complexity of these materials and the restriction on sampling challenge the polymer analysis. [22].

For the proper conservation of artefacts in PS the following facts should be taken into account:

--- Amorphous solid atactic PS (the glass transition temperature being, depending on processing conditions and molecular mass at = 100 °C) is a clear though brittle behaving material, thus it may experience irreversible mechanical damages especially when subjected to impact stresses (impact-sensitive material). *It creates a brittle, almost glassy sound when tapping (butter dishes).* When bending or breaking it smells distinctly of styrene [6].
--- PS it is not very heat resistant and due to accelerating effect of temperature its use should be only limited to 70°C.
--- Non stabilized PS when exposed to solar light yellowed due to photo-oxidation phenomena.
--- PS artefacts, with unreleased internal stresses, may suffer environmental stress cracking when in contact with active liquids and vapours;
--- HIPS items due to the presence of a rubber phase are resistant not only to mechanical and impact stresses but also to stress cracking [23].
--- PS is resistant to aqueous alkali and mineral acids.
--- PS is not resistant to solvents such as gasoline, ketones and aldehydes. Thus such a type of substances must be never used in the course of cleaning operations of PS-made objects.
--- In storing PS artefacts the contact with sulphuric acid should be avoided. As matter of facts it is well known that such an acid substance is capable, by reacting with phenyls, to substitute a hydrogen atoms with the –SO₂H group. The scheme of sulphonation reaction is below depicted.

![Sulphonation reaction scheme](image)

John Morgan in his survey of plastics in historical collections reported, concerning PS artefacts, the hereafter findings:
*During the survey, some colourless, transparent PS objects (e.g. trays imitating moulded or cut glass) were observed to have been subjected to environmental stress crazing, and slight yellowing was also usually apparent. Toughened varieties of PS are not transparent. This material was often found in toy collections and as moulded boxes or containers for the kitchen. It becomes brittle with ageing and should be handled with care. A number of toughened PS objects seen during the survey are thought to have suffered in this way and to have become quite fragile.* [23].

It was found that when PS-based artifacts are indoors stored, under normal light and temperature conditions retain their look and functionality for years. The life time of these objects can be further prolonged if they are maintained under controlled conditions characterized by exposure to free of UV radiation light, relatively low temperatures and proper values of ambient humidity.
In case of HIPS-based items, due to the presence of unsaturated rubbery phases, the presence of oxygen should be also avoided.

Artifacts for outdoors applications or exhibition, manufactured from no stabilized or no properly stabilized PS, will very soon be degraded following photo-oxidation processes induced essentially by the sunlight UV rays and by the presence of oxygen. \textit{<This environmental ageing shows up both as a gradual change in appearance, i.e. yellowing and loss of surface gloss, and also as a decrease in the mechanical strength> [24].}

It must be reminded as objects more dark colored usually show a better resistance to environmental degradation than a pale or transparent product [24].

\textbf{FIGURE 9:} Damage on a box made from sheet polystyrene, 20th century [25].

An example of object in PS with evidence on the surface of damages due to environmental factors is shown in figure 9 [25].

Expanded PS is a white and opaque material characterized by a very low thermal conductivity. Compared to GPPS, EPS presents a lower mechanical strength and elasticity. It must be underlined that EPS decomposes when in contact with acetone, ethyl acetate or toluene. Thus the use of these solvents must be avoided during cleaning or any other conservation procedure established for EPS-based objects like those shown in figures 4 and 7 [6].

In the case of broken object, especially those made on rigid PS, the separated parts can be reassembled and joined together by using a special glue commercialized as “\textit{Polystyrene (poly) cement}” [26]. This cement
\textit{<is only suitable for rigid polystyrene plastic which is the type used for injection molded kits. It works by dissolving the surface of the plastic which then re-hardens. If a bead of poly cement is put between two pieces of plastic, then both faces of the plastic dissolve and meld together so that when they harden they have formed a solid joint. In effect, the two pieces have been welded together, so a}
very good bond is formed that is as strong as the plastic. The drying time will vary mainly depending on how much is applied and the viscosity (thickness) of the glue. Very thin formulas will normally dry in seconds, but the very thick tube glue might take a few hours. Note that even when a bond has formed the plastic may not have fully re-hardened so should be treated with care for a time > (see figure 10) [26].

**FIGURE 10:** Example of commercially sold PS-cements.  
**Top-** Traditional thick polystyrene cement in tubes.  
**Bottom-left-** Medium viscous polystyrene cement in a tube (note the long hollow needle to assist in applying the adhesive with precision) [26].  
**Bottom-right-** Ultra thin or liquid PS-cement looks like water [26].
The disadvantages in using PS-cement are summarized as follows in reference [26]:
< --- If too much is used, then it will completely dissolve through the material being glued and damage it.
--- If any glue is dropped or smeared on the surface of the model it will damage any surface detail > [26].

In the use of PS-cement attention should be paid to the following aspects:
1) The fumes from the glue are toxic. Thus it must be applied only in a well ventilated area.
2) PS-cements dissolve plastic; consequently they have to be applied in a minimum amounts only
< and do not use it in an enclosed space on a model where it will take a long time to dry > [26].
3) The cement should never < be placed into holes and cavities that are not exposed to the air; because it will not be able to dry and will slowly dissolve the surrounding plastic > [26].
4) The contact between the plastic surfaces to be joined, due to the fact that PS-cements are not gap-fillers, has to be absolutely good.

PS-cements are commercialized in three types according to their viscosity. Moreover it must be pointed out that the strength of the adhesive will vary with composition and from one manufacturer to another (see figure 10) [26].
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CHAPTER-TWENTIETH

POLYURETHANES

A) HISTORY, SYNTHESIS, PROCESSING, PROPERTIES AND APPLICATIONS

A.1) SYNTHESIS AND HISTORY OF POLYURETHANES

Polyurethanes (PU) are a large family of synthetic polymers characterized by the presence in their repeat units of urethane (carbamate) linkages [1,2].

In organic chemistry any compound produced by the reaction of an isocyanate (R-N=C=O) and a alcohol (H-O-R'), in conformity with the following reaction, is called urethane, or "carbamate".

![Chemical structure of isocyanate and alcohol](image)

PU are generally obtained by a poly-addition reaction of a polyisocianate with a polyalcohol (polyol) in the presence of catalyst or accelerator of reaction, cross linking agent, chain extenders and other additives and dyes.

An example of synthesis of a typical PU is shown in figure 1 [3, 4].

![Synthesis reaction](image)

**FIGURE 1:** Synthesis reaction that starting from a diisocyanate and a diol (top) leads to a polyurethane. The molecular structure of the repeat unit of the PU, containing the urethane groups -NH-(C=O)-O-, is shown on the bottom side of the figure [3].

When in the synthesis of PU polyesterpolyols are used then the PU are classified as "polyester-based polyurethanes" (PES-PU). PU obtained by using polyetherpolyols are defined as "polyether-based polyurethanes" (PET-PU). The two classes of polymers differ from their properties and then applications. As matter of fact PES-PU have a good thermal and mechanical resistance, excellent
performance against scratch and good chemical resistance against mineral oils and the hydraulic fluids [1,2]. PET-PU show excellent stability to hydrolysis ( contrary to what happen with PES-PU ), flexibility and capability to maintain use properties also at relatively low temperatures [1,2].

Polyesterpolyols are usually synthesized through a condensation reaction between a diol ( in excess ) and a diacid ( for example they may be derived from diethylene glycol and adipic acid ), according to the below reported scheme:

\[ n_{1}R(OH)_{2} + n R'[COOH]_{2} \leftrightarrow \frac{\text{HO-} \text{R-O} \text{C} \text{C} \text{-} \text{R-O} \text{R} \text{OH}}{\text{HO}} + n \text{H}_{2} \text{O} \]

Polyetherpolyols are obtained by reacting an organic oxide and an initiator compound containing two or more active hydrogen atoms (i.e. a dialcohol) in the presence of a base catalyst. The reaction between the ethyleneglycole and the propylene oxide is below depicted [5, 6].

If a trifunctional alcohol such as glycerin is used, a triol will be the final product of the reaction. By a suitable control of the parameters of reactions polyesterpolyols and polyetherpolyols with tailored values of the degree of polymerization (n) may be synthesized.

**FIGURE 2:** The molecular structure of some diisocyanate commonly used in the synthesis of polyurethane.  
Top-left: Hexamethylene diisocyanate (HDI).  
Top-right: Diphenylmethane -4,4'-diisocyanate (MDI).  
Bottom: Toluene-2,4-diisocynate (TDI) [7].
The molecular structures of some of commonly used diisocyanates are reproduced in figure 2. Properties of PU such as hardness, modulus and mechanical resistance strongly depend upon the molecular structure of diisocyanate. On the contrary cold flexibility and resistance to the hydrolysis are controlled by the molecular structure of polyesterpolyols and polyetherpolyols used in the synthesis.

By reacting diisocyanates with diamines polyurea polymers are obtained where along the backbone chains the urethane groups (\(-\text{NH}-(\text{C}=\text{O})-\text{O}^-\)) are replaced by urea groups (\(-\text{NH}-(\text{C}=\text{O})-\text{NH}^-\)). A typical reaction leading to polyurea is below depicted [3].

\[
\begin{align*}
\text{4,4-diisocyanatophenylmethane} & \quad \text{ethylene diamine} \\
\end{align*}
\]

\[
\begin{align*}
\text{a polyurea}
\end{align*}
\]

In the ordinary industrial chemistry linear PU are synthesized according to the following steps [8].

**Step-1 (Prepolymer synthesis)**

A polyesterpolyol or a polyetherpolyol (with very low \(T_g\) and molecular weight between 1000-2000) is allowed to react with a small excess of a rigid diisocyanate to make a "prepolymer" with free isocyanate groups at the chain ends. The reaction (see scheme A) in figure 3 occurs in presence of suitable catalysts. One of those is the diazobicyclo[2.2.2] octane (DABCO) whose molecular structure is below shown [3].

\[
\begin{align*}
\text{N}
\end{align*}
\]

**Step-2 (Chain extension)**

The prepolymer is chain-extended with a diamine to produce the final, and high molecular weight PU (see scheme B) in figure 3.

As can be seen by figure 4 along the axis of the linear PU chains hard segments (the diisocyanate and extender residues) and soft segments (the polyol residues) alternate.

These polymers, considered to be multiblock copolymers, are defined as “Segmented Linear polyurethane”. In the mass condensed state these PU are characterized by a two phase morphology due to the presence of rigid micro domains, formed by the physical aggregation of the hard segments, dispersed in a more disordered matrix constituted by the soft segments (see figure 5) [8,9,10]. In some of Segmented Linear PU two distinguishable \(T_g\) are evidenced corresponding to the two separated phases: The \(T_g\) at lower \(T\) due to the rubber phase while that at higher \(T\) being related to transitions of the hard domains [8].
**FIGURE 3:** The steps in the process of polyurethane synthesis.

A) Scheme of the reaction that by reacting a diisocyanate and a polyesterpolyol or a polyetherpolyol leads to the formation of a PU-prepolymer with a relatively high molecular weight.

B) The prepolymer is chain extended by reacting with a diamine to produce the final high molecular weight PU.
**FIGURE 4:** Structure of a segmented linear polyurethane chain. Stiff rigid blocks and soft rubbery segments alternate along the chain axis.

**FIGURE 5:** The mass morphology in the condensed state of a linear segmented polyurethane. The material presents a two phase structure where hard micro-domains are dispersed in a rubbery phase [10].

The linear PU, whose molecular structure is shown in figure 4, and with a phase-separated morphology of the type described in figure 5, was commercialized by DuPont as Lycra, Spanex or Elastam [11]. In this type of PU the rigid blocks connected by hydrogen linkages act as physical cross linking. Thus at temperature relatively low they behave like a cross linked rubbery system while in the fluid state, where the H-bonds are destroyed they may be processed like a common any thermoplastic material. For such a reason those PU are named as "thermoplastic-elastomers" [8].

As will be later reported, depending on the nature and concentration of raw components and of processing methods PU having an astonishingly variety of different properties have been commercialized.
**FIGURE 6:** Examples of application of polyurethane in the field of modern art furniture from Giovannetti [12]. *Each piece of furniture from the collection incorporates a gas piston mechanism to set the required height. Rendered in rigid, structural polyurethane, the chairs and tables sit atop a chrome steel base.* [12].

**FIGURE 7:** Left- Object and tools in Polyurethane (thermoplastic-elastomeric type) obtained by open casting technology [13].

Right- polyurethane wheels with centre made in cast aluminum, *suitable for environment with atmospheric agents, alcohol and glycol; not suitable for applications where mineral and organic acids, base solutions and saturated vapor are present.* [14].
The chemical industry of PU is now a day capable to produce different types of products, which for their properties are used in a wide range of application sectors (see examples in figures 6, 7 and 8). The most important families of PU are hereafter listed:

--- Rigid/Semirigid Foam
--- Flexible Foam
--- Thermoplastic elastomer/Elastomer
--- Elastic fiber/Synthetic Leather
--- Surface Material and Paint.

In the next chapters the processing methods and properties of those classes of PU together with their main applications and usages will be described in details.

**FIGURE 8:** Polyurethanes in modern art. Sculpture of Piero Gilardi, "Greto autunnale", 2009, manufactured in polyurethane foam, 70 x 70 x 20 cm [15].
HISTORY OF POLYURETHANES: FROM THE EARLY SYNTHESES TO THE NOW A DAY INDUSTRY, PROCESSES AND APPLICATIONS

PU played an important role in the history of polymer science and technology as well as in the history of all chemistry. The most important steps that led to the development of the chemistry and technology of PU are hereafter reported and discussed.

1) **Milestones in the History and applications of Polyurethane**

--- 1848-49- C. A. Wurtz (figure 9) synthesized for the first time aliphatic isocyanates and urethanes [16,17,18].

![Figure 9: Left-Charles Adolph Wurtz, born in Strasbourg, November 26, 1817, president of the French Academy of Sciences, is one of the recognized leaders of modern chemistry [18]. Right- Otto Georg Wilhelm Bayer (born in Frankfurt am Main on November 4, 1902), not related to the family that established the Bayer Group, in 1937 developed the polyurethane chemistry [20].]

--- 1937- Otto Bayer (1902 - 1982) and his coworkers, at the I.G. Farben Laboratories, a subdivision of Bayer Corporation, in Leverkusen, Germany, following a research project aimed at the production of synthetic fibers capable to compete with polyamides, developed at that time in USA, discovered the basic principles of the polyurethane chemistry: he set up the novel polyisocyanate-polyaddition process [17,19, and 20]. Otto Bayer (figure 9-right) first understood that by applying the principle of polyaddition to liquid diisocyanates and polyester and polyether diols would be possible to produce new polymer-based materials with innovative properties. The method used by Bayer and coworkers to produce PU was in effect a modification of the reaction already discovered by C. A. Wurtz on 1848-49.
The basic idea which he documents from March 26 1937 relates to spinnable products made of hexane-1,6-dioisocyanate (HD) and hexa-1,6-diamine (HDA). Publication of German Patent DRP 728981 on November 13 1937: "A process for the production of polyurethanes and polyureas". The team of inventors consisted of: Otto Bayer, Werner Siefken, Heinrich Rinke, L. Orthner and H. Schild [21].

Otto Bayer's basic idea of mixing small volumes of chemical substances together to obtain dry foam materials was seen as unrealistic. But after numerous technical difficulties, Bayer eventually succeeded in synthesizing polyurethane foam. It was to take 10 more years of development work before customized materials could be manufactured on the basis of his invention. Otto Bayer influenced the development of this versatile family of plastics for many years until his death at the age of nearly 80. Thanks to the chemical and entrepreneurial achievements of the inventor of polyurethanes, the Bayer Group still holds a large share of the world market for these materials [20].

The originality of the method discovered by Bayer was essentially based on the fact that by starting from two low mass different molecules with controlled functionality was possible to produce by an addition process, at room temperature and without the formation of any low-molecular weight byproducts to be removed, polymer materials with intrinsic interesting use properties.

--- 1938- Heinrich Rinke produced a polymer from octamethylene diisocyanate and butanediol-1,4. He calls this area of polymers "polyurethanes", a name which was soon to become known worldwide for an extremely versatile class of materials [21].

--- World War-II time- Industrial researches at the laboratories of the Farben-fabriken Bayer, a division of the former I. G. Farbenindustrie, succeeded in developing rigid and flexible PU-foams. PU-rigid foams were developed to be essentially applied in light weight, high strength sandwiches components to be used in the construction of aircrafts [17]. Early applications in this field occurred already on 1940. Interesting to point out that these PU-foams were also used as insulation in submarine and tanks.

--- 1941- PU was used as adhesive between rubber, metal and glass.

--- 1947- A plant for the production in technical amount of isocyanates was established by the Bayer company in Leverkusen.

--- 1942- Researches on PU, especially directed towards applications in the field of coating, adhesives and fibers started in USA particularly at the DuPont Company [17].

