

FILLERS AND REINFORCEMENTS. Many materials may be added to plastics to increase strength, thermal conductivity, resistance to heat distortion, and lower thermal expansion. Table 34.9 classifies the various fillers and reinforcements that are in use. Formerly asbestos was used, but due to its human carcinogenic properties, it is no longer an acceptable filler.

MANUFACTURING PROCESSES¹⁶

General Polymerization Processes

BULK POLYMERIZATION. Polymerization of the monomer in bulk may be carried out in the liquid or vapor state. The monomers and activator are mixed in a reactor and heated or cooled as needed. As most polymerization reactions are exothermic, provision must be made to remove the excess heat. In some cases, the polymers are soluble in their liquid monomers, causing the viscosity of the solution to increase greatly. In other cases, the polymer is not soluble in the monomer and it precipitates out after a small amount of polymerization occurs.

¹⁶Driver, *Plastics Chemistry and Technology*, Van Nostrand Reinhold, New York, 1979.

Table 34.9 Classification of Fillers and Reinforcements

Organic Origin	Inorganic Origin
Cellulosic	Mineral fillers
Wood flour	Calcium carbonate
Shell flour	Mica
Cotton	Kaolin
α -Cellulose	Silica
Paper pulp	Talc
Shredded textiles	Carbide
Sisal	Metallic oxides
Carbonaceous	Sulfates
Graphite filaments	Silicates
Carbon blacks	Titanates
Synthetic	Powdered metals
Aramid yarns and fibers	Iron
	Lead and zinc
	Copper
	Aluminum
	Filaments
	Fiberglass
	Basalt fibers
	Boron and other metals
	Aluminum oxide

SOURCE: Katz and Milewski (eds.), *Handbook of Fillers and Reinforcements for Plastics*, Van Nostrand Reinhold, New York, 1978.

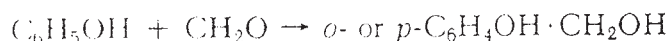
SOLUTION POLYMERIZATION. This method is often used when the exothermic heat is too great to be controlled in bulk polymerization. The monomer and initiator are dissolved in a nonreactive solvent which serves to slow the reaction and thus moderate the heat given off. The heat evolved may be controlled by refluxing the solvent. The polymer concentration usually has to be low to avoid too high a viscosity. This method produces polymers of low to medium molecular weight.

SUSPENSION POLYMERIZATION. In this process the monomer is suspended in water by agitation, and stabilizers such as talc, fuller's earth, and bentonite are added to stabilize the suspension and prevent polymer globules from adhering to each other. Normally, the initiator is soluble in the monomer. Each monomer globule polymerizes as a spherical pearl of high molecular weight. The heat of polymerization is removed by the water, permitting accurate temperature control. The stabilizer must be separated from the polymer, and sometimes, because of partial miscibility of the monomer and water, subsidiary polymerization may occur in the aqueous phase, producing a low molecular weight polymer.

EMULSION POLYMERIZATION. This is similar to suspension polymerization but the monomer is broken up into droplets that form aggregates called micelles. The monomer is on the interior of the micelles, and the initiator is in the water. Soap, or another emulsifying agent, is used to stabilize the micelles. The initiator diffuses into the micelle to start polymer growth. Emulsion polymerizations are rapid and can be carried out at relatively low temperatures. The aqueous phase absorbs the heat evolved by the reaction. Polymers of very high molecular weight can be prepared by this process.

Condensation-Polymerization Products

PHENOLICS. Phenolic resins designate a group of synthetic resins that are probably the most varied and versatile that we know. They may be made from almost any phenolic body and an aldehyde. Phenol-formaldehyde resins constitute by far the greatest proportion, but phenol-furfural, resorcinol-formaldehyde, and similar resins are also included in this group. The product obtained depends primarily on the concentration and chemical nature of the reactants, the nature and concentration of the catalyst used, the temperature and reaction time, and the modifying agents, fillers, and extenders. The initial reaction between the phenol and a mixture of cresols with formaldehyde, using an alkaline catalyst, produces benzyl alcohols:



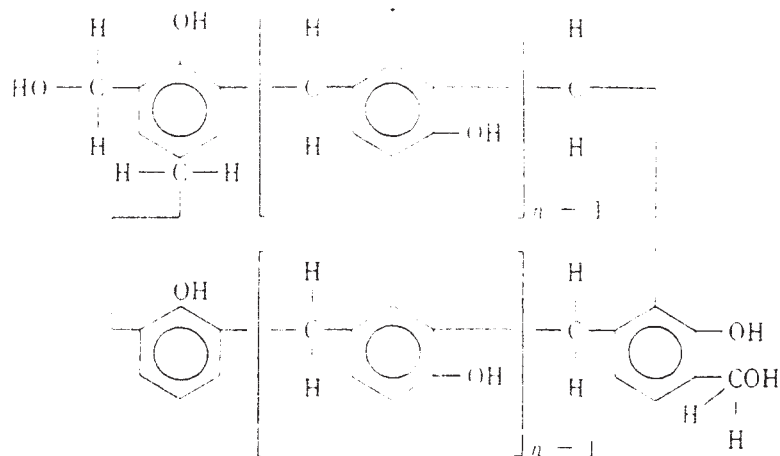
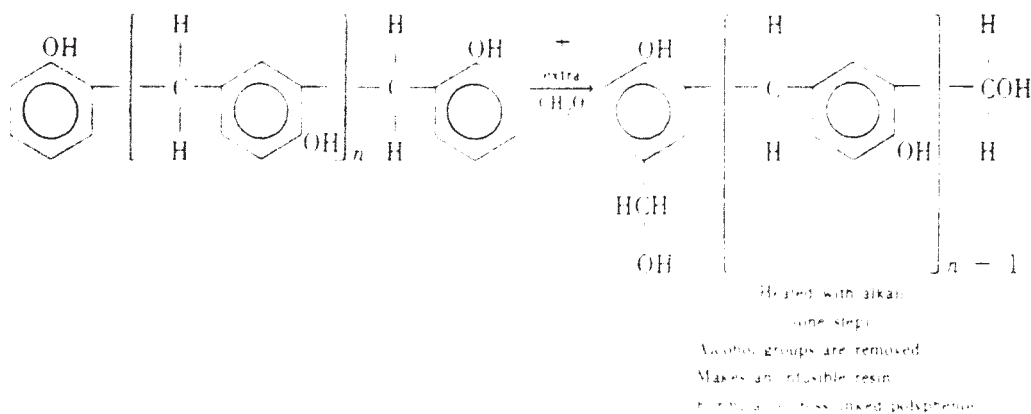
Simultaneously, additional formaldehyde may react to produce both di- and trimethylol-phenols. These alcohols continue to condense and polymerize with each other rapidly and almost violently.¹⁷

¹⁷Butler, Phenol Resin Emulsions, *Am. Dyest. Rep.*, 32 128 (1943); *EPST*, Wiley, New York, 1964.

Phenol-formaldehyde
Reactions: Condensations and Polymerizations

Phenol > 1 formaldehyde : 1
 Any catalyst but generally acid
 A fusible resin (two step)
 Formula: a chain polyphenol

Formaldehyde > 1 phenol : 1
 Any catalyst but generally alkaline
 Makes first a fusible resin
 Formula: a chain polyphenol alcohol

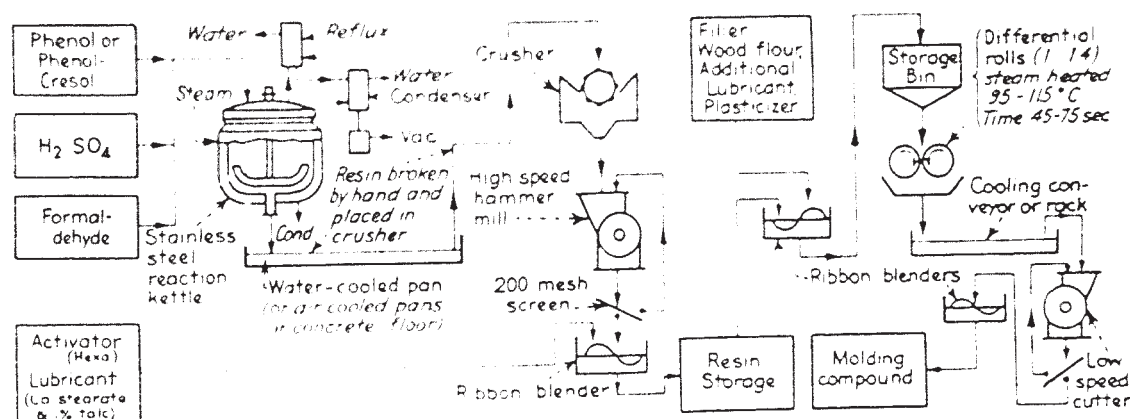


These resins, when classified according to the nature of the reaction occurring during their production, are one of two fundamental types.

1. One-step resins. In these, all the necessary reactants (phenol, formaldehyde, catalyst required to produce a thermosetting resin are charged into the resin kettle in the proper proportions and react together. An alkaline catalyst is used. The resin, as discharged from the kettle, is thermosetting or heat-reactive and requires only further heating to complete the reaction to an infusible, insoluble state.

2. Two-step resins. Only part of the necessary formaldehyde is added in the kettle in making these resin, and an acid catalyst is used. They are permanently fusible or thermoplastic when discharged from the kettle but react with additional formaldehyde to produce a thermosetting resin. This additional formaldehyde is furnished by "hexa" (hexamethylenetetramine). Both one- and two-step resins are used, separately or in combination, in commercial molding materials. Both types are believed to polymerize to similar end products. The two-step scheme is represented in Fig. 34.7,¹⁵ showing the sequences of unit operations and chemical conversions.

¹⁵Phenolic Resin Process Sidesteps Kettle, *Chem. Eng.* 72 (23) 104 (1965) (flowchart).



In order to produce 100 kg of finished molding compound of a typical kind, the following materials (in kilograms) are required

Phenol	42	H ₂ SO ₄	0.1
Formaldehyde	27	Black dye (Nigrosin)	1.3
Wood flour	52	Ca stearate	0.7
Hexa	3.7		

Fig. 34.7. Flowchart for production of a molding compound of the phenol-formaldehyde type

The phenol and formaldehyde are placed in the reaction kettle with the catalyst (sulfuric acid) and heated 3 or 4 h at a temperature of 140 to 163°C.

During condensation, reaction water is eliminated and forms the upper of two layers. This water of reaction is removed under vacuum without the addition of heat.

