

# Synthetic Materials Used in Conservation

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## Introduction

As the most perplexing problem confronting a conservator when using synthetic materials must be the selection of a suitable polymer for a particular application, this paper will be devoted mainly to a discussion of these materials. Other synthetic materials which are not polymeric will be treated towards the end of the paper. Before treating specific polymers it is necessary to know a few general facts about them.

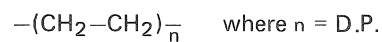
Synthetic polymers (which also can be described as resins, macromolecules or polymeric compounds) are large organic molecules that are formed by repeated chemical reaction that joins small molecules together. These small organic molecules are called "mers" or "monomers". The resulting polymer can be classified into two broad groups according to the physical properties of the material. These groups are called "thermoplastic" and "thermosetting".

## Thermoplastic Polymers

Thermoplastic polymers are those polymeric materials that can be made to flow on the application of heat and pressure. On cooling, the polymer exhibits similar properties to those it had before heating. The cycle of heating and cooling may be repeated many times without the properties of the polymer being changed.

The important structural feature of these thermoplastic polymers is that the monomer units have joined to give long chains; the chains may be branched but are not joined together. The number of monomer units that have got together to form one polymer chain is called the "degree of polymerisation" (abbreviated to D.P.). This number may range from 500 to 100,000 for a particular thermoplastic. In order to envisage the shape of a thermoplastic polymer molecule I will take polyethylene

as an example. Polyethylene has the structure:



If a linear polyethylene molecule with a D.P. of 2,000 (a modest sized polymer) is magnified 100,000,000 times, it would be 66 feet (2,000 cm) long but only 3/8 inches (1 cm) wide<sup>1</sup>. Thus it can be seen that a thermoplastic molecule is very long compared to its cross-sectional area. The important physical properties of thermoplastic polymers, especially when used in conservation, are the solubility of the resin and its glass transition temperature.

## Solubility of Thermoplastic Polymers

Thermoplastic materials are, generally, soluble in organic solvents. This solubility decreases as the D.P. of a particular polymer increases. The viscosity of a polymer solution increases as the D.P. increases (Table 1). In order to overcome the problems of insolubility or very high viscosities when using high D.P. thermoplastics, polymer chemists have prepared these resins as emulsions in water (see "Thermoplastic Emulsions").

Important for the conservator is the property of a thermoplastic to be able to be dissolved in the solvent of application after the solvent has evaporated. Thus if a mistake is made the resin can be removed.

## Glass Transition Temperature

The glass transition temperature ( $T_g$ ) is the temperature below which the polymer is a rigid, glassy solid and above, it exhibits soft, "rubbery" properties. The temperature at which this transition occurs is characteristic of a particular polymer and varies little with increase in D.P. (see Table 1 and Table 2).

Table 1

The effect of degree of polymerisation upon glass transition temperature and viscosity of poly (vinyl acetate).<sup>2</sup>

D.P.	T <sub>g</sub> (°C)	Viscosity*
150	16	1.5
240	17	2.5
600	21	7.0
1,200	24	15.0
1,900	26	25.0
4,000	27	60.0
7,000	28	100
20,000	29	800

\*Viscosity is given in centipoises of an 8.6 percent solution of benzene.

Table 2

The T<sub>g</sub> of some common thermoplastic polymers.

Polymer	T <sub>g</sub> (°C)	Reference
Polyisoprene	-75	3
Poly(ethyl acrylate)	-22	4
Poly(vinylidene chloride)	-17	3
Poly(vinyl butyral)	49	3
Nylon 6-6	50	3
Poly(vinyl alcohol)	85	3
Poly(methyl methacrylate)	105	4

The importance to the user of T<sub>g</sub> is that if a polymer is required with flexible properties, for example for use as an adhesive, the resin should have a T<sub>g</sub> well below ambient temperature. If the polymer has a T<sub>g</sub> above ambient, the T<sub>g</sub> can be lowered by the addition of plasticisers (see section on "Plasticisers").

### Copolymers

Up to now only thermoplastic resins that are formed by one type of monomer reacting have been discussed; these are called "homopolymers". It is a common practice, however, to use more than one monomer in the preparation of these polymers. The resulting polymer is described as a "copolymer". These materials are made to modify the properties of a particular polymer, for example to lower the T<sub>g</sub>, to obtain better solubility, or to improve durability.

Copolymerisation greatly increases the range and properties of thermoplastics available; not only the types of monomers can be varied but also the actual quantity of each monomer on the chain may be changed.

### Plasticisers

There are two ways a thermoplastic can be made more flexible (or the T<sub>g</sub> lowered): by internal or external plasticisation.