--- 1946-1948- In USA DuPont and Monsanto established a pilot plant for producing toluene diisocyanate. At the same time Goodyear Aircraft Corporation and Lockheed Aircraft Corporation developed procedures to produce PU-rigid foams similar to those set up by Bayer in German [17]. These early foams were based on polyesters having a relatively high acid number and some residual water of esterification. The foaming of these systems was the result of the reaction of the isocyanate group with the free carboxyl group and water to yield carbon dioxide [17]. The first commercially available PU, introduced by DuPont Corporation in 1948, used in insulation was a rigid foam.

--- 1949- Polyurethanes having rubber properties, capable to be vulcanized through procedures similar to those used for natural rubber were introduced by Dow Chemical, BASF, and Mobay Corporation. Polyurethane rubbers appeared on the market [19].
--- 1950- The first commercial thermoplastic polyurethane (TPU) was produced, by Bayer-Fabenfabriken in Germany and in the U.S. by B.F. Goodrich. These new materials, present the advantages of having rubber like mechanical properties at relatively low temperature (close to RT) but nevertheless they can be processed as thermoplastics at temperatures well above Tg [22].

--- 1951- Machineries, based on the so called nozzle injection principle, and suitable for the continuous production of PU-rigid and flexible foams were started to be developed at the Farbenfabriken Bayer (Germany) [23].

--- 1952-1954- Polyisocyanates became commercially available.
- A. Hochtlen for the first time developed PU-flexible foams.
- Bayer set up a method and related machineries for producing, on industrial and commercial scale, flexible PU-polyester foams based on toluene diisocyanate (TDI) and polyester polyols [17].

*< The invention of these foams (initially called imitation swiss cheese by the inventors) was thanks to water accidentally introduced in the reaction mix > [24-a].*

To obtain PU-foams, the reaction was carried out in the presence of small amounts of water, which causes, according to the below scheme, the hydrolysis of some of the isocyanate groups and the release, in the course of the process, of gaseous carbon dioxide with the formation and diffusion of bubbles of CO2 that determines the process of expansion and foaming of the reacting mass [24-b].

\[
\begin{align*}
\text{R-N=C=O} + \text{H-O-H} &\rightarrow \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \\
\text{Isocyanate} &\text{Water} \\
\text{R-N-C-OH} &\text{Carbamic Acid}
\end{align*}
\]

\[
\begin{align*}
\text{R-NH}_2 + \text{CO}_2 \uparrow + \text{HEAT} &\rightarrow \begin{array}{c}
\text{OH} \\
\text{OH}
\end{array} \\
\text{Amine} &\text{Carbon Dioxide}
\end{align*}
\]

By using isocyanate and polyols with a functionality higher than 2, as the triol above schematically depicted, a tridimensional foamed cross-linked polymer material will result [24-b].
PU-foams were also produced just by adding to the reactant mass low-boiling non-reactive liquids (i.e. chlorofluorocarbons, methylene chloride, trichloroethane, etc.) capable to act as "physical blowing agent". The vaporization of these liquids is caused by the heat deriving from the exothermic reactions. Polyhalogenated hydrocarbons, commercialized by DuPont under the trade mark "Freon" (for example the trichloro-fluoro-methane commercialized as Freon-11) once widely utilized were successively banned being considered of potential damage to the earth's ozone layer. Now a day hydrocarbons such as propane and butane are employed as blowing agents. By varying the water content and by using suitable surfactants it is possible to tailor the amount and the size of bubbles formed in the foam. The density of PU-foams, an important property as far as type of applications are concerned, is controlled essentially by the amount and nature of blowing agent while surfactants decide about the type of cell structure. In the common industrial practice besides catalysts (for example tin and amines) other additives are used (cross-linking agents, flame retardants, coloring materials, fillers, anti-microbial agent and chain-extending agents) [24-c]). The industry of PU developed two types of foam: flexible (with an open cell structure) and rigid (with a closed cell structure that prevents gas movement between cells) [24-c]). The chemical nature of hydroxyl compounds (polyol) and isocyanates determines the structure of the polymer backbone and then the basic properties of PU-foams. Now a day PU-foams are produced by a one-step, a two-component, or a prepolymer process. A modern manufacturing one-step process used for the production of flexible slab-stock (continuous foam) is described through the scheme of figure 10 [24-c]). According to such a process all the reactants are at the same time metered, mixed, and dispensed onto a conveyor or into a mold.

**FIGURE 10:** A modern manufacturing "batch" process used for the production of flexible PU-foams [24-c]).

The complex chemical and physical transformations occurring along the process line of figure 10 leading to the formation of the final cured flexible (open cells) PU-foams are hereafter briefly described with reference to the scheme of figure 11 where the several distinct, sequential events occurring during the formation of a flexible slab-stock foam are represented [24-d]):
1) Nucleation of tiny gas bubbles- It occurs as soon as the ingredients are mixed.
2) Bubbles growth- The surface of the reactant liquid assumes a creamy look. The mixing time needed to creaming is defined as “Cream Time”.
3) Expansion and thickening phase- Due to the increase in the generation of blowing gases the reactant mass keeps on expanding and thickening. Meanwhile the foam rises it is observed that the number of bubbles remains constant.
4) Gelling- At a certain time gelling occurs and the production of gases stops. The mass ceases to expand. Gradually cells consolidate and gases are ejected out of the mass. The foam at this point is capable to remain standing [24-d]).

**FIGURE 11:** Typical reaction profile for flexible slab-stock foam (with an open cell structure ), see text [24-d]).

**FIGURE 12-left:** A sample of polyurethane, flexible foam [26].
**FIGURE 13-right:** Micrograph showing the open celled structure of a polyurethane flexible foam [27].

< The gelling reaction, or polymerization, continues and the foaming mixture progresses from a liquid to a dry solid. The time required for this to occur is known as the gel time. To test whether a foam bun has gelled, the operator repeatedly inserts a wooden spatula into the gelling mass. When the outer skin of the foam no longer adheres to the spatula on gentle touching, the tack free time has been reached > [24-d]).
As can be seen by figure 10 and 11 once foam blocks are tack free they are sliced into pieces and stored for a suitable time in a curing, and well ventilated area.

The physical and chemical properties, and the heat resistance, of commercial PU-ether and ester based foams are compared in table 1 [24-e]). It can be seen as the chemical composition plays an important role in deciding about most of the characteristics of the PU-foam [25].

**TABLE 1**: See text [24-e]).

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>COLORFOAM (PU-ether-based-foam)</th>
<th>MOLTOPREN (PU-ester-based-foam)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strength</strong></td>
<td>Has strength of approximately 1 kg per square centimeter, and more than 200% elongation percentage.</td>
<td>Is approximately 30 – 100% stronger than COLORFOAM and has the same 200% elongation percentage same as COLORFOAM.</td>
</tr>
<tr>
<td><strong>Flexibility</strong></td>
<td>Excluding special types, exhibits superior recovery and flexibility characteristics regardless of type and extension direction.</td>
<td>They are not as flexible as COLORFOAM and have a harder touch.</td>
</tr>
<tr>
<td><strong>Water Resistance</strong></td>
<td>Water will not penetrate unless physical force is applied. It is also chemically stable against water.</td>
<td>Has similar water absorption characters to COLORFOAM, Under high temperature and high humidly or in the liquid that pH is not neutral, the foam tends to deteriorate earlier.</td>
</tr>
<tr>
<td><strong>Oil Resistance</strong></td>
<td>Will swell when moistened with solvents or oils. When swollen, the strength will decrease, but, since there is no chemical deterioration, it will regain original characteristics after drying.</td>
<td>There is little swelling when moistened with solvents or oils. When moist, there is a minimal strength loss and the material is chemically stable.</td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td>This foam does not have the softening point as thermoplastic resin foam have and will a little melt and gasify at high temperatures.</td>
<td>Similar to COLORFOAM, but a greater amount for melting, making heat sealing possible.</td>
</tr>
</tbody>
</table>
A sample of PU-flexible foam is shown in figure 12 [26]. The typical open celled structure of PU-flexible foam can be seen through the electron micrograph presented in figure 13 [27].

On 1952 the first PU-spandex fibers were produced on a laboratory scale at the Farbenfabriken Bayer who earned a German patent for the corresponding synthesis.

--- 1953-1954- PU found application as “Synthetic leather” for shoe soles production and as foam cushions [19].
-A joint Company between Bayer and Monsanto, named as Mobay Chemical Co., was established in USA on 1954 for the production of flexible polyester PU-foams based on Bayer findings [17].

--- 1956-57- Polyether polyol, poly (tetramethylene ether) glycol, was produced on industrial scale by DuPont. Such a product was obtained by a ring-opening polymerization of tetrahydrofuran (see the below reported reaction).

---1958- Flexible polyether PU-foams started to be used in many sectors due to the set up of the “One Shot” process technology. Such a process was based on the use of polyether polyols with high functionality (e.g., polyoxypropylene adducts of glycerol and trimethyl propane in combination with triethylenediamine and organotin catalysts) and of silicone copolymers as surfactants [17,25]. The one shot process allowed cost saving and the possibility of producing <tailor-fashioned foams to specific end user applications. These developments led to the broad acceptance of flexible foams in the bedding, furniture, and automotive markets> [17].

--- 1958- Introduction of elastic “Spandex Fibers” made from special PU-thermoplastic elastomers<br>The usefulness of the Spandex elastomers lies in their ability to be melt-spun into fibers. This process is impossible with conventional rubbery polymers because they are covalently cross-linked and decompose before melting. However, the Spandex fibers rely on physical cross-links that can be disrupted at high temperature and reformed as the fibers cool> [7]. The molecular structure and the morphology of Spandex fibers were already described through the schemes reported in the figures 4 and 5.

PU-elastic fibers are now a day commercialized by many companies under the generic name of Spandex, nevertheless the most famous are those produced by Du Pont under the trade mark “Lycra”. PU-fibers, as shown by figure 14 were used in the manufacturing of heavy duty industrial wheels as well as in the fabrication of ski pants [28,29].

< Virtually wear-proof, the new material (Spandex) can be compounded and is pourable at RT without special equipment. Tread hardness may be varied ...simply by adjusting the amount of curing agent. Physical characteristics include high impact resistance, high load bearing, improved resistance to elevated temperatures and excellent resistance to oils, gasoline and other hydrocarbons, diluted acids and bases and most chemicals> [28].
FIGURE 14: Heavy duty industrial wheels manufactured by using cast PU-Spandex fibers, see text, [28].

The special properties and the unique elastic behavior of PU-Spandex fibers (classified as segmented PU), produced by dry spinning technique, are explained, considering the scheme of figures 3, 4 and 5, as follows in reference [30]:

<<The fibers are made up of numerous polymer strands. These strands are composed of two types of segments: long, amorphous segments and short, rigid segments. In their natural state, the amorphous segments have a random molecular structure. They intermingle and make the fibers soft. Some of the rigid portions of the polymers bond with each other and give the fiber structure. When a force is applied to stretch the fibers, the bonds between the rigid sections are broken, and the amorphous segments straighten out. This makes the amorphous segments longer, thereby increasing the length of the fiber. When the fiber is stretched to its maximum length, the rigid segments again bond with each other. The amorphous segments remain in an elongated state. This makes the fiber stiffer and stronger. After the force is removed, the amorphous segments recoil and the fiber returns to its relaxed state >> [30].

Fabrics based on PU-Spandex fibers (see figures 15 and 16) present the hereafter listed advantages:
--- Lightweight, comfortable and breathable;
--- Easy colored;
--- Great stretch;
--- Good strength;
--- Long term resistance to body acids;
--- Capability to pull away the moisture from the skin [32].
Lycra fabrics are largely used in the production of exercise clothing, leggings, bathing suits and socks. It is more often used in women's clothing for its form-fitting nature. Most commonly used for cycling clothes, dance costumes or any activity that requires stretch fabric. The thinnest type of Lycra is used in hosiery [32].

**FIGURE 15:** Electron micrograph showing PU-Spandex fibers. It can be seen that each fiber consists of several filaments [31].

**FIGURE 16:** Modern PU industries are capable to offer Lycra fabrics in a wide range of colors [32].
The main elements and basic principles of the dry spinning process, used to obtain PU-elastomers fibers, can be deduced by referring to the scheme of figure 17 [33].

**FIGURE 17:** A dry spinning unit used for the manufacturing of PU-Spandex, elastomeric fibers, see text [33].

The dry spinning technology, looking to figure 17, is described as follows in reference [33]:

*...fiber forming materials are dissolved in volatile solvent. Each spinning unit consists of a pump and spinneret at the top of a tall shaft.... There is an air outlet at the top of the tall shaft and air inlet at the bottom. The fiber spinning solution is forced under pressure from the storage tank to the spinning pump and then through the spinneret.......The fineness of the filament is determined partly by the diameter of the holes but primarily by the relation between the rate at which solution is forced through the spinneret and rate at which the yarn is wind up. When the fiber spinning solution emerging from spinneret meet the warm air, volatile solvent evaporates leaving the filaments, hence coagulation takes place and becomes dried before leaving the chamber.* [33]

In the production of Lycra fibers the raw materials PTMG (polyoxytetramethylene glycol) and MDI (diphenylmethane diisocyanate) are first polymerized in a reactor to form a pre-polymer in presence of diazobicyclo[2.2.2]octane as catalyst. Successively this pre-polymer is dissolved with DMac (dimethyl acetamide), and additives are added. This dope supplies the polymer reactor where polymerization occurs at a controlled temperature. At this stage low molecular weight amines are added to control the molecular weight of the fibers (chain extension step).  

*The dope is precisely metered and discharged by a gear pump mounted on an individual spinning tube, and extruded through nozzles into the spinning tube. In the spinning tubes, extruded dope streams are dried in a high-temperature inert gas flow, vaporizing the solvent and forming spandex*
fibers. Solvent vapor and vent gas are fed to a scrubber and absorbed into a solution for recovery. Spandex multi-fibers are gathered and twisted in the air jet nozzle, and wound on paper tubes with finishing oil applied to avoid sticking and obtain smoothness > [33].

Lycra fibers when exposed to the action of degrading factors such as heat, light, atmospheric contaminants, chlorine, etc., may suffer damages. In order to avoid or reduce those effects the following additives are commonly used:
--- Monomer and polymer hindered phenols as antioxidants.
--- Ultraviolet (UV) screeners, for instance hydroxybenzotriazoles, to shield against light degradation.
--- Stabilizers capable to hinder fiber discoloration deriving from the action of air pollutants (for example compounds with tertiary amine functionality, suitable to interact with the oxides of nitrogen)
--- Anti-mildew systems [33-b]].

< When they are first produced, spandex fibers are white. Therefore, colorants are added to improve their aesthetic appearance. Dispersed and acid dyes are typically used. If the spandex fibers are interwoven with other fibers such as nylon or polyester, special dying methods are required > [33-b].

--- 1960-1969- In 1962 PU-Spandex fibers, under the trade name Lycra, were industrially produced by Du Pont.
PU-based formulations found applications as: Sandwich building panels; Integral skin for armrests and shoe soles; Automobile bumpers [19].
In such a period a new technology, named as “Reaction Injection Molding” (RIM), for the production of PU-foams and PU-elastomers, was introduced first in USA and then in Germany. Between 1966-69 RIM processes were developed by Bayer AG for the molding of high density integral skin rigid PU-foams. These foams commercialized as “Duromer” found application as furniture [17].
The principles at the base of the RIM process (see figure 18) may be summarized as follows:
--- Two highly reactive liquid components, namely the resin component (formed by a blend containing a polyether-based macro-polyol, one or more short diols, a catalyst system and additives and a blowing agent, in the case of foam products) and the isocyanate component, are held in separate temperature controlled feed tanks equipped with agitators (see figure 18) [17,34].
--- The above two components < are fed through supply lines to metering units that precisely meter the reactants, at high pressure, to the mixing head. When injection begins and valves in the mixing head open, the liquid reactants enter a chamber in the mixing head at pressures between 1,500 and 3,000 psi where they are intensively mixed by high-velocity impingement. From the mix chamber, the liquid flows into the mold at approximately atmospheric pressure and undergoes an exothermic chemical reaction, forming the polyurethane polymer in the mold > [34].

By means of PU-RIM process it is possible to produce large parts capable to exhibit the following properties:
--- High strength and low weight;
--- Heat resistance, thermal insulation, dimensional stability;
--- A high level of dynamic properties;
--- Resistance against the degradation actions by many chemicals (inorganic and organic acids including a large number of solvents);
--- Resistance to weathering and aging [34].

It is interesting to point out that relative low processing temperatures (35-66°C) and low injection pressures (30 to 100 psi) make RIM procedures, especially when large parts are considered, more economical than other molding processes [34].

An example of a monitor housing in PU, produced by RIM technology, is shown in figure 19 [36].

