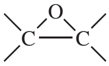
EPOXY RESINS

1. Introduction

Epoxy resins are an important class of polymeric materials, characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxyline group.



The word "epoxy" is derived from the Greek prefix "ep," which means over and between, and "oxy," the combining form of oxygen (1). By strict definition, epoxy resins refer only to uncross-linked monomers or oligomers containing epoxy groups. However, in practice, the term *epoxy resins* is loosely used to include cured epoxy systems. It should be noted that very high molecular weight epoxy resins and cured epoxy resins contain very little or no epoxide groups. The vast majority of industrially important epoxy resins are bi- or multifunctional epoxides. The monofunctional epoxides are primarily used as reactive diluents, viscosity modifiers, or adhesion promoters, but they are included here because of their relevance in the field of epoxy polymers.

Epoxies are one of the most versatile classes of polymers with diverse applications such as metal can coatings, automotive primer, printed circuit boards, semiconductor encapsulants, adhesives, and aerospace composites. Most cured epoxy resins provide amorphous thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, and electrical properties; no volatiles emission and low shrinkage upon cure; and dimensional stability—a unique combination of properties generally not found in any other plastic material. These superior performance characteristics, coupled with outstanding formulating versatility and reasonable costs, have gained epoxy resins wide acceptance as materials of choice for a multitude of bonding, structural, and protective coatings applications.

Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones and are available in a wide range of molecular weights from several hundreds to tens of thousands. The most widely used epoxies are the glycidyl ether derivatives of bisphenol A ($>75\%$ of resin sales volume). The capability of the highly strained epoxy ring to react with a wide variety of curing agents under diverse conditions and temperatures imparts additional versatility to the epoxies. The major industrial utility of epoxy resins is in thermosetting applications. Treatment with curing agents gives insoluble and intractable thermoset polymers. In order to facilitate processing and to modify cured resin properties, other constituents may be included in the compositions: fillers, solvents, diluents, plasticizers, catalysts, accelerators, and tougheners.

Epoxy resins were first offered commercially in the late 1940s and are now used in a number of industries, often in demanding applications where their performance attributes are needed and their modestly high prices are justified. However, aromatic epoxies find limited uses in exterior applications because of their poor ultraviolet (UV) light resistance. Highly cross-linked epoxy thermosets sometimes suffer from brittleness and are often modified with tougheners for improved impact resistance.

The largest use of epoxy resins is in protective coatings ($>50\%$), with the remainder being in structural applications such as printed circuit board (PCB) laminates, semiconductor encapsulants, and structural composites; tooling, molding, and casting; flooring; and adhesives. New, growing applications include lithographic inks and photoresists for the electronics industry.

2. History

The patent literature indicates that the synthesis of epoxy compounds was discovered as early as the late 1890s (2). In 1934, Schlack of I.G. Farbenindustrie AG in Germany filed a patent application for the preparation of reaction products of amines with epoxies, including one epoxy based on bisphenol A and epichlorohydrin (3). However, the commercial possibilities for epoxy resins were only recognized a few years later, simultaneously and independently, by the DeTrey Fréres Co. in Switzerland (4) and by the DeVoe and Raynolds Co. (5) in the United States.

In 1936, Pierre Castan of DeTrey Fréres Co. produced a low melting epoxy resin from bisphenol A and epichlorohydrin that gave a thermoset composition with phthalic anhydride. Application of the hardened composition was foreseen in dental products, but initial attempts to market the resin were unsuccessful. The patents were licensed to Ciba AG of Basel, Switzerland, and in 1946 the first epoxy adhesive was shown at the Swiss Industries Fair, and samples of casting resin were offered to the electrical industry.

Immediately after World War II, Sylvan Greenlee of DeVoe and Raynolds Co. patented a series of high molecular weight (MW) epoxy resin compositions for coating applications. These resins were based on the reaction of bisphenol A and epichlorohydrin, and were marketed through the subsidiary Jones-Dabney Co. as polyhydroxy ethers used for esterification with drying oil fatty acids to produce alkyd-type epoxy ester coatings. Protective surface coatings were the first major commercial application of epoxy resins, and they remain a major outlet for epoxy resin consumption today. Concurrently, epoxidation of multifunctional olefins with peroxy acids was studied by Daniel Swern as an alternative route to epoxy resins (6). Meanwhile, Ciba AG, under license from DeTrey Frères, further developed epoxy resins for casting, laminating, and adhesive applications, and the Ciba Products Co. was established in the United States.

In the late 1940s, two U.S. companies, Shell Chemical Co. and Union Carbide Corp. (then Bakelite Co.), began research on bisphenol A based epoxy resins. At that time, Shell was the only supplier of epichlorohydrin, and Bakelite was a leading supplier of phenolic resins and bisphenol A. In 1955, the four U.S. epoxy resin manufacturers entered into a cross-licensing agreement. Subsequently, The Dow Chemical Co. and Reichhold Chemicals, Inc. joined the patent pool and began manufacturing epoxy resins.

In the 1960s, a number of multifunctional epoxy resins were developed for higher temperature applications. Ciba Products Co. manufactured and marketed *o*-cresol epoxy novolac resins, which had been developed by Koppers Co. Dow developed the phenol novolac epoxy resins, Shell introduced polyglycidyl ethers of tetrafunctional phenols, and Union Carbide developed a triglycidyl *p*-aminophenol resin. These products continue to find uses today in highly demanding applications such as semiconductor encapsulants and aerospace composites where their performance justifies their higher costs relative to bisphenol A based epoxies.

The peracetic acid epoxidation of olefins was developed in the 1950s by Union Carbide in the United States and by Ciba AG in Europe for cycloaliphatic structures. Ciba Products marketed cycloaliphatic epoxy resins in 1963 and licensed several multifunctional resins from Union Carbide in 1965. The ensuing years witnessed the development of general-purpose epoxy resins with improved weathering characteristics based on the five-membered hydantoin ring and also on hydrogenated bisphenol A, but their commercial success has been limited because of their higher costs. Flame-retardant epoxy resins based on tetrabromobisphenol A were developed and commercialized by Dow Chemical for electrical laminate and composite applications in the late 1960s.

In the 1970s, the development of two breakthrough waterborne coating technologies based on epoxy resins helped establish the dominant position of epoxies in these markets: PPG's cathodic electrodeposition automotive primer and ICI-Glidden's epoxy acrylic interior can coatings.

While epoxy resins are known for excellent chemical resistance properties, the development and commercialization of epoxy vinyl ester resins in the 1970s by Shell and Dow offered enhanced resistance properties for hard-to-hold, corrosive chemicals such as acids, bases, and organic solvents. In conjunction with the development of the structural composites industry, epoxy vinyl ester resin composites found applications in demanding environments such as tanks, pipes and ancillary equipment for petrochemical plants and oil refineries, automotive valve covers, and oil pans. More recently, epoxy and vinyl esters are used in the construction of windmill blades for wind energy farms. Increasing requirements in the composite industries for aerospace and defense applications in the 1980s led to the development of new, high performance multifunctional epoxy resins based on complex amine and phenolic structures. Examples of those products are the trisphenol epoxy novolacs developed by Dow Chemical and now marketed by Huntsman (formerly Ciba).

The development of the electronics and computer industries in the 1980s demanded higher performance epoxy resins. Faster speeds and more densely packed semiconductors required epoxy encapsulants with higher thermal stability, better moisture resistance, and higher device reliability. Significant advances in the manufacturing processes of epoxy resins led to the development of electronic-grade materials with lower ionic and chloride impurities and improved electrical properties. Dow Chemical introduced a number of new, high performance products such as hydrocarbon epoxy novolacs based on dicyclopentadiene. The 1980s also witnessed the development of the Japanese epoxy resin industry with focus on specialty, high performing and high purity resins for the electronics industry. These include the commercialization of crystalline resins such as biphenol diglycidyl ether.

More recently, in order to comply with more stringent environmental regulations, there has been increased attention to the development of epoxy resins for high solids, powder, and waterborne and radiation-curable coatings. Powder coatings based on epoxy–polyester and epoxy–acrylate hybrids have continued to grow in the global markets, including new applications such as primer-surfacer and topcoats for automotive coatings. Radiation-curable epoxy–acrylates and cycloaliphatic epoxies showed tremendous growth in the 1990s in radiation-curable applications. These include important and new uses of epoxy resins such as the photoresists and lithographic inks for the electronics industry. Waterborne epoxy coatings are projected to grow substantially.

The continuing trend of device miniaturization in the computer industry, and the explosive growth of portable electronics and communications devices such as wireless cellular telephones in the 1990s demanded new, high performance resins for the PCB market. This has led to the development of new epoxies and epoxy hybrid systems having lower dielectric constants (D_k), higher glass-transition temperatures (T_g), and higher thermal decomposition temperatures (T_d) for electrical laminates. Environmental pressures in the PCB industry have fueled the development of a number of new bromine-free resin systems, but their commercialization is limited because of higher costs.

Significant efforts have been directed toward performance enhancements of epoxy structural composites. Advances have been made in the epoxy-toughening area. Epoxy nanocomposites and nanotube systems have been studied and are claimed to bring exceptional thermal, chemical, and mechanical property improvements. However, commercialization has not yet materialized.

In 1999, Dow Chemical introduced a new epoxy-based thermoplastic resin, BLOX*, for gas barrier, adhesives, and coatings applications.

3. Industry Overview

From the first commercial introduction of diglycidyl ether of bisphenol A (DGEBA) resins in the 1940s, epoxy resins have gradually established their position as an important class of industrial polymers. Epoxy resin sales increased rapidly in the 1970s and continued to rise into the 1980s as new applications were developed (annual growth rate >10% in the U.S. market, Table 1). More recently, the slower growth rates (3–4%) of the U.S., Japanese, and European markets in the 1990s were made up for by the higher growth rate (5–10%) in the Asia-Pacific markets outside of Japan, particularly in Taiwan and China. Epoxy resin growth has historically tracked well with economic developments and demands for durable goods, and so the growth of the epoxy markets in Asia-Pacific is expected to continue into the next decade.

The global market for epoxy resins is estimated at approximately 1.15 million metric tons (MT) for the year 2000 (8). This is an increase of 5% over 1999 demands. The North American market consumed over 330,000 MT of epoxy resins, the European market is estimated at more than 370,000 MT, and the Asian market has surpassed both the North American and European markets by consuming 400,000 MT of epoxy resins. About 50,000 MT of epoxies were consumed in the South American markets. Imports of epoxy resins from Asia into North America has steadily grown to about 120,000 MT in 2000. Epoxy resins

Table 1. **History of U.S. Epoxy Resin Annual Production**[a]

Year	Production, 10^3 MT
1955	10
1960	30
1965	55
1970	79
1975	100
1980	201
1985	347
1990	475
1994	433

[a] Data from U.S. International Trade Commission, *Synthetic Organic Chemicals*. Data include modified and unmodified epoxy resins. Modified epoxy resins include solid epoxy resin (SER), vinyl ester resins, epoxy acrylates, etc. There appear to be some discrepancies in epoxy resin production and market data as reported by different publications and organizations (7). This is primarily due to the fact that some epoxy resins such as liquid DGEBA resins and epoxy novolacs are used as raw materials to produce modified or advanced epoxy resins, which may be further converted to end-use products. Some publications report only unmodified epoxies.

were used with over 400,000 MT of curing agents to produce an estimated 3 million MT of formulated compounds, worth over $20 billion.

Up until the mid-1990s, the major worldwide producers of epoxy resins were Dow Chemical, Shell, and Ciba-Geigy. However, both Shell and Ciba-Geigy have recently divested their epoxy resins businesses. Shell sold their epoxy business to Apollo Management LP (based in New York City) in the year 2000 and the company was renamed Resolution Performance Products. Similarly, Ciba's epoxy business was sold in 2000 to Morgan Grenfell, a London (U.K.)-based private equity firm, and the new company name was Vantico. More recently, in June 2003, the Vantico group of companies joined Huntsman. The Vantico business units are now named Huntsman Advanced Materials. The cycloaliphatic epoxy business of Union Carbide became part of The Dow Chemical Company after their merger in the year 2001. Together, these three producers continue to dominate the world market for epoxy resins, accounting for almost 65 % of the global market. However, this is a reduction from over 70 % of market shares owned by the three largest producers in the 1980s. Smaller producers of epoxy resins for the North American markets are Reichhold (owned by Dainippon Ink and Chemicals), CVC Specialty Chemicals, Pacific Epoxy Polymers, and InChem (phenoxy thermoplastic resins). Suppliers of epoxy derivatives include Ashland Specialty Chemical, UCB Chemicals (Radcure), AOC LLC, Eastman Chemical, and Interplastic Corp.

The market in Europe is similarly dominated by the three big producers: Dow, Resolution, and Huntsman and their affiliated joint ventures. Other smaller epoxy producers include Bakelite AG, LEUNA-Harze, Solutia, SIR

Industriale, and EMS-CHEMIE. Imports from Asia have become significant in recent years.

The last two decades marked the emergence of the Asian epoxy industry. In the 1980s, the Japanese epoxy industry was transformed from a number of joint venture companies with Dow, Shell, and Ciba into independent producers and the emergence of a high number of new producers. This coincides with the development of Japan as a world-class manufacturing base. The Japanese epoxy industry is known for their special focus on high performance, high purity resins for the electronics industry. According to data from the Japan Epoxy Resin Manufacturers Association, the total Japanese market demand is estimated at approximately 200,000 MT for the year 2000. The production capacity is estimated at 240,000 MT annually. Exports accounted for an estimated 40,000 MT in 2000. Major Japanese epoxy resin producers are Tohto Kasei, Japan Epoxy Resins Corp. (formerly Yuka-Shell), Asahi Kasei, Dai Nippon Ink and Chemicals, Dow Chemical Japan, Mitsui Chemicals, Nihon Kayaku, Sumitomo Chemical, and Asahi Denka Kogyo. In Japan, Tohto Kasei is a leading resin producer, with epoxy technology licensing arrangements with numerous resin producers in Asia.

Outside of Japan, there have been significant increases in epoxy market demands and capacity in the 1990s. This is due to the migration of many PCB, electronic, computer, and durable goods manufacturing plants into the region, which has considerably lower manufacturing costs. Nan Ya, a subsidiary of the Formosa Plastics Group based in Taiwan, is emerging as a major epoxy resin producer with some import presence in North America and Europe. Similarly, Kukdo of Korea also exports to the North American and European markets. The output of these two companies now account for an estimated 15% of the world market. In China, there are numerous (more than 200) small domestic producers of epoxy resins. Recently, a number of major epoxy producers have announced joint ventures or plans to build manufacturing plants in China. These include a number of companies with integrated capacity into electrical laminates and PCB manufacturing, following the business model pioneered by the Formosa Plastics Group. Other notable Asian producers include Asia Pacific Resins, Chang Chun, and Eternal Chemical of Taiwan; Thai Epoxy of Thailand; Kumho, LG Chemical, and Pacific Epoxy Resins of Korea; and Guangdong Ciba Polymers, Sinopec Baling Petrochemical, Jiangsu Sanmu, and Wuxi DIC Epoxy Resin of China. The LG Chemical epoxy business was purchased by Bakelite in late 2002. A significant amount of resin produced in Taiwan and China is directed toward electrical laminates applications. The aggressive buildup of epoxy capacity in Asia has put significant pressures on resin prices, particularly the high volume products such as liquid epoxy resins based on bisphenol A (Table 2). But as of January 2004, the epoxy market demand in China alone has increased to more than 500,000 MT (Chinese Epoxy Industry Web site).

Estimated average prices for epoxy resin products in North America are given in Table 3. As with other petrochemical-based products, they depend on crude-oil prices. Prices of multifunctional resins are typically higher. They are based on more expensive raw materials than DGEBA resins and involve more complex manufacturing procedures. A listing of some major epoxy resin producers and the trade names of their products is shown in Table 4.

Table 2. **Epoxy Production Capacity in Asia-Pacific**[a] **(2001)**

Country	Existing capacity, 1000 MT/year	Announced capacity, 1000 MT/year
Japan	240	
Taiwan	239	70
China	100	255
Korea	180	
Thailand	30	
Malaysia	10	
Philippines	10	
Total	*809*	*325*

[a] Compilation of published data by Dow Chemical.

There are numerous suppliers of epoxy curing agents. Some of the major producers are Air Products and Chemicals, Cognis, Degussa, DSM, Huntsman, and Resolution.

4. Classes of Epoxy Resins and Manufacturing Processes

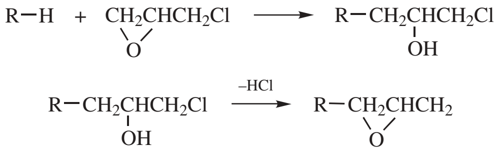
Most commercially important epoxy resins are prepared by the coupling reaction of compounds containing at least two active hydrogen atoms with epichlorohydrin followed by dehydrohalogenation:

Table 3. **U.S. Average Epoxy Resin Prices and Applications (2000)**

Resin	\$/kg	Applications
Liquid epoxy resins (Diglycidyl ether of bisphenol A, DGEBA)	2.2	Coatings, castings, tooling, flooring, adhesives, composites
Solid epoxy resins (SER)	2.4	Powder coating; epoxy esters for coatings; can, drum, and maintenance coatings
Bisphenol F epoxy	4.4	Coatings
Multifunctional		
Phenol epoxy novolac	4.8	Castings, coatings, laminates
Cresol epoxy novolac	8.8	Electronics encapsulants, powder coatings, laminates
Other multifunctional epoxies	11–44	Composites, adhesives, laminates, electronics
Cycloaliphatic epoxies	6.6	Electrical castings, coatings, electronics
Brominated epoxies	3.3–5.5	Printed wiring boards, composites
Epoxy vinyl esters	3.3	Composites
Phenoxy resins	11–17	Coatings, laminates, glass sizing
Epoxy diluents	4–11	

Table 4. **List of Some Epoxy Resin Producers and Their Product Trade Names**

Company	Trade name
Resolution Performance Products	Epon, Eponol, Eponex, Epi-Cure, Epikote
Dow Chemical	D.E.R., D.E.N., D.E.H., Derakane, E.R.L
Hunstman Advanced Materials (formerly Ciba, Vantico)	Araldite, Aralcast
Reichhold Chemical	Epotuf
Nan Ya	NPEL, NPES
Kukdo Chemical	YD
Dainippon Ink & Chemical (DIC)	Epiclon
Tohto Kasei	Epotohto
Japan Epoxy Resin (JER)	Epikote
Asahi Kasei	A.E.R.
Mitsui Chemical	Eponik
Sumitomo Chemical	Sumiepoxy
Thai Epoxy	Epotec
Chang Chun	
InChem	Paphen
Pacific Epoxy Polymers	PEP
CVC Specialty Chemicals	Erysis, Epalloy



$$R{-}H + \underset{\diagdown O \diagup}{CH_2CHCH_2Cl} \longrightarrow R{-}CH_2\underset{OH}{CH}CH_2Cl$$

$$R{-}CH_2\underset{OH}{CH}CH_2Cl \xrightarrow{-HCl} R{-}\underset{\diagdown O \diagup}{CH_2CHCH_2}$$

These included polyphenolic compounds, mono and diamines, amino phenols, heterocyclic imides and amides, aliphatic diols and polyols, and dimeric fatty acids. Epoxy resins derived from epichlorohydrin are termed *glycidyl-based resins*.

Alternatively, epoxy resins based on epoxidized aliphatic or cycloaliphatic dienes are produced by direct epoxidation of olefins by peracids:

$$RCH{=}CHR^{\bullet} + R''COOOH \longrightarrow \overset{\diagup O \diagdown}{RCH{-}CHR^{\bullet}} + R''COOH$$

Approximately 75% of the epoxy resins currently used worldwide are derived from DGEBA. This market dominance of bisphenol A based epoxy resins is a result of a combination of their relatively low cost and adequate-to-superior performance in many applications. Figure 1 shows U.S. consumption of major epoxy resin types for the year 2000.

5. Liquid Epoxy Resins (DGEBA)

The most important intermediate in epoxy resin technology is the reaction product of epichlorohydrin and bisphenol A. It is often referred to in the industry as

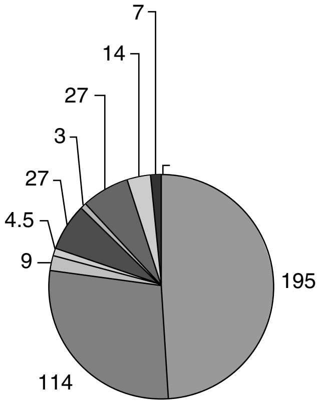
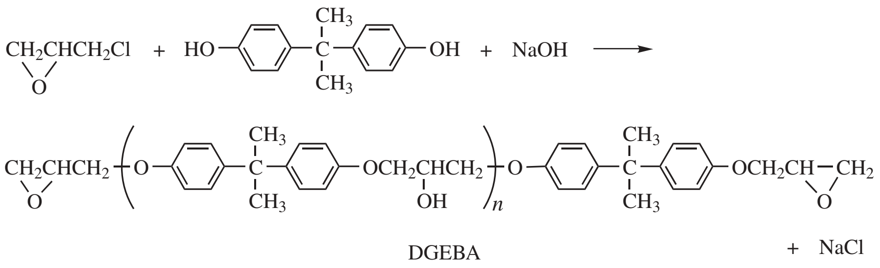


Fig. 1. Major epoxy resin and derivatives markets (10^3 MT). ■ LER; ■ SER; ■ epoxy novolacs; ■ other multifunctional epoxies; ■ brominated epoxies; ■ cycloaliphatic; ■ vinyl esters; and ■ epoxy acrylates.

liquid epoxy resin (LER), which can be described as the crude DGEBA where the degree of polymerization, n, is very low ($n \cong 0.2$):



Pure DGEBA is a crystalline solid (mp 43 °C) with an epoxide equivalent weight (EEW) of 170. The typical commercial unmodified liquid resins are viscous liquids with viscosities of 11,000–16,000 mPa·s (= cP) at 25 °C, and an epoxide equivalent weight of ca. 188.