*External Plasticisers.* External plasticisers are high boiling liquids which are added to a rigid thermoplastic to lower the T<sub>g</sub> by acting as a lubricant between polymer chains. The plasticiser generally has some solvency for the polymer and is added at about 30% by weight of the polymer. The use of external plasticisers has two serious drawbacks when used in conservation. The most significant problem is that the plasticiser will evaporate after a period, even though it has a high boiling point, causing the resin to become brittle. The other disadvantage occurs due to initial migration of the plasticiser to the surface producing a "waxy" surface and making adhesion difficult.

Advantages of external plasticisers are reported<sup>4</sup> to be (a) better release of solvent from thermoplastic solutions containing plasticiser than from solutions without plasticiser and (b) that resins that have been flexibilised in this manner are able to be used over a wider range of temperatures than with the use of internal plasticisers. As these advantages do not outweigh the disadvantages, the conservator should be wary of formulations that contain external plasticisers, and avoid using them if possible.

Many chemicals are used for external plasticisers. They range from esters of phthalic, phosphoric, sebacic or adipic acids to low molecular weight polymers and chlorinated paraffins.

*Internal Plasticisers.* So-called "internal plasticisation" is simply the lowering of the T<sub>g</sub> of a rigid thermoplastic polymer by copolymerisation with a more flexible monomer. As the flexibilising agent is part of the polymer chain, the resin will retain its properties over the whole life of the copolymer. It is not necessary for the more flexible copolymer to be a different chemical type than the rigid polymer. The T<sub>g</sub> of different acrylate polymers are given in Table 3. It can be seen, therefore, that copolymerisation offers to the conservator a better method of obtaining flexibility than using external plasticisers.

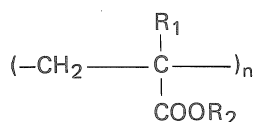
### Thermoplastic Emulsions

It has already been mentioned that thermoplastics with high D.P.s show decreased solvent solubility (or an increase in viscosity). To overcome this tendency and to avoid the use of potentially toxic solvents, polymer chemists have developed water emulsions of thermoplastics. The viscosity of these materials does not depend upon the D.P. of the polymer but on the size of the polymer particle that is emulsified.

Table 3  
The  $T_g$  of acrylic polymers<sup>5</sup>

Polymer	R <sub>1</sub>	R <sub>2</sub>	T <sub>g</sub> (°C)
poly(methyl methacrylate)	-CH <sub>3</sub>	-CH <sub>3</sub>	105
poly(ethyl methacrylate)	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	65
poly(n-butyl methacrylate)	-CH <sub>3</sub>	-C <sub>4</sub> H <sub>9</sub>	22
poly(n-hexyl methacrylate)	-CH <sub>3</sub>	-C <sub>6</sub> H <sub>13</sub>	-5
poly(methyl acrylate)	-H	-CH <sub>3</sub>	-9
poly(ethyl acrylate)	-H	-C <sub>2</sub> H <sub>5</sub>	-22
poly(n-butyl acrylate)	-H	-C <sub>4</sub> H <sub>9</sub>	-56
poly(2-ethyl hexyl acrylate)	-H	-C <sub>8</sub> H <sub>17</sub>	-70

The general formula of a polyacrylate is given by:



From the foregoing it might be inferred that emulsions consist simply of polymer dispersed in water. This is not the case. In practice they have a large number of components. For example a typical emulsion may contain, besides the polymer or copolymer, and water (which is de-ionised to increase the stability of the emulsion), surface active agents, protective colloids (to produce stable emulsions), buffers (to produce a stable pH) and preservative. Because the vehicle for the polymer is water, the preservative is necessary to prevent biological degradation of the surface active agents and the protective colloid as water-soluble cellulosic substances (for example starch) have been used. Some emulsions are prepared using certain polyacrylates or polyvinyl alcohol as the colloid. These emulsions would be less susceptible to biological action before and after application.

Although the polymer content of resin emulsions ranges from 40 to 60%, the expense of shipping water has resulted in a number of firms preparing them in Australia. The conservator should be able to obtain information about the types of copolymers, whether an external plasticiser has been used, and to select a protective colloid that is not susceptible to attack by fungus.

### Thermosetting Polymers

Polymeric resins that cannot be melted or made to flow by the application of heat or pressure are classified as thermosetting polymers. They are

formed when linear polymer chains join together or cross-link, to produce dense, three-dimensional networks where all the monomer units in the sample are coherent. It should be pointed out that there are degrees of cross-linking; natural and synthetic rubber are cross-linked at much wider intervals than thermosetting polymers. This light cross-linking acts as only a constraint on the main polymer chains and produces the elastic properties of rubber. If rubber is intensely cross-linked "hard" rubber or ebonite results.