--- 1970-1980- PU materials, capable to imitate and substitute wood in many fields, were developed.
PU was applied in the production of items suitable for orthopedics and medical applications. Spray building insulation processes were introduced [19].
Around the years 1977-1980 the "Reinforced Reaction Injection Molding" (RRIM) process was developed [17]. As shown by the scheme in figure 20 [37], in one of the liquid component fillers (glass fibers, wollastonite, mica and carbon fibers, etc.) are dispersed.

--- 1981-1995- Innovative processes and PU-based materials led PU to be applied as:
- Surfboards; Energy absorbing foams for passenger safety; Thin wall medical hoses i.e. catheters and bicycle tires [19].

**FIGURE 18:** The principles at the base of the polyurethane Reaction Injection Moulding (RIM) process [35].
**FIGURE 19:** A monitor housing in PU, produced by RIM technology [36].

**FIGURE 20:** The scheme of the RRIM process, see text [37].
The sources of the reactant components used in the PU-synthesis, the types of PU-based products, commercially offered by the modern industry of polyurethanes, together with some of the main corresponding applications, are summarized through the block diagram presented in figure 21 [38].

**FIGURE 21:** Block diagrams reporting the sources of components, the type of polyurethane and some of typical applications especially for flexible and rigid PU-foams [38].

Now a day PU-rigid nano-foams are under development, still at laboratory scale, at the Bayer Material Science Laboratory.  
The process is based on the “Principle of Supercritical Micro-emulsion Expansion”, POSME.  
The objective of such a program is to produce rigid foams with pore sizes of less than 150 nanometers in diameter, see figure 22 [39].  
The advantages expected are hereafter summarized:  
--- Twice the thermal insulation performance of conventional PU-rigid foams;  
--- Contribution to reducing CO₂ emissions;  
--- More storage space for refrigerated goods [39].

The method is described in reference [39] as follows:  
< To synthesize a nanofoam using the POSME method, carbon dioxide (CO₂) and the liquid polyurethane raw materials (polylol and isocyanate) are mixed with the help of special surfactants at a pressure of 200 bar to form a micro emulsion consisting of nanometer-sized droplets filled with CO₂ and encapsulated in surfactants. The pressure is then reduced, causing the CO₂ to expand and the droplets to become bubbles still in the nanometer range. At the same time, the polyurethane raw materials react to form a 3D polymer network that is a rigid polyurethane foam > [39].
FIGURE 22: Micrographs where the cell structure of conventional PU-rigid foams are compared with that of a PU-rigid nano-foams (on the right in figure) produced with the process based on the “Principle of Supercritical Micro Emulsion Expansion, see text [39].

The distribution of PU across the various main fields of application (in USA, year 2008) is represented by the figures reported in Table 2 [19].

It can be seen as building and construction, transportation and furniture and bedding represent the main sector of PU usage.

**TABLE 2:** Distribution of polyurethane according to the type of application field, USA, 2007-08 [19].

<table>
<thead>
<tr>
<th>Application</th>
<th>Amount of polyurethane used (millions of pounds)</th>
<th>Percentage of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Building &amp; Construction</td>
<td>1,459</td>
<td>26.8%</td>
</tr>
<tr>
<td>Transportation</td>
<td>1,298</td>
<td>23.8%</td>
</tr>
<tr>
<td>Furniture &amp; Bedding</td>
<td>1,127</td>
<td>20.7%</td>
</tr>
<tr>
<td>Appliances</td>
<td>278</td>
<td>5.1%</td>
</tr>
<tr>
<td>Packaging</td>
<td>251</td>
<td>4.6%</td>
</tr>
<tr>
<td>Textiles, Fibers &amp; Apparel</td>
<td>181</td>
<td>3.3%</td>
</tr>
<tr>
<td>Machinery &amp; Foundry</td>
<td>178</td>
<td>3.3%</td>
</tr>
<tr>
<td>Electronics</td>
<td>75</td>
<td>1.4%</td>
</tr>
<tr>
<td>Footwear</td>
<td>39</td>
<td>0.7%</td>
</tr>
<tr>
<td>Other uses</td>
<td>558</td>
<td>10.2%</td>
</tr>
<tr>
<td>Total</td>
<td>5,444</td>
<td>100.0%</td>
</tr>
</tbody>
</table>
The following data, concerning the USA market gives an idea of the importance of the role covered by the PU industry in the history of the chemistry.

< The Polyurethane Industry is a $41 billion enterprise and a key element of the U.S. economy. The Polyurethane Industry employs more than 263,000 Americans, operates in over 850 locations in the U.S., and helps create nearly 5 jobs for each job in the polyurethanes industry > [19].

It must be underlined that now a day over three quarters of the global consumption of PU goods is in the form of foams, with flexible and rigid types being approximately equal on the consumer market. This is testified by the pie chart below showed where the geographic distribution of world consumption of PU-foams is described [40].

**FIGURE 23:** Pie chart showing the geographic distribution of world consumption of PU-foams [40].

It must be also reminded as PU-based resins are also used as adhesives. Especially formulated PU adhesives are employed for bonding concrete, natural stones, blocks, bricks and pavers (see example in figure 24) [41].

Some of the properties presented by a commercially available PU-adhesive are hereafter summarized:

- Excellent for frost and thaw cycles;
- Works at above freezing temperature;
- Works on dry and damp surfaces for both concrete and natural stone;
- Fast Cure Time – Permanent Bond in 8-12 hours.
- Bond Strength – minimum 25% stronger than any competition.
- Resistant – against torsion and tension [41].
**FIGURE 24:** Strong polyurethane adhesives are especially formulated for bonding concrete, natural stones, blocks, bricks and pavers [41].
REFERENCES

- Mitsubishi Rayon Engineering Company Limited,
CHAPTER-TWENTY-FIRST

POLYURETHANES

B ) PROPERTIES OF POLYURETHANES IN RELATION TO MOLECULAR STRUCTURE, COMPOSITION AND PROCESSING- METHODOLOGIES AND TESTS FOR THE IDENTIFICATION OF PU IN ARTEFACTS

It was seen as according to molecular structure, composition, additives and processing methodology, it is possible to produce a variety of PU-materials characterized by different properties (see table 1 and 2), thus being capable to cover a large types and number of applications in many technological areas (clothing (Lycra fibers), automotive parts, footwear, furnishings, construction, paints and coatings and biomedical devices) [1].

PU is essentially used as:

--- Thermoplastics;
--- Thermosets;
--- Elastomers;
--- Foams;
--- Paints, coatings and adhesives.

**TABLE 1:** Polyurethanes with a wide range of properties can be produced [1].

<table>
<thead>
<tr>
<th>Polymer characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class (average Mw between crosslinks)</td>
</tr>
<tr>
<td>Elastomer 5000 g/mol</td>
</tr>
<tr>
<td>Thermoplastic 25000 g/mol</td>
</tr>
<tr>
<td>Rigidity (average Mw per branch points)</td>
</tr>
<tr>
<td>Semi-rigid 700-2500 g/mol</td>
</tr>
<tr>
<td>Flexible 2500-20000 g/mol</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Light 50-200 kg/m³</td>
</tr>
<tr>
<td>Medium 200-500 kg/m³</td>
</tr>
<tr>
<td>Heavy 500-700 kg/m³</td>
</tr>
<tr>
<td>Superheavy &gt; 700 kg/m³</td>
</tr>
<tr>
<td>Porosity (average diameter of cells)</td>
</tr>
<tr>
<td>Microporous 0.01-1 μm</td>
</tr>
<tr>
<td>Macroporous 1-100 μm</td>
</tr>
</tbody>
</table>
TABLE 2: According to processing methodologies (left column) PU-materials for various end-uses are produced [1].

<table>
<thead>
<tr>
<th></th>
<th>Foam/ 3D piece</th>
<th>Tubing</th>
<th>Coating</th>
<th>Adhesive</th>
<th>Fiber</th>
<th>Sheet</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection molding</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction injection</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>molding (RIM)</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blow molding</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compression molding</td>
<td>X</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Casting</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
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<tr>
<td>Embedding</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molding (potting)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent molding (dipping)</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
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<td>X</td>
</tr>
<tr>
<td>Banbury</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
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</tr>
<tr>
<td>Calendering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roll mill</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fiber spinning</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spraying</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Thermoplastic PU has a segmented linear chain structure, where the molecular copolymer-like basic structure can be represented as:

\[ P-(D(CD)_n-P)_n \]

Where P indicates the polyol (soft segment terminated with –OH), D the diisocyanate (capable to react with either the polyol or chain extender) and C is the chain extender (usually a low molecular weight molecule with either hydroxyl, or amine end groups) [1]. The hard segment sequence is represented by D(CD)_n.

When in the synthesis, multifunctional polyols and isocyanates are used then a branched or cross-linked structured polymer is obtained.

In segmented PU the end use properties are largely dependent upon the chemical nature and physical characteristics of the three components (P, D, and C) and as well as on the relative chain length of the soft and rigid blocks.

The molecular structures of some macro-glycols, chain extenders and diisocyanates, commonly used in the synthesis of PU, are reproduced in figure 1, 2 and 3 respectively [2].

The effect of the molecular structure of diisocyanate, macroglycol, and glycol upon the 300% modulus of a given PU is shown through the data reported in tables 3, 4 and 5 respectively. While the influence of the molecular structure of the macroglycol on the hydrolytic stability of the same PU is evidenced by table 6 [2].

From the data reported it emerges how strong can be the dependence of PU properties on the molecular nature of the above cited three components.
**FIGURE 1:** Some of the macro-glycols used for the synthesis of Polyurethanes [2].

**FIGURE 2:** Some of chain extenders used in the synthesis of polyurethanes [2].

**FIGURE 3:** Some of diisocyanates used in the synthesis of polyurethanes [2].
**TABLE 3**: Effect of diisocyanate molecular structure on the 300% modulus of a PU $^A$ [2].

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>300% modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-phenylene diisocyanate</td>
<td>23.4</td>
</tr>
<tr>
<td>$\text{O} = \text{O} - \text{C} - \text{N} = \text{O}$</td>
<td></td>
</tr>
<tr>
<td>4,4'-diphenylmethane diisocyanate (MDI)</td>
<td>13.1</td>
</tr>
<tr>
<td>$\text{O} = \text{O} - \text{C} - \text{N} = \text{O}$</td>
<td></td>
</tr>
<tr>
<td>1,3-phenylene diisocyanate</td>
<td>9.7</td>
</tr>
<tr>
<td>$\text{O} = \text{O}$</td>
<td></td>
</tr>
<tr>
<td>2,4-toluene diisocyanate</td>
<td>2.1</td>
</tr>
<tr>
<td>$\text{O} = \text{O}$</td>
<td></td>
</tr>
</tbody>
</table>

$^A$ Polymers made of 2.5 parts of diisocyanate, 1 part of poly(tetramethylene adipate) and 1.5 part of 1,4-bis(2-hydroxyethoxy) benzene.

**TABLE 4**: Effect of macroglycol structure on the 300% modulus of a PU $^A$ [2].

<table>
<thead>
<tr>
<th>Macroglycol</th>
<th>300% modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethylene adipate) glycol</td>
<td>6.2</td>
</tr>
<tr>
<td>Poly (tetramethylene adipate) glycol</td>
<td>9.0</td>
</tr>
<tr>
<td>Poly (hexamethylene adipate) glycol</td>
<td>8.3</td>
</tr>
</tbody>
</table>

$^A$ Polymers made of 2 parts of diphenylmethane-4,4'-diisocyanate, 1 part of macroglycol and 1 part of 1,4 butanediol.

**TABLE 5**: Effect of glycol structure on the 300% modulus of a PU $^A$ [2].

<table>
<thead>
<tr>
<th>Glycol</th>
<th>300% modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>6.9</td>
</tr>
<tr>
<td>Trimethylene glycol</td>
<td>8.3</td>
</tr>
<tr>
<td>Tetramethylene glycol</td>
<td>9.0</td>
</tr>
<tr>
<td>Hexamethylene glycol</td>
<td>7.6</td>
</tr>
</tbody>
</table>

$^A$ Polymers made of 2 parts of diphenylmethane-4,4'-diisocyanate, one part of polytetramethylene glycol and one part of glycol.
TABLE 6: Effect of the macroglycol molecular structure on the hydrolytic stability of a polyurethane [2].

<table>
<thead>
<tr>
<th>Macroglycol</th>
<th>Type</th>
<th>Tens. strength (N)</th>
<th>Elongation at break (%)</th>
<th>300% modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene adipate) glycol</td>
<td>Polyester</td>
<td>40</td>
<td>119</td>
<td>100</td>
</tr>
<tr>
<td>Poly(oxetane-methylene) glycol</td>
<td>Polyester</td>
<td>30</td>
<td>131</td>
<td>75</td>
</tr>
<tr>
<td>Poly(oxetane-methylene) glycol</td>
<td>Polyether</td>
<td>88</td>
<td>105</td>
<td>110</td>
</tr>
<tr>
<td>Poly(oxetane-1,2) glycol</td>
<td>Polyether</td>
<td>88</td>
<td>100</td>
<td>112</td>
</tr>
</tbody>
</table>

* Polymers made of 2 parts of diphenylmethane-p,p'-disocyanate, 1 part of macroglycol and 1 part of 1,4-butane diol; mechanical properties retained after 21 days in H2O at 70°C.

FTIR spectroscopy is a useful technique for assessing the molecular constitution of PU macromolecules. As can be seen from the comparison of the FTIR spectra reproduced in figure 4 by this technique it is possible to differentiate a PU-ether sample from a PU-ester based one.

**FIGURE 4:** The ATR-IR spectra of polyether-PU (R1) and of a polyester-PU (R2) are compared [3].
Some of the most significant IR absorption bands, as can be deduced from the ATR-IR spectrum of a polyurethane adhesive film shown in figure 5, are hereafter listed:

--- N-H stretching at 3350 cm\(^{-1}\)
--- C-H stretching of CH\(_2\) and CH\(_3\) groups at 2866 and 2933 cm\(^{-1}\)
--- C=O stretching at 1730 cm\(^{-1}\)
--- N-H bending at 1602 cm\(^{-1}\)
--- N-C=O symmetric stretching at 1531 cm\(^{-1}\)
--- C-O stretching at 1229 and 1178 cm\(^{-1}\)

The properties of PU strongly depend on the degree of cross-links induced during synthesis. This effect was clearly demonstrated by G. Gultekin et al. who prepared fatty acid-based polyurethane in presence or in absence of a crosslink-catalyst [5]. The scheme of the reaction is shown in figure 6. The structure of polymers was assessed by FTIR and NMR measurements (see figure 7 and 8), and this still indicates as these techniques are very useful for the identification of PU as component of a given object [5]. Moreover as will be reported in following paragraphs FTIR results to be effective also in determining the state of conservation and the degree of degradation of PU-based artifacts.
FIGURE 6: Reaction scheme followed in the synthesis of fatty acid-based polyurethane [5].

FIGURE 7: FTIR spectra of films of fatty acid-based polyurethane prepared in presence (WC) or in absence (NC) of a crosslink-catalyst [5].
The peaked structure of the $^1$H NMR spectrum of PU-WC, shown in figure 8, was explained as follows by G. Gultekin et al.:

The aromatic protons show peaks around 7.18–7.2 ppm and the peak at 2.26 ppm is due to the methylene group attached to the aromatic ring originating from TDI. The urethane N–H proton in TDI-based polyurethane is expected to show peaks between 9.47–9.1 and 8.43–8.38 ppm. The peaks do not appear in the NMR spectra. The absence of these peaks may be due to the existence of hydrogen bonding between C=O and N–H groups in the polymer chain [5].

Concerning the effect of cross-links on the properties of PU samples it was found that:

--- Tensile strength increases with the degree of cross-links, while the opposite occurs as far as elongation at breaks is considered;
--- Films synthesized in absence of crosslink-catalyst are more hydrophilic, and are capable to absorbed more water;
--- Samples synthesized in absence of crosslink-catalyst are characterized by a higher permeability [5].

Moreover it was observed as all films, prepared under the conditions of reference [5], were flexible, and resisted to acid solution [5].
Raman spectroscopy is also commonly used to recognize PU in artifacts. As shown by figure 9, the Raman spectrum of a PU, obtained by reacting castor oil and toluene diisocyanate (TDI), in presence of benzoyl peroxide (BPO) as catalyst, presents typical absorption peaks, whose wave length and intensity are strictly related to the molecular structure of the polymer resultant from polymerization procedure [6].

< The mainly observation from the spectrum (see figure 9) was the absence of $-\text{N}=\text{C}=\text{O}$ absorption at 2270 cm$^{-1}$. As expected, the amount of free isocyanate after the cure is very small, not detectable by the method. Although the typical $\text{N}$$-\text{H}$ urethane absorption appears very weak in Raman spectroscopy the $\text{C}$$-\text{N}$ axial stretch (1550 cm$^{-1}$) one confirm the urethane structure. It is possible also to identify $\text{C}=\text{C}$ and $\text{C}$$-\text{H}$ axial stretch absorptions of aromatic ring at the same wavelengths of infrared spectrum > [6].