The warm, dehydrated, viscous resin is run out of the kettle into shallow trays and allowed to cool and harden. The cooled, brittle resin is crushed and finely ground and becomes the resin binder for molding phenolic resins.

The crushed and ground resin is blended with the activator ("hexa").

Phenolic molding compounds are molded primarily in compression and transfer molds. The powder, mixed with fillers, lubricant, and plasticizers, is further reacted on steam-heated rolls, cooled, and ground. In compression molding the powder is placed in hardened steel molds at a temperature of 132 to 182°C and at pressures from 13.8 to 35 MPa.

In transfer molding the thermosetting material is subjected to heat and pressure in an outside chamber, from which it is forced by means of a plunger into a closed mold where curing takes place.

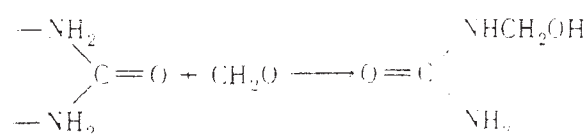
Electronic preheating (in a high-frequency electrostatic field outside the process) of the molding powders, as such or in the form of pellets, prior to mold loading, helps achieve a more rapid cure with less pressure, since it promotes the flow of material in the mold cavity.

The final chemical polymerization reaction, or cure, which takes place in the mold to transform the powder into a rigid, infusible shape of the finished article.

Cast phenolics differ from molding compositions in that no pressure is required to make the composition flow. The phenol and formaldehyde with a basic catalyst (usually sodium or potassium hydroxide) are placed in a metal or stainless-steel kettle and heated from the boiling point to as low as 70°C for a period of 10 min to 3 h. Cooling is done by means of water in the jacket during certain phases of the exothermic reaction. At the proper time (removal of about 75 percent of the water formed), while the resin is still hydrophilic, an organic acid

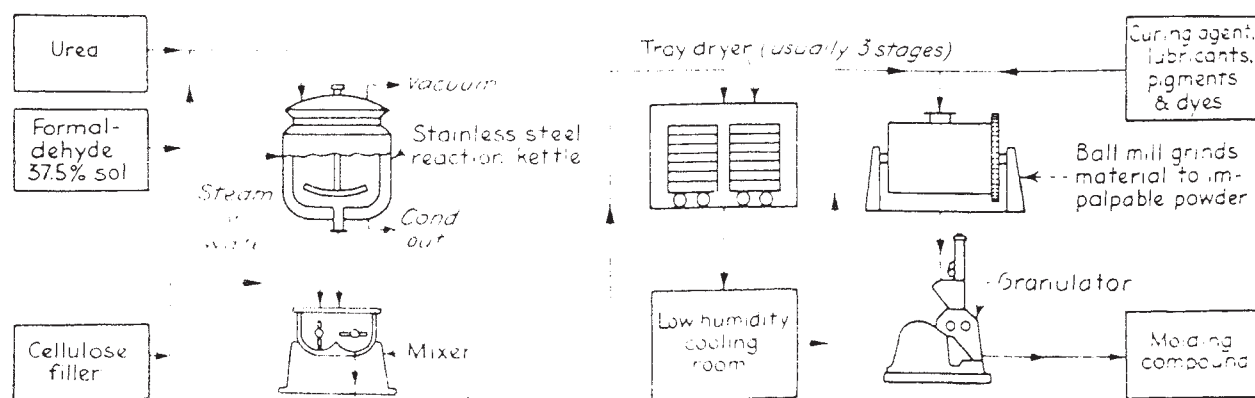
(lactic or maleic acid) is added to neutralize the resin and clarify the color. Before the final dehydration of the resin, plasticizers, pigments, and colors are added to the kettle and mixed with the resin. Dehydration is effected under vacuum at a resin temperature not in excess of 74 to 80°C, and the hot resin is withdrawn and poured into preheated lead molds. The final reaction and hardening take place by curing the resin in the molds at 85°C for periods of 3 to 10 days. The curing ovens are heated with steam under precise temperature control.

AMINO RESINS.¹⁹ Urea-formaldehyde and melamine-formaldehyde condensates are the commercially important amino resins. Other resins in this family utilize sulfonamides, aniline, and thiourea. The simplest condensates are methylolureas and methylolmelamines. A typical low-stage resin is formed when urea (or melamine) is mixed with formaldehyde as shown in Fig. 34.8. The initial reaction of urea (or melamine) with formaldehyde is a simple addition to produce methylol compounds.



Some dimethylol urea ($\text{HOH}_2\text{CNH} \cdot \text{CO} \cdot \text{NHCH}_2\text{OH}$) is also formed. The mechanism of subsequent intercondensation of the methylol compounds has not been established definitely, but there is evidence for the formation of methylene linkages, —NH— , $\text{—CH}_2\text{—}$, —NH— , or ether bridges, $\text{—NH} \cdot \text{CH}_2\text{—O—CH}_2\text{NH—}$, as condensation and curing progress. These water-soluble water-white intermediates are employed in admixture with some form of cellulose before the final reaction and curing to form an infusible, insoluble product. A suitable catalyst and controlled temperature are also needed. Since melamine is not readily soluble in water or formalin at room temperature, it is necessary to heat it to about 80°C to obtain the methylol compounds for melamine-formaldehyde resins.

