POLY VINYL CHLORIDE

POLYAMIDE

Nylon 66

INTERMEDIATES

1. **Adipic Acid**
2. **Hexamethylenediamine**

MANUFACTURING

The nylon 66 salt is prepared by reacting the hexamethylenediamine and adipic acid in boiling methanol, the comparatively insoluble salt (melting point 190-191°C) precipitating out.

A **60% aqueous solution of the salt** is then run into a **stainless steel autoclave** together with a trace of **acetic acid** to limit the molecular weight (9000-15000). The vessel is sealed and **purged** with oxygen-free nitrogen. The temperature and pressure are then controlled as below.

Reaction Conditions at Autoclave Reactor(Stage by Stage)

Stage 1: Temperature raised to about 220°C, pressure of 250 psi (1.7MPa) for 1-2 hours.
Stage 2: Temperature is raised to 270-280°C and steam bled off to maintain the pressure at 250 psi
Stage 3: Pressure is then reduced to atmospheric for one hour

The polymer is extruded by oxygen-free nitrogen on to a water-cooled casting wheel to form a ribbon which is subsequently disintegrated.

Nylon 6

INTERMEDIATES

Caprolactam

Caprolactam is preferred to ω-aminocaproic acid for the manufacture of nylon 6 because it is easier to make and to purify.

MANUFACTURING

Batch Process

Caprolactam, + water (catalyst) + acetic acid (molecular weight regulator) charged into the vessel and reacted under a nitrogen atmosphere at 250°C for about 12 hours. The product consists of about 90% high polymer and 10% low molecular weight material such as the monomer which may be removed by leaching and/or vacuum distillation.

The main characteristics of Nylon are:

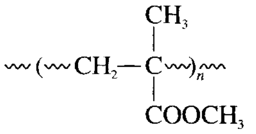
- It has good sliding properties
- Is very abrasion resistant
- Resistant to many oils, greases, diesel, petrol, cleaning fluids
- Strong, tough and rigid
- Electrically insulating
- Easily machined
- Easily welded and bonded very good physical properties
- moisture has significant effect on properties
- very good heat resistance

- excellent chemical resistance
- excellent wear resistance
- moderate to high price

Applications

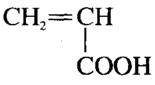
- Fiber applications
  - 50% into tire cords (nylon 6 and nylon 6,6)
  - rope, thread, cord, conveyor belts, and filter cloths.
  - Monofilaments- brushes, sports equipment, and bristles (nylon 6,10)
- Plastics applications
  - bearings, gears, cams
  - rollers, slides, door latches, thread guides
  - clothing, light tents, shower curtains, umbrellas
  - electrical wire jackets (nylon 11)
- Adhesive applications
  - hot melt or solution type
  - thermoset reacting with epoxy or phenolic resins
  - flexible adhesives for bread wrappers, dried soup packets, book bindings

ACRYLICS



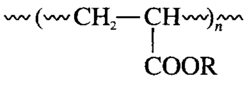
$\sim(\sim CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\sim)_n\sim$

I



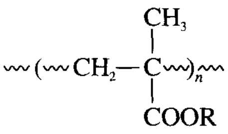
$CH_2=\underset{COOH}{CH}$

II



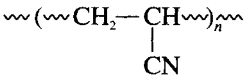
$\sim(\sim CH_2-\underset{COOR}{CH}\sim)_n\sim$

III



$\sim(\sim CH_2-\overset{CH_3}{\underset{COOR}{C}}\sim)_n\sim$

IV



$\sim(\sim CH_2-\underset{CN}{CH}\sim)_n\sim$

V

POLYMERISATION

BULK POLYMERISATION

Bulk polymerisation is extensively used in the manufacture of the sheet and to a lesser extent rod and tube. Methyl methacrylate will polymerise readily and the effect may be observed with non-inhibited samples of monomers during storage. In commercial practice the monomer is supplied with up to 0.10% of an inhibitor such as hydroquinone, which is removed before polymerisation, either by distillation under reduced pressure or, in some cases, by washing with an alkaline solution.

Free-radical polymerisation techniques involving peroxides or azo-di-isobutyronitrile (AIBN) at temperatures up to about 100°C are employed commercially.