\textbf{FIGURE 9:} Raman spectrum of a polyurethane sample obtained by reacting castor oil and toluene diisocyanate (TDI), in presence of benzoyl peroxide (BPO) as catalyst [6].

The presence of PU in artifacts may be also detected by means of miniaturized destructive tests. The procedure of one of the most suitable, “Dimethylaminobenzaldehyde test” is reported as follows in reference [7].

< \textbf{Application:} This is a test used to detect polyamides (nylon), polycarbonates, and, using acetic acid, polyurethanes. This result is obtained by the pyrolysis method.
\textbf{Materials Required:} Pasteur pipettes, cotton swabs, disposable droppers or capillary tubes, alcohol burner, plasticine, methanol, p-dimethylaminobenzaldehyde.
Solution 1 - 14\% (w/v) p-dimethylaminobenzaldehyde in methanol
Solution 2 - Concentrated hydrochloric acid, or concentrated acetic acid (for polyurethane)
\textbf{Procedure}
Heat-seal the capillary end of the pipette. Place the sample in the pipette. A sample the size of the dot on an “i” is amply sufficient. Place two drops of solution 1 and two drops of solution 2 on a cotton swab and place the swab in the pipette. Seal the pipette with Plasticine. Heat the sample over the flame.
If the cotton swab turns blue or red-violet, the sample is a polyamide or a polycarbonate, respectively. These two polymers are very different and cannot be confused. This test is thus very useful for distinguishing polystyrene or acrylic from polycarbonate or polyester from nylon. When performed with acetic acid, this test can also be used to identify polyurethanes. A yellow color indicates a positive test.> [7].

It is well known that the nature of soft segment influences the properties of PU. When the properties of PU based polyether polyols (PU-PET) and the PU based polyesters (PU-PES) are compared, the following conclusions arise:

1) In comparison with PU based polyether polyols, the PU based polyesters are more resistant to oil, grease, solvents and oxidation. They possess better properties related to: tension and tear strength, flex fatigue, abrasion, adhesion and dimensional stability.

2) On the other hand PU based esters are more sensitive to hydrolysis and microbiological attack.

3) The high mechanical properties of PU based polyester can be explained by the greater compatibility between polar polyester flexible segments and polar rigid segments, causing a slower phase separation resulting in better distributed small crystalline rigid blocks.

4) The hydrolysis stability of the ester linkage is inferior to that of the ether linkage in the polyethers, and residual esterification catalysts accelerate the hydrolysis. The hydrolysis resistance of the polyol polyester based PU increases with long chain glycols (1,6-hexane diol) or long chain dicarboxylic (dodecanedioic acid), as a result of the largest hydrophobic portion and small amounts of ester groups.

5) The hydrolysis stability can be improved with additives that react with carboxylic and alcoholic groups, formed during hydrolysis. These additives might be: oxazolines, epoxy compounds, aromatic polycarboxylates and aliphatic monoacids. TPU's based polyester polyols are stabilized by addition of 1 to 2% in weight of aromatic hindered carboxylic acids, that react with the acid generated by ester hydrolysis, which would act as a catalyst of hydrolysis reactions.> [8].

The microstructure at molecular level determines the thermal and mechanical behaviour of PU. The transitions induced by heating in the case of segmented linear thermoplastic polyurethane elastomers (TPU) may be easily evidenced by using techniques such as the dynamic mechanical analysis (DMA) and the differential scanning calorimetry (DSC).

From the DMA measurements, as shown by figure 10, it is possible to quantify the dependence of the tensile modulus (E') and the complex modulus (E'') on the temperature for a sample of TPU. From the diagrams, the following information can be derived [9]:

1) The material presents a glass transition, due to the phase including the soft segments, whose temperature corresponds to that of the maximum of the loss modulus E'' (around -50°C);

2) At higher temperature TPU sample shows a two-stage softening process, which is attributable to the melting of a partially crystalline soft phase, which follows a broad softening of an amorphous hard phase.> [9].

Man Jung Han et al. [10] prepared a series of TPU-elastomers in order to investigate the role of the microphase structure on their thermal behaviour. The segmented TPU-elastomers were constituted of methylene bis(4-phenylisocyanate) (MDI) and 1,4-butanediol as the hard segment and hydroxyl-terminated poly(ethylene adipate) as the soft segments. Samples with different hard segment contents (15-40 wt% ) were synthesised.

The DSC thermograms of samples of the various segmented linear thermoplastic polyurethane elastomers (TPU) prepared as above, with different hard segment content, are shown in figure 11 [10]. It can be seen that all samples show a distinct Tg, attributable to the soft segments, ranging between -35.5 and -32°C. The endothermic peaks around 39°C are accounted for by the melting process of a crystalline phase constituted by the aggregation of soft segments [10].
**FIGURE 10:** the tensile modulus (E') and the complex modulus (E'') of elasticity, for a sample of a commercially TPU, obtained from dynamic mechanical analysis (DMA), are reported as function of temperature [9].

**FIGURE 11:** DSC thermograms of segmented linear thermoplastic polyurethane elastomers (TPU) containing various hard segment content, see text [10].
In the thermograms of the TPU with higher hard segment content (30 and 40 wt%) the slope changes associated with the Tg of the hard segment phase occur at about 85°C. Moreover two broad endothermic peaks at temperatures above 140°C are also observed. These peaks are accounted for by a melting process of crystals composed of hard segment blocks [10].

Lifeng Wu et al. studied, in the case of PU-rigid foams, the influence of factors affecting the mobility of chain segments: crosslink density in the network structure, aromaticity (Ar, weight fraction of aromatic structures in the polymer matrix), polyisocyanurate (PIR) content, plasticizer concentration and index [11]. In this work for the measurements of Tg DMTA was used (values of Tg were determined using the peak of Tan(δ), a quantity that is given by the ratio between the two component of the dynamic modulus, G"/(or E") and G'(or E')).

The materials used in the preparation of various formulations are below listed:
< --- Blended polyols, prepared from individual propylene oxide (PO) to achieve certain average molecular weights (Mn) between cross-links and aromatic contents (Ar).
--- Two catalyst packages: catalyst I yields balanced gel and blow reactions, while catalyst II can further catalyze the PIR reaction.
--- All polyol blends were combined with RUBINATE® M polymeric MDI (NCOv = 31.2, Fm = 2.7) to make PU rigid foams.
--- FYROL® PCF (i.e., Tris(chloroisopropyl) phosphate, TCPP) was used as a plasticizer. It was obtained from Supresta.
--- A standard rigid foam silicone surfactant was supplied by Evonik Degussa > [11].

Some of the results attained are hereafter summarized.

1) The effect of crosslink density
From the diagrams shown in figure 12 it can be seen that the Tg of formulations with lower functionality (i.e. lower crosslink density) show lower Tg temperatures. The formulations 1, 2, 3 cited in the figure 12 have degree of functionality of 4.7, 4.0 and 3.0 respectively [11].
The values of Tg as measured from the peak of Tan(δ) resulted to be:
Formulation 1, Tg= 127°C
Formulation 2, Tg= 116°C
Formulation 3, Tg= 97°C [11].

2) Effect of aromaticity
The dependence of the tensile modulus (G') and of Tan(δ) on the temperature for sample of TPU-rigid foams prepared by using formulations with different aromatic content is shown in figure 13 [11]. Formulations labeled as 1, 4, 5, and 6 in figure 13 are characterized by value of the aromaticity of 29.5%, 31.0%, 33.5% and 36.3% respectively. From the comparison of the Tan(δ) curves it arises that the increase of aromaticity, at a constant crosslink density and at a fixed index of 100, raises the Tg of the PU-rigid foams from 127°C to 151°C [11].

3) Effect of plasticizer
The plasticizer TCPP (6 Tris(chloroisopropyl) phosphate) is widely used in the production of PU-rigid foams due to its effectiveness in reducing viscosity and in acting as flame retardant. The DMTA behavior of four formulations, prepared by adding into the polyol phase, 0 parts, 5 parts, 10 parts and 15 parts of TCPP, is compared in figure 14 [11].
From the trend of the curves of Tan(δ) it emerges that the value of Tg of the PU-rigid foams increases with the increase of plasticizer content (see diagram in figure 15) [1].
FIGURE 12: DMTA curves corresponding to PU-rigid foams produced by using three formulations leading to materials with different values of cross-link density (CD). In figure CD decreases going from formulation 1 to 3, see text [11].

FIGURE 13: DMTA curves corresponding to PU-rigid foams produced by using four formulations with different values of aromaticity (AR). In figure AR increases going from formulation 1 to 6, see text [11].
**FIGURE 14:** DMTA curves of PU-rigid foams produced from four formulations with different plasticizer content. The curves of Tan(δ) refer to formulations where the plasticizer content, from right to left, increases from 0 to 6.2%, see text [11].

**FIGURE 15:** Glass transition temperature (Tg) of PU-rigid foams as a function of weight fraction of plasticizer, TCPP (w/TCPP), added in the polyol phase [11].
The whole of data presented shows that the properties of PU may be strongly modified by changing their molecular structure and constitution. Such a possibility gave to the PU industry the possibility to produce PU capable to achieve desired end properties and then to commercialize systems tailored for a wide range of applications in many different sectors.

The degradation behaviors of PU systems against the various factors of degradation are also strongly dependent upon the molecular structure of their repeat units (i.e. chemical structure of the diisocyanates, of the polyols and the hard/soft segment ratio). Such an issue will be treated in the following chapter.
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CHAPTER-TWENTY-SECOND

POLYURETHANES.

C) DEGRADATION OF POLYURETHANES IN RELATION TO THEIR MOLECULAR STRUCTURE, COMPOSITION AND PROCESSING AND TO THE MAIN CHEMICAL, PHYSICAL AND BIOLOGICAL FACTORS-
STABILIZATION OF PU THROUGH THE USE OF ADDITIVES.

It was seen that commercial polyurethanes, very complex materials, are prepared essentially by condensation reaction between aliphatic or aromatic diisocyanates with ether/ester type polyols in presence of suitable chain extenders and catalysts. Thus the degradation behavior of PU, being strongly dependent upon their molecular constitution and structure, varies considerably from one formulation to another [1,2,3,4].

The most effective processes of degradation capable to induce changes at molecular level in PU systems,
--- Photo-Oxidation;
--- Thermo-Oxidation;
--- Hydrolysis,
are hereafter described.

1) PHOTO/TERMO-OXIDATION OF POLYURETHANES AND HYDROLYSIS

PU systems are capable to react under certain conditions with the oxygen. This degradation process, called “Autoxidation”, determines deep changes in the chemical, physical or mechanical properties of the PU-based resins polyurethane. Quite often, as can be seen by figure 1, this degradation process results in artifact discoloration and causes loss of physical properties [1,2].

\textbf{FIGURE 1:} <Polyurethane foam made with an aromatic isocyanate, which has been exposed to UV light. Readily apparent is the discoloration that occurs over time> [2].
In the case of polyether-based PU it was found that the **thermo-oxidation** starts essentially in the ether region of the macromolecules. The process, that proceeds according to a typical free radical chain mechanism, leads to chain scission reactions according to the scheme depicted in figure 2 [3].

**FIGURE 2:** Thermal decomposition of hydro-peroxides formed in polyether segment of PU [3].

The mechanism described in figure 2 assumes that formation of hydro-peroxides, derived from the polyether segments, following complex reactions between PU, previously formed radicals and oxygen, are thermally decomposed giving rise to different chain scission products [3]. The process, accelerated by traces of metal ion impurities (e.g., copper, iron), causes a fast drop off in the molecular mass [3].

Following **photo-oxidation** ( **Photo-chemically initiated oxidation** ) yellowing, cross-linking and a noticeable decrease in tensile strength and elongation at break are observed in Pu-based materials [4].

From literature data it emerges that, generally, aromatic PU are less stable against the combined action of light and oxygen than the aliphatic ones.

The following trends, have been established for the diisocyanate component respect to photo-stability:

- **Hexamethylene > Toluene > Diphenylamine**

On varying the diol component the light stability decreases in the order:

- **Polyester > Polyether > Polythioethers** [4].

480
As can be seen by the scheme of the mechanism regarding the photo-degradation of aromatic PU, shown in figure 3, chain scission occurs preferentially at the urethane links (i.e. N-C and C-O) [4].

![Diagram](image)

**FIGURE 3:** Simplified scheme for a general picture of the photo-induced degradation of a typical aromatic polyurethane [4].

- Polyurethane based on 4,4'-diphenylmethane disocyanate are the most unstable system. In this case oxidation of the polymer is believed to be due to the presence of benzophenone-type chromophore. On irradiation quinine-imides structure are responsible for the observed photo-yellowing. Polyurethanes, however, also contain high level of hydro peroxides and these again are intimately involved in photosensitized reactions in the polymers > [4].

According to reference [3], photo-oxidation is based also on free radical chain reactions, which involve the formation of hydro-peroxides followed by their disruption and formation of thermal and photolytic breakdown products. Moreover in the case of photo-oxidation it was observed that both aliphatic and aromatic segments of PU chains are vulnerable to free radical attack [3].

The reactions occurring during the photooxidation of MDI-based PU, involving just the MDI residues, are described through the scheme reported in figure 4 [3]. The degradation is favored by the fact that the hydrogen is easily abstracted. It can be seen that in the course of the process highly colored conjugated quinine-imides-type molecules are formed [3]. This finding accounts for the coloration observed in degraded samples.

- Aliphatic isocyanate-based PUs often yields less coloration than the corresponding aromatic PUs because of the absence of products absorbing above 400 nm. A PU soft segment containing a polyether macrodiol is less stable toward photo-oxidation than a polyester one of a similar molar mass > [3].

From above it results that commercial PU need to be stabilized not only against heat but also against UV-light.

Such objective is attained by the use of radical scavengers, e.g., phenol antioxidants or hindered amines (HALS), and UV absorbers, e.g., benzotriazoles and hydroxybenzophenones. Synergistic combinations of all three types of antioxidants (e.g., hindered phenol, high molar mass HALS and benzotriazole) should offer effective stabilization for PU > [3].
L. Irusta and M. J. Fernandez-Berridi investigated the photo-oxidative behavior of aliphatic segmented PU (ester and ether based) in order to assess the role of both the chemical structure (ether or ester) and molecular mass of the soft segment in the process of degradation [5]. The PU samples < were irradiated in an accelerated weathering device equipped with a xenon arc light source > [5]. The effects of degradation were assessed by FTIR and DSC techniques.

First of all L. Irusta and M. J. Fernandez-Berridi analyzed the photo-oxidation mechanism of the carbamate moiety in the case of linear non-segmented PU (LNS-PU). These materials were obtained < from 1,4-butanediol and hexamethylene disocyanate by precipititative hydrogen transfer polymerization > [5].

The FTIR spectra of LNS-PU, before and after irradiation are compared in figure 5. The most significant IR-characteristic band frequencies of the above PU are summarized in table 1 [5].

The entity of the modifications caused by irradiation at molecular level was assessed in reference [5] by analyzing the variations of the intensity and shape of some specific bands. The results of this analysis led to the following results:

--- A decrease in the intensity of the bands related to the stretching vibration of N-H groups (3320 cm\(^{-1}\)) and to the amide-II (1540 cm\(^{-1}\)), see figure 6. A decrease of the intensity of these bands indicates a loss of the urethane structure following irradiation.

--- A band broadening in the carbonyl stretching vibration region (1800-1650 cm\(^{-1}\)) with the appearance of a shoulder at 1755 cm\(^{-1}\) [5].

It must be pointed out that the amount of loss in FTIR intensity of the above mentioned bands resulted to be in the case of LNS-PU rather low [5].
**FIGURE 5:** FTIR spectra of samples of linear non segmented-polyurethane (LNS-PU) before (OH) and after (250 OH) of irradiation [5].