¹⁹Lichtenberg, MPE, 1981–1982, p. 12; ECT, 3d ed., vol. 2, 1978, pp. 440–469

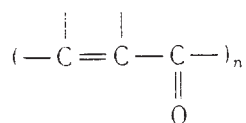


In order to produce 100 kg of molding compound, the following materials (in kilograms) are required

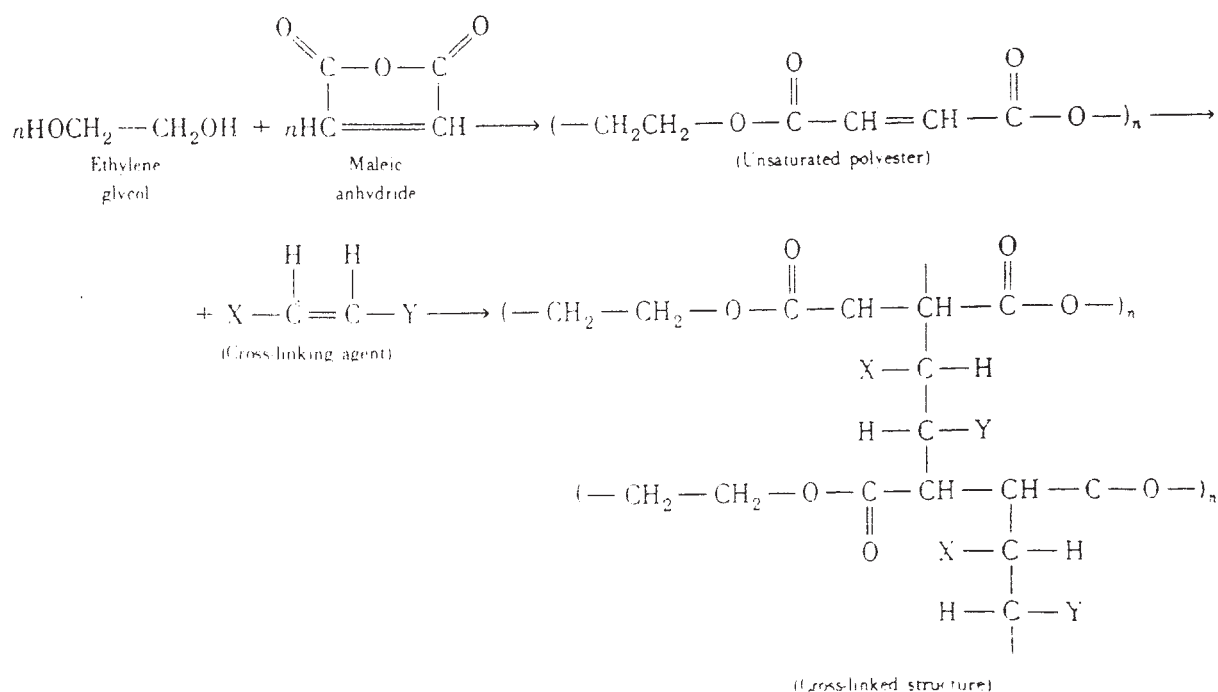
Urea	42	Cellulose filler	40
Formaldehyde	42	Curing agent, lubricant and dye	1.8

Fig. 34.8. Flowchart for the manufacture of a molding compound of the urea-formaldehyde type.

POLYESTER RESINS.²⁰ Polyester resins are complex esters formed when a difunctional alcohol is reacted with a dibasic acid or anhydride. Since the reaction takes place at both ends of the chain, long molecules are possible and a plurality of ester groups is obtained. Unsaturated polyesters are produced when any of the reactants contain unsaturation, such as



Unsaturated polyesters can be formed in two steps, condensation of the acid and alcohol to form a soluble resin, and then addition of a cross-linking agent to form the thermosetting resin. Typical reactions are:



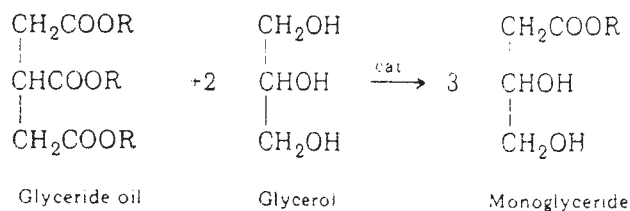
The condensation reaction is carried out in an insulated stainless-steel or glass-lined kettle. The reactants are usually charged through a manhole (since some of the reactants are solids, i.e., phthalic anhydride, fumaric acid, etc.). An inert gas such as nitrogen is introduced by bubbling it up through the reactants, to keep out oxygen (which may cause discoloration and gelation of the resin).

A mixture is heated to reaction temperature (usually about 200°C) and held from 4 to 20 h as continual mixing takes place. By-product water and the inert gas are removed continuously during the reaction (most of the vaporized glycol is returned by the reflux condenser). When the desired degree of condensation has been attained, generally under vacuum, the product is cooled to prevent premature gelation. The polycondensation product (very viscous) is pumped to the blending tank and mixed with the cross-linking agent (usually 2 to 4 h). The resin is transferred to drums for shipment and storage. For the process flowchart²¹ for manufacturing polyester film (Mylar) and polyester fiber (Dacron), see Chap. 35.

²⁰ECT, 3d ed., vol. 18, 1982, pp. 549-574.