SUSPENSION POLYMERISATION

The reaction temperature was **80°C** initially but this **rose to 120°C because of the exothermic reaction**. Polymerisation was complete in about **an hour**.

Properties

1. Commercial poly(methyl methacrylate) is a hard, rigid, transparent material,
2. Extremely good weathering resistance compared with other thermoplastics
3. Tougher than polystyrene, but is less tough than cellulose acetate or the ABS polymers.
4. Light transmission of normal incident light through a parallel sheet of acrylic material free from blemishes is about 92%.
5. Good electrical insulator for low-frequency work, but is inferior to such polymers as polyethylene and polystyrene, particularly at high frequencies.

Applications

a) Display signs, illuminated and non-illuminated, and for both internal and external use.
b) Lighting fittings
c) Glazing material
d) Roof lights, motor cycle windscreens
e) Transparent guards for foodstuffs, machines and even baby incubators may be fabricated simply from acrylic sheet.

Acrylic sheet is also employed for many other diverse applications, including baths and wash-basins, in a wide range of colours, and are cheaper and much lighter than similar products from other materials.

Acrylonitrile Butadiene Styrene (ABS)

Production

Today the term ABS usually refers to a product consisting of discrete cross-linked polybutadiene rubber particles that are grafted with SAN and embedded in a SAN matrix.

To produce ABS polymers, styrene and acrylonitrile are added to polybutadiene latex and the mixture warmed to about 50°C to allow absorption of the monomers. A water-soluble initiator such as potassium persulphate is then added to polymerise the styrene and acrylonitrile. The resultant materials will be a mixture of

1. Polybutadiene
2. Polybutadiene grafted with acrylonitrile and styrene
3. Styrene-acrylonitrile copolymer

The presence of graft polymer is essential since straightforward mixtures of polybutadiene and styrene-acrylonitrile copolymers are weak. In addition to emulsion processes such as those described above, mass and mass/suspension processes are also of importance.

Properties

- ✓ High toughness
- ✓ High impact resistance,
- ✓ Very good dimensional stability,
- ✓ Good heat distortion Resistance (relative to the major tonnage thermoplastics)
- ✓ Good low-temperature properties
- ✓ Capability of being electroplated without great difficulty.

Applications

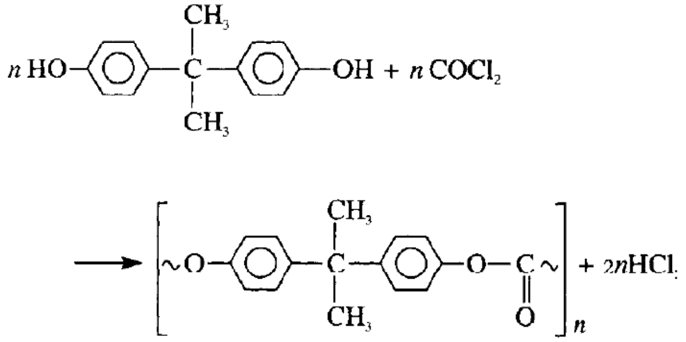
- ✓ Automotive Applications - fascia panels, door covers, door handles, radiator grilles, ventilation system components, heater housings, seat belt fastenings, console panels, loudspeaker housings, interior trim and other uses. Electroplated ABS continues to be used for nameplates, reflectors and other parts where a bright reflecting surface is a requirement.
- ✓ Household appliances – Body cover for washing machine, refrigerator, telephones etc
- ✓ Consumer electronic equipment - Body cover for printer, fax, UPS etc.
- ✓ Refrigerator sheeting
- ✓ Toys
- ✓ Recreational equipment,
- ✓ Luggage