EEW is the weight of resin required to obtain one equivalent of epoxy functional group. It is widely used to calculate reactant stoichiometric ratios for reacting or curing epoxy resins. It is related to the epoxide content (%) of the epoxy resin through the following relationship:

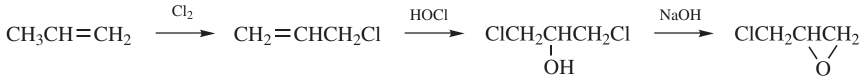
$$\text{EEW} = \frac{43.05}{\%\text{Epoxide}} \times 100$$

where 43.05 is the molecular mass of the epoxide group, $-C_2H_3O$. Other equivalent terminologies common in the industry include *weight per epoxide* (Wpe) or *epoxide equivalent mass* (EEM).

The outstanding performance characteristics of the resins are conveyed by the bisphenol A moiety (toughness, rigidity, and elevated temperature performance), the ether linkages (chemical resistance), and the hydroxyl and epoxy groups (adhesive properties and formulation latitude; reactivity with a wide variety of chemical curing agents).

LERs are used in coatings, flooring and composites formulations where their low viscosity facilitates processing. A large majority of LERs are used as starting materials to produce higher molecular weight (MW) solid epoxy resins (SER) and brominated epoxy resins, and to convert to epoxy derivatives such as epoxy vinyl esters, epoxy acrylates, etc. The bisphenol A derived epoxy resins are most frequently cured with anhydrides, aliphatic amines, phenolics, or polyamides, depending on desired end properties. Some of the outstanding properties are superior electrical properties, chemical resistance, heat resistance, and adhesion. Cured LERs give tight cross-linked networks having good strength and hardness but have limited flexibility and toughness.

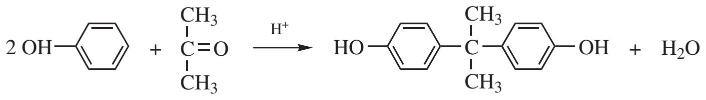
Epichlorohydrin, or 3-chloro-1,2-epoxy propane (bp 115 °C), is more commonly prepared from propylene by chlorination to allyl chloride, followed by treatment with hypochlorous acid. This yields glycerol dichlorohydrin, which is dehydrochlorinated by sodium hydroxide or calcium hydroxide (9).



$$CH_3CH{=}CH_2 \xrightarrow{Cl_2} CH_2{=}CHCH_2Cl \xrightarrow{HOCl} ClCH_2\underset{OH}{CH}CH_2Cl \xrightarrow{NaOH} ClCH_2\underbrace{CHCH_2}_{O}$$

In industrial practices, epichlorohydrin is produced by direct chlorohydroxylation of allyl chloride in chlorine and water (10–13). Alternatively, a new epichlorohydrin process has been developed and commercialized by Showa Denko (14) in Japan in 1985. It involves the chlorination of allyl alcohol as the precursor and is claimed to be more efficient in chlorine usage.

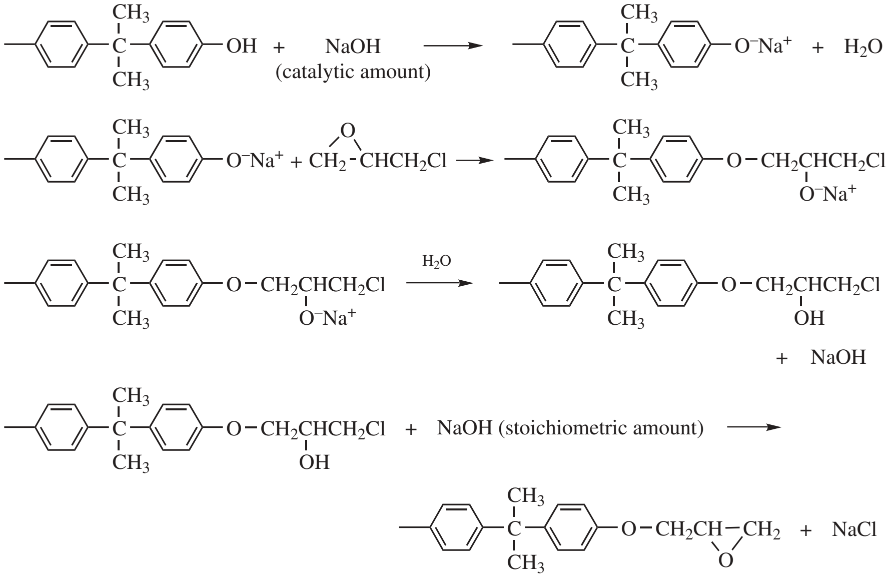
Bisphenol A (mp 153 °C), or 2,2-bis(*p*-hydroxyphenyl)propane, is prepared from 2 moles of phenol and 1 mole of acetone (15,16)



Bisphenol A based liquid epoxy resins are prepared in a two-step reaction sequence from epichlorohydrin and bisphenol A. The first step is the base-catalyzed *coupling* of bisphenol A and epichlorohydrin to yield a chlorohydrin.

Bases that may be used to catalyze this step include sodium hydroxide, lithium salts, and quaternary ammonium salts. Dehydrohalogenation of the chlorohydrin intermediate with a stoichiometric amount of base affords the glycidyl ether. Manufacturing processes can be divided into two broad categories according to the type of catalyst used to couple epichlorohydrin and bisphenol A (17,18).

5.1. Caustic Coupling Process. In this process, caustic is used as a catalyst for the nucleophilic ring-opening (coupling reaction) of the epoxide group on the primary carbon atom of epichlorohydrin by the phenolic hydroxyl group and as a dehydrochlorinating agent for conversion of the chlorohydrin to the epoxide group:



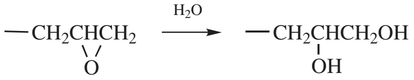
In caustic coupling processes, caustic (20–50 % sodium hydroxide in water) is slowly added to an agitated mixture of epichlorohydrin and bisphenol A. The highly exothermic coupling reaction proceeds during the initial stages. As the coupling reaction nears completion, dehydrochlorination becomes the predominant reaction. A high ratio (usually 10:1) of epichlorohydrin/bisphenol A is charged to the reactor to maximize the yield of monomeric ($n = 0$) DGEBA. At a 10:1 level of epichlorohydrin/bisphenol A, the $n = 0$ monomer comprises $>85\,\%$ of the reaction product mixture.

5.2. Phase-Transfer Catalyst Process. Alternatively, the coupling reaction and dehydrochlorination can be performed separately by using phase-transfer coupling catalysts, such as quaternary ammonium salts (19), which are not strong enough bases to promote dehydrochlorination. Once the coupling reaction is completed, caustic is added to carry out the dehydrochlorination step. Higher yields of the $n = 0$ monomer ($>90\,\%$) are readily available via this method.

Many variations of these two basic processes are described in process patents (20,21), including the use of co-solvents and azeotropic removal of water to facilitate the reactions and to minimize undesirable by-products such as insoluble polymers. The original batch methods have been modified to allow for continuous or semicontinuous production. New developments have been focused on improving manufacturing yield and resin purity.

The description of liquid DGEBA resins presented so far is oversimplified. In reality, *side reactions* result in the formation of low levels of impurities that both decrease the epoxide content from the theoretical amount of 2 per molecule and affect the resins properties, both before and after curing (22). The five common side reactions are as follows:

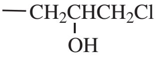
1. *Hydrolysis of epoxy groups.* Unavoidable hydrolysis of the epoxide ring gives a small amount (0.1–5 %) of monohydrolyzed resin (MHR) or α-glycol. It has been reported that dispersability of pigments are enhanced and rates of epoxy resin curing with diamines can be dramatically increased by higher levels of MHR (23).



$$-\mathrm{CH_2}\underset{\diagdown O \diagup}{\mathrm{CHCH_2}} \xrightarrow{\mathrm{H_2O}} -\mathrm{CH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH_2OH}$$

α-glycol formation

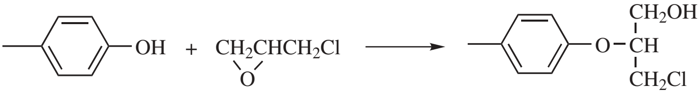
2. *Incomplete dehydrochlorination* results in residual saponifiable or hydrolyzable chloride:



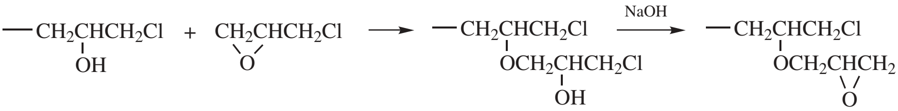
$$-\mathrm{CH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH_2Cl}$$

Incomplete dehydrochlorination increases the level of hydrolyzable chloride in the resin, which affects its suitablity for applications requiring superior electrical properties. In addition, hydrolyzable chlorides can affect reactivity by neutralizing basic catalysts such as tertiary amines. Many formulators adjust their formulations according to resin hydrolyzable chloride content. Typical hydrolyzable chloride contents of LERs range from <100 ppm for electronic grade resin to 200–1000 ppm for standard grade resins.

3. *Abnormal addition of epichlorohydrin,* i.e., abnormal phenoxide attack at the central carbon of epichlorohydrin results in an end group that is more difficult to dehydrochlorinate:



4. *Formation of bound chlorides* by reaction of epichlorohydrin with hydroxy groups in the polymer backbones:



$$-\mathrm{CH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH_2Cl} + \underset{\diagdown O \diagup}{\mathrm{CH_2CH}}\mathrm{CH_2Cl} \longrightarrow -\mathrm{CH_2}\underset{\underset{\mathrm{OH}}{\mathrm{OCH_2CHCH_2Cl}}}{\mathrm{CH}}\mathrm{CH_2Cl} \xrightarrow{\mathrm{NaOH}} -\mathrm{CH_2}\underset{\mathrm{OCH_2}\underset{\diagdown O \diagup}{\mathrm{CHCH_2}}}{\mathrm{CH}}\mathrm{CH_2Cl}$$

The bound chloride is not readily saponified with metal hydroxide solutions and is analyzed as part of the total chloride of the resin. Typical total chlorides values are 1000–2000 ppm.

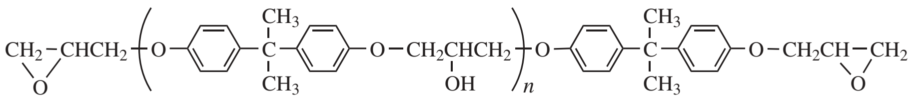
5. *Higher oligomer formation.* Reaction of a phenolic terminal group with another epoxy resin molecule instead of an epichlorohydrin molecule gives epoxy resins with broader oligomer distribution and increased viscosity

($n = 1$ and higher oligomers). Typical LERs contain 5–15% of the higher oligomers, mostly $n = 1$ and $n = 2$ compounds.

Pure DGEBA is a solid melting at 43 °C. The unmodified commercial liquid resins are supercooled liquids with the potential for crystallization, depending on purity and storage conditions. This causes handling problems, particularly for ambient cure applications. Addition of certain reactive diluents and fillers can either accelerate or retard crystallization. Crystallization-resistant, modified resins are available. A crystallized resin can be restored to its liquid form by warming.

6. Solid Epoxy Resins Based on DGEBA

High molecular weight (MW) SERs based on DGEBA are characterized by a repeat unit containing a secondary hydroxyl group with degrees of polymerization, i.e., n values ranging from 2 to about 35 in commercial resins; two terminal epoxy groups are theoretically present.



The epoxy industry has adopted a common nomenclature to describe the SERs. They are called type "1," "2" up to type "10" resins, which correspond to the increased values of n, the degree of polymerization, EEW, MW, and viscosity. Examples of SERs are D.E.R. 661, 662, 664, 667, 669 resins from Dow Chemical, and Epon 1001 to 1009 series from Resolution. A comparison of some key properties of LERs and SERs is shown in Table 5.

SERs based on DGEBA are widely used in the coatings industry. The longer backbones give more distance between cross-links when cross-linked through the terminal epoxy groups, resulting in improved flexibility and toughness. Furthermore, the resins can also be cured through the multiple hydroxyl groups along the backbones using cross-linkers such as phenol–formaldehyde resoles or isocyanates to create different network structures and performance.

SERs are prepared by two processes: the *taffy* process and the *advancement* or *fusion* process. The first is directly from epichlorohydrin, bisphenol A, and a stoichiometric amount of NaOH. This process is very similar to the *caustic coupling* process used to prepare liquid epoxy resins. Lower epichlorohydrin to bisphenol A ratios are used to promote formation of high MW resins. The term *taffy* is derived from the appearance of the advanced epoxy resin prior to its separation from water and precipitated salts.

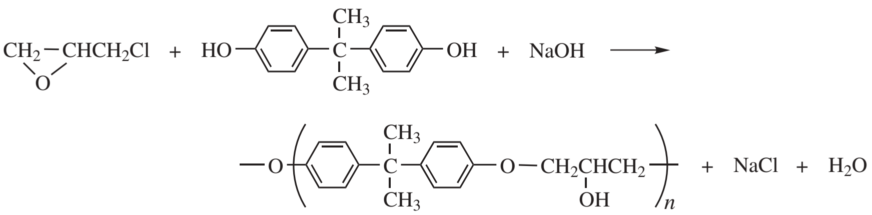


Table 5. **DGEBA-Based Epoxy Resins**

Resin type	n value[a]	EEW	Mettler softening point, °C	Molecular weight (M_w)[b]	Viscosity at 25 °C, mPa · s (= cP)
Low viscosity LER	< 0.1	172–176		~ 350	4,000–6,000
Medium viscosity LER	~ 0.1	176–185		~ 370	7,000–10,000
Standard grade LER	~ 0.2	185–195		~ 380	11,000–16,000
Type 1 SER	~ 2	450–560	70–85	~ 1,500	160–250[c]
Type 4 SER	~ 5	800–950	95–110	~ 3,000	450–600[c]
Type 7 SER	~ 15	1,600–2,500	120–140	~ 10,000	1,500–3,000[c]
Type 9 SER	~ 25	2,500–4,000	145–160	~ 15,000	3,500–10,000[c]
Type 10 SER	~ 35	4,000–6,000	150–180	~ 20,000	10,000–40,000[c]
Phenoxy resin	~ 100	> 20,000	> 200	> 40,000	

[a] n value is the number-average degree of polymerization which approximates the repeating units and the hydroxyl functionality of the resin.

[b] Molecular weight is weight average (M_w) measured by gel-permeation chromatography (GPC) using polystyrene standard.

[c] Viscosity of SERs is determined by kinematic method using 40 % solids in diethylene glycol monobutyl ether solution.

In the taffy process, a calculated excess of epichlorohydrin governs the degree of polymerization. However, preparation of the higher molecular weight species is subject to practical limitations of handling and agitation of highly viscous materials. The effect of epichlorohydrin–bisphenol A (ECH–BPA) ratio for a series of solid resins is shown in Table 6.

In commercial practice, the *taffy* method is used to prepare lower MW solid resins, i.e., those with maximum EEW values of about 1000 (type "4"). Upon completion of the polymerization, the mixture consists of an alkaline brine solution and a water–resin emulsion. The product is recovered by separating the phases, washing the taffy resin with water, and removing the water under vacuum. One disadvantage of the taffy process is the formation of insoluble polymers, which create handling and disposal problems. Only a few epoxy producers currently manufacture SERs using the taffy process. A detailed description of a taffy procedure follows (24).

A mixture of bisphenol A (228 parts by weight) and 10 % aqueous sodium hydroxide solution (75 parts by weight) is introduced into a reactor equipped with a powerful agitator. The mixture is heated to ca. 45 °C and epichlorohydrin (145 parts by weight) is added rapidly with agitation, giving off heat. The temperature is allowed to rise to 95 °C, where it is maintained about 80 min.

Table 6. **Effect of Epichlorohydrin–Bisphenol A Ratio on Resin Properties of Taffy SERs**

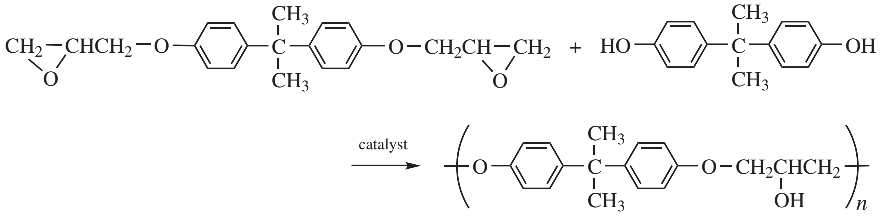
Mole ratio ECH/BPA	EEW	Softening point, °C
1.57:1.0	450–525	65–75
1.22:1.0	870–1025	95–105
1.15:1.0	1650–2050	125–135
1.11:1.0	2400–4000	145–155

for completion of the reaction. Agitation is stopped, and the mixture separates into two layers. The heavier aqueous layer is drawn off and the molten, taffy-like product is washed with hot water until the wash water is neutral. The taffy-like product is dried at 130 °C, giving a solid resin with a softening point of 70 °C and an EEW of ca. 500.

Alternatively, epichlorohydrin and water are removed by distillation at temperatures up to 180 °C under vacuum. The crude resin/salt mixture is then dissolved in a secondary solvent to facilitate water washing and salt removal. The secondary solvent is then removed via vacuum distillation to obtain the taffy–resin product.

Resins produced by this process exhibit relatively high α-glycol values, i.e., ca. 0.5 eq/kg, attributable to hydrolysis of epoxy groups in the aqueous phase. Although detracting from epoxide functionality, such groups act as accelerators for amine curing. Resins produced by the taffy process exhibit n values of 0, 1, 2, 3, etc, whereas resins produced by the *advancement* process (described below) exhibit mostly even-numbered n values because a difunctional phenol is added to a diglycidyl ether of a difunctional phenol.

An alternative method is the chain-extension reaction of liquid epoxy resin (crude DGEBA) with bisphenol A, often referred to as the *advancement* or *fusion process* (25) which requires an advancement catalyst:



The advancement process is more widely used in commercial practice. Isolation of the polymerized product is simpler, since removal of copious amounts of NaCl is unnecessary. The reaction can be carried out with or without solvents. Solution advancement is widely practiced by coatings producers to facilitate handling of the high MW, high viscosity epoxy resins used in many coating formulations. The degree of polymerization is dictated by the ratio of LER to bisphenol A; an excess of the former provides epoxy terminal groups. The actual MW attained depends on the purity of the starting materials, the type of solvents used, and the catalyst. Reactive monofunctional groups can be used as chain terminators to control MW and viscosity build.

The following formula can be used to calculate the relative amount of bisphenol A that must be reacted with epoxy resin to give an advanced epoxy resin of predetermined EEW:

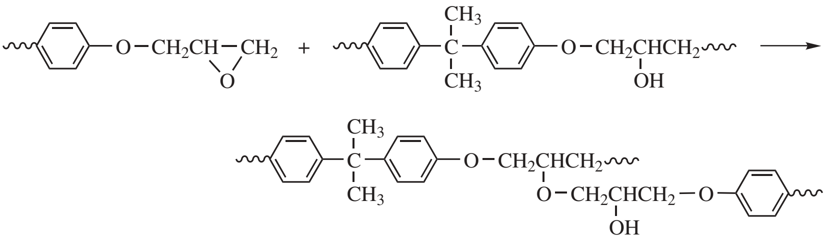
$$\text{Bis A} = \frac{\text{EEW}_\text{i}^{-1} - \text{EEW}_\text{f}^{-1}}{\text{EEW}_\text{i}^{-1} + \text{PEW}^{-1}}$$

where Bis A is the mass fraction of bisphenol A in the mixture prior to advancement, EEW_i is the EEW of the epoxy resin that is to be advanced, EEW_f is the

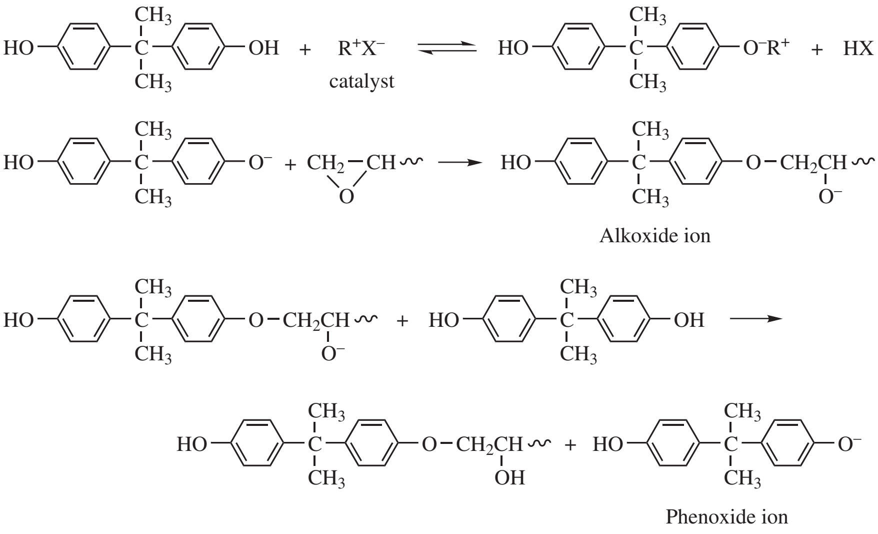
EEW of the advanced epoxy resin, and PEW is the phenol equivalent mass of the bisphenol, which is 114 g per equivalent for bisphenol A.