**TABLE 1:** FTIR band frequencies of polyurethanes with molecular structure described in reference (see text) [5].

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Relative intensity</th>
<th>Main assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3420</td>
<td>v, w</td>
<td>ν (N–H) free</td>
</tr>
<tr>
<td>3320</td>
<td>s</td>
<td>ν (N–H) associated</td>
</tr>
<tr>
<td>3050</td>
<td>m</td>
<td>Overtones of amide II band</td>
</tr>
<tr>
<td>1725</td>
<td>vs</td>
<td>ν C=O in ester</td>
</tr>
<tr>
<td>1701</td>
<td>sh</td>
<td>ν C=O associated in urethane</td>
</tr>
<tr>
<td>1584</td>
<td>vs</td>
<td>ν C=O associated ordered in urethane</td>
</tr>
<tr>
<td>1540</td>
<td>s</td>
<td>ν C–N + δ N–H (amide II)</td>
</tr>
<tr>
<td>1475</td>
<td>w</td>
<td>δ CH₂</td>
</tr>
<tr>
<td>1263</td>
<td>s</td>
<td>ν C–N + δ N–H (amide III)</td>
</tr>
<tr>
<td>1250</td>
<td>s</td>
<td>ν C–O–C in ester</td>
</tr>
<tr>
<td>1180</td>
<td>s</td>
<td>ν C–O–C in ether</td>
</tr>
<tr>
<td>1110</td>
<td>s</td>
<td>ν C–O–C in ether</td>
</tr>
<tr>
<td>773</td>
<td>w</td>
<td>δ oop in COO urethane</td>
</tr>
<tr>
<td>638</td>
<td>w</td>
<td>w (N–H) amide V</td>
</tr>
</tbody>
</table>

w = weak; m = medium; s = strong; vs = very strong; sh = shoulder;
ν = stretching; δ = bending; w = wagging; δ oop = out of plane bending.
According to the Authors <the results are consistent with a mechanism...where an induced oxidation on carbon atoms in a position to urethane N-H groups take place, leading to the formation of primary hydro-peroxy groups. These groups are likely to decompose into alkoxy and hydroxy radicals. The main route of evolution of this pair of radicals involves a cage reaction that leads to the formation of acetyl-urethane functions. The acetyl-urethane group is the responsible for the shoulder (1755 cm⁻¹) appearing in the carbonyl stretching vibration region. As conclusion photo-oxidation of aliphatic carbamate groups follows the induced oxidation mechanism....the oxidation extent being low> [5].

Linear segmented PU (LS-PU) were synthesized in solution by using a catalyzed pre-polymer technique based on the following reactants and solvents:
--- Polytetramethyleneoxide (Mw=650, PTMO650 or Mw=2000, PTMO2000), for the preparation of ether-based PU;
--- Poly (ε-caprolactone) (Mw=1250, PECA1250 or Mw=2000, PECA2000), for the preparation of ester-based PU;
--- Hexamethylene diisocyanate (HDI), for the synthesis of aliphatic PU;
--- Toluene diisocyanate (TDI), for the synthesis of aromatic PU;
--- 4,4′-methylene bis(4-phenyl diisocyanate) (MDI), for the synthesis of aromatic PU;
--- 1,4-Butan diol (BD) as chain extender;
--- Stannous octoate as catalyst;
--- Monochlorobenzene;
--- N,N′-dimethyl formamide [5].

Several LS-PU materials were prepared differing, as shown in Table 2, in soft segment molecular structure and length, and in % amount of hard segment [5].

**TABLE 2: Description and nomenclature of segmented-PU synthesized in reference [5], see text.**

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Chain extender</th>
<th>Soft segment</th>
<th>% Hard segment</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI</td>
<td>BD</td>
<td>—</td>
<td>100</td>
<td>HDI10BD</td>
</tr>
<tr>
<td>HDI</td>
<td>BD</td>
<td>PTMO650</td>
<td>46</td>
<td>HT6.46</td>
</tr>
<tr>
<td>HDI</td>
<td>BD</td>
<td>PTMO2000</td>
<td>22</td>
<td>HT2.22</td>
</tr>
<tr>
<td>HDI</td>
<td>BD</td>
<td>PECA1250</td>
<td>31</td>
<td>HCl31</td>
</tr>
<tr>
<td>HDI</td>
<td>BD</td>
<td>PECA1250</td>
<td>22</td>
<td>HCl2.22</td>
</tr>
<tr>
<td>HDI</td>
<td>BD</td>
<td>PECA2000</td>
<td>22</td>
<td>HC2.22</td>
</tr>
</tbody>
</table>

The effects of irradiation on the two samples of polyether based LS-PU (HT6.46 and HT2.22, in table 2) were evidenced through the comparison of FTIR spectra before and after exposure to the UV light. From the analysis of those spectra (see figures 6 ad 7) it emerges that:
--- Significant changes following irradiation are produced in IR spectra of both materials.
--- The intensity of the band centered at 1110 cm⁻¹, related to the stretching vibration of C-O-C groups of PTMO, strongly decreases.
--- No evidence of new peaks are observed [5].
**FIGURE 6**: Infrared spectra of the polyether-based PU, labeled as HT6.46, and whose molecular composition is described in table 2, before (OH) and after irradiation (407H) [5].

**FIGURE 7**: Infrared spectra of the polyether-based PU, labeled as HT2.22, and whose molecular composition is described in table 2, before (OH) and after irradiation (212H) [5].
Moreover, as can be seen by the diagrams in figures 8 and 9, the samples suffered a weight loss. Such a finding is accounted for by assuming that \( \text{weight loss is directly related to the photo-oxidation of ether soft segments in poly(ether-urethanes)} \) [5].

For sake of comparison in figures 8 and 9 the plots of the remaining weight loss of LS-PU materials based on 4,4’-methylene bis (4-phenyl disocyanate) (MDI) or Toluene disocyanate (TDI), against time of irradiation are also reported (samples are labeled as MT and TT respectively). It can be seen that LS-PU samples based on aromatic disiocyanates result to be more stable to the irradiation than corresponding aliphatic-based materials [5].

**FIGURE 8:** Remain weight after irradiation for different samples of polyether based LS-PU of aliphatic and aromatic nature.

Samples labeled as HT6.46, MT6.54 and TT6.47 correspond to polyether based LS-PU synthesized by using hexamethylene diisocynate (HDI), 4,4’-methylene bis (4-phenyl diisocynanate) (MDI) and toluene diisocyanate (TDI) respectively. The length of the soft segment (PTMO, Mw=650) is practically the same as well as the hard segment content (46%) [5].

From table 3 it can be seen that the Tg of the soft phase (Tgs) of samples of polyether based LS-PU strongly depend upon composition. The fact that in some sample the values of Tgs are higher than those of pure PTMOS phase (around ~90°C) indicates that a process of phase mixing occurs [5].
The degradation induced by irradiation on urethane containing segments was followed by plotting the normalized area of the amide II band as function of the time of exposure. It was found that the oxidation of the urethane group is higher in the formulation where the soft segments (PTMO) is present than in the case of non-segmented ones. On the other hand the oxidation magnitude of the urethane group increases as both molecular weight and % increases (> see figure 10) [5].

From the examination of the FTIR spectra of poly(ε-caprolactone) based aliphatic polyester urethanes (PECAPU), before and after exposure to irradiation the following information were obtained:
1) "There is no apparent change in the overall spectral bands even because from the spectra it is not possible to isolate the characteristic vibration bands of the ester groups" [5].
2) From the analysis of the dependence of the intensity of the Amide II band upon the time of exposure it emerges that PECAPU are more prone to degrade than LNS-PU
3) From the comparison of the behavior of segmented polyester and polyether based PU it can be seen that the degree of degradation of urethane groups results to be higher in polyether-PU than in polyester-PU (especially at longer time of exposure to irradiation) [5].

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TABLE 3: The glass transition temperature of the soft polyether segment for different samples of polyether based LS-PU of aliphatic (HT) and aromatic nature (TT or MT), see text [5].

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Soft segment</th>
<th>% Hard segment</th>
<th>Nomenclature</th>
<th>$T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI</td>
<td>PTMO650</td>
<td>46</td>
<td>HT6.46</td>
<td>-53</td>
</tr>
<tr>
<td>HDI</td>
<td>PTMO2000</td>
<td>22</td>
<td>HT2.22</td>
<td>-81</td>
</tr>
<tr>
<td>TDI</td>
<td>PTMO650</td>
<td>47</td>
<td>TT6.47</td>
<td>-19</td>
</tr>
<tr>
<td>TDI</td>
<td>PTMO2000</td>
<td>22</td>
<td>TT2.22</td>
<td>-75</td>
</tr>
<tr>
<td>MDI</td>
<td>PTMO650</td>
<td>54</td>
<td>MT6.54</td>
<td>11</td>
</tr>
<tr>
<td>MDI</td>
<td>PTMO2000</td>
<td>28</td>
<td>MT2.28</td>
<td>-72</td>
</tr>
<tr>
<td>—</td>
<td>PTMO650</td>
<td>0</td>
<td>PTMO650</td>
<td>-89</td>
</tr>
<tr>
<td>—</td>
<td>PTMO2000</td>
<td>0</td>
<td>PTMO2000</td>
<td>-93</td>
</tr>
</tbody>
</table>

TDI: toluene diisocyanate; MDI: 4,4'-methylene bis(4-phenyl diisocyanate).

FIGURE 10: Normalized absorption band of the Amide II band as function of the irradiation time for samples of polyether based NLS-PU (HDIBD) and LS-PU (HT22, HT6.46) (see text) [5].

From their studies L. Irusta and M. J. Fernandez-Berridi reached the hereafter reported conclusions:
--- <The results obtained support the photo-oxidation mechanism proposed in the literature for aliphatic PU: induced oxidation of the methylene groups in a position to the N-H groups> [5].
--- <Photo oxidation of urethane groups in segmented aliphatic polyether and polyester urethane proceeds by the same mechanism as in non segmented PU. However, the extent of the photo oxidation reaction is higher in segmented polyether and polyester urethanes than in non segmented ones> [5].
--- *The magnitude of the photo oxidation of urethane linkage is higher in poly-ether-PU than in polyester-PU* [5].

From the above cited findings it emerges as the chemical nature and molecular weight of the soft segment play an important role in controlling the photo-degradation behavior of the urethane linkages [5].

As already underlined the thermo (photo) oxidative degradation behavior of PU artifacts is strongly dependent upon the molecular structure of their repeat units (i.e. chemical structure of the diisocyanates and the hard/soft segment ratio).

The above statement was confirmed by the studies performed by V. Rek and others where the chemical and structural changes produced by the exposure to UV radiation to molecularly differing PU elastomer samples where compared [6].

**FIGURE 11, left:** FTIR spectra of aromatic isocyanate-based polyurethane elastomer PU-M4. (a) before and (b) after UV irradiation (see text) [6].

**FIGURE 12, right:** FTIR spectra of aromatic isocyanate-based polyurethane elastomer PU-M2. (a) before and (b) after UV irradiation (see text) [6].

In the above study samples of PU-elastomer were obtained according to a two-step procedure. First, prepolymers were prepared from poly(caprolactone) glycol (M=1250) by reacting with the corresponding isocyanate at NCO/OH ratios of 2/1 and 4/1. The prepolymers were then chain extended with 1,4-butandiol and the mixture was press-molded in a platen press at 100°C.

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One set of PU, labeled as PU-M2 or PU-M4, was based on an aromatic isocyanate (4,4'-diphenylmethane diisocyanate) (MDI), while another one, based on cycloaliphatic isocyanate (4,4'-dicyclohexylmethane diisocyanate) (H12-MDI) was named as PU-W2 or PU-W4 (the numbers 2 or 4 indicate values of the NCO/OH ratios of 2/1 and 4/1 respectively) [6].

The modifications in the chemical structure of the polyurethane elastomers as a result of UV irradiation, carried out using a quartz-mercury vapor lamp (W 400) at room temperature, were followed by Fourier Transform Infra-Red Spectroscopy (FTIR), see figures 11-12.

After irradiation the following changes were observed in the FTIR spectra of PU Elastomers based on aromatic isocyanate (see figures 11 and 12):

--- The absorption due to the carbonyl group in non-exposed polyurethane elastomers was split into two bands. The one at the lower frequency (1729 cm⁻¹) is attributed to the hydrogen bonded urethane carbonyl group while that at 1735 cm⁻¹ to the ester and non-bonded urethane carbonyl groups.

--- The ratio of absorptions at 1729 to 1735 cm⁻¹ increased with increasing hard segment concentration.

--- The resolution of the peaks from the carbonyl groups decreased as a result of UV irradiation.

--- The new band appeared at 3500 cm⁻¹ was assigned to the non-bonded NH group.

**FIGURE 13, left:** FTIR spectra of cycloaliphatic isocyanate-based polyurethane elastomer PU-W2. (a) before and (b) after UV irradiation [6].

**FIGURE 14, right:** FTIR spectra of cycloaliphatic isocyanate-based polyurethane elastomer PU-W4. (a) before and (b) after UV irradiation (see text) [6].

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--- The ratio of aromatic group absorption at 1600 cm\(^{-1}\) to the carbonyl group absorptions at 1729 and 1735 cm\(^{-1}\) decreased after UV irradiation as well as the ratio of caprolactone ester group absorption (1100-1300 cm\(^{-1}\)) to carbonyl group absorptions [6].

--- Both aromatic isocyanate-based polyurethane elastomers, PU-M2 and PU-M4, underwent a color change upon UV irradiation due to the transformation to quinoid structure [6].

The effects of irradiation on the FTIR spectra of PU- elastomers based on cycloaliphatic isocyanate (PU-W2 and PU-W4) shown in Figures 13 and 14, in reference [6] were summarized as follows.

< --- The absorption of carbonyl groups changed significantly with UV irradiation. New bands appeared in the range of 1640 to 1690 cm\(^{-1}\), indicating possible formation of amide and substituted amide groups.

--- Overall changes with UV irradiation were more pronounced with the cycloaliphatic isocyanate-based polyurethane elastomer with the higher hard segment concentration (PU-W4) than that with lower hard segment concentration (PU-W2).

--- A new band appeared at 3500 cm\(^{-1}\) in both elastomers after UV irradiation, similarly to the aromatic based polyurethane elastomers ....and can again be explained by the possible formation of non-bonded NH groups.

--- IR spectra of cycloaliphatic-based elastomers indicated that photodegradative processes occurred mostly on the hard segment structure [6].

The samples after degradation were also characterized by dynamic mechanical and differential scanning calorimetry in order to assess modifications induced by photo-oxidative degradative processes on thermal and mechanical behavior eventually related to structural and morphological changes associated with influence of the flexibility of the amorphous soft segments and their interaction with hard segments [6].

Some of the conclusions reached are hereafter summarized.

1) PU-elastomers based on the cycloaliphatic isocyanate (PU-W) result to be more affected by the exposition to UV even though they did not change color with UV irradiation.

2) In the case of PU-W samples, it was found that the degree of degradation is higher in samples with higher hard segment concentration. PU-W4 samples became brittle after 100 hours of UV irradiation.

3) PU-elastomers based on the aromatic isocyanate (PU-M) that show color changes following UV irradiation, they exhibited better retention of mechanical and thermal properties than those based on the cycloaliphatic isocyanate.

4) Resistance to photo-oxidative degradation was enhanced with increase of the hard segment concentration in PU-M samples.

5) The tensile properties of the PU-M samples did not change after 100 hours of exposure to UV irradiation.

6) The IR spectra of PU-M samples exhibited changes in IR-carbonyl group absorption in agreement with photo-oxidative degradation processes involving the hard segments.

7) The Tg of the soft segment increased with UV irradiation in PU-W4 samples; the opposite was observed in the PU-W2.

8) The un-aged PU-W4 samples exhibited two distinct glass transition temperatures, connected to the presence of segregated soft and hard segments. Following UV irradiation, mixing of these segments occurred [6].

The results attained showed that the photo-oxidative behavior of the investigated PU-elastomers results to be strongly depending on the chemical structure of the diisocyanate and the hard/soft segment ratio.
From literature data it results that

*The Hydrolytic degradation of PU* occurs, according to an auto-catalytically process, at the (amide) urethane linkage. The process (accelerated by acids and proteolytic enzymes such as the Hydrolases) as can be seen by the reaction scheme of figure 15, leads to chain scissions (monomer precursor are formed). This determines a molecular weight decrease followed by a rapid deterioration of mechanical properties [3].

![Figure 15: Hydrolytic degradation of PU backbone](image)

The above reported results combined with other findings published in scientific and technical literature lead to the conclusion that PU macromolecules, according to their polyester or polyether structure may be attacked by free radicals in combination with oxygen and or hydrolysis in combination with hydrogen ions and water on variety of reaction sites according to the scheme shown in figure 16 [7].

II ) STABILIZATION OF POLYURETHANES- ADDITIVES

To stabilize PU against the action of oxygen, light and heat several types of additives are commonly used. These additives according to their chemical structure and functionality act in different ways. The most common used additives to stabilize PU are hereafter briefly described.

1 ) Antioxidants — according to their mode in acting against degradation processes, and with reference to the cycles reported in figure 17, they are usually classified in:

--- *Primary Antioxidants* — mainly acting in Cycle 1 of Figure 17 as chain-breaking antioxidants, are sterically hindered phenols. Primary antioxidants react rapidly with peroxy radicals (ROO•) to break the cycle [1]. Irganox®1010 and Irganox 245, whose molecular structures are depicted in figure 18, are examples of primary antioxidants. *Secondary arylamines, another type of primary antioxidant, are more reactive toward oxygen centered radicals than are hindered phenols. Irganox 5037 is an example of a secondary arylamine* [1] (see molecular structure in figure 19).
--- **Secondary Antioxidants** - *acting in Cycle II of figure 17, react with hydroperoxide (ROOH) to yield non-radical, non-reactive products and are, therefore, frequently called hydroperoxide decomposers.* An example of secondary antioxidant is the Irgafos® 168 (see molecular structure in figure 20) [1].