The important physical properties of a thermosetting polymer are its insolubility in organic solvents, its hardness and toughness. The conservator has to be cautious in using these polymers for once formed their intractability makes them extremely difficult or impossible to remove, if a mistake is made.

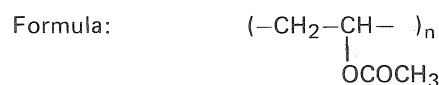
The final cross-linked polymer, being insoluble, cannot be applied from a solvent. The resin must be made in situ. The thermoset may be prepared in one of two ways. The first method which is the more common involves the formation of a "pre-polymer" which is, normally, a linear (thermoplastic) with a low D.P. and is therefore readily soluble. Prepolymers are designed to react further with a monomer, or with themselves, to form the thermosetting polymer. The second method is to form the polymer entirely from monomers.

### Specific Polymers

#### Vinyls

This group includes poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl acetals), polystyrene, acrylates and methacrylates. They are all thermoplastics and are available to the conservator either as powders or granules which may be dissolved in a solvent, as solutions, or emulsions. All these polymers give a clear resin.

#### *Poly(vinyl acetate) (P.V.A.)*



Properties: As the  $T_g$  is around ambient temperature the D.P. of the polymer will predetermine its use. The resin is stable to light (does not "yellow"), but can hydrolyse with moisture under slightly acid or alkaline conditions. The polymer is able to support the growth of mould if nutrients are available, mainly due to the water permeability of the polymer.

Solubility: As the polymer is an ester it is very soluble in ester solvents (polymers are most soluble in solvents that are similar to the polymer in chemical structure: like dissolves like). P.V.A. is also soluble in aromatics (toluol), lower alcohols

(methanol and ethanol) and ketones (acetone). It is not soluble in aliphatic hydrocarbons (hexane and petroleum ethers).

Uses: As adhesives, the copolymer with dibutyl maleate or ethylene is reported to give excellent adhesive properties<sup>6</sup>. Emulsions of P.V.A., because of their excellent adhesion and good flexibility, are used as a consolidant and surface coating for bone, ivory, glass and ceramics<sup>7</sup>, although their tendency to imbibe dirt and grow mould would seem to limit these applications. P.V.A. with a higher  $T_g$  when dissolved in an organic solvent is used as a surface consolidation for glass and ceramics<sup>7</sup> and as a varnish for painted surfaces.

*Poly(vinyl alcohol) (P.V.A.L.)\**



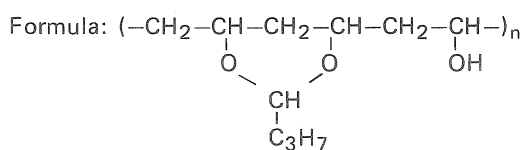
Properties: Although the  $T_g$  is  $85^\circ\text{C}$  it is reasonably flexible at ambient temperatures. P.V.A.L. can be obtained as a powder or as an emulsion. As it is prepared from poly(vinyl acetate) there are some acetate groups remaining on the polymer chain. The polymer is resistant to the effect of sunlight although some cross-linking may occur.

Solubility: Only useful solvent is water, the maximum solubility occurs at  $70^\circ\text{C}$  and the more acetate groups the greater the solubility<sup>9</sup>. Heating the polymer to about  $100^\circ\text{C}$  causes a reaction which decreases its water solubility. The polymer is resistant to most organic solvents except alcohols and ketones.

Uses: As an adhesive for cellulosic materials with P.V.A. The polymer is an effective barrier against low water soluble gases for example oxygen and as it does not change the surface texture has been used in the preservation of old fabrics. P.V.A.L. water solutions tend to grow mould (a preservative should be added), and the dry polymer becomes "tacky" under high humidity conditions. The free hydroxyl ( $-\text{OH}$ ) groups on P.V.A.L. can be used to prepare a thermosetting polymer when reacted with amino resins.

*Poly(vinyl butyral) (P.V.B.)*

P.V.B. is an example of the polyvinyl acetals and as it is the most important it will be the only one discussed. It is prepared from P.V.A.L.



Properties: As can be seen from the formula the reaction to produce P.V.B. leaves some of the hydroxyl groups. A typical commercial resin has the formula.<sup>11</sup>

poly(vinyl butyral)	75–77%
poly(vinyl alcohol)	18–21%
poly(vinyl acetate)	1%

The unreacted hydroxyl gives the polymer excellent adhesion characteristics with glass and cellulose and they can be cross-linked with amino resins. The  $T_g$  of P.V.B. is given as  $49^\circ\text{C}$ <sup>8</sup> and the solid resin is a clear, tough resin at ambient temperatures, resistant to sunlight and insensitive to moisture.