In a typical advancement process, bisphenol A and a liquid DGEBA resin (175–185 EEW) are heated to ca. 150–190 °C in the presence of a catalyst and reacted (i.e., advanced) to form a high MW resin. The oligomerization is exothermic and proceeds rapidly to near completion. The exotherm temperatures are dependent upon the targeted EEW and the reaction mass. In the cases of higher MW resins such as type “7” and higher, exotherm temperatures of > 200 °C are routinely encountered.

Advancement reaction catalysts facilitate the rapid preparation of medium and high MW linear resins and control prominent side reactions inherent in epoxy resin preparations, eg, chain branching due to addition of the secondary alcohol group generated in the chain-lengthening process to the epoxy group (26,27). Nuclear Magnetic Resonance (NMR) spectroscopy can be used to determine the extent of branching (28).



Conventional advancement catalysts include basic inorganic reagents, eg, NaOH, KOH, Na_2CO_3, or LiOH, and amines and quaternary ammonium salts. One mechanism proposed for the basic catalysts involves proton abstraction of the phenolic compound as the initiation step:



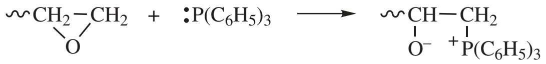
The phenoxide ion then attacks the epoxy ring, generating an alkoxide, which immediately abstracts a proton from another phenolic OH group. This is called the propagation step. Regeneration of the phenoxide ion repeats the cycle. The potential for side reactions increases after the phenolic OH groups have been consumed, particularly in melt (i.e., fusion) polymerization reactions.

One key disadvantage of catalysts based on inorganic bases and salts is the increased ionic impurities added to the resin, which is not desirable in certain applications.

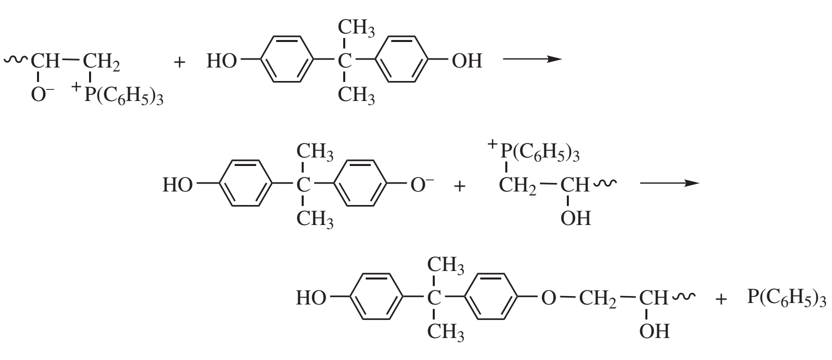
Imidazoles, substituted imidazoles, and triethanolamine have been patented as advancement catalysts (29). However, most of the inorganic bases, salts, and amines produce resins with broad MW distribution and viscosity instability. This is due to poor catalyst selectivity and the continuing activity of the catalyst after completion of the advancement reaction.

Alternatively, a broad class of catalysts derived from aryl or alkyl phosphonium compounds were developed. Extensive patent literature claims a high order of selectivity (30,31). Selections of the phosphonium cation and counter ion have been shown to affect initiation rate, catalyst selectivity, catalyst lifetime, and, consequently, product quality and consistency. Some of the phosphonium salts are deactivated at high temperatures by the reaction exotherm, and are claimed to give better resin stability in terms of viscosity, EEW, and MW during the subsequent finishing steps (32–35).

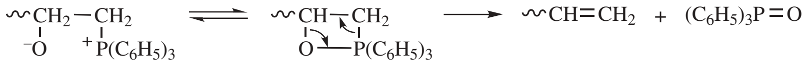
Few mechanistic studies have been published on the selectivity of phosphonium compounds, but one publication describes the role of triphenylphosphine in advancement catalysis (36). Nucleophilic attack by triphenylphosphine opens the epoxy ring, producing a betaine:



Proton abstraction from bisphenol A yields the phenoxide anion, forming a phosphonium salt. The phenoxide reacts with the electrophilic carbon attached to the positive phosphorus regenerating the catalyst:



When the bisphenol A is consumed, the betaine decomposes into a terminal olefin and triphenylphosphine oxide:

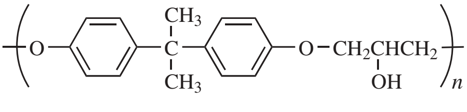


Branched epoxies (37) are prepared by advancing LER with bisphenol A in the presence of epoxy novolac resins. Such compositions exhibit enhanced thermal and solvent resistance.

SERs are available commercially in solid form or in solution. MW distributions of SERs have been examined by means of theoretical models and compared with experimental results (38). Taffy-processed resins were compared with advancement-processed resins by gel-permeation chromatography (GPC) and high performance liquid chromatography (HPLC) (39) in conjunction with statistical calculations. The major differences are in the higher α-glycol content and the repeating units of oligomers. Resin viscosity and softening points are also lower with taffy resins. In addition, certain formulations based on taffy resins exhibit different behavior in pigment loading, formulation rheology, reactivity, and mechanical properties compared to those based on advancement resins.

6.1. SER Continuous Advancement Process. The recent literature review indicates efforts to develop continuous advancement processes to produce SERs. Companies seek to improve process efficiencies and product quality. One of the major deficiencies of the traditional batch advancement process is the long reaction time, resulting in EEW and viscosity drift, variable product quality, and gel formation. In addition, it is difficult to batch process higher MW, higher viscosity SERs such as types “9” and “10” resins. Shell patented several versions of the continuous resin advancement processes using modified reactor designs (40). Dow Chemical received patents covering the uses of reactive extrusion (41) (REX) to produce SERs and other epoxy thermoplastic resins (42). The latter process makes use of a self-wiping twin-screw extruder. LER, bisphenol A, and catalyst are fed directly to the extruder to complete the resin advancement reaction in several minutes compared to the traditional several hours in a batch process. The process is claimed to be very efficient and is particularly suitable for the production of high molecular weight SERs, phenoxy resins, and epoxy thermoplastic resins. Compared to the traditional taffy processes used to produce phenoxy resins, the chemistry is salt-free, and the resins made via the REX process are fully converted in a matter of minutes, significantly reducing manufacturing costs. Additional benefits include reduced lot-to-lot variations in MW distribution, the flexibility to make small lots of varying molecular weights with minimal waste, and the ability to make custom resins with a variety of additives such as pigments and flow modifiers.

6.2. Phenoxy Resins. *Phenoxy resins* are thermoplastic polymers derived from bisphenol A and epichlorohydrin. Their weight-average molecular weights (M_w) are higher (i.e., >30,000) than those of conventional SERs (i.e., 25,000 maximum). They lack terminal epoxides but have the same repeat unit as SERs and are classified as polyols or polyhydroxy ethers:



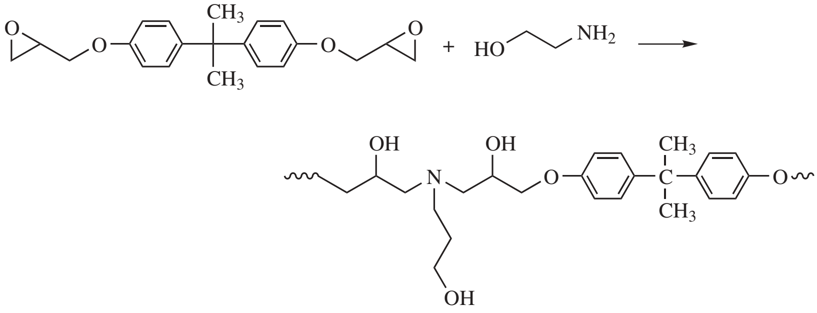
Phenoxy resins were originally developed and produced by Union Carbide (trade names PKHH, PKHC, PKHJ) using the taffy process. The process involves reaction of high purity bisphenol A with epichlorohydrin in a 1:1 mole ratio.

Alternatively, phenoxy resins can be produced by the fusion process which uses high purity LER and bisphenol A in a 1:1 mole ratio. High purity monomers and high conversions are both needed to produce high MW phenoxy resins. The effects of monomer purity on phenoxy resin production are significant: monofunctional components limit MW, and functionality > 2 causes excess branching and increased polydispersity. Solution polymerization may be employed to achieve the MW and processability needed (43). This, however, adds to the high costs of manufacturing of phenoxy resins, limiting their commercial applications.

The phenoxies are offered as solids, solutions, and waterborne dispersions. The majority of phenoxy resins are used as thermoplastics, but some are used as additives in thermoset formulations. Their high MW provide improved flexibility and abrasion resistance. Their primary uses are in automotive zinc-rich primers, metal can/drum coatings, magnet wire enamels, and magnetic tape coatings. However, the zinc-rich primers are being phased out in favor of galvanized steel by the automotive industry. Smaller volumes of phenoxy resins are used as flexibility or rheology modifiers in composites and electrical laminate applications, and as composite honeycomb impregnating resins. A new, emerging application is fiber sizing, which utilizes waterborne phenoxies. Literature references indicate their potential uses as compatiblizers for thermoplastic resins such as polyesters, nylons, and polycarbonates because of their high hydroxyl contents.

Current producers of phenoxy resins include the Phenoxy Specialties division of InChem Corp., Resolution, Huntsman, Tohto Kasei, and DIC.

6.3. Epoxy-Based Thermoplastics. Some of the new epoxy products developed in the past few years are the thermoplastic resins based on epoxy monomers. Polyhydroxy amino ether (44,45) (PHAE) was commercialized by Dow Chemical in 1999 and trade named BLOX (Dow Chemical Co.). It is produced by the reaction of DGEBA with monoethanol amine using the reactive extrusion process. The high cohesive energy density of the resin gives it excellent gas-barrier properties against oxygen and carbon dioxide. It also possesses excellent adhesion to many substrates, optical clarity, excellent melt strength, and good mechanical properties. The product has been evaluated as a barrier resin for beer and beverage plastic bottles, as thermoplastic powder coatings, and as a toughener for starch-based foam (46). Another epoxy thermoplastic resin under development by Dow is the polyhydroxy ester ether (PHEE). It is a reaction product of DGEBA with difunctional acids. The ester linkage makes it suitable for biodegradable applications (47).

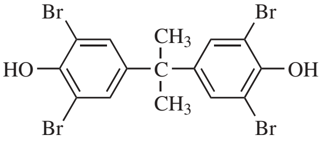


Polyhydroxy amino ether (PHAE) resin

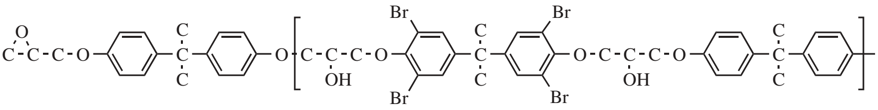
7. Halogenated Epoxy Resins

A number of halogenated epoxy resins have been developed and commercialized to meet specific application requirements. Chlorinated and brominated epoxies were evaluated for flame retardancy properties. The brominated epoxy resins were found to have the best combination of cost/performance and were commercialized by Dow Chemical in the late 1960s.

7.1. Brominated Bisphenol A Based Epoxy Resins. Many applications of epoxy resins require the system to be ignition-resistant, eg, electrical laminates for PCBs and certain structural composites. A common method of imparting this ignition resistance is the incorporation of tetrabromobisphenol A (TBBA), 2,2-bis(3,5-dibromophenyl)propane, or the diglycidyl ether of TBBA, 2,2-bis[3,5-dibromo-4-(2,3-epoxypropoxy)phenyl]propane, into the resin formulation. The diglycidyl ether of TBBA is produced via conventional liquid epoxy resin processes. Higher MW resins can be produced by advancing LERs or diglycidyl ether of TBBA with TBBA. The lower cost, advanced brominated epoxies based on LERs and TBBA containing ca. 20 wt.% Br are extensively employed in the PCB industry. The diglycidyl ether of TBBA (ca. 50 wt.% Br) is used for critical electrical/electronic encapsulation where high flame retardancy is required. Brominated epoxies are also used to produce epoxy vinyl esters for structural applications. Very high MW versions of brominated epoxies are used as flame-retardant additives to engineering thermoplastics used in computer housings.



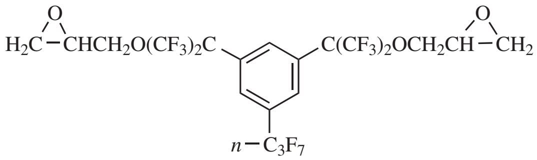
Tetrabromo bisphenol A



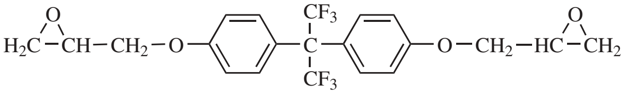
Advanced brominated epoxy resin

In order to meet increased requirements of the PCB industry for higher glass-transition temperature (T_g), higher thermal decomposition temperature (T_d), and lower dielectric constant (D_k) products, a number of new epoxy resins have been developed (48,49).

7.2. Fluorinated Epoxy Resins. Fluorinated epoxy resins have been researched for a number of years for high performance end-use applications (50). Fluorinated epoxies are highly resistant to chemical and physical abuse and should prove useful in high performance applications, including specialty coatings and composites, where their high cost may be offset by their special properties and long service life. The following fluorinated diglycidyl ether, 5-heptafluoropropyl-1,3-bis[2-(2,3-epoxypropoxy) hexafluoro-2-propyl] benzene, illustrates an example of fluoroepoxy resins (51) under development.



This resin is a viscous, colorless liquid (bp 118 °C at 20 Pa · s) that contains 52 wt. % fluorine. It has a low surface tension, which makes it a superior wetting agent for glass fibers. The reactivity of this resin with amine or anhydride curing agents is comparable to epoxy resins based on bisphenol A and results in a thermoset that has a low affinity for water and excellent chemical resistance. Another fluorinated epoxy resin derived from hexafluorobisphenol A was introduced to the marketplace aiming at the anticorrosion coatings market for industrial vessels and pipes. The key disadvantages of fluorinated epoxies are their relatively high costs and low T_g, which limit their commercialization (52).



8. Multifunctional Epoxy Resins

The multifunctionality of these resins provides higher cross-linking density, leading to improved thermal and chemical resistance properties over bisphenol A epoxies.

8.1. Epoxy Novolac Resins. Epoxy novolacs are multifunctional epoxies based on phenolic formaldehyde novolacs. Both epoxy phenol novolac resins (EPN) and epoxy cresol novolac resins (ECN) have attained commercial importance (53). The former is made by epoxidation of the phenol–formaldehyde condensates (novolacs) obtained from acid-catalyzed condensation of phenol and formaldehyde (see PHENOLIC RESINS). This produces random *ortho*- and *para*-methylene bridges.

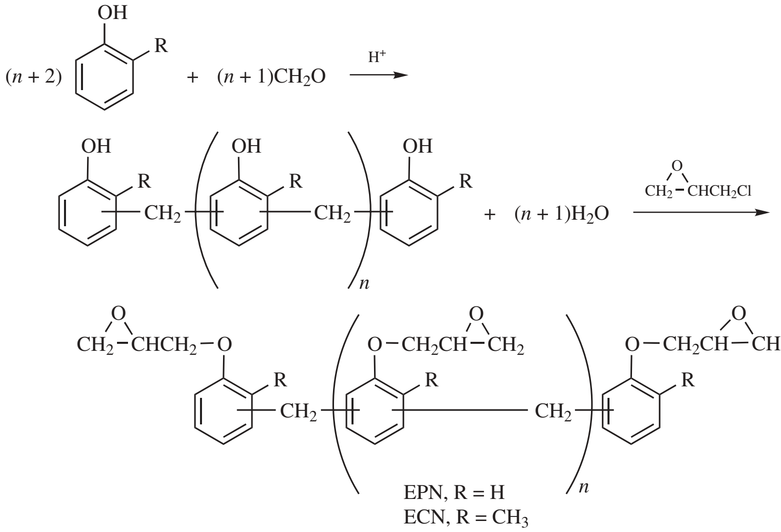


Table 7. **Typical Properties of Epoxy Phenol Novolacs**

Property	D.E.N. 431,[a] EPN 1139[b]	D.E.N. 438,[a] EPN 1138[b]	D.E.N. 439[a]
n	0.2	1.6	1.8
EEW[c]	175	178	200
viscosity, mPa · s (= cP)	1,400[d]	35,000[d]	3,000[e]
softening point[f]			53
color, Gardner	1	2	2

[a] The Dow Chemical Co.

[b] Huntsman.

[c] Epoxide equivalent weight.

[d] Temperature of measurement = 52 °C.

[e] Temperature of measurement = 100 °C.

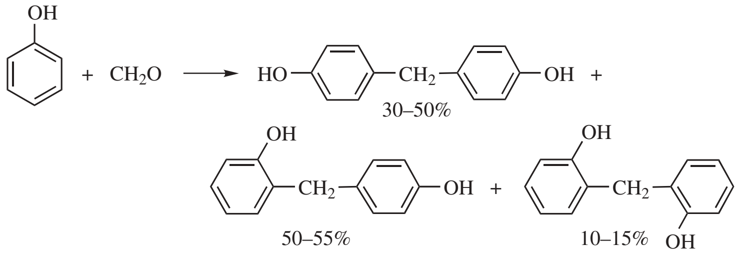
[f] Durran's mercury method.

An increase in the molecular weight of the novolac increases the functionality of the resin. This is accomplished by changing the phenol or cresol to formaldehyde ratio. Epoxidation with an excess of epichlorohydrin minimizes the reaction of the phenolic OH groups with epoxidized phenolic groups and prevents branching. The epoxidation is similar to the procedure described for bisphenol A. EPN resins range from a high viscosity liquid of $n = 0.2$ to a solid of $n > 3$. The epoxy functionality is between 2.2 and 3.8. Properties of epoxy phenol novolacs are given in Table 7. When cured with aromatic amines such as methylenedianiline, the heat distortion temperatures (HDT) of EPN-based thermosets range from 150 °C to 200 °C, depending on cure and post-cure schedules

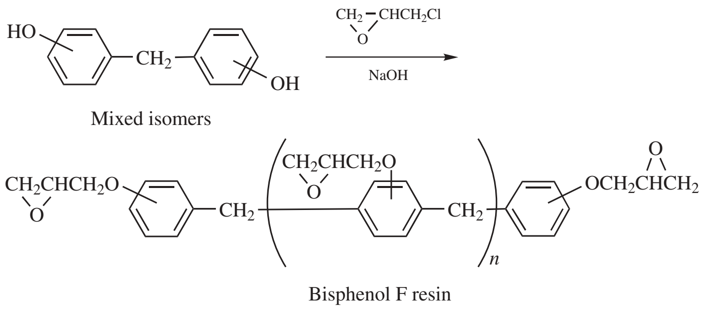
Curing agents that give the optimum in elevated temperature properties for epoxy novolacs are those with good high temperature performance, such as aromatic amines, catalytic curing agents, phenolics, and some anhydrides. When cured with polyamide or aliphatic polyamines and their adducts, epoxy novolacs show improvement over bisphenol A epoxies, but the critical performance of each cure is limited by the performance of the curing agent.

The improved thermal stability of EPN-based thermosets is useful in elevated temperature services, such as aerospace composites. Filament-wound pipe and storage tanks, liners for pumps and other chemical process equipment, and corrosion-resistant coatings are typical applications which take advantage of the chemical resistant properties of EPN resins. However, the high cross-link density of EPN-based thermosets can result in increased brittleness and reduced toughness.

Bisphenol F Epoxy Resin. The lowest MW member of the phenol novolacs is bisphenol F, which is prepared with a large excess of phenol to formaldehyde; a mixture of *o,o′*, *o,p′*, and *p,p′* isomers is obtained:



Epoxidation yields a liquid bisphenol F epoxy resin with a viscosity of 4000–6000 mPa · s (= cP), an EEW of 165, and $n \cong 0.15$.