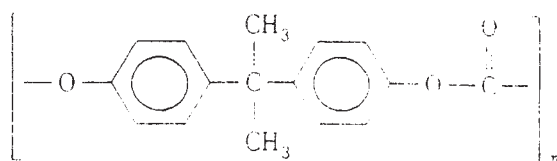
²¹MPE, 1981-1982; ECT, 3d ed., vol. 18, 1982, pp. 549-574.

ALKYD RESINS. The processing equipment (reaction kettle and blending tank) used for unsaturated polyesters can also be used for manufacturing alkyd resins. These are a particular kind of polyester formed by the reaction of polyhydric alcohols and polybasic acids. The most common method of preparation is the "fatty acid" method in which a glyceride oil is catalytically treated with glycerol at 225 to 250°C. The glyceride oil is simultaneously esterified and de-esterified to a monoglyceride.

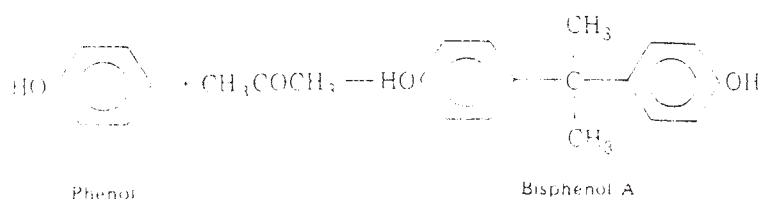


The monoglyceride plus a dibasic acid yields an alkyd resin

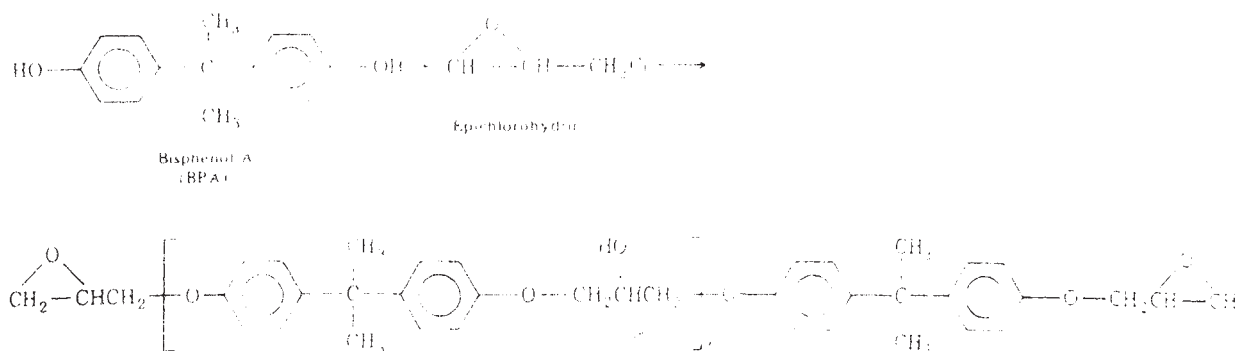
POLYCARBONATES. These resins are a special variety of polyester in which a derivative of carbonic acid is substituted for adipic, phthalic, or other acid and a diphenol is substituted for the more conventional glycols. A number of methods for the preparation of polycarbonates have been described, of which the melt process and the phosgenation process are the most important.²² Their general formula is



EPOXY RESINS. The most common epoxy resins are formed by the reaction of bisphenol A with epichlorohydrin. Bisphenol A is made from phenol and acetone

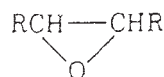


Bisphenol A plus epichlorohydrin gives resins of the following general structure



²²ECT, 3d ed., vol. 18, 1981, pp. 479-494

If the value of n is low, the resin is liquid; if n is 25 the resin is a hard, tough solid. However, any resin containing one or more epoxide groups is an epoxy resin.²³



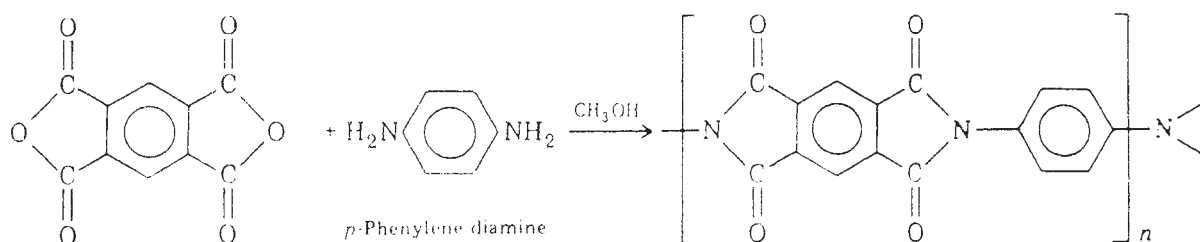
Epoxide group

Most commercial resins are not 100% diepoxides but may contain some other terminal groups such as glycol, phenolic, or chlorohydrin.

The epoxy resins are really intermediates, and must be cured, or cross-linked, to yield a useful resin. Cross-linking occurs by the opening of the epoxide ring caused by addition of a curing agent which must have active hydrogen atoms. Amines, acid anhydrides, and mercaptans are the most usual compounds used as curing agents.

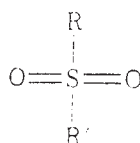
Depending upon molecular weight, epoxy resins have a great many uses ranging from adhesives to can and drum coatings. They have excellent chemical resistance, particularly to alkalis, very low shrinkage on cure, excellent adhesion and electrical insulating properties, and ability to cure over a wide range of temperatures.