POLYCARBONATES

Production

Phosgenation Process

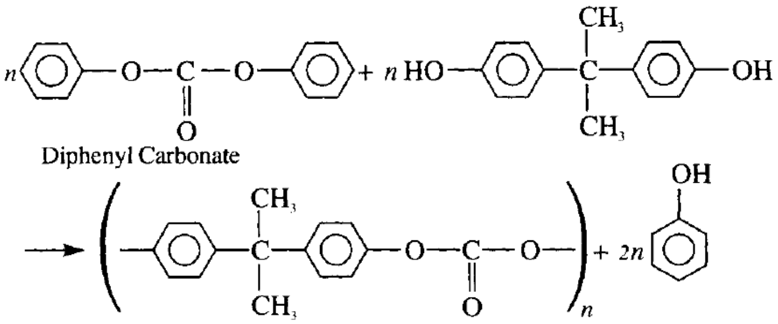
Today the most important process is that of **interfacial polymerisation**. In a typical process the disodium salt of bisphenol A in an alkaline aqueous solution or suspension is reacted with phosgene in the presence of an inert organic solvent such as methylene chloride, chlorobenzene, tetrahydrofuran or dioxane. Reaction temperatures are in the range 10-35°C. The polymer is recovered by washing the organic phase with water, neutralisation of the caustic soda and either precipitation of the polymer by a non-solvent or evaporation of the solvent by thorough washing.



Ester Exchange Process

In this method the reaction is typically carried out at 180-220°C at 20-30mmHg pressure until 80-90% of the phenol of condensation has been removed. The temperature is then gradually raised to 290-300°C and the pressure reduced to 1 mmHg or below. The melt viscosity increases considerably during this period and the reaction is stopped while the material can still be forced out of the kettle by an inert gas.

The high melt viscosity limits the molecular weights obtainable and although number average molecular weights of 50000 can be obtained it is difficult to attain values of above 30 000 without special equipment.



PROPERTIES

- Outstanding impact strength—even at low temperatures
- Good mechanical properties over a broad temperature range
- Excellent dimensional stability, even at elevated temperatures
- Outstanding optical properties
- Low birefringence [for compact disc (CD) manufacture]
- Natural water-clear transparency
- Ability to be integrally colored to form transparent, translucent, or opaque parts in virtually any hue and a wide variety of special effects for parts with high aesthetics

- Amenability to plating, painting, and in-mold decoration
- Product purity and safety for food-contact and medical applications (many BPA-PC grades have agency compliance around the globe)
- Good thermal stability [relative thermal index (RTI) to 125°C]
- Good electrical insulating properties (although it can be made electroconductive via additives)
- Good ultraviolet (UV) stability and weatherability
- Very good flame retardancy, inherent V-2 rating.
- Good processability with fast cycle times

APPLICATIONS

Electronic Components

Polycarbonate is mainly used for electronic applications that capitalize on its collective safety features. Being a good electrical insulator and having heat resistant and flame retardant properties, it is used in various products associated with electrical and telecommunications hardware. It also serves as dielectric in high stability capacitors.[3]

Construction materials

The second largest consumer of polycarbonates is the construction industry, e.g. for dome lights, flat or curved glazing, and sound walls.

Data storage

A major application of polycarbonate is the production of Compact Discs, DVDs, and Blu-ray Discs. These discs are produced by injection molding polycarbonate into a mold cavity that has on one side a metal stamper containing a negative image of the disc data, while the other mold side is a mirrored surface. Typical products of sheet/film production include applications in advertisement (signs, displays, poster protection).[3]

Automotive, aircraft, and security components

In the automotive industry, injection-molded polycarbonate can produce very smooth surfaces that make it well-suited for direct (without the need for a basecoat) metalised parts such as decorative bezels and optical reflectors. Its uniform mold shrinkage results in parts with greater accuracy than those made of polypropylene. However, due to its susceptibility to environmental stress cracking, its use is limited to low-stress applications. It can be laminated to make bullet-proof "glass", although "bullet-resistant" is more accurate for the thinner windows, such as are used in bullet-resistant windows in automobiles. The thicker barriers of transparent plastic used in teller's windows and barriers in banks are also polycarbonate.

So-called "theft-proof" large plastic packaging for smaller items, which cannot be opened by hand, is uniformly made from polycarbonate.

The cockpit canopy of the F-22 Raptor jet fighter is made from a piece of high optical quality polycarbonate, and is the largest piece of its type formed in the world.

Niche applications

Polycarbonate, being a versatile material with attractive processing and physical properties, has attracted myriad smaller applications. The use of injection molded drinking bottles and glasses and food containers has stirred serious controversy

Many kinds of lenses are manufactured from polycarbonate, automotive headlamp lenses, lighting lenses, sunglass/eyeglass, lenses, and safety glasses. Other miscellaneous items: including durable, lightweight luggage, MP3/digital audio player cases, ocarinas, computer cases, riot shields, visors, instrument panels, and blender jars. Many toys and hobby items are made from polycarbonate parts, e.g. fins, gyro mounts, and flybar locks for use with radio-controlled helicopters.[6]

Polycarbonate is also used as a printing substrate for nameplate and other forms of industrial grade under printed products. The polycarbonate provides a barrier to wear, the elements, and fading.