This unmodified, low viscosity liquid resin exhibits slightly higher functionality than unmodified bisphenol A liquid resins. Crystallization, often a problem with liquid bisphenol A resins, is reduced with bisphenol F resin. Consequently, noncrystallizing LERs which are blends of DGEBA and bisphenol F epoxy are available. Epoxy resins based on bisphenol F are used primarily as functional diluents in applications requiring a low viscosity, high performance resin system (eg solvent-free coatings). Higher filler levels and faster bubble release are possible because of the low viscosity. The higher epoxy content and functionality of bisphenol F epoxy resins provide improved chemical resistance compared to conventional bisphenol A epoxies. Bisphenol F epoxy resins are used in high solids, high build systems such as tank and pipe linings, industrial floors, road and bridge deck toppings, structural adhesives, grouts, coatings, and electrical varnishes.

Cresol Epoxy Novolacs. The *o*-cresol novolac epoxy resins (ECN) are analogous to phenol novolac resins. ECNs exhibit better formulated stability and lower moisture adsorption than EPNs, but have higher costs. ECN resins are widely used as base components in high performance electronic (semiconductors) and structural molding compounds, high temperature adhesives, castings and laminating systems, tooling, and powder coatings. Increasing demands by the semiconductor industry has led to significant advances in ECN resin manufacturing technologies to reduce impurities, mainly the ionic content, hydrolyzable chlorides, and total chlorides. The use of polar, aprotic solvents, such as dimethyl sulfoxide (DMSO), as a co-solvent to facilitate chloride reduction has been patented (54). Typical high purity ECN resins contain <1000 ppm total chlorides and < 50 ppm hydrolyzable chlorides.

The melt viscosity of these resins, which are solids at room temperature, decreases sharply with increasing temperature (Table 8). This affords the formulator an excellent tool for controlling the flow of molding compounds and facilitating the incorporation of ECN resins into other epoxies, eg, for powder coatings. While Ciba-Geigy was the first producer of ECN resins, many Japanese companies (Nippon Kayaku, Sumitomo Chemical, DIC, and Tohto Kasei) supply the majority of high purity ECN resins for the semiconductor industry today. Other suppliers are based in Korea and Taiwan.

Glycidyl Ethers of Hydrocarbon Epoxy Novolacs. In response to the increased performance demands of the semiconductor industry, hydrocarbon

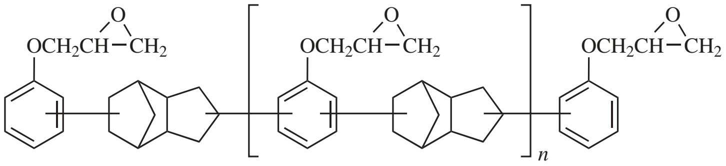
Table 8. **Typical Properties of Epoxy Cresol Novolac Resins**[a]

Property	ECN 1235	ECN 1273	ECN 1280	ECN 1299
molecular weight	540	1080	1170	1270
EEW[b]	200	225	229	235
softening point, °C	35	73	80	99
epoxide functionality	2.7	4.8	5.1	5.4

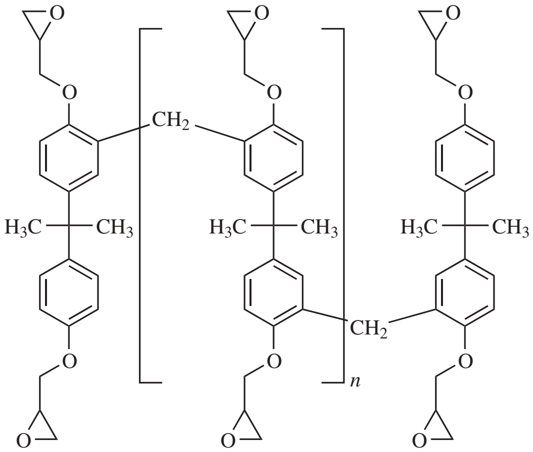
[a] Huntsman.

[b] Epoxide equivalent weight.

epoxy novolacs (HENs) were developed by Dow Chemical in the 1980s. HENs exhibit a much lower affinity for water compared to cresol or phenol epoxy novolacs. This translates directly into increased electrical property retention, which is important in the reliability of an electronic device encapsulated in the resin. An epoxy resin that is typical of this class is based on the alkylation product of phenol and dicyclopentadiene (55) ($n = 0.1$), 2,5-bis[(2,3-epoxypropoxy) phenyl]octahydro-4,7-methano-5*H*-indene (272 EEW; softening point 85 °C; η at 150 °C 0.4 Pa · s). The product is available from Huntsman as TACTIX* 556. Similar products based on *o*-cresol are commercialized in Japan by DIC (EPICLON HP-7200L).



Bisphenol A Epoxy Novolacs. Bisphenol A novolacs are produced by reacting bisphenol A and formaldehyde with acid catalysts. Epoxidation of the bisphenol A novolacs gives bisphenol A epoxy novolac (BPAN) with improved thermal properties such as T_g, T_d of the epoxy-based electrical laminates.

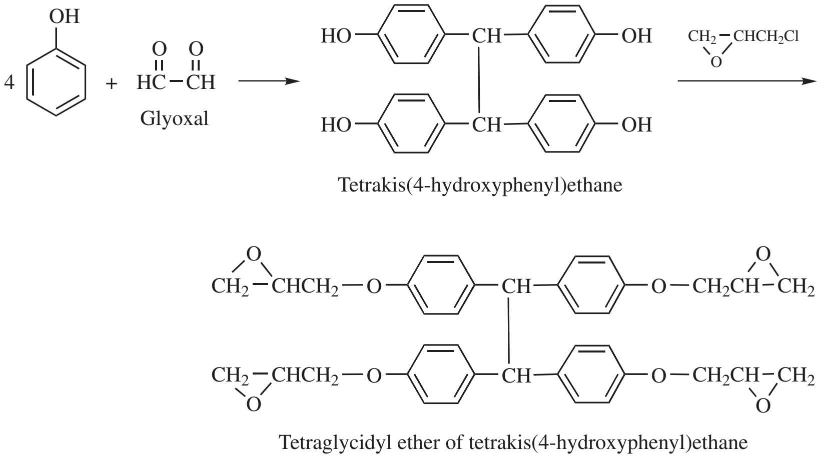


Bisphenol A epoxy novolac

8.2. Other Polynuclear Phenol Glycidyl Ether Derived Resins.

In addition to the epoxy novolacs, there are other epoxy resins derived from phenol–aldehyde condensation products. New applications that require increased performance from the epoxy resin, particularly in the electronics, aerospace, and military industries, have made these types of resins more attractive despite their relatively high cost.

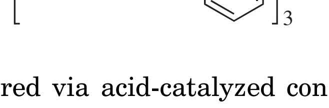
Glycidyl Ether of Tetrakis(4-hydroxyphenyl)ethane. One of the first polyfunctional resins to be marketed (by Shell) is based on 1,1,2,2-tetrakis[4-(2,3-epoxypropoxy)phenyl]ethane (56). It is used primarily as additives in standard epoxy resin formulations for electrical laminates, molding compounds, and adhesives in which increased heat distortion temperature and improved chemical resistance are desired. Tetrakis(4-hydroxyphenyl)ethane is prepared by reaction of glyoxal with phenol in the presence of HCl. The tetraglycidyl ether (mp ca. 80 °C, and an EEW of 185–208) possesses a theoretical epoxide functionality of 4.



Tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane

The commercial products Araldite 0163 (Huntsman) and Epon 1031 (Resolution) are tan-colored solids. They are widely used in high temperature resistance electrical laminates for high density PCBs and military applications. Their costs are typically higher than those of phenol and cresol epoxy novolacs.

Trisphenol Epoxy Novolacs. In the 1980s, new trifunctional epoxy resins based on tris[4-(2,3-epoxypropoxy)phenyl]methane isomers were introduced by Dow Chemical to help close the performance gap between phenol and cresol epoxy novolacs and high performance engineering thermoplastics (57). These products were later sold to Ciba-Geigy and continued to be marketed under the TACTIX* 740 and XD 9053 trade names by Huntsman.

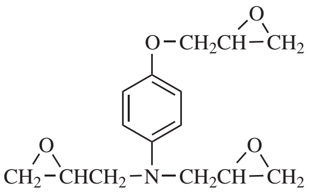


The resins are prepared via acid-catalyzed condensation of phenol and a hydroxybenzaldehyde, eg, salicylaldehyde, to afford the trifunctional phenol, which is epoxidized with epichlorohydrin. These resins range from semisolids (162 EEW; Durran softening point 55 °C; η at 60 °C 11.5 Pa · s, at 150 °C 0.055 Pa · s) to nonsintering solids (220 EEW; Durran softening point 85 °C; η at 150 °C 0.45 Pa · s).

The semisolid resins are used in advanced composites and adhesives where toughness, hot-wet strength, and resistance to high temperature oxidation are required. Their purity, formulated stability, fast reactivity, and retention of electrical properties over a broad temperature range make the solid resins suitable for use in the semiconductor molding powders industry. The trisphenol-based epoxies command significant high prices ($28–48/kg), limiting their uses.

8.3. Aromatic Glycidyl Amine Resins. Among the multifunctional epoxy resins containing an aromatic amine backbone, only a few have attained commercial significance. Their higher costs limit their uses to critical applications where their costs are justified. Glycidyl amines contain internal tertiary amines in the resin backbone, hence their high reactivity. Epoxy resins with such built-in curing catalysts are less thermally stable than nitrogen-free multifunctional epoxy resins.

Triglycidyl Ether of p-Aminophenol. The triglycidyl derivative of *p*-aminophenol was originally developed by Union Carbide (58) and is currently marketed by Huntsman under the designation MY 0500 and 0510. Epoxidation of *p*-aminophenol is carried out with a large excess of epichlorohydrin under carefully controlled conditions, since the triglycidylated resin exhibits limited thermal stability and polymerizes vigorously under the influence of its tertiary amine moiety.

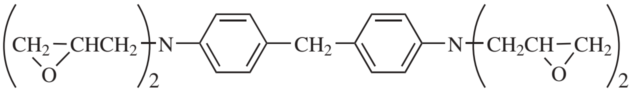


Triglycidyl-*p*-aminophenol

The resin exhibits a low viscosity, 2500–5000 mPa · s (= cP) at 25 °C, and an EEW of 105–114; a molecularly distilled version (0510) has a viscosity of 550–850 mPa · s (= cP) at 25 °C and an EEW of 95–107. It is considerably more reactive toward amines than standard bisphenol A resins. The trifunctional resin permits curing at low temperatures, i.e., 70 °C, and rapidly develops excellent elevated-temperature properties. Used as additives to increase cure speed, heat resistance, and T_g of bisphenol A epoxy resins, it has utility in such diverse applications as high temperatures adhesives, tooling compounds, and laminating systems.

Tetraglycidyl Methylenedianiline (MDA). These resins are used as binders in graphite-reinforced composites and are the binders of choice for many military applications. Epoxidation of MDA is carried out with stoichiometric excess of epichlorohydrin and under carefully controlled conditions to avoid rapid polymerization side reactions.

The tetrafunctional glycidylated MDA resins range in viscosity from 5000 to 25,000 mPa · s (= cP) at 50 °C and have an EEW of 117–133; they are commercially available as Araldite MY 720 (Huntsman) and Epiclon 430 (DIC). When used in combination with the curing agent 4,4′-diaminodiphenylsulfone (DADS), it is the first system to meet the performance requirements set by the aerospace industry and is the standard against which other resin systems are judged (59). Because of its outstanding properties, this resin is often used as the primary resin in high heat resistance formulations for military applications, despite its high costs (~ $22/kg). Among its attributes are excellent mechanical strength, high T_g, good chemical resistance, and radiation stability.



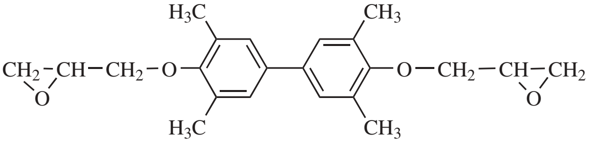
N,*N*,*N*′,*N*′-Tetraglycidyl-4,4′-diaminodiphenylmethane

Another commercially important aromatic glycidyl amine resin is triglycidyl isocyanurate (TGIC), which is discussed in the “Weatherable Epoxy Resins” section.

9. Specialty Epoxy Resins

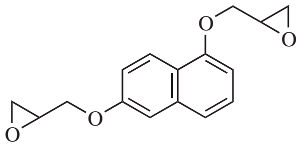
9.1. Crystalline Epoxy Resins Development.

A number of new epoxy resins used in epoxy molding compounds (EMC) have been developed by Japanese resin producers in response to the increased performance requirements of the semiconductor industry. Most notable are the commercialization of crystalline epoxies based on biphenol by Yuka-Shell (60):

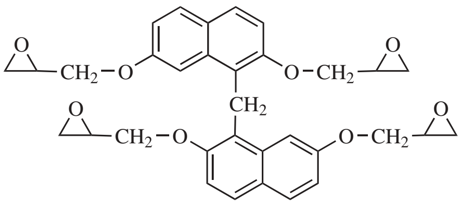


Diglycidyl ether of tetramethyl biphenol

The very low viscosity of these crystalline, solid epoxies when molten allows very high filler loading (up to 90 wt. %) for molding compounds. The high filler loading reduces the coefficient of thermal expansion (CET) and helps manage thermal shock and moisture and crack resistance of molding compounds used in new, demanding semiconductor manufacturing processes such as Surface Mount Technology (SMT). It should be noted that cured thermosets derived from these crystalline resins do not retain crystallinity. Recently, a number of capacity expansions were announced for biphenol epoxies (sold as YX-4000 resin by Japan Epoxy Resins Corporation, formerly Yuka-Shell). DIC has developed dihydroxy naphthalene based epoxies (61) as the next generation product for this high performance market. Prices for crystalline epoxies are generally high ($22–26/kg), limiting their uses to high end applications.

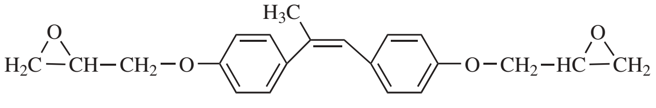


Diglycidyl ether of 1,5-dihydroxy naphthalene



Tetraglycidyl ether based on dihydroxy naphthalene

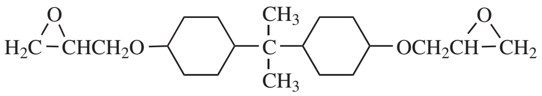
Dow Chemical developed liquid crystalline polymers (LCP) based on diglycidyl ether of 4-4′-dihydroxy-α-methylstilbene in the 1980s (62,63). Liquid crystal thermoplastics and thermosets based on this novel chemistry showed excellent combinations of thermal, mechanical, and chemical properties, unachievable with traditional epoxies. However, commercialization of these products has not materialized.



Diglycidyl ether of 4-4′-dihydroxy-α-methylstilbene

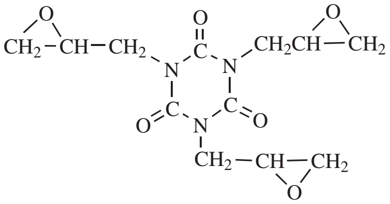
9.2. Weatherable Epoxy Resins. One of the major deficiencies of the aromatic epoxies is their poor weatherability, attributable to the aromatic ether segment of the backbone, which is highly susceptible to photoinitiated free-radical degradation. The aromatic ether of bisphenol A absorbs UV lights up to about 310 nm and undergoes photocleavage directly. This in turn produces free radicals that lead to oxidative degradation of bisphenol A epoxies, resulting in chalking. Numerous efforts have been devoted to remedy this issue, resulting in a number of new weatherable epoxy products. However, their commercial success has been limited, primarily because of higher resin costs and the fact that end users can topcoat epoxy primers with weatherable coatings based on other chemistries such as polyesters, polyurethanes, or acrylics. The following epoxy products when formulated with appropriate reactants can provide certain outdoor weatherability.

Hydrogenated DGEBA. In 1976, Shell Chemical Co. introduced epoxy resins based on the diglycidyl ether of hydrogenated bisphenol A, 2,2-bis[4-(2,3-epoxypropoxy)cyclohexyl]propane (232–238 EEW; η at 25 °C 2–2.5 Pa · s).



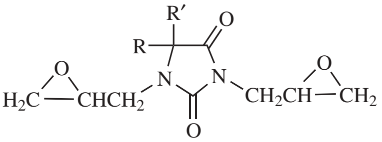
These resins resist yellowing and chalking because of their aliphatic structure. Epoxy resins based on hydrogenated bisphenol A are made by the epoxidation of the saturated diol, 2,2-bis(4-hydroxycyclohexyl)propane or 2,2-bis(4-hydroxycyclohexyl)propane with epichlorohydrin, or by the hydrogenation of a low molecular weight DGEBA resin (64). Commercially available products include an Epalloy 5000 resin from CVC. One disadvantage is their much higher costs, and consequently, the products have not found broad acceptance in the industry. Furthermore, cross-linked networks based on hydrogenated bisphenol A epoxies lose some of the characteristic temperature and chemical resistances inherent with the bisphenol A backbone.

Heterocyclic Glycidyl Imides and Amides. In the 1960s, considerable work was devoted to preparing triglycidyl isocyanurate, 1,3,5-tris(2,3-epoxypropyl)-1,3,5-perhydrotriazine-2,4,6-trione (65). The epoxidation of cyanuric acid with epichlorohydrin gives triglycidyl isocyanurate (TGIC), marketed as PT 810 by Huntsman. It is a crystalline compound (mp 85–110 °C) with an EEW of ca. 108. Miscibility with organic compounds is limited. Because of its excellent weatherability, TGIC is widely used in outdoor powder coatings with polyesters (66), despite its higher cost (∼ $12/kg).



Triglycidyl isocyanurate

Hydantoin-Based Epoxy Resins. These resins were commercialized by Ciba-Geigy. Hydantoins are prepared from carbon dioxide, ammonia, hydrogen cyanide, and ketones via the Bucherer reaction and can be epoxidized with epichlorohydrin (67). Cured and uncured resin properties depend greatly on the nature of the substituents R and R′. The hydantoin derived from acetone furnishes a low viscosity, water-dispersable epoxy resin, 5,5-dimethyl-1,3-bis(2,3-epoxypropyl)-2,4-imidazolidinedione ($R = R' = CH_3$; 145 EEM; η at 25 °C 2.5 Pa · s). A nonsintering solid epoxy resin is obtained if $R = R' = -(CH_2)_5-$.



When cured with aromatic amines or anhydrides, these resins show high heat distortion temperatures and excellent adhesion and weatherability. A variety of applications are suggested for these new resins, particularly in applications in which a non-yellowing epoxy resin is desirable.

9.3. Elastomer-Modified Epoxies. Epoxy thermosets derive their thermal, chemical, and mechanical properties from the highly cross-linked networks. Consequently, toughness deficiency is an issue in certain applications. To improve the impact resistance and toughness of epoxy systems, elastomers such as BF Goodrich's CTBN rubbers (carboxyl-terminated butadiene nitrile) are often used as additives or pre-reacted with epoxy resins (68). Most commonly used products are reaction adducts of liquid epoxy resins (DGEBA) with CTBN in concentrations ranging from 5 wt. % to 50 wt. %. They have been shown to give improved toughness, peel adhesion, and low temperature flexibility over unmodified epoxies. Primary applications are adhesives for aerospace and automotive and as additives to epoxy vinyl esters for structural composites. Formation of adducts of epoxy resins and CTBN is promoted by triphenylphosphine or alkyl phosphonium salts. Other elastomers used to modify epoxies include amine-terminated butadiene nitrile (ATBN), maleated polybutadiene and butadiene–styrene, epoxy-terminated urethane prepolymers, epoxy-terminated polysulfide, epoxy–acrylated urethane, and epoxidized polybutadiene.

10. Monofunctional Glycidyl Ethers and Aliphatic Glycidyl Ethers

A number of low MW monofunctional, difunctional, and mutifunctional epoxies are used as reactive diluents, viscosity reducers, flexiblizers, and adhesion promoters. Recent trends toward lower VOC, higher solids and 100 % solids epoxy formulations have resulted in increased utilization of these products. Most of these epoxies are derived from relatively compact hydroxyl-containing compounds, such as alcohols, glycols, phenols, and epichlorohydrin. Epoxidized vegetable oils, such as epoxidized linseed oils, are also used as reactive diluents. They are produced using a peroxidation process and are discussed in more detail in the cycloaliphatic epoxies and epoxidized vegetable oils section. Typically, these products have very low viscosity (1–70 cP at 20 °C) relative to LERs (11,000–16,000 cP). They are often used in the range of 7–20 wt.% to reduce viscosity of the diluted system to 1000 cP. However, the uses of reactive diluents, especially at high levels, often result in decreased chemical resistance and thermal and mechanical properties of the cured epoxies.