2) **Light Stabilizers** - The most common used light stabilizers belong to the following families:

- Ultraviolet Light Absorbers (UVAs) - *< UV absorbers protect against photodegradation by competing with the polymer for absorption of ultraviolet light.... An ideal UVA should be very light stable, and should have high absorption over the UV range from 290 to 400 nanometers.* [1].

Molecules derivatives of benzotriazole, commercialized as “Tinuvin” belong to this class of UVAs (see examples in figure 21) [3].

--- Hindered Amine Light Stabilizers (HALS) - *Several theories have been advanced to explain the mechanism of stabilization by HALS, of which the most widely held involves efficient trapping of free radicals with subsequent regeneration of active stabilizer moieties.* [1]. Examples of Hindered Amine Light Stabilizers (HALS) commonly used for the stabilization of PU are shown in figure 22 [1,3].

---

**FIGURE 16:** The most probable sites of oxidative and hydrolytic degradation attack in polyether-PU (R₁) and polyester-PU (R₂) macromolecules [7].
FIGURE 17: The cycles describing the action of antioxidants in stabilizing PU against oxidation (see text) [1].
FIGURE 18: Examples of primary antioxidants (see text) [3,1].

FIGURE 19: The molecular structure of the Irganox 5057, an example of a secondary arylamine primary antioxidant (see text) [3].

FIGURE 20: The molecular structure of the Irgafos 168, an example of a secondary antioxidant (see text) [3].
FIGURE 21: Molecules derivatives of benzotriazole, commercialized as "Tinuvin" used as Ultraviolet Light Absorbers (UVAs), see text [3,1].

FIGURE 22: Examples of Hindered Amine Light Stabilizers (HALS) commonly used for the stabilization of PU [3,1].

Some of the effects that additives may have on some properties of thermoplastic-PU (TPU) are evidenced through the diagrams shown in figures 23 and 24 [1]. The results lead to the conclusion that:

<After 500 hours Dry Xenon exposure, all three UV absorbers (Tinuvin 571, Tinuvin 328, and Tinuvin 327) show significant protection of color and retention of original elongation and tensile properties > [1].

The Scanning Electron Microscope micrographs reported in figure 25 demonstrate <that a combination of a hindered amine (Tinuvin 765) and ultraviolet absorber (Tinuvin 328) can help protect the cell structure of a polyether polyurethane foam. Note that the cell structure of the stabilized foam looks similar to the unexposed foam even after 150 hours of Xenon exposure > [1].
**FIGURE 23:** Influence of the addition of additives on the discoloration of TPU plaques (1.5mm) exposed to the action of artificial light (see conditions in figure and text) [1].

**FIGURE 24:** Influence of additives on the tensile strength and elongation retention of TPU plaques (1.5mm) following exposure to artificial light (the arrows indicate the TPU control behavior) [1].
FIGURE 25: Surface micro-crazing of Foamed Polyether Urethane
during exposure to light in unstabilized and stabilized samples (see text).
Top-left- Unexposed sample, Magnification: 1,000X.
Top-right- Unstabilized sample. Exposure: 150 hours in Xenon Weather-
Ometer. Magnification: 1,000X.
Bottom- Stabilized sample. Exposure: 150 hours in Xenon Weather-
Ometer, magnification: 1,000X, stabilization system: 0.5% Tinuvin 328 +
0.5% Tinuvin 765 [1].

III) OTHER TYPES OF ADDITIVES FOR PU

The most widely used non-antioxidant additives are “Lubricants” and “Plasticizers”.

i) Lubricants— They are used to avoid the sticking of the highly viscous melt PU to the metal
surfaces of machinery in the course of processing. Now a day almost all commercial lubricants,
belong to one of the below indicated chemical families:

--- Amides;
--- Hydrocarbon waxes;
--- Fatty acids ester;
--- Fatty acids;
--- Metallic soaps [3].
Ethylene-bis-stearamide, whose molecular structure is described in figure 26, and used as a lubricant, is an example of compound characterized by a good balance of "internal" and "external" lubricating properties [3].

i) **Plasticizers** – They have essentially the function to enhance the degree of flexibility (reduce rigidity degree) of PU macromolecules by lowering their glass transition temperature (Tg).

The most used plasticizers are typically organic liquids belonging to the family of phthalate esters (see figure 26 for structure) [3]. Some of the problems concerning the use of plasticizers are so described in reference [3]:

![Chemical structure of some non-antioxidant (lubricants and plasticizers) additives for PU](image)

**FIGURE 26:** Chemical structure of some non-antioxidant (lubricants and plasticizers) additives for PU [3].

*When the polymer is heated in the presence of a plasticizer, an intimate mix of polymer and plasticizer is formed in the melt. On cooling of the melt, plasticizer molecules develop specific weak interactions (van der Waals forces) with the polymer chains. These plasticizer molecules are, therefore, relatively mobile and are able to migrate easily to the surface, with subsequent loss to the*
contact environment coupled with the loss of material flexibility. Leaching of plasticizer molecules become even more severe in applications which require the use of PU elastomers in tubings for transporting hydrophobic fluids. Since plasticizer molecules usually possess relatively long alkyl chains, they screen the polymer chains from each other, thereby preventing them from "re-forming" the chain-chain interactions that give the un-plasticized polymer its rigidity $> [3]$. 

The fact that in PU materials so many types of additives are used poses a severe problem when the conservation and maintenance of related artifacts is to be afforded. In such a contest sophisticated analytical instrumental methodologies need to be applied to identify, determine and characterize the large number of additives presents in commercial PU-formulations.
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CHAPTER-TWENTY THIRD

POLYURETHANES

D) DEGRADATION OF POLYURETHANE ARTIFACTS AND REMEDIES
SOME CASE HISTORIES

It was seen that commercial polyurethanes are offered to the users as thermoplastics, rubbers, fibers, flexible and rigid foams, adhesives and paints.

Many artifacts in PU, due to their intrinsic artistic, historical and design value are collected in several museums and private houses. For example in costume collections many items such as coats, jackets, belts, shoes, and purses are made starting from PU materials, which include, bonded fabrics, spandex, synthetic suede, leather look fabrics and water repellant materials[1].

Materials based on PU, as described in previous chapters, suffers degradation when are exposed to the action of light, heat, and chemicals. Moreover PU-materials, unlike most synthetic polymers, may be also vulnerable to biological deterioration by microorganisms such as fungi [1]. It is interesting to point out as in such a contest PU based on polyesters seem to be more susceptible than those based on polyether [2]. Moreover it was clearly established as PU-foams are more susceptible to degradation than mass PU. This behavior is accounted for by taking into consideration the fact that foamed materials present <a greater surface area for oxidation to take place and are frequently made by blowing air or nitrogen through the liquid polymer> [3].

When items fabricated from foamed-PU are coated or surface painted then their resistance against ageing is sensibly enhanced [3]. As matter of facts the surface layer in such objects acts as protective barrier against the action of various degrading factors.

The above conclusions were confirmed by the work performed at the “Netherland Institute for Cultural Heritage” on a sculpture entitled, “Still Life of Watermelons”, of Piero Giraldi (1967), made in PU-ether-foam based material [3].

By using infrared spectroscopic analysis it was demonstrated that the coated-painted areas resulted to have a better state of conservation in comparison to unpainted regions of the sculpture [3].

Piero Giraldi (1942, Turin, Italy), an Italian designer and artist, created many sculptures in polyurethane foam coated by colored paints. Examples of pieces made by this artist, exhibited in many museums of modern art and widely collected all around the world, are shown in figure 1 [4,5].

In reference [1] the most common symptoms of degradation observed in design valuable costumes PU-made are:

--- Discoloration
--- Cracking
--- Delaminating of layers
--- Distortion (bubbling) of the exterior fabric [1]

Moreover it was found that <Solvents used for dry-cleaning can soften adhesives holding the layers together. As the material breaks down it often becomes sticky due to plasticizers migrating to the surface. Plasticizers can stain adjacent materials and corrode metals......>
Deterioration of bonded fabrics usually occurs when the polyurethane foam starts to break down causing the backing to separate from the base fabric. Polyurethane foams can yellow, become brittle, and crumble. Multi-layered garments can be discolored if the underlying layer of polyurethane has yellowed [1].

![Figure 1](image_url)  
**FIGURE 1:** Pieces made by Piero Gilardi in PU-foam covered by colored paints at the surface.  

In reference [2] it was underlined as, following degradation/ageing generally PU-items stiffen becoming more brittle. Objects made in PU-flexible foams and PU-suede become friable and crumble [2].

*<PU-materials are subject to both oxidation and hydrolysis but, except under very moist conditions oxidation predominates and is accelerated by light and/or heat. A brown discoloration usually accompanies deterioration > [2].>*

In general it can be said that items made in PU, whatever the nature of the starting material is, are susceptible to chemical degradation resulting in discoloration followed by a loss of mechanical performances. The chemical composition plays also a very important role as already written. For example it was observed that PU fabricated by using aromatic diisocyanates result to be more vulnerable to oxidation [3]. *<Degradation can be accompanied by a pungent odor > [3].*

It must be still underlined that the primary cause of degradation of PU artifacts is related to oxidation processes, nevertheless especially in the case of polyester-based PU the exposition in environment with high value of relative humidity reactions of hydrolysis may occur. This process determines the breaking of primary and secondary bonds in PU macromolecules, which produces a sharp detriment in the physical properties of the material components [3].
Hereafter some examples of artifacts in PU showing various types and degrees of deterioration are presented and discussed as "Case History" suitable to get information about the best practices to be followed for conservation and maintenance of such kind of items.

1) The "Globe Chair"

The "Globe Chair" also known as the "Ball Chair" was designed by the Finnish designer Eero Aarnio. One exemplary was acquired by the Victoria and Albert Museum in 1969. After almost 40 year the state of conservation of the artifacts was described as follows in reference [6]:

< Now, several decades after manufacture, many of the modern materials used in the manufacture of the 'Globe Chair' have changed in their appearance and mechanical properties...... The chair therefore required radical treatment....... While the fibre glass reinforced polyester shell had remained stable with the external gel-coat suffering only minor abrasions, the appearance within the shell had changed dramatically. The interior had begun to hang limply rather than maintaining the crisp profile intended by Aarnio. The adhesive applied between the orange-red show cover textile and the foam under-upholstery had degraded and failed, leaving the textile unsupported, especially on the top interior of the shell where the textile hung down. The upholstery within the shell is lined with five concave segments or wedges of pre-formed polyurethane foam with a show covering of an orange, plain weave wool textile. This is stitched to a self piping on the inner rim of the shell with the underside of the textile adhered to the foam. The edges of the fabric covering the five segments overlap onto the underside of the foam and were adhered in place. Based on visual and ultra-violet light examination before treatment, the foam appeared to be merely held in place by compression of the foam segments. As the foam still maintains some flexibility when compressed and has not degraded into a powdery dust (which is the degradation typically seen in foams), it was decided that it should be retained and a treatment that might enhance its longevity be considered. Whilst being aware that the textile would outlive the foam indefinitely, we aimed to create an option enabling future re-treatment and the opportunity of removing degraded foam while retaining the show cover > [6].>

From the above analysis it was decided to undertake a deep direct restoration plan whose details, depicted by D. Melchar, N. Bamforth in reference [6], are hereafter literally reported:

< Based on the gathered information, we conducted informal testing using several recommended adhesives and methods. We experimented with two types of adhesives for the interface between the fabric and foam: the first was a 2:1 mixture of Lascaux 360 HV and 498 HV, thermoplastic acrylic adhesives, in test concentrations by volume of 50%, 25%, and 10% diluted in de-ionized water; (Lascaux 360 HV and 498 HV are dispersion of a thermoplastic acrylic polymer on the basis of methyl methacrylate and butyl acrylate. The two types 360 HV and 498 HV are thickened with acryl-buty1-ester ) [7] )

the second was Beva 371 film, a thermoplastic elastomeric polymer mixture

( BEVA is a registered trademark for a thermoplastic, elastomeric polymer mixture. BEVA® 371 was developed by Gustav Berger in 1970. It is composed of Elvax (ethylene vinyl acetate [EVA] copolymer), Ketone Resin N (polycyclohexanone), A-C copolymer (EVA), Cellolyn 21 (phthalate
ester of hydroabietyl alcohol and paraffin. BEVA® 371 is an opaque gel at room temperature that produces a matte, waxy finish. It has been used for relining paintings and as a consolidant for paintings, leather and textiles [8].

Impranil® DLV, a polyurethane dispersion, was tested as a consolidant for the foam

(Impranil DLV/1 is an anionic aliphatic polycarbonate-ester-polyether polyurethane dispersion; is suitable for the formulation of textile coatings for use in numerous applications [9].)

Our results provided us with the following information:
- Impregnation of the foam with Impranil DLV was a necessary step, otherwise the adhesives stuck either too well or not enough to the foam
- The Lascaux bond was very weak between the textile and foam
- Beva 371 film worked well in combination with the Impranil but was difficult to remove from the textile.

After these findings...a textile conservator, suggested that, in addition to coating the foam with Impranil, we should try conservation-grade nylon net as a carrier for the Beva. The addition of the net would aid removal of the Beva 371 film and thus help to reduce the adhesive residue left on the textile when it needs to be removed in future. This combination proved to be the most successful test we conducted. To initiate treatment, the textile was peeled back to the inner rim of the shell exposing the foam. The manufacturer’s adhesive between the textile and foam had degraded leaving the textile almost adhesive free. Fourier Transform Infrared Spectroscopy (FTIR)......on the original adhesive indicated that this was a neoprene (rubber based) adhesive, which degrades in the presence of oxygen. Based on this information, it was not surprising the interface had failed...... To facilitate the treatment, V&A Technical Services technicians built a cradle to support the shell and allow removal of the metal base plate, providing flexibility and accessibility to rotate the chair and attain the correct upholstered profile. It was decided to apply the adhesives in-situ so that the stitched edge of the textile around the inner rim of the chair would not need to be disturbed (Figure 2). Using this method, one foam wedge at a time could be worked on. To begin the multi-step process, the foam was coated with Impranil and allowed to dry (Figure 3). A template, based on the size of the foam wedges, was made to prepare a net and Beva film. This was first adhered together on a work surface with a heated spautula and barriers of Melinex film and then laid onto the foam. Darts had to be cut in the Beva/net layer to enable it to lay flat on the concave surface of the foam. It was then adhered onto the surface of the foam with a heated spautula and barrier of Melinex. After this application, the textile was then laid onto the Beva/net and heated with the spautula, but due to poor adhesive penetration into the textile there was an insufficient bond to hold the textile in place. To increase the adhesive bond, an additional layer of Beva film was then applied to the topside of the net. The additional layer of adhesive successfully held the textile in place resulting in a clean, crisp profile on the interior of the shell (Figure 4).

The original materials have been kept, the shell’s interior profile has been restored and the treatment executed anticipates the eventuality of the foam’s degradation and replacement while retaining the original show cover textile > [6].
FIGURE 2- Top-left: The 'Globe Chair', exposed interior, see text [6].
FIGURE 3-Top-right: Applying Imprani® DLV to the chair, see text [6].
FIGURE 4-Bottom: The 'Globe Chair', adhering textile to Beva net, see text [6].
2) The “Pratone”

The Pratone (figure 5), designed by Gruppo Sturm for Gufram (Italy, 1971), is an over sized large grass stars making up an artificial lawn where one can comfortably lie down. This accessory creates a fresh look to a room and also a relaxing armchair to lie back in. Made from expanded polyurethane and painted green in Guflac water washable paint [10].

It is to be pointed out as the Pratone belongs to a series of modern sculptural pieces made from polyurethane foam called “Multipli”. These artifacts are now a day on display in the most important museums of contemporary art and design all around the world [10].

The fundamental points of the Gufram philosophy are: research and innovation, quality, design. With an emphasis on creative freedom over the functional demands imposed by production, Gufram took part of the radical movements of ground breaking design with new materials. Gufram’s modern design objects show the many influences of pop art, conceptual art, illusionism, naturalism and modern art [10].

**FIGURE 5:** The “Pratone” designed by Gruppo Sturm for Gufram (Italy, 1971), made from expanded polyurethane and painted green in Guflac water washable paint [10].
Judith Butzer demonstrated that it was possible in 1999, after almost thirty years from its production, to provide suitable methodologies for the restoration of a Dusseldorf Pratone, manufactured in nineteen seventies, [11].

The coating, as it emerged from the analysis of the micrographs of the cross section (see figure 6, top-right) resulted to be constituted by three layers: A top transparent film, a green layer with addition of a white pigment or extender capable to <correct the irregularities in the surface of the dark green layer beneath> [11].

Moreover it was observed that <the adhesion between the bottom layer and the foam support is good> [11].