Solubility: P.V.B. is soluble in alcohols, or glycol ethers. The solubility in esters and ketones has to be determined for the particular grade of resin. P.V.B. is not soluble in hydrocarbon solvents.

Uses: For the consolidation of a wide range of materials. For more flexible polymer (where it is used as a consolidant for fibres) it needs to be plasticised. For the production of a matt finish dilute solutions should be used.

*Methacrylates* This range of polymers is available to the conservator as solids, resin solutions, emulsions, or free monomers. The use of free monomer is interesting because they are low in viscosity and can be used as 100% solids applications. They are, therefore, ideal for use in consolidation of wood or stone.

Some mention should be made of the methods used to polymerise methacrylate monomers.

Methods for the polymerisation of methacrylates:

The method that has been most widely used is to mix the monomer with an initiator (usually an organic peroxide) and to heat this mixture to decompose the initiator and start the polymerisation. This method has the disadvantages of:

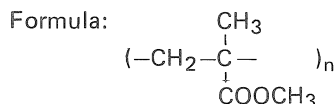
1. Initiators can be unstable on storage.
2. Heat needs to be supplied to the article being consolidated. The temperature may need to be  $90^\circ\text{C}$ .
3. As the polymerisation generates heat, this heat and the heat necessary to decompose the initiator may be detrimental to the artifact being consolidated.

\*While P.V.A.L. is a suggested abbreviation for poly(vinyl alcohol) by the American Society for Testing and Materials (A.S.T.M.), the use of P.V.A. for poly(vinyl acetate) is not an A.S.T.M. suggestion. P.V.A. has been retained, however, as it is common usage in Australia as an abbreviation for poly(vinyl acetate).

Another method widely reported<sup>12, 13</sup> is the use of  $\gamma$ -radiation from a cobalt-60 source at radiation dosages of 1 to 5 megarad to prevent damage to the substrate and to control the evolution of heat. This method needs the availability of a cobalt-60 source and the polymerisation has to be carried out in the absence of oxygen (that is under a nitrogen or carbon dioxide atmosphere). An interesting development of this is the use of water-soluble methacrylate monomers (for example 2-hydroxyethyl methacrylate) in the consolidation of water-logged wood and hardening of the monomer with  $\gamma$ -radiation<sup>14</sup>.

The best method of polymerising methyl methacrylate seems to be the use of an initiator with another chemical called an activator. The use of these two reagents causes the initiator to decompose slowly at room temperature or slightly above. Schaffer<sup>13</sup> has recommended the use of bis-4-6-butylcyclohexyl peroxydicarbonate as the initiator and pyridine as the activator. This method still requires the use of an inert atmosphere.

#### *Poly(methyl methacrylate) – P.M.M.A.*



Properties: P.M.M.A. is a very strong impact resistant polymer with excellent clarity and lack of colour. The resin is reported to show good light stability if formulated with certain initiators<sup>15</sup>.

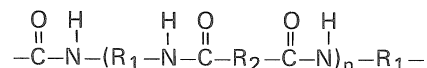
As P.M.M.A. has a high  $T_g$  it is only suitable where a rigid polymer can be used. For flexibility it is internally plasticised with n-hexyl methacrylate or butyl acrylate. The homopolymer shows poor adhesion to substrates and copolymerisation to give a polar group in the polymer backbone improves this. Typical groups that are used are hydroxyl ( $-\text{OH}$ ), carboxylic acid ( $-\text{COOH}$ ) or amine ( $-\text{NH}_2$ )<sup>15</sup>.

Solubility: P.M.M.A. is soluble in aromatic solvents (toluol or xylene) and shows limited solubility in aliphatics or lower alcohols. It is also soluble in ketones, esters and chlorinated hydrocarbons<sup>16</sup>.

Uses: For the consolidation of many artifacts. It should be noted that when using the polymer for consolidation of stone or ceramics with high salt content, crystallisation of the salt may cause the consolidated surface to lift off<sup>7</sup>. The more flexible copolymer emulsions are used for adhesives, and the resin solutions as lacquers for treating metal surfaces. Specially prepared acrylics can be cross-linked.

#### *Polyamides – Nylons*

Nylons have the general formula:



– For nylon 66,  $\text{R}_1 = \text{C}_6\text{H}_{12}$  and  $\text{R}_2 = \text{C}_4\text{H}_8$ . These types of nylons have not been used in conservation because of their low solubility, and some chemical modification may be carried out to increase the solubility. One method is to methylate nylon 66, that is change one of the  $-\text{NH}$  groups to  $-\text{NCH}_3$ . This increases the solubility of the polymer in ethanol. In the preparation of "soluble nylon", nylon 66 is reacted with formaldehyde. This modification changes the  $-\text{NH}$  group to N-methylol group,  $-\text{NCH}_2\text{OH}$ , also called N-hydroxy methyl group.