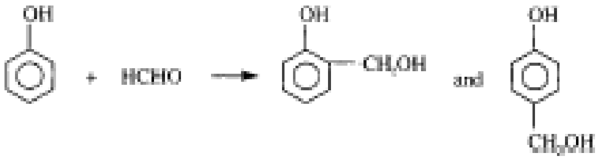
Medical applications

Some polycarbonate grades are used in medical applications and comply with both ISO 10993-1 and USP Class VI standards (occasionally referred to as PC-ISO). Class VI is the most stringent of the six USP ratings. These grades can be sterilized using steam at 120 °C, gamma radiation, or by the ethylene oxide (EtO) method.[7] However, scientific research indicates possible problems with biocompatibility. Dow Chemical strictly limits all its plastics with regard to medical applications

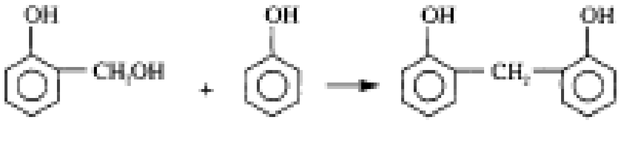
PHENOL FORMALDEHYDE RESIN

NOVOLAKS

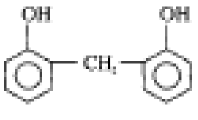
The novolaks are prepared by reacting phenol with formaldehyde in a molar ratio of approximately 1 : 0.8 under acidic conditions. Under these conditions there is a slow reaction of the two reactants to form the o- and p-hydroxymethylphenols



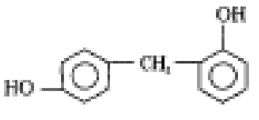
These then condensate rapidly to form products of the bis(hydroxyphenyl)-methane (HPM) type.



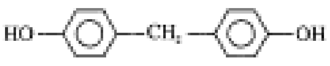
There are three possible isomers and the proportions in which they are formed will depend on the pH of the reaction medium. Under the acid conditions normally employed in novolak manufacture the 2,4'- and 4,4'-HPM compounds are the main products



2,2'-HPM

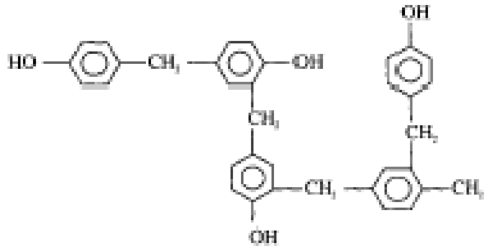


2,4'-HPM



4,4'-HPM

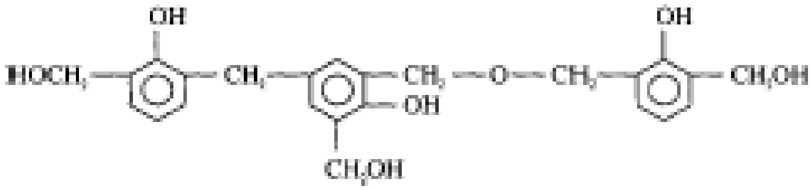
These materials will then slowly react with further formaldehyde to form their own methylol derivatives which in turn rapidly react with further phenol to produce higher polynuclear phenols. Because of the excess of phenol there is a limit to the molecular weight of the product produced, but on average there are 5-6 benzene rings per molecule. A typical example of the many possible structures is shown in.



The novolak resins themselves contain no reactive methylol groups and do not form cross-linked structures on heating.