POLYIMIDES. Compounds containing two anhydride groups will react with primary amines or isocyanates to form polyimide polymers which are very stable, linear polymers.



Polymellitic dianhydride

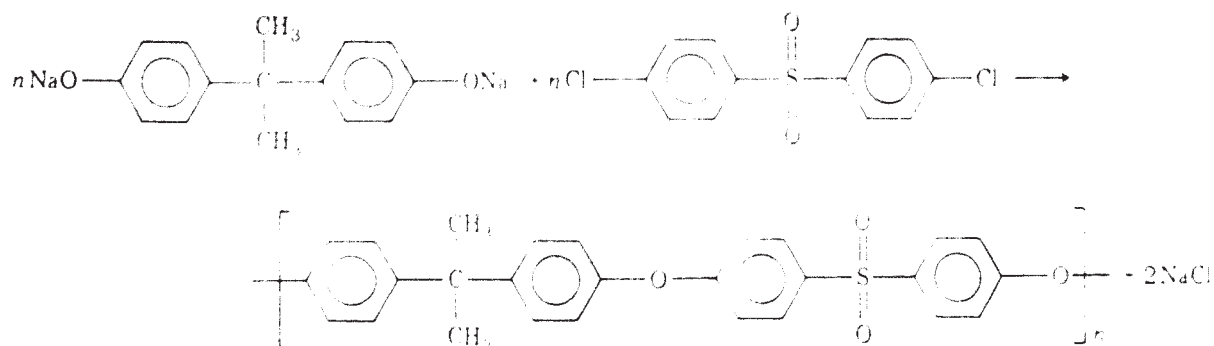
POLYSULFONES.²⁴ These are both aliphatic and aromatic polymers that contain the structural unit



They are resistant to high temperatures and are ultrastable. Their resistance to autoclave sterilization makes them useful for medical instruments and trays. Other uses are microwave cookware, coffee decanters, and corrosion-resistant piping. A typical preparation is the reaction of disodium bisphenol A with 4,4'-dichlorodiphenylsulfone.

²³Bauer, The Versatile Epoxies, *CHEMTECH* 10 (11) 692 (1980).

²⁴ECT, 3d ed., vol. 18, 1982, p. 832; Steinberg, Substituting Polyketones and Polysulfones for Polyethylene, *Chem. Eng. Prog.* 72 (9) 75 (1976); Fried, Polymer Technology, Part I, *Plast. Eng.* 38 (6) 49 (1982).



Addition Polymerization

POLYOLEFINS. *Polyethylene* was the first, and still is the largest in production, of polyolefin plastics. Imperial Chemical Industries (ICI) of England inadvertently discovered the white waxy solid in 1933 while attempting to react ethylene with benzaldehyde in an autoclave. The original ICI process operated at 50 to 300 MPa. This was one of the highest-pressure processes employed in the organic chemical industry.

Two types of polyethylene have been available.²⁵ High-density polyethylene (HDPE) produced by low-pressure methods, is used mainly for blow-molded containers and injection-molded articles and pipe. Low-density polyethylene (LDPE) produced by high-pressure methods, is used mainly for plastic films. Within the past five years new processes for producing low-density polyethylene at lower pressures have been introduced. These new low-density polymers have a small amount of α -olefin as comonomer and are called linear low-density polyethylene (LLDPE). Union Carbide's process uses butene. Dow and DuPont use octene, and Phillips uses hexene. The structural differences between the high- and low-density polyethylenes are in the structure of the polymer chain. Low-density polyethylene's chain is highly branched with both short- and long-chain branches, and the high-density material has very few side chains. The new LLDPE contains short side chains that are spaced uniformly and periodically on the long backbone chain. HDPE has a density greater than 0.960 g/cm³. LDPE's density ranges from 0.910 to 0.940, and the commercial LLDPE density usually ranges between 0.918 and 0.940.

Figure 34.9 shows a high-pressure process using oxygen or peroxides for catalysts. Polyethylene manufacture requires high-purity ethylene, and the first steps involve the demethanizer, where a mixture of methane-ethylene is removed and recycled. The feed passes to a deethanizer, where 99.8% ethylene is taken overhead, and the bottoms, ethane, recycled. A free-radical yielding catalyst, such as a peroxide, is added to the high-purity ethylene, compressed to operating pressure (150 MPa), and fed to the tubular reactor which is maintained at 190°C. The reaction takes place in solution. Conversion per pass is about 30 percent. The effluent from the reactor passes to a high-pressure separator in which the unconverted ethylene is removed and recycled. The polyethylene is extruded, pelletized, and dried.

One of the low-pressure processes to produce LLDPE is that of Union Carbide's Unipol process as shown in Fig. 34.10.²⁶ The purified ethylene, and 1-butene for comonomer, are fed

²⁵Paschke, The Outlook for High-Density Polyolefin, *Chem. Eng. Prog.* **76**: 1-74 (1980); LDPE Goes Low Pressure, *Chem. Eng.* **S5**: 1-25 (1978); ECT, 3d ed., vol. 16, 1981, p. 355; *Chem. Eng.* **89** (25) 17 (1982).