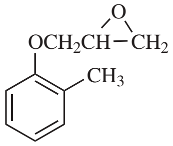
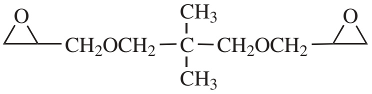
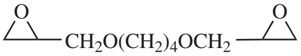
Important products include butyl glycidyl ether (BGE), alkyl glycidyl ethers of C8–C10 (Epoxide 7) and C12–C14 (Epoxide 8), *o*-cresol glycidyl ether (CGE), *p-tert*-butyl glycidyl ether, resorcinol diglycidyl ether (RDGE), and neopentyl glycol diglycidyl ether (Table 9). While BGE is the most efficient viscosity reducer and has been widely used in the industry for many years, it has been losing market share because of its volatility and obnoxiousness. Phenyl glicidyl ether (PGE) is no longer used by many formulators because of its toxicity. The industry trend is moving toward longer chain epoxies such as Epoxide 8 or neopentyl glycol diglycidyl ether.

Major suppliers of these products are Resolution, Air Products, Ciba Specialty Chemicals, Huntsman, CVC Specialty Chemicals, Pacific Epoxy Polymers, and Exxon.

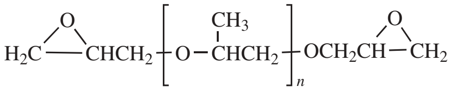
An example of multifunctional aliphatic epoxies is the triglycidyl ether of propoxylated glycerine (Heloxy 84) from Resolution. A similar product is based on epoxidized castor oil (Heloxy 505). These products are used primarily as viscosity reducers while increasing functionality and cross-linking density of the cured systems.

Epoxy resins based on long-chain diols, such as the diglycidyl ether of polypropylene glycol [α,ω-bis(2,3-epoxypropoxy)poly(oxypropylene)] (305–335 EEW; η at 25 °C 0.055–0.10 Pa · s), are used as flexibilizing agents to increase a thermo-

Table 9. **Some Common Commercial Glycidyl Ether Reactive Diluents**

Name	Structure
n-Butyl glycidyl ether	 $CH_3(CH_2)_3OCH_2CH{-}CH_2$
C12–C14 Aliphatic glycidyl ether	 $C_{12}{-}C_{14}OCH_2CH{-}CH_2$
o-Cresol glycidyl ether	
Neopentylglycol diglycidyl ether	
Butanediol diglycidyl ether	

set's elongation and impact resistance. Because of the low reactivity of the aliphatic diols toward epichlorohydrin, these epoxies are produced by first coupling the diols with epichlorohydrin using phase-transfer catalysts such as ammonium salts or Lewis acid catalysts (boron trifluoride, stannic chloride), followed by epoxidation with caustic (69,70). A prominent side-reaction is the conversion of aliphatic hydroxyl groups formed by the initial reaction into chloromethyl groups by epichlorohydrin. The resultant epoxy resins are known to have lower reactivity toward conventional amine curing agents relative to bisphenol A epoxies. Dow Chemical manufactures D.E.R. 732 and D.E.R. 736 aliphatic epoxy resins. They are derived from polyglycols with different chain lengths.



Polyglycidyl ethers of sorbitol, glycerol, and pentaerythritol are used as adhesion promoters for polyester tire cords. Their high chloride content improves adhesion to rubber.

11. Cycloaliphatic Epoxy Resins and Epoxidized Vegetable Oils

Resins based on the diepoxides of cycloaliphatic dienes were first commercialized in the 1950s by Union Carbide Corp. The combination of aliphatic backbone, high oxirane content, and no halogens gives resins with low viscosity, weatherability, low dielectric constant, and high cured T_g. This class of epoxy is popular for

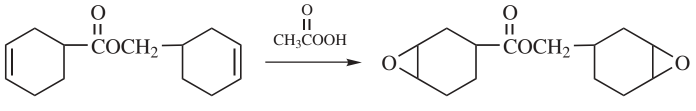
Table 10. **Comparative Viscosities of Cycloaliphatic Epoxies, Epoxidized Oils, and DGEBA**

Epoxy type	Viscosity, mPa·s(= cP)	EEW
Cyclo Diepoxy ERL-4221[a] (3′,4′-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate)	400	135
DGEBA	11000	190
Linseed Oil Epoxy	730	168

[a] Trademark of the Dow Chemical Co.

diverse end uses including auto topcoats, weatherable high voltage insulators, UV coatings, acid scavengers, and encapsulants for both electronics and optoelectronics. A comparison of some properties of two common aliphatic epoxies with those of LER (DGEBA) is shown in Table 10.

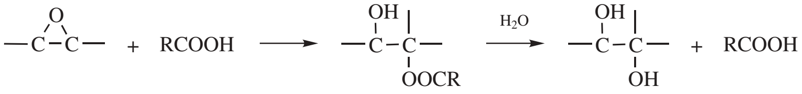
The preferred industrial route to cycloaliphatic epoxy resins is based on the epoxidation of cycloolefins with peracids, particularly peracetic acid (71). Few side reactions are encountered. Some properties of various commercial products are given in Table 11. The peracid cannot be made *in situ* because the cyclic olefins are sensitive to impurities generated in this process.



3′-Cyclohexenylmethyl
3-Cyclohexenecarboxylate

3′,4′-Epoxycyclohexylmethyl
3,4-Epoxycyclohexanecarboxylate

An important secondary reaction is the acid-catalyzed hydrolysis of the epoxide groups. The reaction is minimized at low temperatures and strongly depends on the constituents and the reaction medium.

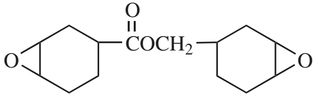
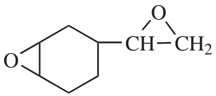
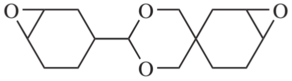
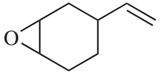
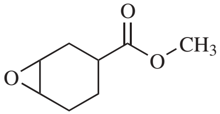
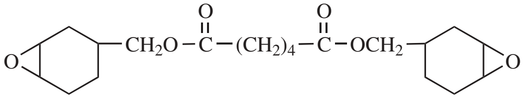


$$-\overset{O}{C-C}- + RCOOH \longrightarrow -\underset{}{\overset{OH}{C}}-\underset{OOCR}{C}- \xrightarrow{H_2O} -\overset{OH}{C}-\underset{OH}{C}- + RCOOH$$

The cycloaliphatic epoxides are more susceptible to electrophilic attack because of the lower electronegativity of the cycloaliphatic ring relative to the bisphenol A aromatic ether group in DGEBA resins. Consequently, cycloaliphatic epoxies do not react well with conventional nucleophilic epoxy curing agents such as amines. They are commonly cured via thermal or UV-initiated cationic cures. In addition, cycloaliphatic epoxy resins are low viscosity liquids that can be thermally cured with anhydrides to yield thermosets having a high heat distortion temperature. They are often used as additives to improve performance of bisphenol A epoxies. Their higher prices ($6.60–8.80/kg) have limited their commercial applications to high end products.

The largest end uses of cycloaliphatic epoxies in order of volume are electrical, electronic components encapsulation, and radiation-curable inks and coat-

Table 11. **Cycloaliphatic Epoxy Resins**

Chemical name	Structure	Commercial products	EEW	Viscosity, mPa · s (= cP) at 25 °C
3′,4′-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate		ERL-4221 UVR-6110	131–143	350–450
3,4-Epoxycyclohexyloxirane		CY-179 ERL-4206	70–74	15
2–(3′,4′-Epoxycyclohexyl)-5,1″-spiro-3″,4″-epoxycyclohexane-1,3-dioxane		ERL-4234	133–154	7,000–17,000
Vinyl cyclohexene monoxide		VCMX	124	5
3,4-Epoxycyclohexanecarboxylate methyl ester		ERL-4140	156	6
Bis(3,4-epoxycyclohexylmethyl) adipate		ERL-4299 UVR-6128	180–210	550–750

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[a] Epoxide equivalent weight.

[b] Unless otherwise stated.

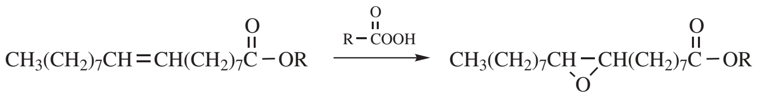
[c] Union Carbide, division of The Dow Chemical Co.

[d] Huntsman.

[e] At 38 °C.

ings. A potentially large volume application is UV-curable metal can coatings for beer can exterior and ends, but the market has not been growing significantly in recent years. Other uses include acid scavengers for vinyl-based transformer fluids and lubricating oils; filament winding for aerial booms and antennas; and as viscosity modifier for bisphenol A LERs in tooling compounds. An epoxy silicone containing cycloaliphatic epoxy end groups and a silicone backbone is used as radiation-curable release coatings for pressure-sensitive products. Dow Chemical is the largest producer of cycloaliphatic epoxies. Daicel of Japan has entered the cycloaliphatic epoxy resin market.

Epoxidation of α-olefins, unsaturated fatty acid esters, and glycerol esters is affected readily by peracids including *in situ* peracids generated from hydrogen peroxide and carboxylic acids.



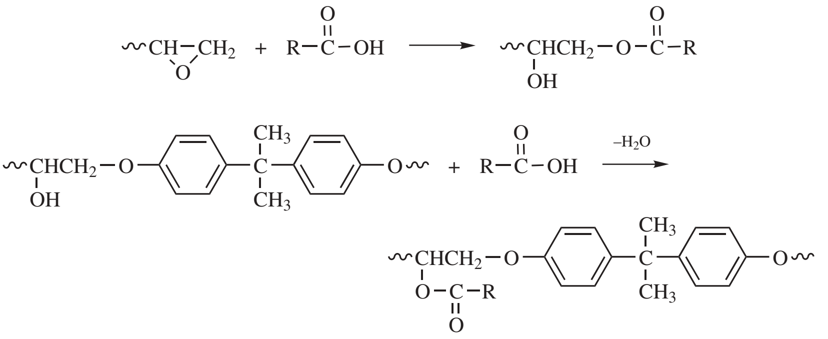
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}-OR \xrightarrow{R-\overset{O}{\overset{\|}{C}}OOH} CH_3(CH_2)_7\underset{O}{\underbrace{CH-CH}}(CH_2)_7\overset{O}{\overset{\|}{C}}-OR$$

α-Olefin epoxies find utility as reactive diluents for coatings and as chemical intermediates for lubrication fluids. Larger volume epoxidized soybean and linseed oils are most frequently used as secondary plasticizers and co-stabilizers for PVC.

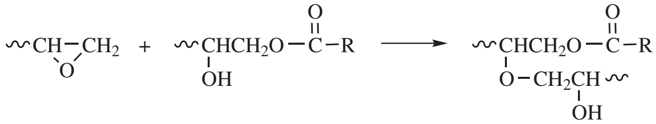
12. Epoxy Esters and Derivatives

12.1. Epoxy Esters.

The esterification of epoxy resins with commercial fatty acids is a well-known process that has been employed for industrial coatings for many years. The carboxylic acids are esterified with the terminal epoxy groups or the pendant hydroxyls on the polymer chain.



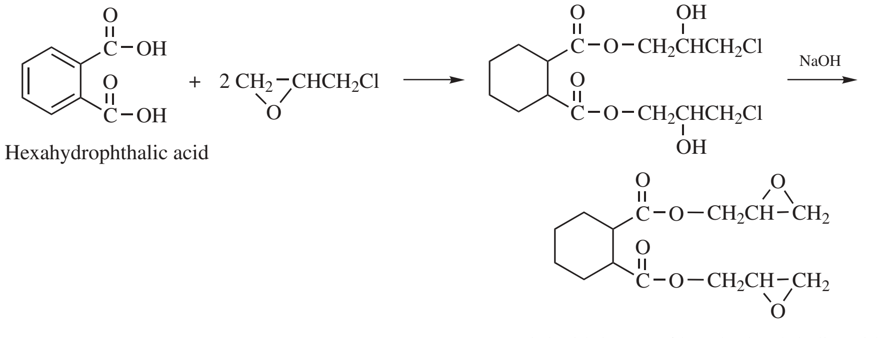
A wide variety of saturated and unsaturated fatty acids are utilized to confer properties useful in air-dried, protective, and decorative coatings. Typical fatty acids include tall oil fatty acids, linseed oil fatty acid, soya oil fatty acid and castor oil fatty acid. A medium molecular weight SER, a so-called 4-type, is commonly used. Catalysts such as alkaline metal salts (Na_2CO_3) or ammonium salts are essential to prevent chain branching and gelation caused by etherification of the epoxy groups.



Esterification is generally conducted in an inert atmosphere at 225–260 °C, with sparging to remove by-product water. The course of the reaction is monitored by acid number to a specified end point and by viscosity. The product is then dissolved in a solvent (72).

Metallic driers are incorporated in unsaturated ester solutions to promote cure via air-drying, i.e., oxidative polymerization of the double bonds of the fatty acids. Chemical resistance is generally lower than that of unmodified epoxy resins cured at ambient temperatures with amine hardeners. Epoxy esters are also used to produce anodic electrodeposition (AED) coatings by further reaction with maleic anhydride followed by neutralization with amines to produce water-dispersable coatings. Epoxy esters were widely used as automotive primer-surfacer and metal can ends coatings for many years, but are being replaced by other technologies. Their high viscosity limited their uses in low solids, solvent-borne coatings. Waterborne epoxy esters are now available and are used in flexographic inks for milk cartons.

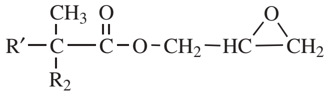
12.2. Glycidyl Esters. Glycidyl esters are prepared by the reaction of carboxylic acids with epichlorohydrin followed by dehydrochlorination with caustic:



Diglycidyl ester of hexahydrophthalic acid

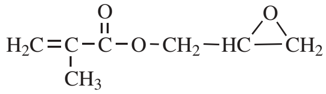
The viscosity of these esters is low, i.e., ca. 500 mPa · s (= cP), and their reactivity resembles that of bisphenol A resins. Similar epoxy resin derived from dimerized linoleic acid is also commercially available. They are often used as flexiblizing agents instead of epoxidized long-chain diols.

The *glycidyl ester of versatic acid* or neodecanoic acid is an example of high MW monoglycidyl aliphatic epoxy. The molecule is highly branched, thus providing steric effects to protect it from hydrolysis, resulting in good weatherability and water resistance. On the other hand, it suffers from high viscosity, and therefore it is not an effective diluent. It is often used to improve scrubability, chemical resistance, and weatherability of coatings. The product is commercially available from Resolution (Cardura E-10) and Exxon (Glydexx N-10).



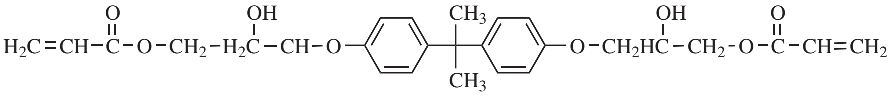
Where R′s = alkyl or substituted alkyls
Glycidyl ester of versatic acid

A commercially important glycidyl ester is *glycidyl methacrylate (GMA)*, a dual functionality monomer, containing both a terminal epoxy and an acrylic C=C bond. It is produced by the reaction of methacrylic acid with epichlorohydrin. The dual functionality of GMA brings together desirable properties of both epoxies and acrylics, eg, the weatherability of acrylics and chemical resistance of epoxies, in one product. GMA is useful as a comonomer in the synthesis of epoxy-containing polymers via free-radical polymerization. The resultant epoxy-containing polymers can be further cross-linked. An example of such polymers is GMA acrylic, which is an acrylic copolymer, containing about 10–35 % by weight of GMA. Cure is by reaction with dodecanedioic acid. Its primary uses are in automotive powder coatings. GMA-containing polymers are also used as compatiblizers for engineering thermoplastics, in adhesives and latexes, and as rubber and asphalt modifiers (73). Dow Chemical and Nippon Oils & Fats are two major producers of GMA.



Glycidyl methacrylate (GMA)

12.3. Epoxy Acrylates. Epoxy resins are reacted with acrylic acid to form epoxy acrylate oligomers, curable via free-radical polymerization of the acrylate C=C bonds initiated by light (74). UV lights are most commonly used, but electron beam (EB) curing is becoming more common because of its decreasing equipment costs. This is a fast-growing market segment for epoxy resins because of the environmental benefits of the UV cure technology: low to zero VOC, low energy requirements. Major applications include coatings for overprint varnishes, wood substrates, and plastics. Radiation-cured epoxy acrylates are also growing in importance in inks, adhesives, and photoresists applications. The 2001 global market for epoxy acrylates was estimated at 40,000 MT with an annual growth rate projected to be 8–10 %.

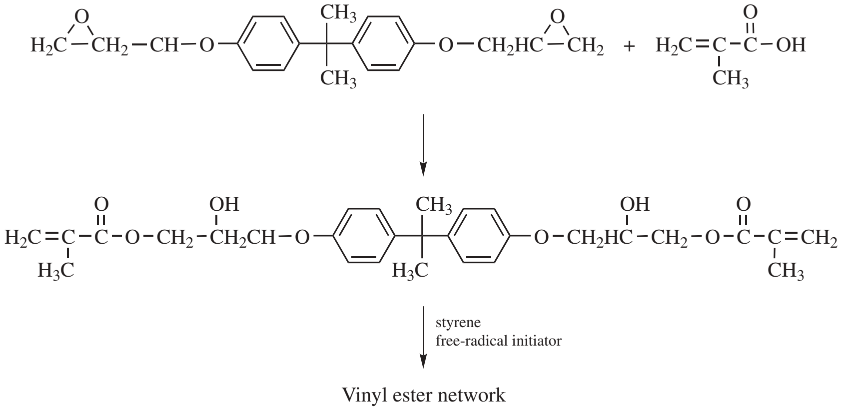


Epoxy acrylate based on DGEBA

Liquid epoxy resins such as DGEBA are most commonly used to produce epoxy acrylates. When higher thermal performance is required, multifunctional epoxies such as epoxy novolacs are used. Epoxy acrylates from epoxidized soybean oil and linseed oil are often used as blends with aromatic epoxy acrylates to reduce viscosity of the formulations. Major producers of UV-curable epoxy acrylates are UCB, Radcure, Dow Chemical, Sartomer, and Henkel.

12.4. Epoxy Vinyl Esters. A major derivative of epoxy resins is the epoxy vinyl ester resin. Originally developed by Dow Chemical (75,76) and Shell Chemical in the 1970s, it is considered a high performance resin used in glass-reinforced structural composites, particularly for its outstanding chemical resistance and mechanical properties. The resins are made by reacting epoxy resins with methacrylic acid and diluted with styrene to 35–40% solvent by weight. Liquid epoxy resins (DGEBA) are commonly used. Epoxy novolacs are used where higher thermal or solvent resistance is needed. Brominated epoxies are also used to impart flame retardancy for certain applications. In the final formulation, peroxide initiators are added to initiate the free-radical cure reactions of the methacrylic C=C bonds and styrene to form a random copolymer thermoset network.

The vinyl ester functionality of the epoxy vinyl esters provides outstanding hydrolysis and chemical resistance properties, in addition to the inherent thermal resistance and toughness properties of the epoxy backbone. These attributes have made epoxy vinyl esters a material of choice in demanding structural composite applications such as corrosive chemicals storage tanks, pipes, and ancillary equipment for chemical processing. Other applications include automotive valve covers and oil pans, boats, and pultruded construction parts. Significant efforts have been devoted to improve toughness and to reduce levels of styrene in epoxy vinyl ester formulations because of environmental concerns. In addition to Dow Chemical, other major suppliers of epoxy vinyl esters include Ashland, AOC, DSM, Interplastic, and Reichhold (DIC).



12.5. Epoxy Phosphate Esters. Dow Chemical developed the epoxy phosphate ester technology in the 1980s (77). Epoxy phosphate esters are reaction products of epoxy resins with phosphoric acid. Depending on the stoichiometric ratio and reaction conditions, a mixture of mono-, di- and triesters of phosphoric acid are obtained. Subsequent hydrolysis of the esters is used as a way to control the distribution of phosphate and glycol end groups and product viscosity. Epoxy phosphate esters can be made to disperse in water to produce waterborne coatings. They are used primarily as modifiers to improve the adhesion property of nonepoxy binders in both solvent-borne and waterborne systems for container and coil coatings.

13. Characterization of Uncured Epoxies

Most industrial chemicals and polymers are not the 100 % pure, single chemicals as described in their general chemical structures. In the case of epoxy resins, they often contain isomers, oligomers, and other minor constituents. As a first requirement, one would need to know the epoxy content or EEW of the epoxy resin so the proper stoichiometric amount of cross-linker(s) can be calculated. However, a successful thermoset formulation must also have the proper reactivity, flow, and performance. Consequently, other epoxy resin properties are required by the formulators and supplied by the resin producers.

Liquid epoxy resins are mainly characterized by epoxy content, viscosity, color, density, hydrolyzable chloride, and volatile content (78). Less often analyzed are α-glycol content, total chloride content, ionic chloride, and sodium. Solid epoxy resins are characterized by epoxy content, solution viscosity, melting point, color, and volatile content. Less often quoted are phenolic hydroxyl content, hydrolyzable chloride, ionic chloride, sodium, and esterification equivalent. Table 12 lists analytical methods adopted by ASTM (79) as standard testing methods for epoxy resins.