RESOLS

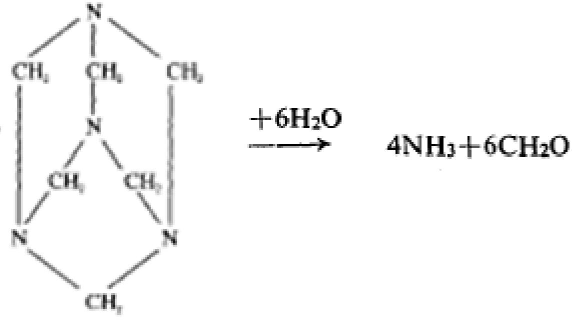
A resol is produced by reacting a phenol with an excess of aldehyde under basic conditions. In this case the formation of phenol-alcohols is rapid but their subsequent condensation is slow. Thus there is a tendency for polyalcohols, as well as monoalcohols, to be formed. The resulting polynuclear polyalcohols are of low molecular weight. Liquid resols have an average of less than two benzene rings per molecule, while a solid resol may have only three to four. A typical resol would have the structure shown in Figure



Heating of these resins will result in cross-linking via the uncondensed methylol groups or by more complex mechanisms. The resols are sometimes referred to as one-stage resins since cross-linked products may be made from the initial reaction mixture solely by adjusting the pH. On the other hand the novolaks are sometimes referred to as two-stage resins as here it is necessary to add some agent which will enable additional methylene bridges to be formed.

Crosslinking (Hardening)

For novolac, Hexa is used almost universally as the hardener. Hexamethylene tetramine or simply hexa, most commonly used as the cross-linking agent, decomposes under heat and using the moisture present to generate formaldehyde (the curing agent) and ammonia (the curing catalyst).



The resols may be hardened by heating and/or by addition of catalysts. Hardening of the novolaks may be brought about by addition of hexamethylenetetramine (hexa, hexamine). Because of the exothermic reaction on hardening (cure) and the accompanying shrinkage, it is necessary to incorporate inert materials (fillers) to reduce the resin content.

PROPERTIES OF PHENOLIC MOULDINGS

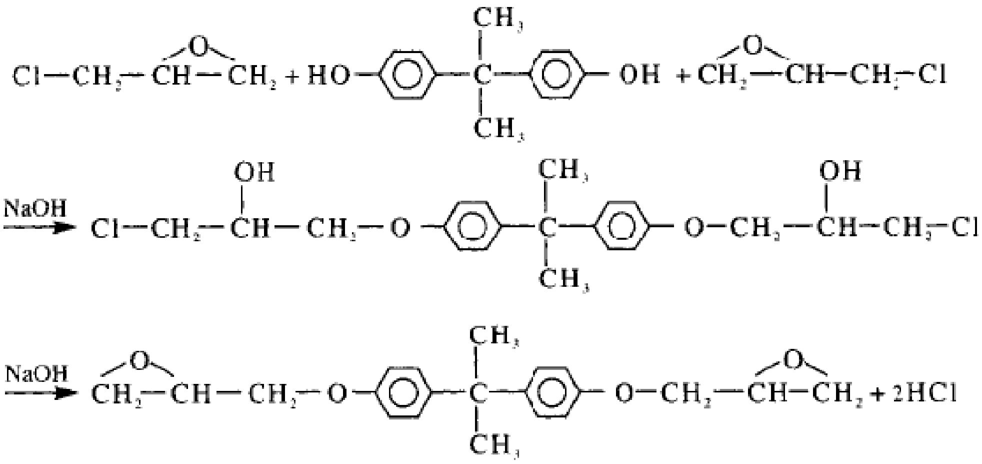
- Since the polymer in phenolic mouldings is cross-linked and highly interlocked, phenolic mouldings are hard,
- Heat-resistant insoluble materials.
- The chemical resistance of the mouldings depends on the type of filler and resin used. Simple phenol-formaldehyde materials are readily attacked by aqueous sodium hydroxide solution but cresol- and xylenol-based resins are more resistant.
- The resins are stable up to 200°C.
- As the mouldings are polar, the electrical insulation properties are not outstanding
- Poor arc tracking resistance under conditions of high humidity.

APPLICATIONS

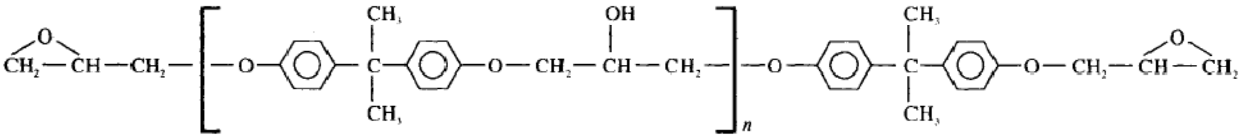
- Domestic plugs and switches
- Insulators.
- In the car industry phenol-formaldehyde mouldings are used in fuse-box covers, distributor heads and in other applications where good electrical insulation together with good heat resistance are required
- Heat-resistant grades are finding use in saucepan handles, saucepan lid knobs, lamp housings, cooker handles, welding tongs and electric iron parts.
- Laminates