#### *Soluble Nylon – N-hydroxy Methyl Nylon 66.*

Formula: See above.

Properties: This thermoplastic resin is flexible and does not contract on drying. A film of the resin is permeable to water vapour. As the N-hydroxy methyl groups are reactive the polymer may cross-link after application and thus become difficult to remove.

Solubility: Soluble in the lower alcohols and alcohol/water mixtures when hot, tends to gel when cooled below  $40^\circ\text{C}$ . Reheating will give, again, a clear solution.

Uses: Used widely for the surface consolidation of friable materials. Soluble nylon has been recommended as a surface coating for bone and ceramics for safe transport<sup>7</sup>. Reactive polyamides are used as a cross-linking agent for epoxy resins.

#### *Poly(ethylene Glycols) – P.E.G.*

Formula:  $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n-\text{CH}_2\text{OH}$

Properties: A wide range of these thermoplastic materials are available. They differ only in the degree of polymerisation or molecular weight. The lower molecular weight polymers are liquids and the higher molecular weight materials hard waxes. The liquid poly(ethylene glycols) are hygroscopic.

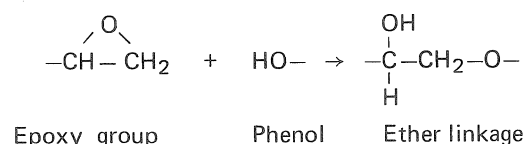
Solubility: All the P.E.G.s are soluble in water.

Uses: P.E.G. of molecular weight 1,000 is very popular as a consolidant for water-logged wood<sup>7, 17, 18</sup> where water in the wood is replaced by immersing the wet wood in baths of P.E.G. solutions, starting with dilute solutions and gradually increasing the concentration. Care should be taken when using hot solutions of P.E.G. to prevent degradation to lower molecular weight hygroscopic polymers. Low molecular weight

P.E.G. (400) has been used successfully for flexibilising old leather.

#### Epoxy Resins

Epoxy resins are thermosetting polymers prepared by the reaction of a prepolymer with a cross-linking agent, called a "hardener". The prepolymer is produced by reacting epoxy groups with a phenol to give an ether linkage:



The D.P. of the prepolymer is kept low in order to give good solubility and is able to be cross-linked through its residual epoxide or hydroxyl groups. While there are many possible prepolymers, depending on the type of phenol used, commercial resins are made from condensing epichlorohydrin with diphenylol propane to give a solid diglycidyl ether (the prepolymer) with a D.P. of approximately 13<sup>20</sup>. Amines are normally used as hardeners for these prepolymers.

Formula: See above.

Properties: By careful selection of the hardener (see below) the cross-linking reaction will produce little heat and very little shrinkage on curing. The cross-linked resin has good adhesion to all substrates, is tough with good abrasion resistance, transparent with good resistance to sunlight.

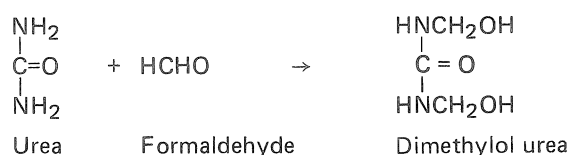
Uses: Epoxy resins have been used in the consolidation of wooden artifacts. For this purpose Munnikendan<sup>21</sup> has suggested a mixture which gives low viscosity, slow cure (for ease of application and heat dissipation) and a flexible final polymer. The mixture he obtained was butanediol diglycidyl ether (a low viscosity epoxy prepolymer), propylene diglycidyl ether (as an internal plasticiser), menthane diamine (a hardener that gives slow cure) and about 5% methyl ethyl ketone (a solvent to decrease viscosity). The use of epoxy resins in the consolidation of stone has been shown to contribute to poor results on accelerated chemical weathering tests<sup>22</sup>. Because of their good adhesion to all types of substrates they make excellent bonding agents.

The use of epoxy resins in conservation is, however, limited as they are thermosetting and give glossy surfaces.

#### Amino Resins

This group covers urea-formaldehyde (U.F.) and malamine-formaldehyde (M.F.) resins. As with epoxy resins, U.F. and M.F. are purchased as prepolymers and both these prepolymers are water

soluble. The prepolymer is produced by reacting formaldehyde with urea (or malamine) to give a dimethylol urea:



Both the U.F. and M.F. prepolymer may be cross-linked at room temperature by addition of acid catalyst to give a thermosetting polymer.

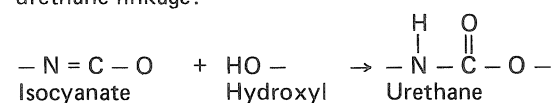
Formula: See above.