In addition, gel-permeation chromatography (GPC), high performance liquid chromatography (HPLC) (39,80), and other analytical procedures such as nuclear magnetic resonance (NMR) (28) and infrared spectroscopy (IR) (81) are performed to determine MW, MW distribution, oligomer composition, functional groups, and impurities.

Table 12. **Uncured Epoxy Resin Test Methods**

Test Item	Unit	Condition	ASTM method
EEW			D1652-97
viscosity, neat	cP[a]	25 °C	D445-01
viscosity, solution	cSt[b]	25 °C	D445-01
viscosity, melt	cSt[b]	150 °C	D445-01
viscosity, ICI Cone and Plate	Pa · s		D4287-00
viscosity, Gardner–Holdt			D1545-98
color, Co-Pt			D1209-00
color, Gardner			D1544-98
color, Gardner in solution			D1544-98
moisture	ppm		E203-01
softening point	°C		D3104-99

[a] cP = mPa · s.

[b] cSt = mm^2/s.

Resin components such as α-glycol content and chloride types and levels are known to influence formulation reactivity and rheology, depending on their interactions with the system composition such as basic catalysts (tertiary amines) and/or amine curing agents. Knowing the types and levels of chlorides guides formulators in the adjustment of their formulations for proper reactivity and flow.

Epoxide Equivalent Weight. The epoxy content of liquid resins is frequently expressed as *epoxide equivalent weight (EEW)* or *weight per epoxide (WPE)*, which is defined as the weight in grams that contains 1 g equivalent of epoxide. A common chemical method of analysis for epoxy content of liquid resins and solid resins is titration of the epoxide ring by hydrogen bromide in acetic acid (82). Direct titration to a crystal violet indicator end point gives excellent results with glycidyl ethers and cycloaliphatic epoxy resins. The epoxy content of glycidyl amines is determined by differential titration with perchloric acid. The amine content is first determined with perchloric acid. Addition of tetrabutylammonium iodide and additional perchloric acid generates hydrogen iodide, which reacts with the epoxy ring. The epoxy content is obtained by the second perchloric acid titration to a crystal violet end point.

In another procedure, a halogen acid is generated by the reaction of an ionic halide salt, eg, tetraethylammonium bromide in acetic acid with perchloric acid with subsequent formation of a halohydrin; the epoxy group is determined by back-titration with perchloric acid using crystal violet indicator (83). The end point can be determined visually or potentiometrically. A monograph on epoxide determinations was published in 1969 (84). This is the method adopted by ASTM and is currently used by most resin producers.

Viscosity of epoxy resins is an important characteristic affecting handling, processing, and application of the formulations. For example, high viscosity LERs impede good mixing with curing agents, resulting in inhomogeneous mixtures, incomplete network formation, and poor performance. On the other hand, too low viscosity would affect application characteristics such as coverage and appearance.

Viscosities of liquid resins are typically determined with a Cannon–Fenske capillary viscometer at 25 °C, or a Brookfield viscometer. The viscosity depends on the temperature, as illustrated in Figure 2. Viscosities of solid epoxy resins are determined in butyl carbitol (diethylene glycol monobutyl ether) solutions (40% solids content) and by comparison with standard bubble tubes (Gardner–Holdt bubble viscosity). The Gardner color of the same resin solution is determined by comparison with a standard color disk. Recently, data have been reported for solid epoxy resins using the ICI Cone and Plate viscometers, which are much more time-efficient because they do not require sample dissolution.

Hydrolyzable chloride (HyCl) content of liquid and solid epoxy resins is determined by dehydrochlorination with potassium hydroxide solution under reflux conditions and potentiometric titration of the chloride liberated by silver nitrate. The solvent(s) employed and reflux conditions can influence the extent of dehydrochlorination and give different results. The "easily hydrolyzable" HyCl content, which reflects the degree of completion of the dehydrochlorination step in the epoxy resin manufacturing process, is routinely determined by a

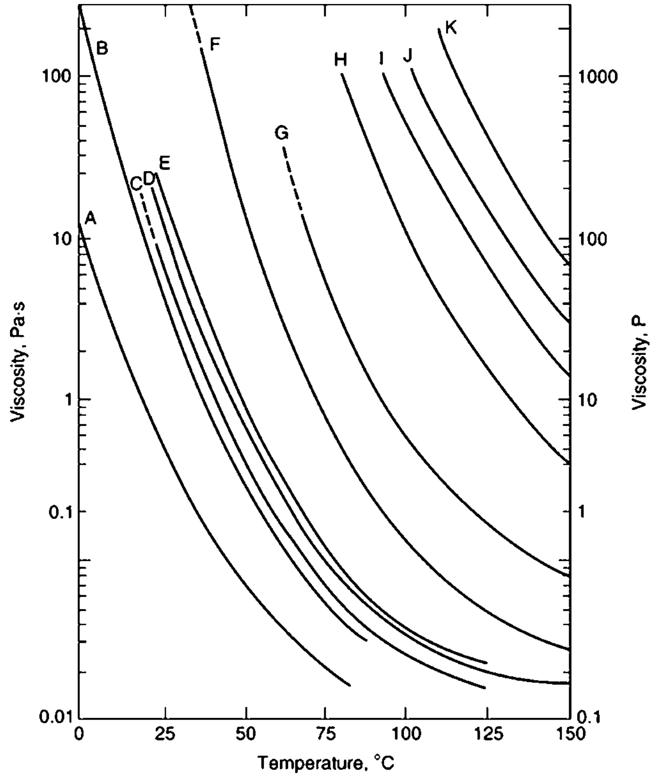


Fig. 2. Viscosity–temperature profiles for bisphenol A epoxy resins with the following EEW (epoxide equivalent weight): A, 175–195 and 195–215 diluted resins; B, 172–178; C, 178–186; D, 185–192; E, 190–198; F, 230–280; G, 290–335; H, 450–550; I, 600–700; J, 675–760; K, 800–975.

method using methanol and toluene as solvents. This is the method most commonly used to characterize LER and SER.

For epoxy resins used in electronic applications, such as cresol epoxy novolacs, more powerful polar aprotic solvents such as dioxane or dimethyl formamide (DMF) have been used to hydrolyze the difficult-to-hydrolyze HyCls, such as the abnormal chlorohydrins and the organically "bound" chlorides. The issue here is the inconsistency in results obtained by different methods (78). The presence of ionic hydrolyzable chlorides and total chlorides has been shown to affect electrical properties of epoxy molding compounds used in semiconductor encapsulation (85). For these applications, producers offer high purity grade epoxy resins with low ionic, hydrolyzable and total chloride contents.

Total chloride content of epoxy resins can be determined by the classical Parr bomb method in which the sample is oxidized in a Parr bomb, followed by titration with silver nitrate (78). The major disadvantage of this method is that it is time-consuming. Alternatively, X-ray fluorescence has been used successfully as a simple, nondestructive method to determine total chloride of epoxy resins. The method, originally developed by Dow Chemical, has been under consideration for adoption by ASTM.

The "ball and ring" and Durran's methods traditionally measure the softening point of SERs, which is important in applications such as powder coatings. The Durran's method involves heating a resin sample topped with a certain weight of mercury in a test tube until the resin reaches its softening point and flows, allowing the mercury to drop to the bottom of the test tube. The method is accurate but involves handling of highly hazardous mercury at elevated temperatures. The Mettlers' softening point method is more widely used recently because of its simplicity.

The esterification equivalent of solid resins is defined as the weight in grams esterified by one mole of monobasic acid. This value includes both the epoxy and hydroxyl groups of the solid resin. It is determined by esterification of the sample with acetic anhydride in the presence of pyridinium chloride, followed by titration with sodium methoxide to a thymol blue–phenolphthalein end point.

Molecular structure of epoxy resins. Infrared spectroscopy (IR) is used to determine the epoxide content of resins as well as their structure. A compilation of IR spectra of uncured resins has been published (86) and their use in quality control and identification of components of resin blends has been described. Recently, near IR (NIR) has emerged as a useful tool to characterize epoxy resins (87).

NMR has been utilized to characterize epoxy resins, formulations and cured networks. It has been shown to be useful in determining the level of branching in epoxy resins and isomers distribution in epoxy novolacs (88,89).

GPC and HPLC are utilized to characterize both liquid and solid epoxy resins (90). MW and MW distributions are obtained from GPC measurements, but differences in chemical composition of resin samples are more apparent from HPLC chromatograms because of better resolution (91).

HPLC has proven to be a good fingerprinting tool to characterize LERs and SERs. Chromatograms of liquid epoxy resins (crude DGEBA) indicate a homologue distribution of $n = 0$, 85%, and, in a specific case, $n = 1$, 11.5%, although the values obtained depend on the source of the liquid resin. HPLC analysis of both liquid and solid epoxy resins has been studied in some detail using normal-phase and reversed-phase columns, respectively (39).

The difference between taffy-processed and fusion advancement solid resin can be noted in HPLC chromatograms. In the advancement process, the even-membered oligomers predominate, whereas taffy-produced resins exhibit both even- and odd-numbered oligomers. Compounds that contribute to hydrolyzable chloride and α-glycol content can be quantified by HPLC. The presence of branched chain components is detectable in studies using an improved reversed-phase gradient HPLC method (92,93). Excellent reviews of applications of chromatographic techniques to the analysis of epoxy resins are available (94).

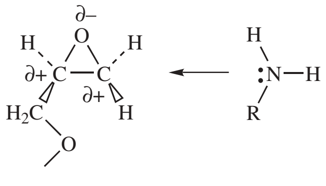
14. Curing of Epoxy Resins

With the exception of the very high MW phenoxy resins and epoxy-based thermoplastic resins, almost all epoxy resins are converted into solid, infusible, and insoluble three-dimensional thermoset networks for their uses by curing with cross-linkers. Optimum performance properties are obtained by cross-linking (qv) the right epoxy resins with the proper cross-linkers, often called hardeners or curing agents. Selecting the proper curing agent is dependent on the requirements of the application process techniques, pot life, cure conditions, and ultimate physical properties. Besides affecting viscosity and reactivity of the formulation, curing agents determine both the types of chemical bonds formed and the degree of cross-linking that will occur. These, in turn, affect the chemical resistance, electrical properties, mechanical properties, and heat resistance of the cured thermosets.

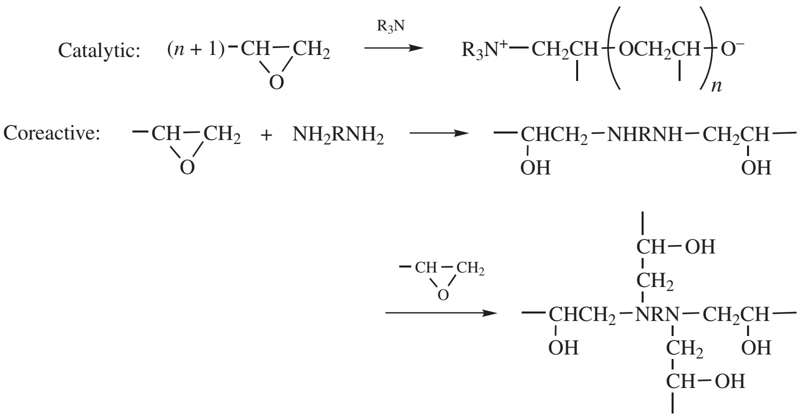
Epoxy resins contain two chemically reactive functional groups: epoxy and hydroxy. Low MW epoxy resins such as LERs are considered difunctional epoxy monomers or prepolymers and are mostly cured via the epoxy group. However, as the MW of SERs increases, the epoxy content decreases, whereas the hydroxyl content increases. High molecular weight SERs can cross-link via reactions with both the epoxy and hydroxyl functionalities, depending on the choice of curing agents and curing conditions. Reaction of the epoxy groups involves opening of the oxirane ring and formation of longer, linear C–O bonds. This feature accounts for the low shrinkage and good dimensional stability of cured epoxies. The polycondensation curing via hydroxyl groups is often accompanied by generation of volatile by-products, such as water or alcohol, requiring heat for proper cure and volatiles removal.

It is the unique ability of the strained epoxy ring to react with a wide variety of reactants under many diverse conditions that gives epoxies their versatility (95). Detailed discussions on the probable electronic configurations, molecular orbitals, bond angles, and reactivity of the epoxy ring are available in the literature (96).

Compared to noncyclic and other cyclic ethers, the epoxy ring is abnormally reactive. It has been postulated that the highly strained bond angles, along with the polarization of the C–C and C–O bonds account for the high reactivity of the epoxide. The electron-deficient carbon can undergo nucleophilic reactions, whereas the electron-rich oxygen can react with electrophiles. It is customary in the epoxy industry to refer to these reactions in terms of anionic and cationic mechanisms. The terminology was attributed to the fact that an anionic intermediate or transition state is involved in a nucleophilic attack of the epoxy while a cationic intermediate or transition state is formed by an electrophilic curing agent (97). For the sake of clarity, the nucleophilic and electrophilic mechanism terminology is used in this article.



Curing agents are either catalytic or coreactive. A catalytic curing agent functions as an initiator for epoxy resin homopolymerization or as an accelerator for other curing agents, whereas the coreactive curing agent acts as a comonomer in the polymerization process. The majority of epoxy curing occurs by nucleophilic mechanisms. The most important groups of coreactive curing agents are those with active hydrogen atoms, eg, primary and secondary amines, phenols, thiols, and carboxylic acids (and their anhydride derivatives). Lewis acids, eg, boron trihalides, and Lewis bases, eg, tertiary amines, initiate catalytic cures.



The functional groups surrounding the epoxide resin also affect the curing process. Steric factors (98,99) can influence ease of cure. Electron-withdrawing groups adjacent to the epoxide ring often enhance the reactivity of the epoxy resin to nucleophilic reagents, while retarding its reactivity toward electrophilic reagents (98,100,101). In general, aromatic and brominated aromatic epoxy resins react quite readily with nucleophilic reagents, whereas aliphatic and cycloaliphatic epoxies react sluggishly toward nucleophiles (102).

Figure 3 shows the pseudo first-order kinetic response for the disappearance of the epoxy in buffered methanol solutions (lines are for clarity only).

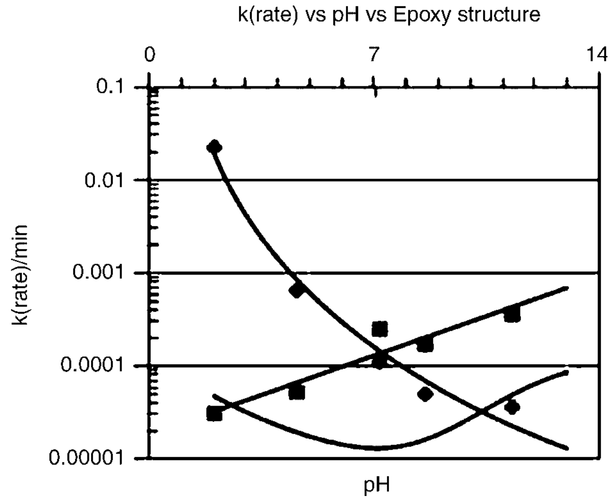


Fig. 3. Effects of pH on reaction rates of epoxies. ◆ Cyclohexene oxide; ■ phenylglycidyl ether; △ vinyl cyclohexane oxide.

Table 13. **U.S. Consumption of Curing Agents for Epoxy Resins (2001)**

Curing agents	Consumption, 10^3 MT	Market percentage
Amine functional compounds	50	48
Aliphatic amines and adducts	16	
Polyamides	14	
Amidoamines	9	
Cycloaliphatic amines	6.8	
Phenalkamines	1.8	
Dicyandiamide (DICY)	1.8	
Aromatic polyamines	0.9	
Carboxylics	37	36
Polycarboxylic polyesters	22	
Anhydrides	15	
Resole resins	9	9
Amino formaldehydes	4.5	
Phenol formaldehyde	4.5	
Novolacs and other phenolics	2.7	2.6
Polysulfides and polymercaptans	14	1.3
Catalysts	3.2	3
Anionic	3.1	
Cationic	0.1	
Others	0.9	< 1

Clearly the epoxy structure dramatically influences the cure response of the epoxy as a function of pH. Cycloaliphatic epoxies are fast-reacting under low pH conditions. Aromatic glycidyl ethers are faster under high pH conditions. These results generally agree with "practical" cures: aromatic epoxies are easily cured with amines and amidoamines. Cycloaliphatics are cured with acids and superacids. The behavior of the aliphatic epoxies is more complex but on balance is similar to that of cycloaliphatics.

In 2001, the U.S. market for epoxy curing agents was estimated at 165×10^3 MT (see Table 13), while approximately 318×10^3 MT of epoxy resins was consumed. The most commonly used curing agents are amines, followed by carboxylic-functional polyesters and anhydrides.

A description of advantages, disadvantages and major applications of typical curing agents is given in Table 14.

Table 14. **Curing Agents for Epoxy Resins**

Type	Advantages	Disadvantages	Major applications
Aliphatic amines and adducts	Low viscosity; ambient cure temperature; little color; low cost	Short pot life; rapid heat evolution; critical mix ratio; some are moderately toxic; high moisture absorption; blush; carbonation; limited high temperature performance (< 100 °C)	Flooring; civil engineering; marine and industrial coatings; adhesives; small castings

Table 14 (*Continued*)

Type	Advantages	Disadvantages	Major applications
Cycloaliphatic amines	Low viscosity; long pot-life; room temperature (RT) cure and heat-curable; adhesion to wet cement; good color; low toxicity; good electrical, mechanical, thermal properties (high T_g)	Slower reactivity; high costs	Flooring; paving; aggregate; industrial coatings; adhesives; tooling; composites; castings
Aromatic amines	Excellent elevated temperature performance (150 °C); good chemical resistance; long pot life; low moisture absorption	Solids; incompatibility with resins; long cure cycles at high temperature (150 °C); toxicity	High performance composites and coatings; adhesives; electrical encapsulation
Amidoamines	Low viscosity; reduced volatility; good pot life; ambient cure temperature; convenient mix ratios; good toughness	Poor performance at high temperature ($< 65\,^{\circ}C$); some incompatibility with epoxies	High solids, solvent-free coatings; floorings; concrete bonding; troweling compounds
Polyamides	Good mix ratios; pot life; RT cure; good concrete wetting; flexibility; low volatility and toxicity	High viscosity; low temperature performance; poor color; higher cost	Marine and maintenance coatings; civil engineering; castings; adhesives
Anhydrides	Low exotherm; good thermal (high T_g), mechanical, electrical properties; low shrinkage and viscosity; long pot life; little color	Long cure cycles at high temperature (200 °C)	Composites; castings; potting; encapsulation
Catalytic	Long pot life; high temperature resistance	Brittle; moisture-sensitive	Adhesives; prepregs; electrical encapsulation; powder coatings
Dicyandiamide	Good electrical properties; high temperature resistance; latent systems	Incompatibility with epoxy resins	Electrical laminates; powder coatings; single-package adhesives
Carboxylic-terminated polyesters	Good weatherability, corrosion resistance, and mechanical properties; low cost	Poor chemical resistance	Powder coatings
Isocyanates	Fast cure at low temperature; good flexibility and solvent resistance	Moisture-sensitive; toxic	Powder coatings; maintenance coatings

Table 14 (*Continued*)

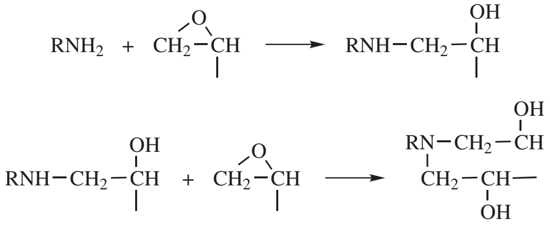
Type	Advantages	Disadvantages	Major applications
Phenol–formaldehyde, novolacs	Good chemical resistance, electrical properties, shelf stability, and compatibility with epoxies; high temperature resistance	High melting solids; high temperature cure; poor UV stability	Molding compounds; powder coatings; electrical laminates
Polysulfides and polymercaptans	RT rapid cure times; flexible systems; moisture insensitive	Poor performance at high temperature; odorous	Consumer adhesives; sealants; traffic paints
Melamine–formaldehyde	Good color and hardness; stable one-component systems	High temperature cure	Stove paints; can coatings
Urea–formaldehyde	Stable one-component systems; little color; low cost	High temperature cure; formaldehyde emission	Fast-bake enamels; stove primers; can and drum coatings
Phenol–formaldehyde resoles	Stable one-component systems; excellent chemical resistance	High temperature cure; brittle; gold color	Baked enamels; can, drum and pail coatings; high temperature service coatings

15. Coreactive Curing Agents

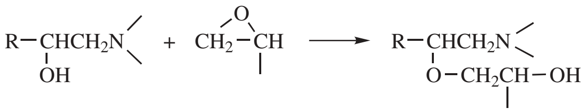
Commercially, epoxy resins are predominantly cured with coreactive curing agents. Following are important classes of epoxy coreactive curing agents.

15.1. Amine Functional Curing Agents. This section describes one of the most important classes of epoxy coreactive curing agents.