EPOXY RESIN

The reaction scheme suggests that diglycidyl ether would be prepared by a molar ratio of *2:* 1 epichlorohydrin : bis-phenol A, probability considerations indicate that some higher molecular weight species will be produced. Experimentally, it is in fact found that when a *2:* 1 ratio is employed, the yield of the diglycidyl ether is less than 10%. Therefore, in practice two to three times the stoichiometric quantity of epichlorhydrin may be employed. In a typical laboratory scale preparation 1 mole of bis-phenol A is dissolved in 4 moles of epichlorohydrin and the mixture heated to 105-110°C under an atmosphere of nitrogen. The solution is continuously stirred for 16 hours while 2 moles of sodium hydroxide in the form of 30% aqueous solution is added dropwise. A rate of addition is maintained such that reaction mixture remains at a pH which is insufficient to colour phenolpthalein. The resulting organic layer is separated, dried with sodium sulphate and may then be fractionally distilled under vacuum.



The general formulae for glycidyl ether resins may thus be represented by the structure shown

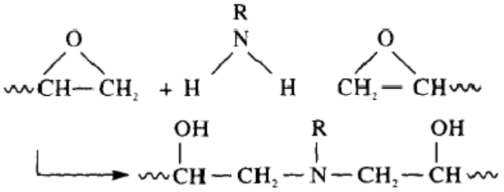


CURING OF GLYCIDYL ETHER RESINS

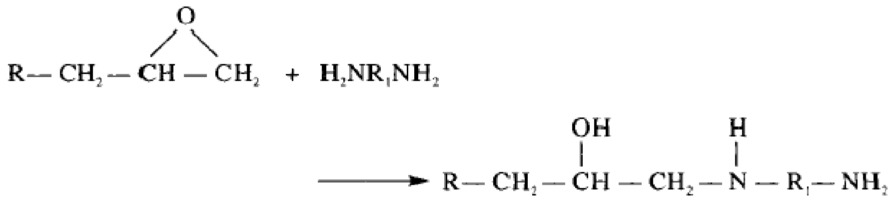
Amine Hardening Systems

Diethylenetriamine and *triethylenetetramine* are highly reactive primary aliphatic amines with five and six active hydrogen atoms available for crosslinking respectively. Both materials will cure glycidyl ether at room temperature.

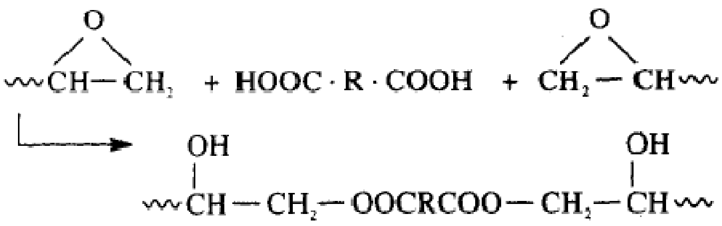
With amines,



With diamines,

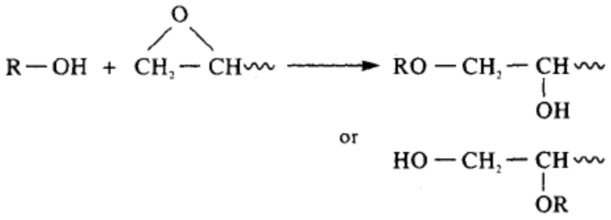


Acid Hardening Systems



Curing with Hydroxyl Group

The epoxy-hydroxyl reaction may be expressed as



Mercaptan Hardening Systems

Both amines and acid anhydrides are extensively used cross-linking agents. The resins may also be modified by reacting with other polymers containing hydroxyl or mercaptan groupings, e.g.

Advantages of Epoxy Resins over Polyester Resins

Superior heat resistance, chemicals and alkali resistance, mechanical properties and aging resistance.