Properties: U.F. and M.F. polymers are clear and colourless. M.F. shows better hardness, moisture resistance, light stability and less shrinkage than U.F.

Uses: M.F. has been used in the consolidation of wood where the advantages of low viscosity, water soluble prepolymer that hardens slowly without heat are apparent. Although the resins are used in textiles commercially, they do not appear to be used for this purpose in conservation.

#### Polyurethanes — P.U.

"Polyurethane" is a generic term and applies to any polymer that is formed by the reaction of an isocyanate with an hydroxyl group to give a urethane linkage:



The isocyanate generally used is toluene diisocyanate (TDI). For increased light stability 1,6-hexamethylene diisocyanate (HDI) is recommended<sup>23</sup>. Numerous other isocyanates are commercially available for particular applications. As most isocyanates are toxic, due mainly to their high vapour pressure, this is lowered by preparing an adduct with an alcohol or water. The hydroxyl group may be obtained from a thermoplastic polyester, or from polyesters based on vegetable oils. Vegetable oil based P.U. is not recommended for use in conservation as it cross-links and becomes brittle with time.

Methods for curing polyurethanes:

There are five categories into which the curing of polyurethanes are normally divided. Only the types that use ambient temperature and saturated polyesters will be reviewed.

1. One pack moisture cured — these are saturated polyesters mixed with the isocyanate adduct that cure on exposure to atmospheric moisture. It is obvious that these P.U. resins have to be protected from moisture when not being used and that they are only useful for surface coatings.

2. Two pack catalyst cured — the isocyanate adduct is mixed with a "catalyst" just prior to application. The "catalyst" may be an hydroxy amine which reacts with the isocyanate or a true catalyst of the metal soap type.

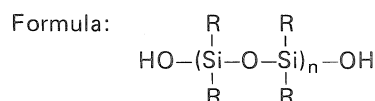
3. Two pack polyol cured — the P.U. resin is obtained by mixing the polyester (polyol) and isocyanate before application.

Formula: See above.

Properties: P.U. resins may be prepared as thermoplastic or thermosetting polymers which are hard and inflexible or flexible enough to coat rubber or leather. The resins are clear and show some degradation in sunlight. To minimise this, aliphatic isocyanates are used and ultra-violet and anti-oxidants are added. The resin has good adhesion to most substrates.

Uses: Little has been reported about the use of this resin in conservation and its main use would be as a surface coating, although the high gloss of the coating would detract from its use in this application.

#### Silicone Resins



(where R = organic groups for thermoplastic resins or R = —O—Si—O— for thermosetting polymers.)

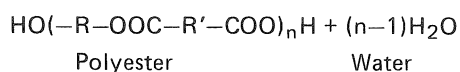
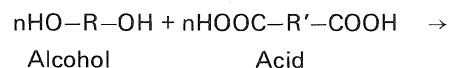
Properties: Silicone resins can range from liquids to hard resins. They all show extremely good water and light resistance. The thermosetting resins are generally cured above 200°C and this limits their use in consolidation.

Uses: These resins are used commercially in moisture resistant fabrics and have been tested as a lubricant for deteriorated wool<sup>24</sup>. In this application the silicone used was found to be of no use and contributed to greater dirt pick-up than any other lubricant tested. A moisture-curing silicone for the treatment of masonry is commercially available<sup>25</sup>.

This preparation is applied as a solution in an organic solvent it is claimed to show good penetration.

#### Polyester Resins

The generic name "polyester" refers to polymers that result from the esterification reaction between an organic acid and alcohol:



If the acid and alcohol have two reactive groups each (as shown in the equation above) a linear (thermoplastic) polymer is obtained. With an alcohol (or acid) with three reactive groups per molecule reacting with an acid (or alcohol) with two groups, the polymer resulting is cross-linked (thermosetting).

*Unsaturated Polyesters.* The group of polyesters finding the widest use in conservation are the unsaturated polyesters. These are thermosetting resins which are prepared from a low molecular weight, linear polyester produced from an unsaturated acid. The polyester is dissolved in a reactive monomer, typically styrene, to give a solution of medium viscosity. Just prior to application an initiator (usually an organic peroxide) is added to the unsaturated polyester-monomer solution to start the cross-linking reaction through the double bonds of the monomer and polyester. In order to facilitate this reaction at room temperatures, it is normal for a promoter or accelerator to be added also.

The main advantage of unsaturated polyesters lie in using a liquid resin or nearly 100% solids which results in little shrinkage on curing. As the cross-linking reaction is exothermic high temperatures may be reached if large volumes of the resin are used.

The important disadvantages of these resins are they are thermosetting (not able to be dissolved after curing has finished), they are susceptible to degradation by ultra-violet light and the resin will hydrolyse in moist alkaline or acid conditions.