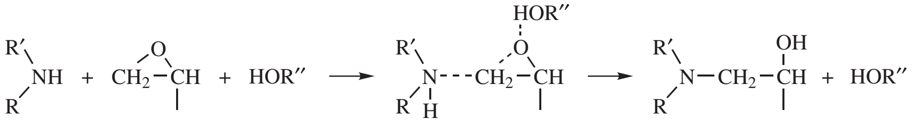
Primary and Secondary Amines. Primary and secondary amines and their adducts are the most widely used curing agents for epoxy resins, accounting for close to 50% of all the epoxy curing agents used in the United States in 2001. The number of amine hydrogen atoms present on the molecule determines the functionality of an amine. A primary amine group, one which has two hydrogens bound to it, will react with two epoxy groups while a secondary amine will react with only one epoxy group. A tertiary amine group, which has no active hydrogen, will not react readily with the epoxy group, but will act as a catalyst to accelerate epoxy reactions. Reactions of a primary amine with an oxirane group or an epoxy resin are shown in the following (103).



It has been reported that primary amines react much faster than secondary amines (101,104). Reaction of an epoxy group with a primary amine initially produces a secondary alcohol and a secondary amine. The secondary amine, in turn, reacts with an epoxy group to give a tertiary amine and two secondary hydroxyl groups. Little competitive reaction is detectable between a secondary hydroxyl group in the backbone and an epoxy group to afford an ether (100), provided a stoichiometric equivalent or excess amine is maintained. However, with excess epoxy, the secondary hydroxyl groups formed gradually add to the epoxide groups (105). This reaction can be catalyzed by tertiary amines.



Hydroxyl compounds accelerate the rate of amine curing. A mechanism has been proposed (100) in which the hydroxyl group hydrogen bonds to the oxygen atom on the epoxy group, rendering the methylene group more susceptible to attack by the nucleophilic amine. Reactivity is proportional to the hydroxyl acidity and functionality; phenolics, aryl alcohols, and polyfunctional alcohols afford the best results.



In general, reactivity of amines toward aromatic glycidyl ethers follows their nucleophilicity: aliphatic amines > cycloaliphatic amines > aromatic amines. Aliphatic amines cure aromatic glycidyl ether resins at room temperature (RT) without accelerators, whereas aromatic amines require elevated temperatures. However, with the help of accelerators, the cure rates of aromatic amines can approach those of some aliphatic amines. In general, the steric and electronic effects of substituents of the epoxy and the amine influence the reaction rate of an amine with an epoxy resin.

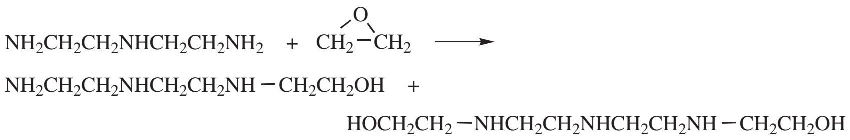
Aliphatic Amines. The liquid aliphatic polyamines such as polyethylene polyamines (PEPAs) were some of the first curing agents used with epoxies. They give good RT cures with DGEBA-type resins. The low equivalent weights of the ethylene amines give tightly cross-linked networks with good physical properties, including excellent chemical and solvent resistance but limited flexibility and toughness. Good long-term retention of properties is possible at temperatures up to 100 °C. Short-term exposure to higher temperatures can be tolerated. Certain aliphatic amines cured epoxies will blush (or bloom) under humid conditions. This undesirable property has been attributed to the incompatibility of some amine curing agents with epoxy resins. Incompatible amines can exude to the surface during cure and react with atmospheric carbon dioxide and moisture to form undesirable carbamates (carbonation). This, in turn, leads to gloss reduction and intercoat adhesion and recoatability problems in coating applications (106).

$$\underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2} \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

$$\underset{\text{Carbonic acid}}{H_2CO_3} + \underset{\text{Amine}}{RNH_2} \longrightarrow \underset{\text{Carbamic acid}}{RNHCOOH} + \underset{\text{Water}}{H_2O}$$

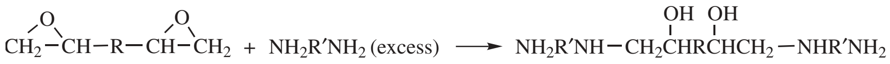
$$\underset{\text{Carbamic acid}}{RNHCOOH} + \underset{\text{Amine}}{R'NH_2} \longrightarrow \underset{\text{Carbamate}}{R'NH_3^{+}{-}OCONHR}$$

Mixing ratios with epoxy resin are very critical, and working pot lives are too short for some applications. Aliphatic polyamines are hygroscopic and volatile, have bad odor, and cause dermatitis if improperly handled. Another disadvantage is high exotherm in thick sections or large mass parts that can lead to thermal decomposition. Consequently, significant efforts have been devoted toward remedying these shortcomings by modifications of the polyethylene polyamines. Adducts with epoxy resins (resin adducts), carboxylic acids (polyamides, amidoamines), ketones (ketimines), and phenols/formaldehyde (Mannich bases) (107) are widely used commercially. Longer chain alkylenediamines such as hexamethylenediamine (HMD) and polyetheramines (polyglycol-based polyamines) have also been developed. Currently, very small amounts of unmodified polyamines are used as curing agents for epoxies. They are primarily used to produce epoxy adducts (up to 90 %). Chemical modification by reaction with epoxy groups to yield epoxy adducts affords products with better handling properties, lower vapor pressure, reduced tendency to blush, and less critical mix ratio. For example, diethylenetriamine (DETA) readily reacts with ethylene oxide in the presence of water to give a mixture of mono- and dihydroxyethyl diethylenetriamine with a longer pot life and fewer dermatitic effects than free DETA.



$$NH_2CH_2CH_2NHCH_2CH_2NH_2 + \overset{\;O\;}{CH_2{-}CH_2} \longrightarrow$$
$$NH_2CH_2CH_2NHCH_2CH_2NH{-}CH_2CH_2OH + HOCH_2CH_2{-}NHCH_2CH_2NHCH_2CH_2NH{-}CH_2CH_2OH$$

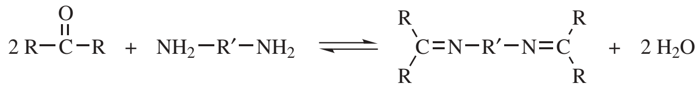
Resinous adducts are produced by reaction of excess diamine with epoxy resins.



$$\overset{O}{CH_2{-}CH}{-}R{-}\overset{O}{CH{-}CH_2} + NH_2R'NH_2\,(\text{excess}) \longrightarrow NH_2R'NH{-}CH_2\overset{OH}{C}HR\overset{OH}{C}HCH_2{-}NHR'NH_2$$

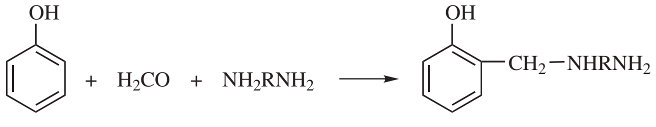
The higher molecular weight of the adduct affords a more desirable, forgiving ratio of resin to curing agent, lower water absorption, and better resin compatibility.

Ketimines. Ketimines are the reaction products of ketones and primary aliphatic amines. In the absence of reactive hydrogens, they do not react with epoxy resins. They can be considered blocked amines or latent hardeners, since they are readily hydrolyzed to regenerate the amines. They have low viscosity, cure rapidly when exposed to atmospheric humidity, and are useful in high solids coatings. Similar products have been obtained with acrylonitrile.



$$2\,R{-}\overset{O}{\overset{\|}{C}}{-}R + NH_2{-}R'{-}NH_2 \rightleftharpoons R_2C{=}N{-}R'{-}N{=}CR_2 + 2\,H_2O$$

Mannich Base Adducts. Mannich base adduct is the reaction product of an amine with phenol and formaldehyde.



The resultant product has an internal phenolic accelerator. Compared to unmodified amines Mannich base adducts have lower volatility, less blushing and carbonation, and, despite their higher MW, faster reactivity.

Polyetheramines. Polyetheramines are produced by reacting polyols derived from ethylene oxide or propylene oxide with amines. The more commercially successful adducts are based on propylene oxide and are available in different MWs (JEFFAMINE* from Huntsman). The longer chain backbone provides improved flexibility but slower cure rate. Chemical and thermal resistance properties are also reduced. Polyetheramines are often used in combination with other amines in flooring, and adhesive and electrical potting applications.

Cycloaliphatic Amines. Cycloaliphatic amines were originally developed in Europe, where their use as epoxy curing agents is well established. Compared to aliphatic amines, cycloaliphatic amines produce cured resins having improved thermal resistance and toughness. Glass-transition temperatures (T_g) approach those of aromatic amines ($> 150\,^\circ C$), while percent elongation can be doubled. However, chemical resistance is inferior to that of aromatic amines. Because cycloaliphatic amines are less reactive than acyclic aliphatic amines, their use results in a longer pot life and in the ability to cast larger masses. Unmodified cycloaliphatic amines require elevated temperature cure, but modified systems are RT-curable. Properly formulated, they can give an excellent balance of properties: fast cure, low viscosity, low toxicity, good adhesion to damp concrete, and excellent color stability. They are, however, more expensive than other types of curing agents.

Isophorone diamine (IPDA), bis(4-aminocyclohexyl)methane (PACM), and 1,2-diaminocyclohexane (1,2-DACH) are the principal commercial cycloaliphatic polyamine curing agents. IPDA is the largest volume cycloaliphatic amine. Commercial cycloaliphatic amines are formulated products. In addition to the cycloaliphatic amines, other components such as aliphatic amines and plasticizers are also included to improve RT cure speed and end-use properties. One popular formulation consists of IPDA used in combination with trimethylhexamethylenediamines (TMDA) or *meta*-xylenediamine (MXDA), and plasticizers/accelerators such as nonyl phenol or benzyl alcohol. In some ambient cure coating applications, cycloaliphatic amines can be reacted with phenol and formaldehyde to form the Mannich base products, which have an internal phenol accelerator and cure readily at ambient temperatures.

The largest market for cycloaliphatic amines is in flooring, followed by high solids coatings, composites, adhesives, castings, and tooling. Cycloaliphatic amines experienced significant growth in the early 1990s as replacements for more toxic aromatic amines such as MDA. However, anhydrides have been more successful at replacing aromatic amines in composite applications.

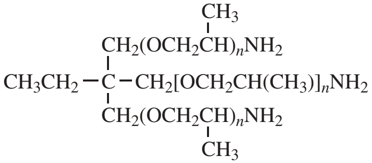
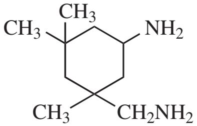
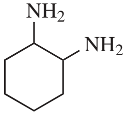
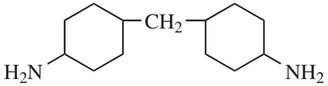
Aromatic Amines. Because of conjugation, aromatic amines have lower electron density on nitrogen than do the aliphatic and cycloaliphatic amines. Consequently, they are much less reactive toward aromatic epoxies. They have longer pot-lives and usually require elevated temperature cures. Aromatic amines are usually solid at room temperature. These hardeners are routinely melted at elevated temperatures and blended with warmed resins to improve solubility. Eutectic mixtures of *meta*-phenylenediamine (MPD) and methylenedianiline (MDA or DDM) exhibit a depressed melting point resulting in an aromatic hardener that remains a liquid over a short period of time. MDA or 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulfone (DDS or DADPS), and MPD are the principal commercial aromatic amines. A new aromatic amine, diethyltoluenediamine (DETDA) has gained more significant uses in recent years.

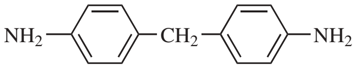
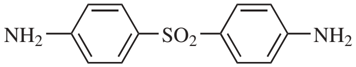
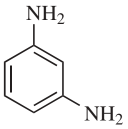
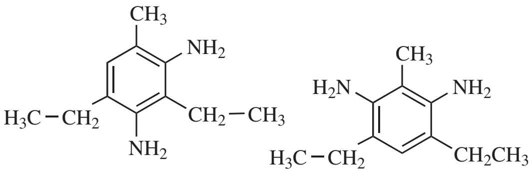
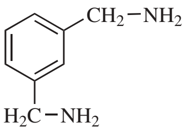
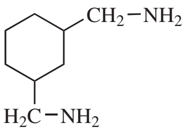
Epoxies cured with aromatic amines typically have better chemical resistance and higher thermal resistance properties than products cured with aliphatic and cycloaliphatic amines. Their best attribute is their retention of mechanical properties at long exposures to elevated temperatures (up to 150 °C). Consequently, they are widely used in demanding structural composite applications such as aerospace, PCB laminates, and electronic encapsulation. 4,4′-DDS is the standard curing agent used with a multifunctional amine epoxy (MY 720) for high performance aerospace and military composite application. 3,3′-DDS is used in aerospace honeycomb for its excellent peel strength. MDA, which has excellent mechanical and electrical properties, is the most widely used aromatic curing agent, but recently has been classified as a potential human carcinogen and its volume has been declining. Alkyl-substituted MDAs such as tetraethyl-MDA have been developed with lower toxicity and improved performance (108,109). However, none of the replacement products has the performance/cost combination of MDA. Anhydrides and cycloaliphatic amines have been used to replace aromatic amines in a number of composite applications. Efforts have been made to develop ambient-curable aromatic amines by adding accelerators such as phenols to MDA.

Arylyl Amines. These amines have cycloaliphatic or aromatic backbones, but the amine functional groups are separated from the backbone by methylene groups (benzylic amines and hydrogenated derivatives). Consequently, arylyl amines are much more reactive toward epoxies than aromatic amines while having improved thermal and chemical resistance over aliphatic amines. Fast cures at ambient and sub-ambient are possible with arylyl amines. These amines are more widely used in Japan and Europe than in North America *meta*-Xylylene diamine (MXDA) and its hydrogenated product, 1,3-bis(aminomethyl cyclohexane) (1,3-BAC) are popular arylyl amines.

The commercial polyamine curing agents are given in Table 15.

Table 15. **Commercial Amine Curing Agents**

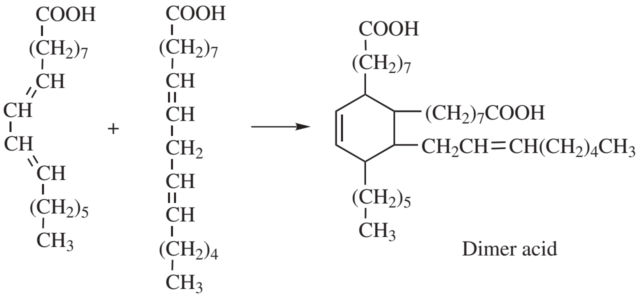
Formula	Name	Abbreviation
Aliphatic		
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	Diethylenetriamine	DETA
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	Triethylenetetramine	TETA
 $NH_2\overset{CH_3}{\overset{\mid}{C}}HCH_2(OCH_2\overset{CH_3}{\overset{\mid}{C}}H)_nNH_2$	Poly(oxypropylene diamine)	
 $CH_3CH_2-\overset{CH_2(OCH_2\overset{CH_3}{\overset{\mid}{C}}H)_nNH_2}{\overset{\mid}{\underset{\underset{CH_2(OCH_2\underset{\underset{CH_3}{\mid}}{C}H)_nNH_2}{\mid}}{C}}}-CH_2[OCH_2CH(CH_3)]_nNH_2$	Poly(oxypropylene triamine)	
$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_3NH_2$	Poly(glycol amine)	
	*N*-Aminoethylpiperazine	AEP
Cycloaliphatic		
	Isophorone diamine	IPDA
	1,2-Diaminocyclohexane	DACH
	Bis(4-aminocyclohexyl)methane	PACM

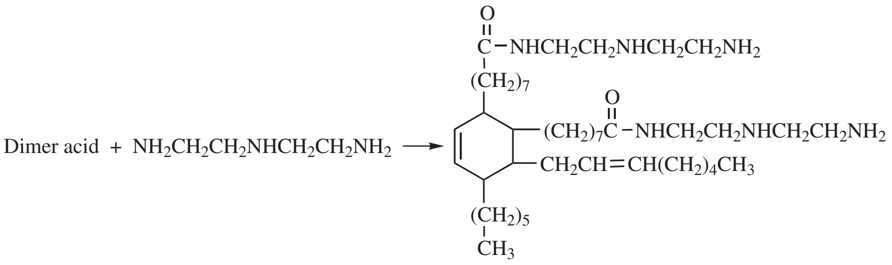
Aromatic		
	4,4′-Diamino-diphenylmethane	MDA, DDM
	4,4′-Diaminodiphenyl sulfone	4,4′-DDS
	*m*-Phenylenediamine	MPD
	Diethyltoluenediamine	DETDA
Arylyl amines	*meta*-Xylene diamine	MXDA
		
	1,3-Bis(aminomethyl cyclohexane)	1,3-BAC

The stoichiometric quantity of polyamine used to cure an epoxy resin is a function of the molecular weight and the number of active hydrogens of the polyamine (amine equivalent weight, AEW) and the EEW or equivalent weight of epoxy resin; it is expressed as follows:

$$\left(\frac{\mathrm{AEW}}{\mathrm{EEW}}\right) \times 100 = \text{parts by weight polyamine per 100 parts by weight epoxy resin}$$

Polyamides. Polyamides are one of the largest volume epoxy curing agents used. They are prepared by the reaction of dimerized and trimerized vegetable-oil fatty acids with polyamines. Dimer acid is made by a Diels–Alder reaction between 9,12- and 9,11-linoleic acids. Subsequent reaction with diethylenetriamine or other suitable multifunctional amines yields the amine-terminated polyamides. They are available in a range of molecular weights and compositions.



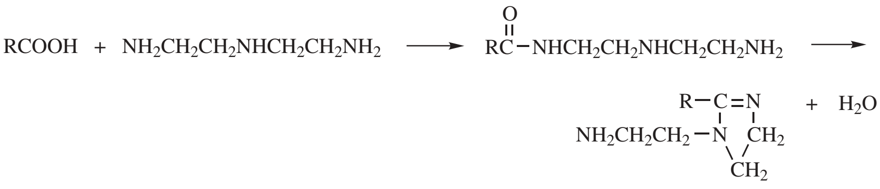


Polyamides are extremely versatile curing agents. The polyamides react with the epoxide group through the terminal amine functionality. The unreacted amide NH groups in the backbone provide good intercoat adhesion and the fatty acid structures provide good moisture resistance and mechanical properties. Wetting of cement surfaces is excellent. As a result of their relatively higher molecular weight, the ratio of polyamide to epoxy is more forgiving than with low MW polyamines. They are inexpensive, less toxic to handle; give no blushing; exhibit readily workable pot lives; and cure under mild conditions. Polyamides are mainly used in coating and adhesive formulations, mostly in industrial maintenance and civil engineering applications. The various MW polyamides exhibit different degrees of compatibility with epoxy resins. To ensure optimum properties, the polyamide/epoxy mixture must be allowed to react partly before being cured. This partial reaction assures compatibility and is known as the *induction period.*

Disadvantages of polyamides include slower cure speeds and darker color than polyamine-cured epoxies. Polyamide-cured epoxies lose structural strength rapidly with increasing temperature. This limits their use to applications not subjected to temperatures above 65 °C. Formulations with tertiary amines, phenolic amines, or co-curing agents help to speed up cures at low temperatures. Alternatively, polyamides derived from polyamines with phenolic-containing carboxylic acids are called *phenalkamines* (110). These curing agents have low viscosity and fast ambient cure speed and are widely used in on-site marine coatings and concrete deck applications.

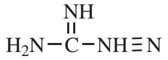
The high viscosity of polyamides limits their uses primarily to low solids coatings, which have been losing ground to higher solids coatings. Waterborne polyamides have been developed for use with waterborne epoxies, but their growth has been modest over the past decade because the conversion to waterborne epoxy coatings has been slower than expected. Commercial polyamides include the Versamid resins from Cognis, Ancamide resins from Air Products, and Epicure resins from Resolution.

Amidoamines. Amidoamines have all the properties of polyamides, except for a significantly lower viscosity, which make them useful in high solids and solvent-free coating formulations. They are prepared by the reaction of a monofunctional acid like tall-oil fatty acid with a multifunctional amine such as DETA, resulting in a mixture of amidoamines and imidazolines.



Imidazoline is formed by intramolecular condensation at high reaction temperatures. Commercial amidoamines are produced with different imidazoline contents to regulate reactivity and cured product performance. The pot life/reactivity of amidoamines varies with imidazoline content. High imidazoline content offers longer pot life and semi-latent curing activated by moisture. They are particularly useful in wet concrete applications. Like the polyamides, amidoamines can be used over a range of levels to enhance a specific property. However, amidoamines offer several advantages over aliphatic amines and polyamides. They offer more convenient mix ratios, increased flexibility, and better moisture resistance than aliphatic polyamines, and they offer lower color and viscosity than polyamides. Consequently, the volume of amidoamines has grown significantly in the past decade.