Epoxy as Universal Adhesive

- ✓ Excellent adhesion,
- ✓ Very good cohesion,
- ✓ Low creep and
- ✓ Low shrinkage on cure
- ✓ Absence of volatiles

The above properties make epoxy as an excellent adhesive, bonding or cementing material for metal-to-metal, metal to-ceramics, metal-to-plastics and various other combination of substrates.

APPLICATIONS

- High strength adhesives and cementing agents, in the building industry and road surfacing
- Surface coatings
- Potting and encapsulation of electronic components
- Glass fibre reinforced cast objects and laminates
- Laminates in flooring
- Moulding powders

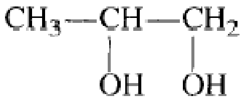
UNSATURATED POLYESTER RESINS

The polyester laminating resins are viscous, generally pale yellow coloured materials of a low degree of polymerisation (~ 8 - 10), i.e. molecular weight of about 2000. They are produced by condensing a glycol with both an unsaturated and a saturated dicarboxylic acid. The unsaturated acid provides a site for subsequent cross-linking whilst provision of a saturated acid reduces the number of sites for cross-linking and hence reduces the cross-link density and brittleness of the end-product. In practice the polyester resin, which may vary from a very highly viscous liquid to a brittle solid depending on composition, is mixed with a reactive diluents, such as styrene. This eases working, often reduces the cost and enhances reactivity of the polyester.

Selection of Raw Materials

Diols

1,2-Propylene glycol is probably the most important glycol used in the manufacture of the laminating resins. It gives resins which are less crystalline and more compatible with styrene than those obtained using ethylene glycol.



$CH_3—CH(OH)—CH_2(OH)$

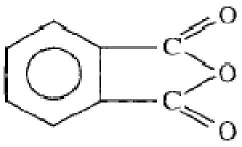
1,2-Propylene Glycol

$HO•CH_2•CH_2•O•CH_2•CH_2•OH$

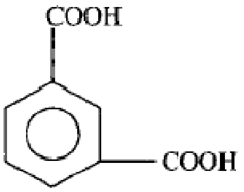
Diethylene Glycol

Saturated acids

The prime function of the saturated acid is to space out the double bonds and thus reduce the density of cross-linking. Phthalic anhydride is the most commonly used for this purpose because it provides an inflexible link and maintains the rigidity in the cured resin. It has been used in increasing proportions during the past decade since its low price enables cheaper resins to be made. The most detrimental effect of this is to reduce the heat resistance of the laminates but this is frequently unimportant.



Phthalic Anhydride



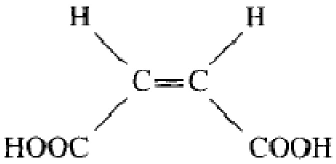
Isophthalic Acid

$HOOC(CH_2)_4COOH$

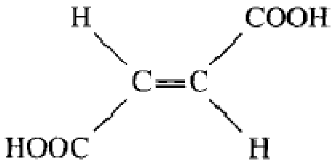
Adipic Acid

Un-Saturated acids

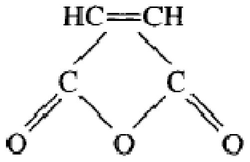
Most conventional general purpose resins employ either maleic acid (usually as the anhydride) or its trans-isomer fumaric acid (which does not form an anhydride) as the unsaturated acid.



Maleic Acid



Fumaric Acid



Maleic Anhydride

Diluents

Because of its low price, compatibility, low viscosity and ease of use, styrene is the preferred reactive diluent in general purpose resins. Methyl methacrylate is sometimes used, but as it does not copolymerise alone with most unsaturated polyesters, usually in conjunction with styrene in resins for translucent sheeting. Vinyl toluene and diallyl phthalate are also occasionally employed.

Production of Resins

Polyester laminating resins are produced by heating the component acids and glycols at 150-200°C for several hours, e.g. 12 hours. In order to obtain a good colour and to prevent premature gelation, the reaction is carried out under an inert blanket of carbon dioxide or nitrogen. The reaction mixture is agitated to facilitate reaction and to prevent local overheating. A typical charge for a general purpose resin would be:

Propylene glycol	146 parts
Maleic anhydride	114 parts
Phthalic anhydride	86 parts