²⁶New Route to Low-Density Polyethylene, *Chem. Eng.* **86**: 26-30 (1979); A Step Up for LLDPE Know-How, *Chem. Week* **130** (13) 11 (1982).

cess steps and cut costs and energy requirements. The basic catalyst, used for the past 20 years, is titanium trichloride with aluminum chloride present as a solid solution in the titanium trichloride matrix. It is made by treating aluminum with titanium tetrachloride.



Various improvements have been made, such as by addition of a third component, such as diethyl or triethyl aluminum chloride, to modify the crystal structure and by making a supported catalyst. Other improvements have been made by closely guarded trade-secret means. Typical processing schemes have been described.²⁷ In the United States polypropylene is produced by solution polymerization (Eastman), hydrocarbon slurry (Hercules, Solvay, Amoco, Eastman), propylene slurry (Phillips, Dart Industries), and in the gas phase (Northern Petrochemicals). The two new processes are the gas-phase and propylene slurry.

The propylene slurry process does not require any other hydrocarbon, which simplifies feedstock inventory and recycle systems. The reaction takes place in a reactor which consists of a large-diameter pipe assembled in a loop configuration. The propylene, catalyst, and cocatalyst are fed to the loop continuously. The slurry of polypropylene in liquid propylene is discharged continuously to a vessel where polymerization terminating agents are added. Washing with liquid propylene and flashing off the propylene yields a powder which is extruded and pelletized.

An interesting battle was waged over the patent rights to crystalline polypropylene. In contention were DuPont, Montedison, Standard Oil of Indiana, and Phillips Petroleum. Originally Montedison had a patent dated February 6, 1973, but in 1980 the courts declared that Montedison had committed fraud during a patent examiner's meeting, and awarded prior invention rights to Phillips. The stakes were, and are, millions of dollars in licenses and royalties. In 1982 the U.S. Supreme Court upheld the lower court and awarded patent rights to Phillips who will now be issued a patent.²⁸

VINYL RESINS.²⁹ The polyvinyl resins are synthetic materials made from compounds having a vinyl ($-\text{CH}=\text{CH}_2$) group. The most important members of this class are polyvinyl acetate, polyvinyl chloride, polyvinyl alcohol, and polyvinyl acetals and copolymers of vinyl chloride with vinyl acetate, and vinylidene chloride. See Fig. 34.11 for a simplified flowchart for vinyl resins. *Polyvinyl acetate* may be prepared by introducing a benzene solution of vinyl acetate containing the desired catalyst into a jacketed vessel. At a temperature of about 72°C, the mixture boils and the vapors are condensed and returned to the kettle. After about 5 h at a gentle boil, the reaction mixture is run to a still, and the solvent and unchanged vinyl acetate are removed by steam distillation. The molten resin is then either run into drums, where it solidifies, or extruded into rods and sliced into flakes. Polyvinyl acetate is used primarily in paints and adhesives. About 20 percent of the vinyl acetate produced is used to make polyvinyl alcohol.

The largest branch of the vinyl family is *polyvinyl chloride* (PVC). The popularity of PVC is due to its excellent physical properties, its ability to be compounded for a wide range of applications, its ease of processing, and its relatively low cost.

²⁷Short, Polypropylene: Processes, Catalysis, Economics, *CHEMTECH* 11 (4) 238 (1981); Cipriani and Trischman, New Catalyst Cuts Polypropylene Costs and Energy Requirements, *Chem. Eng.* 88 (8) 50 (1981); ECT, 3d ed., vol. 16, 1981, pp. 453-469.

²⁸*Plast. World* 40 (7) 10 (1982)

²⁹MPE, 1981-1982; *Hydrocarbon Process.* 60 (11) 233 (1981).

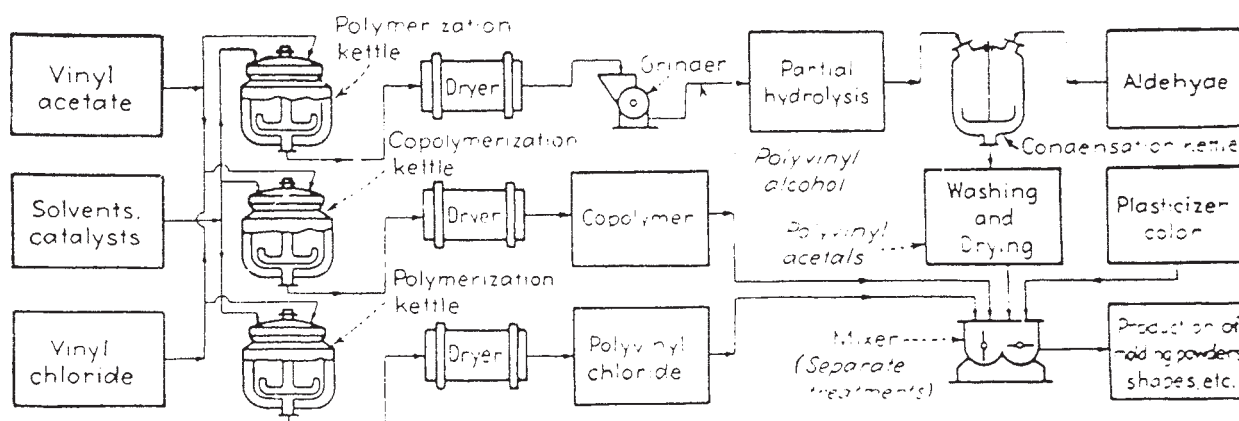
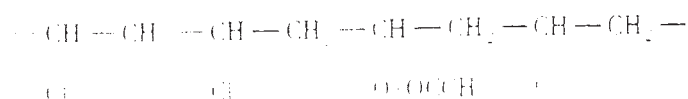


Fig. 34.11. Flowchart for polyvinyl resin manufacture.