The phases concerning the restoration of voids with deep tears observed on the blades were described as follows (see figure 6 bottom, from left to right):

<...i) Filling with a foam filler. ii) A piece of gauze is fitted into the area of loss, supporting both, foam filler and iii) subsequent coating with a mixture of dry pigments, Plextol B500 and glass-spheres and iv) the final retouching> [11].

From the above reported cases it can be concluded that direct actions of restoration may be afforded with success in repairing damaged artifacts in polyurethane.

**FIGURE 6:** State of conservation of the Dusseldorf “Pratone”. Are evidenced the main operations of restoration performed (see details in the text) [11].
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http://www.stardust.com/pratone.html
CHAPTER-TWENTY FOURTH

GENERAL REMARKS ABOUT THE CONSERVATION OF PLASTIC OBJECTS.

Synthetic plastics due to the broad spectrum of properties they are capable to offer are extremely versatile materials. Since the beginning of the synthetic "Era" their demand increased rapidly becoming the most used materials in many applications.

<The development of the plastic industry has been a phenomenal episode in the history of materials science. With large scale development taking place only within the last 60 years, the use of plastics in product design & manufacture has spiralled at a rate unrivalled by conventional materials.

The range & types of plastics now available to the designer & engineer are greater than at any previous stage in the history of the polymer industry >[1].

It must be also underlined that plastics contributed to the development of decorative arts. As matter of fact, because they may be easily processed, colored, molded and shaped in a wide range of forms and structures plastics offered the opportunity to sculptors, artists, architects, and designers to produce objects characterized by novel artistic forms and functions (see examples in figure 1 and 2) [2,3].

FIGURE 2-right: Garden Egg Chair, Germany (designed, 1968, manufactured, 1971).
Materials and Techniques: Lacquered, molded polyurethane with synthetic textile upholstery over polyurethane foam padding [3].
Many classes of plastics are typically cheap, lightweight, readily molded and shaped into all kinds of forms and structures, and, since their introduction in the 1930s have opened up incredible new design possibilities for sculptors, architects, and designers [4].

It is well known, in such a contest, the significant role that plastic materials such as polyurethane, polyester and polyamide, in twentieth century fashion design and fabrics, earned [5].

It was also seen as in our time many artifacts, manufactured from formulations based on synthetic polymers, are more and more present in private as well as in public collections and museums being considered of cultural, historical and artistic value.

**FIGURE 3**: Artifacts in plastics showing signs of degradation (discoloration and yellowing).

**Top-left**: A piece of twenty-year-old polyurethane-based plastic. The plastic has yellowed significantly and lost flexibility since it was manufactured [6].

**Top-right**: Plastic discoloration in classic super-Nintendo machines [7].

**Bottom-left**: Telephone set showing plastic discoloration caused by exposure to heat and light overtime.

**Bottom-right**: The telephone set after restoration by using suitable repainting and special spray-on coating to prevent discoloration [8].
FIGURE 4:
Right- Discoloration observed in plastics of a computer mouse due to the presence of brominated flame retardants used as additives.
Left- The same object following restoration performed
<with the help of some UV light and Oxiclean in addition
to 3% hydrogen peroxide to > [9-a)].

Regrettably in many of the plastic artifacts, stored or on display in museums or in private house collections, clear symptoms of degradation (discoloration/yellowing (see figures 3 and 4), crazing and cracking (see figure 5, 6 and 7), warping, stickiness, the latter being essentially caused by the migration of plasticizers toward surfaces) are observed. Contrary to this some other plastic objects result to be quite stable showing no deterioration signs even after exposure to atmospheric factors [4]. Nevertheless it must be underlined that, as reported in figure 3 and 4, in some cases apparently effective active conservation treatments have been already undertaken [8,9-a].

Most of plastics especially in outdoors applications suffer the action of external degradation factors that leads to chemical and physical damages such as reduction in molecular weight and a lowering in mechanical properties as well as chemical modifications induced by the presence of reactive pollutants and chemical degradation caused by air-borne biological agents.

In the case of transparent artefacts weathering may reduce the transparency inducing surface opacity while in the case of pigmented objects discolouration was quite often observed.

Moreover it was seen that following exposure to natural outdoor weathering many plastic artefacts become brittle presenting a noticeable decrease in strength and in toughness essentially due to the breaking of macromolecular chains.

This effect of weathering that drastically reduces the performance of many polymers is, as a result, a very complex process whose mechanisms are not easy to be understood. Consequently appropriate non-destructive and effective tests capable to monitor, in situ, the early evolution of damages by following the variations in some of the material properties have to be still implemented. Moreover such a tests should help preferentially in to prevent damages thus avoiding the starting of synergetic effects of the various concomitantly acting factors of deterioration.
**FIGURE 5-LEFT:** Crazes formed in transparent polymers are easily observed with the use of backlighting methods. Visual inspection is the most commonly used technique for the early detection of crazing in polymers and composites. Visual inspection of transparent or translucent polymers should be conducted using backlighting. This causes diffraction of light from the sides of the craze allowing them to be observed more clearly [9-b].

**FIGURE 6-RIGHT:** Red dye penetrant used to expose hairline cracking around bolt hole in a plastic molding. Dye penetrants are widely used for failure analysis. However, care should be taken when using them for monitoring a component that is to remain in service as the penetrant can act as an ESC agent [9-b].

**FIGURE 7:** Transmission electron micrograph of a thin section through a craze in polystyrene showing fibrils that traverse the craze. The photo shows a high resolution microscopy photograph of a crazing crack (micron is about 50 times smaller than a hair diameter). The crack surfaces are connected with fibrils - i.e. groups of polymer chains that run across the crack and have not yet been broken [9-c].
The combination of techniques as infrared and Raman spectroscopy and gel permeation chromatography (GPC) are very effective in following alteration of the chemical structure in polymers induced by weathering (this includes an increase both in the concentration of carbonyl or C=C groups resultant photo-oxidation and in the degree of scission and/or cross-links).

From a study accomplished by Smithers Rapra [1] it was possible to conclude as degradation or deterioration processes in plastic products are essentially due <to the cumulative effects of synergies between creep, fatigue, temperature, chemical species, UV & other environmental factors> [1]. Moreover following the results attained in the course of the above mentioned study was possible to elaborate the chart, reported in figure 8, which highlights the relative weight that environmental stress cracking (ESC), fatigue, notched static rupture, thermal degradation, UV degradation & chemical attack may have in processes of deterioration of plastic-made objects [1].

It is interesting to point out as in some circumstances it can be possible to correlate the type of damage suffered by a plastic object with the modes and mechanism due to a specific acting factor of degradation. The results of this exercise are below reported [1].

<table>
<thead>
<tr>
<th>Mechanical Modes</th>
<th>Deformation &amp; distortion due to creep &amp; stress relaxation, Yielding, Crazing Brittle Fracture due to Creep rupture (static fatigue), Notched creep rupture, Fatigue (slow crack growth from cyclic loading), High energy impact, Wear &amp; abrasion. Thermal fatigue Degradation – thermo-oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Modes</td>
<td>Dimensional instability Shrinkage Combustion Additive extraction Solvation, Swelling, Dimensional instability &amp; additive extraction Oxidation</td>
</tr>
<tr>
<td>Chemical modes</td>
<td>Acid induced stress corrosion cracking (SCC) Hydrolysis (water, acid or alkali) Halogenation Environmental stress cracking (ESC) Biodegradation</td>
</tr>
<tr>
<td>Radiation Modes</td>
<td>Photo-oxidative degradation (UV Light) Ionising radiation (gamma radiation, X rays)</td>
</tr>
<tr>
<td>Synergistic Modes</td>
<td>Weathering – effects due to photo &amp; thermo-oxidation, temperature cycling, erosion by rain &amp; wind-borne particles &amp; chemical elements in the environment</td>
</tr>
</tbody>
</table>
The above conclusions in reference [1] are commented as follows:

*When analysing the key failure modes of plastics they can be broken down into the following categories: mechanical, thermal, radiation and chemical. Classification of failure mode by mechanism shows that mechanical failure is the predominant mechanism although it is often preceded by one or more of the other classifications* [1].

According to reference [1] damages in plastic materials are favoured by:

--- **Poor material** – this includes:
The substitution with a cheaper material, the use of the wrong grade of polymer and of pigments, fillers, lubricants or plasticisers.

--- **Poor Design**

--- **Poor processing** - this includes:
Use of inappropriate process equipment
Post-moulding shrinkage (see figure 9-a)
Warping / distortion
Degradation (process temperature too high, residence time in the barrel too long, shear heating)
Residual stress
Molecular orientation
Development of low or excessive crystallinity.

Plastic objects suffer the prolonged application of stresses cycle, which may produce dramatic mechanical degradation (see figure 9-b). In such a case the restoring of the functionality is only exceptionally attained. Thus the object can be only saved as it is in its present state of conservation in order to give evidence of a certain type of artifact, function or production process.
**FIGURE 9-a:** Optical micrograph, polarized light, showing a spherulite in a quenched film of a sample of poly[ethylene-block-(L,L-lactide)]. During quenching the polymer film shrinks. The colors and circular crazes are caused by the resulting tensions [9-d)].

**FIGURE 9-b:** Hard (polyurethane) shell of a ski boot broken by material fatigue.
The artifacts in plastics, of cultural value, are generally characterized by the hereafter reported peculiarities:

1) Most of them are manufactured by assembling parts constituted by different materials (other plastics, metals, wood, etc.), see figure 10-a) [10-a].
2) Plastic components are generally multi-component compounds, which include additives, pigments, dyes, and fillers.
3) The interaction between the different phases may give rise to unexpected harmful chemical and physical interactions between the various components.
4) The knowledge of the overall chemical composition of the artifacts may be not easily to be established even because, especially in the case of artistic pieces, sampling is restricted; thus non-destructive tests should be as a rule used. This means that most of the destructive traditional test used for polymer identification and characterization, based on the taking away of a tiny sample and dissolving, heating or decomposing it to perform the analysis have to be in principle avoided.

In the conservation of plastic artefacts great attention has to be paid to chemical nature and reactivity of additives (plasticisers and stabilisers, etc.) used as they possibly will induce degradation processes, which may influence the effectiveness of conservative procedures. This requires the necessity of the application of non-destructive methods of analysis suitable for the identification of the molecular structure of the additives most used in the past for the processing of polymers [11]. Modern methods of instrumental diagnostic have to be used and also implemented to afford the above mentioned critical points.

From the above critical issues it results as, in the case of plastic objects, proper conservation measures, which include: cleaning and maintenance procedures, direct restoration and inhibitive or protective actions, are not easy to be planned and accomplished. Moreover it comes out the necessity of the elaboration of more appropriate and suitable protocols for the preservation of artifacts in plastics in which best practices suitable to slow down the processes of degradation are established and described, taking into consideration the fact that in the manufacturing of objects a wide variety of polymers, having different characteristics and then degradation pathway, as well as many types of additives, are used. Thus it may be concluded that the conservation of artifacts in plastics, especially those of relevant artistic value (see some exemplary in figure 10-b) represents at the moment still a significant challenge for which large effort of research are needed.

< There is, therefore, a need for standards that will actively promote and encourage the maintenance and long term preservation of plastics artefacts > [5].
**FIGURE 10-a)**-Left: Muticomponent sculpture. “Reclaimed Objects Sculptures” by Sayaka Kajita Ganz. *For my sculptures I use plastic utensils, toys and metal pieces among other things. I only select objects that have been used and discarded.* [10-a].

**FIGURE 10-b)**-Right: An ethereal plastic sheet like a flying carpet [10-b].

**FIGURE 10-c)**

**Left:** Plastic bottle Chinese pagoda [10-b].

**Right:** Plastic bags filled with plastic bags, see text [10-b].
SOME GENERAL RECOMMENDATIONS CONCERNING THE CONSERVATION OF PLASTIC ARTEFACTS

It was already seen as in the course of the twentieth century synthetic polymers (i.e. bakelite, polyvinylchloride, polyurethanes, polystyrene, polypropylene, polyethylene and many others) were used to create objects, interesting from artistic or historical point of view, acknowledged as to be part of the world of cultural heritage. It was also pointed out as quite a number of these items have to face unpredictable rapid degradation phenomena.

According to the now a day’s policy of many museums it should be expected that the number of artefacts with plastic components collected will rapidly raise with time.

With the increase of artifacts entirely made by plastics or only containing part in plastics in museums or collections conservators have to face a wide range of problems connected with their preservation.

The proper conservation of these artifacts constitutes nowadays still a very complex challenge [12,13,14,15,16].

<...there is a lack of knowledge and agreement about the way we can exhibit, clean and store them in order to lower their deterioration rate>[13].

Hereafter some recommendations, aiming at defining the best strategies to improve preservation and maintenance procedures of plastics artifacts, in order to prolong their life, including measures suitable to evaluate and establish practices and risk related to the exhibition, cleaning and protection are suggested and discussed.

In the above context it must be still underlined as the availability of analytical techniques based on instrumental diagnostic suitable not only to define the chemical nature of material components of the artefacts but also to identify the types of damages and then assessing the state of conservation of such items is absolutely necessary. As matter of fact the knowledge of those characteristics represents a necessary background from which the most appropriate active and passive actions (including maintenance) to be undertaken to prolong the life time of those precious objects is strongly depending.

In planning proper conservation and maintaining procedures of plastic objects all conservators or curators have to pay attention to the fact that quite often the starting material is a multi-component compound with a very complicated composition. Thus the assessment of the chemical nature of all components, including polymer and additives used in the formulation should be preliminary accomplished.

Curators of collections of plastic objects had to recognize that plastics behave dissimilarly than traditional materials and, therefore, their conservation procedures had to be conceived on innovative criteria taking into consideration especially the below listed issues [17].

--- Plastics, extremely numerous and dissimilar, are, more or less, vulnerable to the action of degradation factors.
--- Malignant plastics (cellulose nitrate, cellulose acetate, polyvinylchloride, polyurethanes) induce injure to other materials following the emission of reactive products while undergoing degradation.
--- Plastics have a specific chemical composition based on a complex formulation of which polymers are the main components. Thus each one must be considered as an individual material with their own specific characteristics.
--- Plastics usually undergo < degradación in a more dramatic way than the more traditional materials. This is because the deterioration of plastics has a relatively long induction period followed by accelerating degradation. ...what looks in fine shape one day may be a pile of dust six months later > [17].

--- Contrary to what happens in the case of other type of materials it can be observed as in the case of plastics even < a relatively innocent treatment, e.g. swabbing a surface with solvent or adhering broken parts, may result in much more severe damage appearing at a later date > [17].

--- Generally degradation of plastics is related to irreversible chemical processes, which can hardly be inverted. Thus proper conservation actions may only have the goals of slowing down the rate of such phenomena. Of course the success of conservation procedures requires that they are to be applied as soon as the first signs of degradation appear. This means that suitable monitoring systems capable to call the attention to museum professionals have to be installed ( chemical and physical eyes and noses ).

--- The control of the environment, as well as the accurate choice of storage conditions is necessary for the preservation of plastics. < As commercial packaging systems are extremely expensive and often contain non-essential elements, a knowledge of the different degradation chemistries involved allows the most cost-effective system to be chosen > [17].

--- A strategy finalized at the looking into the long-standing effects of conservation treatments on selected degraded plastics has to be planned taking into consideration the fact that minimal interventive treatments, cleaning for example, are presently undertaken also in the case of some modern artifacts ( see the case of the pieces of pop furniture from the 1960s and 70s shown in figure 11 ) [17].

**FIGURE 11:** Modern plastic furniture from the Victoria and Albert museum collection on which minimal cleaning procedures are already applied [ 17].
**Guide lines aiming at define an overall approach for the conservation of plastic artefacts**

It is generally assumed that the modern approach to the conservation of plastic-made objects is essentially based on the following three main pillars:

--- Analysis of the state of conservation of the object and monitoring its evolution against time;
--- Application of suitable direct stabilization, consolidation and protective procedures;
--- Activation of inhibitive (non direct) preservation measures for protection and maintenance.

Some details about the various actions specific of each of the above single pillars are below reported.

I ) **Analysis of the state of conservation of the object and monitoring its evolution against time**

It is mainly based on the following actions:
1 ) Identification of the chemical structure of all the components (base-polymer, polymers, additives, fillers and pigments) of the formulation from which the objects was manufactured.
2 ) Recognition of the manufacturing technique applied.
3 ) Definition of age, use function and exposition to the action of adverse factors of degradation.
4 ) Searching for the most common signs of degradation (surface bloom, crazing or cracking, discolouration, surface tackiness, surface oiliness, stress or distortion, surface chalkiness, etc.) and assessing their degree and evolution with time in order to determine if the degradation is stabilized or still ongoing.

Concerning the identification of plastics it was found as many of the tests available <were found to have serious drawbacks which make them unsuitable for use by the conservator in the studio. As well as requiring toxic chemicals, many of the results are subjective. Most of the tests only appear to work when the identity of the material is already indicated in some other way. Testing completely unknown samples showed the results to be highly ambiguous> [17].