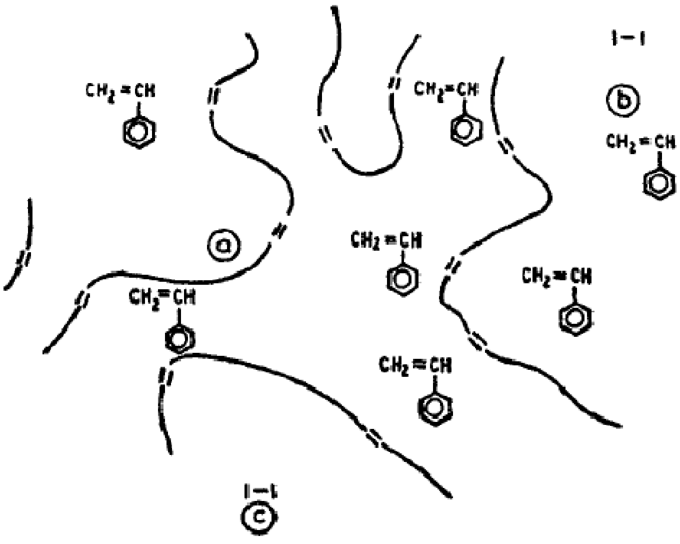
The molar ratios of these three ingredients in the order above is 1.1 : 0.67 : 0.33. The slight excess of glycol is primarily to allow for evaporation losses. Xylene is often used used to facilitate the removal of water of condensation by means of azeotropic distillation. The reaction is followed by measuring the acid number of small samples periodically removed from the reactor. (The acid number is the number of milligrams of potassium hydroxide equivalent to the acidity present in one gram of resin.) Where there are equimolecular proportions of glycol and acid the number average molecular weight is given by 56000/acid number. Since there is some deviation from equimolecular equivalence in practice, care should be taken in using this reationship. Reaction is usually stopped when the acid number is between 25 and 50, the heaters are switched off and any xylene presents is allowed to boil off into a receiver.

When the resin temperature drops below the boiling point of the reactive diluent (usually styrene) the resin is pumped into a blending tank containing suitability inhibited diluent.

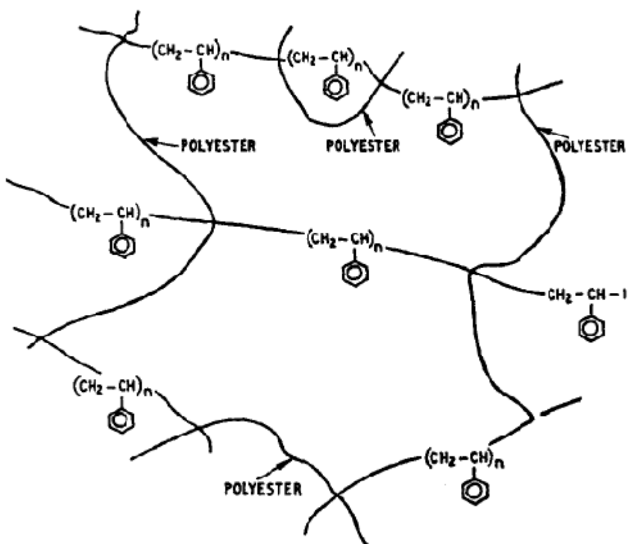
Curing Systems

The cross-linking reaction is carried out after the resin has been applied to the glass fibre. In practice the curing is carried out either at elevated temperatures of about 100°C where compression mouldings are being produced, or at room temperature in the case of large hand lay-up structures.

1) Benzoyl peroxide is most commonly used for elevated temperature curing. The peroxide is generally supplied as a paste (~50%) in a liquid such as dimethyl phthalate to reduce explosion hazards and to facilitate mixing. The curing cycle in pressure moulding processes is normally less than five minutes.
2) In the presence of certain aromatic tertiary amines such as dimethylaniline, benzoyl peroxide will bring about the room temperature cure of general purpose polyester resins.
3) More frequently either methyl ethyl ketone peroxide (MEKP) or cyclohexanone peroxide is used for room temperature curing in conjunction with a cobalt compound such as a naphthenate, octoate or other organic solvent-soluble soap. The peroxides (strictly speaking polymerisation initiators) are referred to as 'catalysts' and the cobalt compound as an 'accelerator'. Other curing systems have been devised but are seldom used.



(1) Structures present in polyester resin ready for laminating:



(2) Structures present in cured polyester resin.