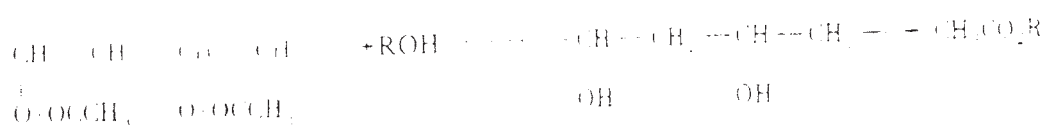
The liquid monomer is formed into tiny globules by vigorous stirring in water containing a suspending agent. A typical recipe lists 100 parts of water, 100 parts of liquid vinyl chloride, 1 part of a persulfate catalyst, and 1.5 parts of an emulsifier such as sodium lauryl sulfate. The autoclave operates at 40 to 45°C for 72 h to give a yield of 90 percent of polymer with a particle size of 0.1 to 1.0 μm . Recovery of these particles may be accomplished by spray-drying, or by coagulation by acid addition. A PVC compound can be tailor-made to achieve whatever balance of properties is desired by using plasticizers, stabilizers, lubricants, and fillers. Almost 40 percent of the U.S. production is used to manufacture construction pipe.

Copolymers of vinyl chloride and other vinyls retain the toughness and chemical resistance of PVC but are more flexible. Studies of these copolymers were carried out because of the practical limitations (high molding temperature, poor heat stability, etc.) encountered with PVC in its early development. The monomers of both acetate and chloride are mixed with a solvent and catalyst and polymerized in an autoclave to yield a copolymer which may be represented in part as follows:



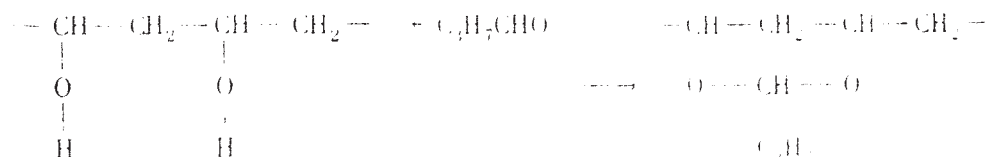
Although the acetate-chloride ratio can be varied over wide limits to give resinous products suitable for a great variety of applications, the more important copolymers usually contain a preponderance of chloride.

Vinyl Alcohol Resins. These resins are made from polyvinyl acetate which is first reacted with alcohol to yield polyvinyl alcohol and then condensed with aldehydes to give a group of resins. The polyvinyl acetate is reacted with alcohol under controlled conditions with a trace of either acid or alkali which replaces the acetyl groups with hydroxyl groups to yield polyvinyl alcohol.



This method of preparation is used because polyvinyl alcohol cannot be prepared by direct polymerization since the monomer vinyl alcohol is an unknown compound and exists as the enol form of acetaldehyde (CH_3CHO). Polyvinyl alcohol is a unique plastic because it is plas-

ticized by water and is completely soluble in an excess of water. Polyvinyl alcohol reacts with an aldehyde under the influence of heat and in the presence of an acid catalyst, such as sulfuric or hydrochloric acid, and the result is a typical acetal. Polyvinyl butyral is formed as follows:



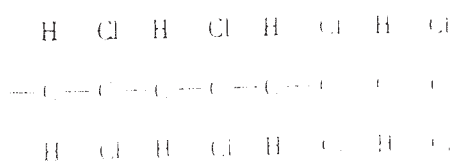
The corresponding formal and acetal are



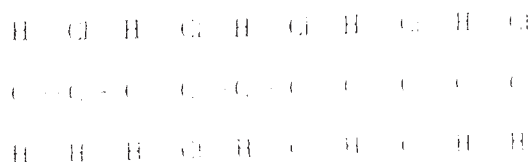
In actual commercial production, the hydrolysis and condensation reactions are never carried to completion because it has been found that the presence of residual acetyl and hydroxyl groups gives the resins better properties.

Polyvinyl butyral is usually extruded as a sheet for the interlayer for safety glass. Some polyvinyl acetals can be compression-molded at temperatures from 100 to 130°C and injection-molded at temperatures from 170 to 190°C. Polyvinyl formals can be molded by either compression or injection, depending upon the softening point.

Vinylidene Resins. This class of resins was introduced in 1940 and is formed by the polymerization of the monomeric vinylidene chloride, $\text{CH}_2=\text{CCl}_2$, or vinylidene fluoride. These resins may be represented as:



or the monomer may be copolymerized with vinyl chloride to give a new product represented as:



The resins formed by copolymerization range from a flexible material having a softening point of about 70°C to a hard, thermoplastic solid with a softening point of 150°C. Their higher softening point indicates a greater degree of crystalline character. If the fibrous crystals are not oriented, the vinylidene chloride has a tensile strength of 55 MPa, which is an ordinary value. If the crystals are oriented by drawing, however, the tensile strength may be increased to about 410 MPa. These resins may be fabricated by compression or injection