The analysis of material components requires the availability in situ of techniques such as X-ray fluorescence (XRF), optical microscopy, Fourier-transform infrared spectroscopy (FTIR), Raman microscopy, ultra violet, visible spectroscopy and others.

II ) **Direct stabilization, consolidation and protective procedures**

Stabilization of degraded plastics should be performed through active-interventive conservation methodologies. Active approaches, with the now days knowledge, are difficult to be accomplished. In many cases inhibitive non-direct treatments are at the moment preferred.

The reasons are related to the fact that due to the chemical specificity of most of plastic families it may occur that:
--- Cleaning agents, solvents, adhesives and consolidants may be the source of severe damages when applied to degraded objects made by plastics [18].
--- Coatings by adhering to plastics surfaces may cause the swelling, softening and/or the dissolution of the substrates thus altering the look of the items [18].

Transparent coating, based on low density polyethylene, LDPE, characterized by a lower hardness,
stiffness and strength than HDPE (high-density PE), and a higher ductility may be used as a surface protective coating for other plastics [19].

Transparent epoxy resins coatings, resistant to high temperatures/humidity, may be also used. Some of those formulations produces high strength, rigid, chemical resistant bonds, and adheres to similar and dissimilar materials such as metals, glass, ceramics, wood, vulcanized rubbers, and plastics [20].

Silicone Elastomer compounds, combining flexibility, high insulation properties and high temperature resistance are recommended for high performance sealing and joining of metals, plastics, electrical insulations, protective coatings and formed-in-place gaskets [21].

High performance adhesives, sealants, coatings, potting and encapsulation compounds and impregnation resins are commercialized by The Master Bond Inc. Company, < The product line offers over 3,000 grades of specially designed formulations of acrylcs, anaerobics, cyanoacrylates, epoxies, latex, polyamides, polyurethanes and silicone systems to provide an optimal solution for even the most extreme applications > [21].

A permanent protective coating technology based on polysiloxane inorganic compounds was commercialized as Ecolkote [22]. This technology has been developed to offer enhanced benefits in the areas of long term retention of cosmetic appearance, chemical resistant, ease of maintenance and, when used within the correct anti-corrosive environment, it offers the best available long term resistance to the corrosive damage that nature can inflict on metals, gel-coat, paint and wood even when exposed in the most aggressive environments [22].

![Diagram](image)

**FIGURE 12:** By introducing a siloxane functional group to an acrylic organic polymer a hybrid coating material can be obtained, see text [23].
FIGURE 13: Morphology of the organic-inorganic hybrid coating material (GLASCA), see text [23].

By introducing a siloxane functional group to an acrylic organic polymer, and by starting a sol-gel reaction at the said functional group, a hybrid coating material can be obtained. The method followed to synthesize such hybrid products is schematically delineated in figure 12. The product is commercialized under the trade name “GLASCA” [23].

FIGURE 14: The gloss retention of organic-inorganic hybrid coating material is compared with those of other type of protective agents, see text [23].
As can be seen by the micrograph shown in figure 13 the structure of such coating is characterized by the fact that the phases (organic polymer, siloxane inorganic polymer) uniformly disperses into nano order dimension [23].

From the diagrams shown in figure 14 it emerges as the organic-inorganic hybrid coating material presents a superior weather resistance and can be used for outdoor applications [23].

![Morphology of a nanotech-protective coating](image)

**FIGURE 15:** Morphology of a nanotech-protective coating [24].

Protective coating obtained through the use of nanotechnology has been recently developed. It was observed that protective coatings with a nano-morphology (see figure 15), present better physical characteristics being capable to make the material-substrate more water repellent, more resistant to scratch, dirt, oil, and easy to clean. This helps in a more correct preservation of the objects contributing to improve its life span [24].

Some of the protective coating methods above described can be effective in the case of plastic objects, nevertheless at the moment still much more research and experimentation need to be accomplished.

Concerning direct restoration techniques are concerned it must be also taken into the right consideration the fact that generally:

*< Deterioration of plastics cannot be stopped under the usual indoor climate conditions comfortable for people. Active preservation treatments such as applying protective coatings and paints are complex for technical and ethical reasons. Any coating which adheres successfully to a plastics surface must also soften the surface, thereby increasing the damage and altering the original appearance. This is unacceptable for museum objects > [12].>*

Many plastics may be attacked by a number of chemical substances, having various reactivity and functionality, which may produce also irreversible chemical changes and structural modifications. These are the reasons why in surface cleaning procedures all chemicals capable to act as stress cracking and/or as degrading agents have to be always avoided [14,15].

The problem concerning the choice of proper cleaning agents is particularly relevant when plastic artefacts made by amorphous polymers with a Tg higher than RT, and then in a glassy state, are concerned. As matter of fact in such a case stress-cracking, "silent killer process", occurs as a consequence of contact with substances such as, acids, alcohols, cosmetic creams, soaps,
oils, grease, etc., which may be active as stress cracking agents. It is well known that stress cracking is one of the most common causes of unexpected brittle failure of thermoplastics polymers known. Research has shown that the exposure of polymers to liquid chemicals accelerate the crazing process [16].

The Ray-Ran Company has developed a “Stress Cracking Apparatus” (see figure 16) [16]. The, designed in accordance with the ASTM D1693 test method, it is simple to use and an extremely cost effective method of determining a polymer material’s susceptibility to stress cracking when exposed to different environments such as soaps, wetting agents, oils and detergents. The material is cut to shape with the die cutter provided and notched and then the test sample bent into a "U" section to induce the required stress. The samples are placed into the sample holders which are then transferred to the glass test tubes. These tubes are filled with the selected environment and heated. At timed intervals the samples are checked for any cracks developing adjacent to the notch. The number of failures is recorded [16].

**FIGURE 16:** The “Stress Cracking Apparatus” developed by the Ray-Ran Company, see text [16].
III) Inhibitive (non direct) preservation measures for protection and maintenance

Most of the pollutants present in the environment (oxygen, water, gaseous atmospheric pollutants, liquid acids and alkalis, etc.), due to the chemical reactivity of polymers and additives, represents a potential factor degradation. Consequently modern diagnostics based on chemical analytical instrumental techniques should be used to determine the most suitable environment for single class of plastics collected and also to monitor its evolution against time taking into consideration the fact that some class of plastics following degradation emits by-products in the environment. Thus the composition and the concentration of such substances have to be also defined.

The conservation of plastic-based artefacts requires preventive actions, which essentially involve the introduction of chemical and/or physical devices capable in to keep under control and mitigate the effects of the environmental main degradation factors. The main goal of these protective measures will be then the reduction of the rate of the degradation processes.

Under such contest the main effective environmental factors needed to be inhibited and kept under control are:

--- Light;
--- Oxygen;
--- Humidity;
--- Temperature;
--- Ventilation;
--- Air pollutants and presence of chemicals as by-products of degradation processes.

The control of the atmosphere where object is forced to reside includes:

- environmental monitoring and advice;
- lighting and solar control policies and implementation;
- dust monitoring;
- technical examination of artifact constituents and response to environments;
- insect pest management;
- display cases [17-a].

As general rule plastic objects should be stored in cool (the temperature should be kept stable and never above 15°C), ventilated, dry, and dust free environment. Consequently humid or airless storage areas must be avoided [17-b].

The light used should be attenuated with the UV component filtered. It is a good practice to keep artefacts in plastics, when not in display, in almost dark places.

An environmental monitoring system, called “Object Centered Environmental Analysis Network”, <a radio network of data loggers spanning the Museum and its outstations, sending continually updated data (temperature, relative humidity, light, UV, flood) back to a central computer server was developed. The Museum (the Victoria and Albert Museum) is now using this technology and will be using state-of-the-art IT techniques to manage the data and allow a far greater level of access to this same data > [13].

The development of light dosimeters experienced at the Victoria and Albert Museums is shown in figure 17 [13].
Concerning the exposition to light the following recommendations were suggested by J. Morgan [5]:

--- <With those plastics most susceptible to photo-degradation (e.g. polyethylene, polypropylene, nylon, cellulose nitrate, cellulose acetate and perhaps toughened polystyrene) the level of illumination should not exceed 50 Lux. With most other plastics a maximum level of 100 Lux is considered acceptable, although the possible effect of light on colorants should also be taken into consideration.> [5].

![Image](image.png)

**FIGURE 17:** Light dosimeters being tested in the galleries of Victoria and Albert Museum, as part of the LiDo project [13].

In the case of humidity, assuming that the majority of plastics absorb moisture J. Morgan suggests:

< A stable relative humidity of approximately 55% appears satisfactory for most plastics. Although a lower level may be better for plastics susceptible to degradation by hydrolysis (e.g. cellulose nitrate, cellulose acetate and polyesters) > [5].

The problem of ventilation may be especially relevant when objects made by malignant plastics are taken into consideration. Such objects as already written have to be isolated in order to avoid the chemical contamination of other items stored in their proximity.

Of course in the case of malignant plastics suitable systems should be developed to buffer and trap the poisonous degradation products trying to reduce their emission in the surrounding atmosphere avoiding the presence of other objects in vicinity made by materials that may be attacked by the emitted products.

In the above circumstances, artifacts in flexible PVC, which release plasticizers and/or hydrochloric acid, must be stored far away from other objects made by materials, which are chemically sensitive to those reactive species. This especially includes items made on textiles, paper and metals [14,15].

In conclusion any malignant plastics (celluloid, cellulose acetate, polyvinylchloride, polyurethane, etc.,) as general rule have to be isolated from other materials to prevent their deterioration.
The protection of plastic items against the main environmental factors of degradation it can be conveniently accomplished by keeping those objects in a room or case with controlled atmosphere where special chemical devices suitable to remove, by adsorption or by neutralizing processes, the most important agents which give origin to damages [18,25].

<...tailor made scavengers such as activated charcoal or Ageless help to create a low oxygen environment. Ageless is a reactive powdered iron and is normally used to prolong the shelf-life of dry foods by absorbing oxygen. Epoxidised soyabean oil (ESBO), has also been tested with encouraging results as an acid absorbing coating on degrading cellulose nitrate > [25].

![FIGURE 18: Oxygen absorbers have as active component iron powder [26].](image)

Most oxygen absorbers are based on the use, as active component, of iron powder and a small quantity of water. In some cases the formulation may contain other ingredients to enhance effectiveness (see figure 18) [26].

The humidity is usually controlled by means of desiccants, which incorporate hygroscopic substance (i.e. silica gel). More sophisticated desiccants contains humidity indicators able to show, by color changes, the degree of water-saturation of the desiccant. One commonly used indicator is cobalt chloride (CoCl₂). Anhydrous cobalt chloride is blue. When it bonds with two water molecules, (CoCl₂·2H₂O), it turns purple. Further hydration results in the pink hexaaquacobalt (II) chloride complex [Co(H₂O)₆]Cl₂ [27] (see figure 19 and 20).

Epoxidised soyabean oil (ESBO, as shown by figure 21 are epoxidized glycerol fatty esters [28].

Environmental air pollution monitoring devices suitable to notice the presence of specific chemicals even at small concentration and/or capable to detect the by-products of degradation processes are strongly welcomed. Research effort in such a contest will be highly appreciated by curators.

In deciding the best conditions which have to be chosen for a place where objects in plastics have to be stored it must be taken into consideration the facts that those conditions may suit well for a certain class of plastics and not for others.
<It is most unlikely that the best environmental conditions can be provided for every object in a collection...It will not be possible...to provide ideal conditions for storing and displaying all plastics> [5].

**FIGURE 19-20:** Left, typical silica gel desiccant device. Right, more sophisticated desiccants contain humidity indicators able to show, by color changes, the degree of water-saturation of the desiccant [27].

**FIGURE 21:** Molecular structure of epoxidised soya bean oil. They are epoxidized glycerol fatty esters, see text [28].
Particularly difficult appears to be the finding of the best environmental conditions when the artefacts are manufactured by using dissimilar type of plastics and materials. In such a case the chosen environment will be a compromise which takes into consideration the characteristics of the various components as far as degradation behaviour is concerned. Of course the negative synergies which may arise from the chemical and/physical interactions between contaminants produced in the course of degradation by the different materials have to be taken also into a proper account.

It was already underlined as any modern approach to the conservation of plastic artefacts cannot be effective without the availability and the support of proper methods of “Analytical Chemistry Diagnostics” [11]. As matter of fact the appropriate applications of these instrumental analytical procedures gives the opportunity to answer to the following questions:

1) **What is the nature of the plastics which are the main components of the artifacts in the collection?**

   This includes the knowledge of:
   --- Overall composition and chemical structure of components, which constitute the items.

2) **What is the condition of the plastic artifacts stored in the collection?**

   This includes the knowledge of:
   --- Type of damages, including still actives factors;
   --- Mechanisms of degradation.

3) **Are there degradation products (solid, liquid, gaseous) emitted by polymer objects during storage and what are the risks and damages they may cause?**

3) **Should the conservation being based on active-direct actions (cleaning and consolidation) or inhibitive non-direct procedures are sufficient?**

From another side, in case of active or interventive conservation approaches proper methods of “Analytical Chemistry Diagnostics” give the possibility to characterize the:
   --- Molecular structures, the reactivity and compatibility of materials used;
   and to assess the:
   --- Durability, the reversibility and environmentally sustainability of the procedures applied.

In case of inhibitive conservation approach effective methods of chemical instrumental analysis needed in order to weigh up the development on time of Exogenous Factors of Degradation:
   --- Temperature, humidity, oxygen, light, chemical pollutants,

present in the storage or display environment allowing thus the monitoring and the correlation between damages and time.

As previously underlined analytical instrumental techniques are also very effective in defining the “Malignant” nature of plastics such as celluloid, cellulose acetate, polyvinylchloride, polyurethanes and others.
By their application it is possible to assess the origin, the chemical structure and the reactivity of the corrosive products emitted in the environment following internal degradation processes (i.e. hydrogen chloride, nitric acid and acetic acid in the case of polyvinylchloride, celluloid and cellulose acetate respectively).

Polyurethane foams are widely present in museum collections either as part of the artifacts, or as a material for their conservation. Unfortunately it was observed as many of PU foam artifacts are in poor condition and often exhibit specific form of damages. Such materials are very difficult to be preserved and protected (see figure 22 and 23) [29,30].

A. Lattuati-Derieux, S. Thao-Heu and B. Lavédrine, in a quite recent investigation, were able to demonstrate as by using procedures based on attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and non-invasive headspace solid-phase micro extraction coupled with gas chromatography and mass spectrometry (HS-SPME-GC/MS) it was possible to evaluate the chemical nature of the volatile fractions emitted by PU foams following degradation caused by some environmental factors (i.e. humidity, temperature and daylight) [31].

In this paper, the formation of alcohol and acid raw products for polyester-based polyurethane PU(ES) and glycol derivatives for polyether-based polyurethane PU(ET) during natural and artificial ageing is confirmed. These main products can be considered as degradation markers for PU foams. <Results show that artificial and natural ageing provide similar analytical results, and confirm that the dominant degradation paths for PU(ES) and for PU(ET) are hydrolysis and photo-oxidation, respectively. Lastly, we highlight that non-invasive HS-SPME-GC/MS analysis allows distinguishing between PU(ES) and PU(ET) at any point of their degradations.>

The above results lead to the conclusion that PU-foams have to be considered as part of malignant plastics, due to the emission, following degradation, of reactive volatile organic compounds (alcohol and acid raw products for PU(ES) and glycol derivatives for PU(ET)) [31].

Thus it may be conclude as in the case of both, Preventive or Inhibitive and Active or Interventive approaches [18], chemical non destructive analytical instrumental procedures represent, now a day, a non-replaceable tools for the conservation of plastic artefacts [32].

It must be also recognized as research and studies still seem necessary to evaluate the applicability of new appearing non destructive and in situ analytical methods for the assessment of the state of conservation of objects stored in museums and for the estimation of the benefit of a micro environment to improve artifact conservation [33].

The overall topics treated in the present volume leads to the conclusion that under the present time unfortunately it must be recognized that more information and research efforts, concerning the procedures most suitable for a safe exhibition, cleaning and storing of plastic items, which are capable to lower their degradation rate, are still needed.
This is especially imperative in the case of art museum collections where artifacts made by using artificial polymers ( cellulose nitrate, cellulose acetate ) and synthetic polymers ( polyvinyl chloride, polyurethane and others ), which are most sensible to degradation, behaving also as malignant plastics, are collected [32].

As the number of objects manufactured in plastics collected and stored in museums is continuously rising, conservators have to face a wide range of problems connected with their maintenance and protection. The acquisition of a more appropriate background of knowledge relating to the best practices for both preventive and interventive conservation treatments effective in extending significantly the lifetimes of plastic-based components represents still today a challenge for all curators and scientists.

At moment, based upon present understanding it can be concluded that to preserve plastic artifacts with artistic and historical value a drastic implementation of investigations finalized at getting more suitable guidelines seem to be still considered highly necessary.
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