## Miscellaneous Synthetic Materials

### Fungicides

As polymer emulsions are water-based and have nutrients that will support the growth of micro-organisms, the manufacturer is faced with not only the problem of in-can stability but also the prevention of fungus or mould growth after application. In an attempt to overcome these problems certain chemicals, which are toxic to these organisms, are added to commercial preparations. These chemicals are broadly classified as "fungicides".

Historically alkyl mercury compounds, for example phenyl mercuric acetate (P.M.A.), have been used as fungicides. Recently the use of these chemicals in commercial preparations has been questioned on the grounds of their toxicity and a large number of "non-toxic" fungicides have been tested. Barium metaborate (B.M.B.) is an example of these new generation fungicides.

For the prevention of fungus in solvent-based systems, pentachlorophenol (P.C.P.) is widely used. All fungicides are fugitive, that is they slowly

evaporate or sublime from the polymer and thus there will be a decrease in fungicidal activity with time. The conservator is, therefore, recommended to be careful in the use of preparations that are subject to fungus growth.

#### *Ultra-Violet Absorbers*

One of the most important sources of degradation of both synthetic and natural polymers is light in the ultra-violet region of the spectrum. Synthetic polymers that are more susceptible to this form of decay (for example polyesters, vinyls and polystyrene) are normally formulated with the addition of complex organic compounds generally described as "ultra-violet absorbers". These chemicals have the ability to absorb ultra-violet light without being changed by it. Chemicals used for this purpose are substituted benzophenones and triazoles. As these chemicals are also fugitive, the conservator is advised to place consolidated artifacts out of direct sunlight. Clear polymer sheets are available which incorporate ultra-violet absorbers and are used to protect artifacts. These sheets are prepared from polyvinyl acetate or flexibilised poly(methyl methacrylate) P.M.M.A. tubes with ultra-violet absorbers can be obtained to fit over fluorescent lights.

#### Testing of Synthetic Materials Used in Conservation

There are two main reasons for wishing to test a material for a particular application. The first is to determine if the material is suitable for the job for which it is to be applied and the second to ascertain, in a condensed period of time, the long term effectiveness of the material. The latter is often referred to as accelerated testing. As very few of the test methods available to the conservator are non-destructive, the material to be tested has to be applied to a substrate as similar as possible to the artifact. It is then hoped that results with this system are able to be transferred to the synthetic material/artifact system.

This list of suppliers was obtained from O.C.C.A.A. Raw Materials Index, 3rd Edition, 1969. A new Index is being prepared and should be available at the end of 1976. Copies of the Index and a Supplement (1972) may be obtained for \$10 (plus postage)\*.

#### *Supplier*

Albright & Wilson (Aust) Ltd.  
B.A.S.F. Aust Ltd.  
B.P. Aust Ltd.  
Bayer Aust Ltd.  
Borden Chemical Co. (Aust) Pty Ltd.  
Brown & Dureau Ltd.  
Robert Bryce & Co. Ltd.

#### *Class of Polymer Available*

P.U., silicones, acrylics, acrylic emulsions, P.V.A. emulsions.  
Vinyls, acrylics.  
M.F., U.F., vinyls, acrylics.  
Silicones, acrylics.  
Epoxy, polyamides, P.V.A. emulsions.  
Silicones.  
Epoxy, polyamides, acrylics, vinyls, U.F. and M.F.

*Accelerated Testing.* Accelerated testing can be designed to test the effects of sunlight, humidity and temperature changes and atmospheric pollutants on the synthetic material. An example of an apparatus used is given in A.S.T.M. D2565 - 70. In this specification a xenon arc lamp source is used to simulate sunlight and cyclic changes in humidity and temperature are prescribed. This is a method for accelerating any possible degradation, the extent of this degradation has to be determined by testing a suitable physical property of the system. The effects of atmospheric pollutants may be accelerated by subjecting the system to high concentrations of the pollutants at elevated temperatures.

In the field of surface coatings it has been found difficult to collate the results from accelerated testing with actual field results. This must be the case, also, where synthetic materials are used in conservation as artifacts are normally stored away from sunlight, changes in atmospheric conditions and pollutants.

#### Conclusion

This paper is only an outline of some aspects of polymer chemistry and a review of the more important synthetic materials used in conservation. The conservator should not be deterred from using these synthetic materials because of the abundance of different types from which to choose. Nearly all the polymeric materials discussed are manufactured in Australia. The plastics industry is very competitive with many different polymers used in consumer durables able to perform equally under similar conditions. Thus most firms use technical service in order to successfully compete in the market. The expertise, therefore, for the correct selection and use of these materials is available in Australia. Before approaching a company for technical service, the conservator should have an idea of type of polymer or, at least, a good idea of the requirements that the polymer has to fulfil.



Dow Chemical Aust Ltd.	Epoxy, silicones and vinyls.
Dow Corning Aust Pty. Ltd.	Silicones.
Croda Federal Chemicals Ltd.	Polyurethanes.
Ciba-Geigy Aust Ltd.	Epoxy and polyamides.
Frankston Manufacturing Pty. Ltd.	Epoxy.
W. F. Hamilton (Chemicals) Pty. Ltd.	Epoxy, acrylics, and P.V.A. emulsions.
Hardie Trading Ltd.	Silicones and polyamides.
A. C. Hatrick Chemicals Pty. Ltd.	Epoxy, M.F., U.F., P.U., acrylics, P.V.A. and acrylic emulsions.
Hoechst Aust Ltd.	U.F., M.F., P.U., P.V.A., P.V.B., acrylics and emulsions.
I.C.I.A.N.Z.	P.U., silicones and acrylics.
Kemrez Chemicals	Epoxy, U.F., M.F., P.U., polyamides, acrylics, P.V.A. and acrylic emulsions.
Jordon Chemical Works (A'sia) Pty. Ltd.	Epoxy, U.F., M.F., P.U., and acrylics.
Meggitt Ltd.	P.U.
Monsanto Aust Ltd.	U.F., M.F., and P.V.A. emulsions.
Resinous Chemicals	U.F. and M.F.
Rohn & Haas Aust Pty. Ltd.	Acrylics and acrylic emulsions.
Revertex (Aust) Pty. Ltd.	P.V.A. and acrylic emulsions.
Shell Chemical (Aust) Pty. Ltd.	Epoxy, and polyamides.
Union Carbide Aust Pty. Ltd.	Silicones, epoxy, and vinyls.
Westminster Chemical Co. Pty. Ltd.	P.U., P.V.A. emulsions and acrylics.

\*The Index may be obtained from: Mr. C. C. Coleman, 26 East Parade, Eastwood, N.S.W. 2122.

## References

- 1 Billmeyer, F. W., 1970, *Textbook of Polymer Science*, 2nd ed., Wiley-Interscience, Sydney.
- 2 Skeist, I., Ed., 1962, *A Handbook of Adhesives*, Reinhold, New York.
- 3 Nielsen, L. E., 1962, *Mechanical Properties of Polymers*, Reinhold, New York.
- 4 Solomon, D. H., 1967, *The Chemistry of Organic Film Formers*, Wiley, Sydney.
- 5 Burell, H., 1962, *Offic. Dig. Federation Soc. Paint Tech.*, 34: 131.
- 6 Berger, G. A., 1972, *Studies in Conservation*, 17: 173-194.
- 7 Pearson, C., 1974, *Aust. O.C.C.A. Proc. & News*, 11: 10-12.
- 8 Ravve, A., 1967, *Organic Chemistry of Macromolecules*, Arnold, London.
- 9 Pritchard, J. G., 1970, *Poly(vinyl Alcohol) Basic Properties and Uses*, Reinhold, New York.
- 10 A.S.T.M. D 1600 - 75, 1975 *Annual Book of ASTM Standards*, Part 35, Pa.
- 11 Hoechst Tech. Bulletin, *Mowital B Poly(vinylbutyral)*, Edition: 7062.
- 12 Munnikendam, R. A., 1967, *Studies in Conservation*, 12: 70-75.
- 13 Schaffer, E., 1974, *Studies in Conservation*, 19: 212-221.
- 14 Munnikendam, R. A., 1973, *Studies in Conservation*, 18: 97-99.
- 15 Green, K. H., 1974, *Surface Coatings*, 144-152, N.S.W.U. Press.
- 16 *Modern Plastics Encyclopedia*, 1971, vol. 47, McGraw-Hill, New York.
- 17 Seborg, R. M., and Inverarity, R. B., 1962, *Studies in Conservation*, 7: 111-120.
- 18 Organ, R. M., 1959, *Conservation*, 4: 96-105.
- 19 Schaffer, E., 1974, *Studies in Conservation*, 19: 66-67.
- 20 Adomenas, A., 1974, *Surface Coatings*, 124-130, N.S.W.U. Press.
- 21 Munnikendam, R. A., 1972, *Studies in Conservation*, 17: 202-204.
- 22 Lal Gauri, K., 1974, *Studies in Conservation*, 19: 100-101.
- 23 Reti, R., 1974, *Surface Coatings*, 110-123, N.S.W.U. Press.
- 24 Delacorte, M., Sayre, E. V., and Indicator, N., 1971, *Studies in Conservation*, 16: 9-17.
- 25 Dow Corning Tech. Bulletin, *Information About Masonry Treatments*, No. 23-051A-01.