Dicyandiamide. Dicyandiamide (DICY) is a solid latent hardener (mp 208 °C). Its latent nature is due to its insolubility in epoxy resins at RT. DICY can be mixed with epoxy resins to provide a one-package formulation with good stability up to 6 months at ambient temperatures. Cure of epoxies with DICY occurs with heating to 150 °C. It is often used with imidazoles as catalysts. DICY offers the advantage of being latent (reacts with epoxy resin upon heating and stops reacting temporarily when the heat is removed). This partially cured or “B-staged” state is ideal for prepreg applications. Typically, DICY is used at levels of 5–7 parts per 100 parts of liquid epoxy resins and 3–4 parts per 100 parts of solid epoxy resins.



$$H_2N-\overset{\overset{\displaystyle NH}{\|}}{C}-NH\equiv N$$

DICY

DICY is one of the first curing agents to be used with epoxy resins. It cures with epoxies to give a highly cross-linked thermoset with good mechanical strength, thermal properties, and chemical resistance, and excellent electrical properties. Because of its latency, low quantity requirements and excellent balance of properties, DICY is a widely used curing agent in powder coating and electrical laminate applications. These two applications account for 85% of DICY consumption as epoxy curing agent.

The curing mechanism is rather complex, involving several simultaneous reactions. There are a number of conflicting proposed mechanisms in the literature. One study proposed the initial reaction of all four active hydrogens with epoxy resin catalyzed by tertiary amine catalysts followed by epoxy homopolymerization. The last step involves reactions between the hydroxyl groups of the epoxy resin with the cyano group (108,109). One of the more recent and plausible mechanisms of DICY cure with epoxies is that of Gilbert and co-workers (111). The Gilbert mechanism is summarized in Figure 4. Gilbert and co-workers investigated the reaction of DICY with methyl glycidyl ether of bisphenol A (MGEBA). Products were analyzed using HPLC, NMR, and FTIR. On the basis of products that were isolated and characterized, Gilbert and co-workers proposed the mechanism shown in Figure 4.

The first step in the mechanism is the reaction of DICY with epoxy to form the alkylated DICY. This was confirmed by the imide IR peak at 1570 cm^{-1}. The second step involves further alkylation of the nitrogen that reacted in step 1, to form the *N*,*N*-dialkyldicyandiamide. No alkylation of the other amino group was suggested. The third step is the intramolecular cyclization step to form a zwitterionic five-membered intermediate. This involves the intramolecular reaction of the secondary alcohol formed in step 2 with the imide functionality ($-C=N-$). This is in contrast with the Zahir mechanism (112) where the intramolecular cyclization involves the hydroxy and the nitrile groups. The fourth step involves the elimination of ammonia and the formation of 2-cyanoimidooxazolidine. The formation of this heterocycle is consistent with the observed bathocromic IR shift from 1570 cm^{-1} to 1650 cm^{-1}. The ammonia that is eliminated can then react with epoxy to form a trifunctional cross-link. The last step involves the hydrolysis of the oxazolidine to form the oxazolidone and cyanamide. The hydrolysis step accounts for the formation of the carbonyl group.

15.2. Carboxylic Functional Polyester and Anhydride Curing Agents.

Carboxylic polyesters and anhydrides are the second most important class of epoxy curing agent. Together, they constitute 36% of the total curing agent volume used in the U.S. market (2001 data). Polyesters have been growing rapidly in powder coatings formulations with epoxy resins, consuming the highest tonnage of epoxy curing agents. This is driven in part by the conversion to the more environmentally friendly powder coating technologies, and in part by the

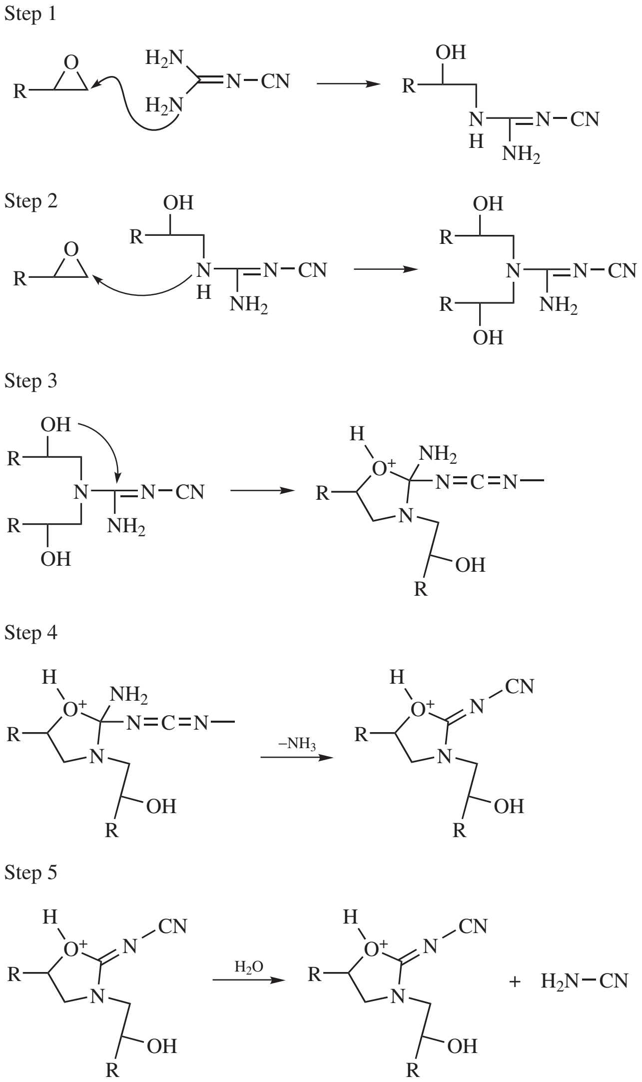


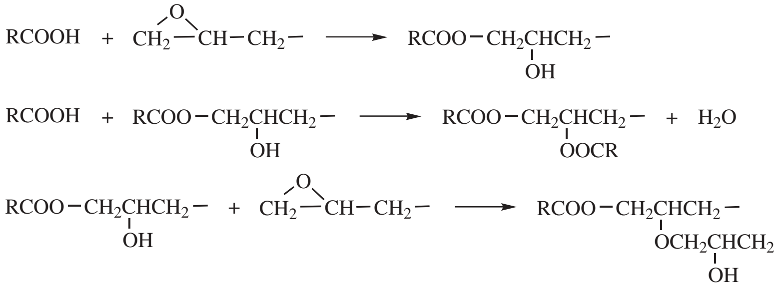
Fig. 4. The Gilbert mechanism for the DICY curing of epoxy. From Ref. (111).

versatility and cost efficiency of polyester–epoxy hybrid powder coatings. Anhydrides have been successfully replacing more toxic aromatic amines in composites. They account for 70% of the volume of curing agents used in structural composite applications. Both polyesters and anhydrides are used in heat-cured applications only.

Carboxylic Functional Polyesters. The reaction of polyacids with polyalcohols produces polyesters. The terminal functionality is dictated by the ratio of the reactants. By virtue of their relatively cheap, widely available raw materials and good flexibility and weatherability, acid functional polyesters are used in hybrid epoxy powder coatings for a wide range of applications. For applications requiring good weatherability, triglycidyl isocyanurate (TGIC) is often used as curing agent for acid functional polyesters.

Terephthalic acid, trimellitic anhydride, and neopentyl glycol are commonly used raw materials to produce polyesters. Other acids, anhydrides, and glycols can also be used to modify functionality, MW, viscosity, and mechanical properties (after curing) of the polyesters. This versatility of the polyester building blocks allows many useful combinations of epoxy–polyester hybrid systems to be developed for a wide range of applications (113). Major applications include coatings for metal furniture, general metal finishing, appliances, machinery and equipment, automotive, and wood. Automotive is a new, large, and fast growing market with many car makers converting to primer-surfacer based on epoxy–polyester powder coatings. Wood coatings are a new, emerging market.

The curing mechanism of epoxy–polyester thermosets involves reaction of the acid functionality with epoxy followed by esterification of the epoxy hydroxyl groups with the acids (114). Compounds such as amines and phosphonium salts catalyze these reactions. Water is a condensation reaction by-product that must be allowed to escape during the curing process to avoid coating defects.



The first product is a β-hydroxypropyl ester, which reacts with a second mole of carboxylic acid to yield a diester. The hydroxyl ester can also undergo polymerization by reaction of its secondary hydroxyl group with an epoxy group.

Acid Anhydrides. Anhydrides are some of the very first epoxy curing agents used, and they remain a major class of curing agents used in heat-cured structural composites and electrical encapsulation. Their consumption volume equals that of all aliphatic amines and adducts in 2001 in the United States. While the carboxylic-terminated polyesters find widespread uses in coatings, anhydride use in coatings is minimal.

Epoxy–anhydride systems exhibit low viscosity and long pot life, low exothermic heats of reaction, and little shrinkage when cured at elevated temperatures. The low exotherm heat generation is a unique attribute of anhydrides, making them suitable for uses in large mass epoxy cures. Curing is slow at temperatures below 200 °C and is often catalyzed by Lewis bases or acids. Post-cure is often needed to develop optimum properties. Tertiary amines such as benzyldimethylamine, dimethylaminomethylphenol, tris(dimethylaminomethyl)phenol, boron trihalide amine complexes, stannic chloride, ammonium salts, phosphonium salts, and substituted imidazoles are effective catalysts. Proper catalyst concentration (0.5–2.5 % of resin weight) is critical, depending on the types of anhydrides and resins used and the cure schedules, and is known to affect high temperature performance.

Cured epoxy–anhydride systems exhibit excellent thermal, mechanical, and electrical properties, and are used in filament-wound epoxy pipe, PCB laminates, mineral-filled composites, and electrical casting and encapsulation applications. Anhydride-cured epoxies also have better aqueous acid resistance than similar amine-cured systems. Anhydrides are the principal curing agents for cycloaliphatic and epoxidized olefin resins in electrical casting and potting. Some key physical properties of exemplary epoxy resins cured with hexahydrophthalic anhydride are shown in Table 16.

The mechanism of anhydride cure is complex and controversial because of the possibility of several competing reactions. The uncatalyzed reaction of epoxy resins with acid anhydrides proceeds slowly even at 200 °C; both esterification and etherification occur. Secondary alcohols from the epoxy backbone react with the anhydride to give a half ester, which in turn reacts with an epoxy group to give the diester. A competing reaction is etherification of an epoxy with a secondary alcohol, either on the resin backbone or that formed during the esterification, resulting in a β-hydroxy ether. It has been reported that etherification is a probable reaction since only 0.85 equivalents of anhydrides are required to obtain optimum cross-linked density and cured properties (103).

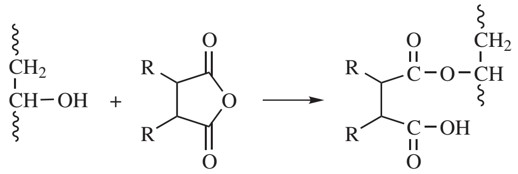
Table 16. **Formulation and Properties of Epoxy Resins Cured With Hexahydrophthalic Anhydride**

	DGEBA	3′,4′-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate	Hexahydrophthalic acid diglycidyl ester
formulation			
resin, pbw[a]	100	100	100
hexahydrophthalic anhydride, pbw[a]	85	105	100
accelerator type	tertiary amine	metal alkoxide salt	quaternary ammonium salt
pbw[a]	3	12	4
cure schedule, h at °C	2 at 100 1 at 150	4 at 120	4 at 80 4 at 140
typical cured properties at 25 °C			
tensile strength, MPa[b]	65	68	83
tensile modulus, MPa[b]	3400	3300	3000
flexural strength, MPa[b]	131	89	127
flexural modulus, MPa[b]	3400	3000	3000
elongation, %	5.0	2.7	3.5
compressive strength, MPa[b]	124	151	124
heat-deflection temperature, °C	120	150	105
water absorption, % weight gain[c]	0.5	0.4	0.4
dielectric constant at 60 Hz	3.4	3.3	3.5
dissipation factor at 60 Hz	0.006	0.005	0.007
volume resistivity, $\Omega \cdot \mathrm{cm} \times 10^{16}$	2.0	10.0	3.0

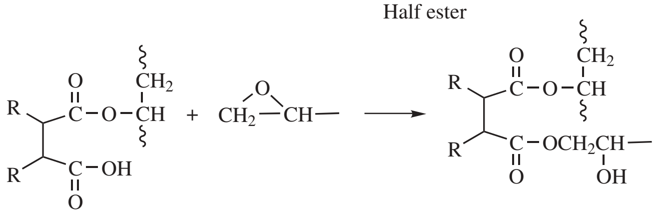
[a] Parts by weight.

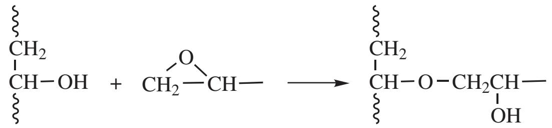
[b] To convert MPa to psi, multiply by 145.

[c] After boiling for 1 h.

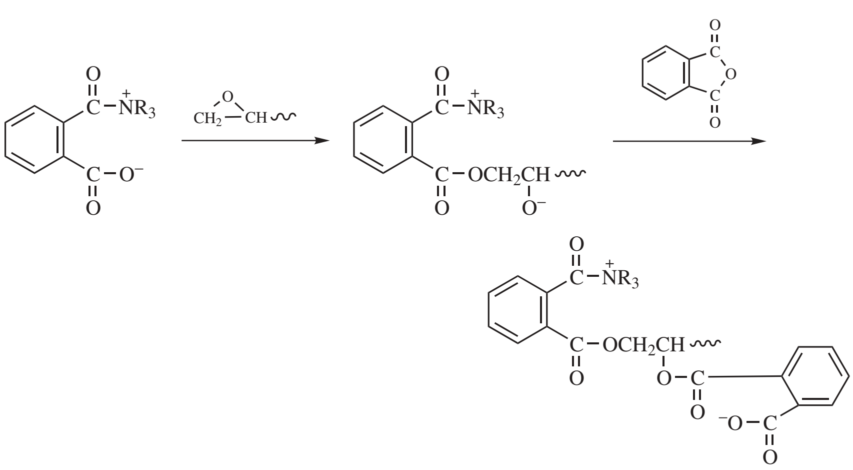


Half ester





Lewis bases such as tertiary amines and imidazoles are widely used as epoxy–anhydride catalysts. Conflicting mechanisms have been reported for these catalyzed reactions (115). The more widely accepted mechanism (103) involves the reaction of the basic catalyst with the anhydride in the initiation step to form a betain (internal salt). The propagation step involves the reaction of the carboxylate anion with the epoxy group, generating an alkoxide. The alkoxide then further reacts with another anhydride, propagating the cycle by generating another carboxylate which reacts with another epoxy group. The end result is the formation of polyester-type linkages. In practice, it has been observed that optimum properties are obtained when stoichiometric equivalents of epoxy and anhydride are used with high temperature cures, which is consistent with this mechanism and does not involve etherification reactions. At lower anhydride/epoxy ratios (0.5:1) and lower cure temperatures, some etherifications can take place by reaction of the alkoxide with an epoxy group.



Numerous structurally different anhydrides can be used as epoxy curing agents, but the most widely used are liquids for ease of handling. The most important commercial anhydrides are listed in Table 17. Methyltetrahydrophathalic anhydride (MTHPA) is the largest volume anhydride, used in filament-winding composites. Phthalic anhydride (PA) is the next largest volume and is inexpensive; so it is used widely in mineral-filled laboratory bench top manufacturing, which requires low exotherm heat generation to avoid cracking. Dodecylsuccinic anhydride (DDSA) has a long aliphatic chain in the backbone and is used as blends to improve flexibility. Benzophenonetetracarboxylic dianhydride (BTDA) is a relatively new, multifunctional anhydride developed for high temperature applications, capable of achieving a high cross-linking density with a heat distortion temperature (HDT) of 280 °C. It has been used as a replacement for more toxic aromatic amines. Tetrachlorophthalic anhydride (TCPA) is used in epoxy powder coatings for small electronic components with flame-retardancy requirements.

15.3. Phenolic-Terminated Curing Agents.

Phenolics form a general class of epoxy curing agents containing phenolic hydroxyls capable of reacting with the epoxy groups. They include phenol-, cresol-, and bisphenol A terminated epoxy resin hardener. More recent additions include bisphenol A based novolacs. Cure takes place at elevated temperatures (150–200 °C) and amine catalysts are often used.

The bisphenol A terminated hardeners are produced using liquid epoxy resins and excess bisphenol A in the resin advancement process. They are essentially epoxy resins terminated with bisphenol A. They are popular in epoxy powder coating applications for rebar and pipe, providing more flexible epoxy coatings than the novolacs.

The novolacs are produced via the condensation reaction of phenolic compounds with formaldehyde using acid catalysts. They are essentially precursors to epoxy novolacs. Novolacs are multifunctional curing agents and can impart higher cross-link density, higher T_g, and better thermal and chemical resistance than other phenolics. Cresol novolacs provide higher solvent and moisture resistance, but are more brittle than their phenol novolac counterparts. Recently, bisphenol A based novolacs have been used in electrical laminate formulations to improve thermal performance (T_g and T_d) (116). Novolacs are widely used in composites, PCB laminates, and electronic encapsulation applications. Their uses in coatings are limited to high temperature applications such as powder coatings for down-hole oil-field pipe coatings.

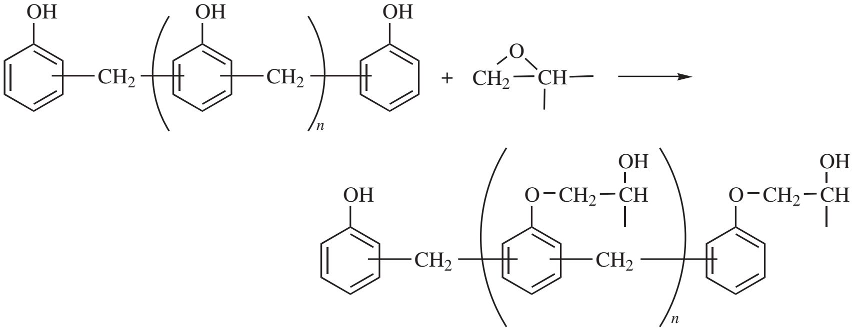
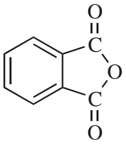
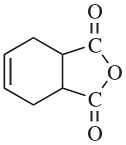
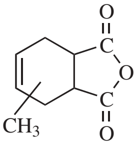
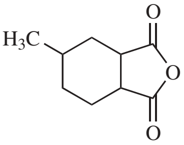
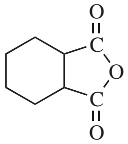
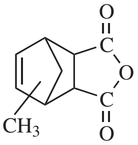
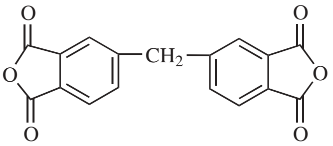
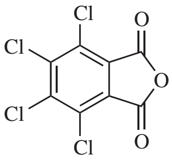
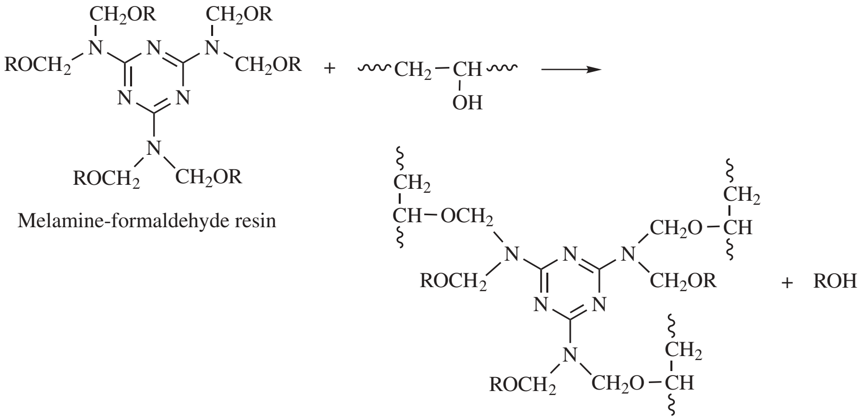


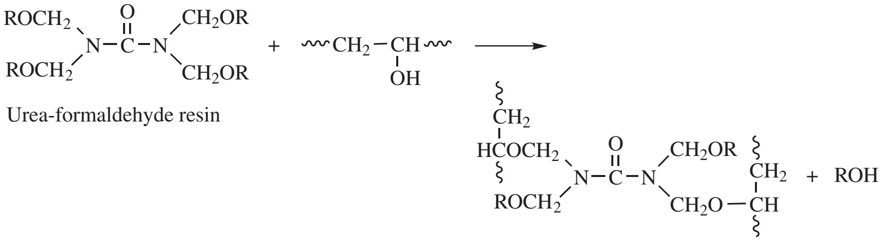
Table 17. **Commercially Important Anhydride Curing Agents**

Name	Structure
Phthalic anhydride (PA)	
Tetrahydrophthalic anhydride (THPA)	
Methyltetrahydrophthalic anhydride (MTHPA)	
Methyl hexahydrophthalic anhydride (MHHPA)	
Hexahydrophthalic anhydride (HHPA)	
Nadic methyl anhydride or methyl himic anhydride (MHA)	
Benzophenonetetracarboxylic dianhydride (BTDA)	
Tetrachlorophthalic anhydride (TCPA)	

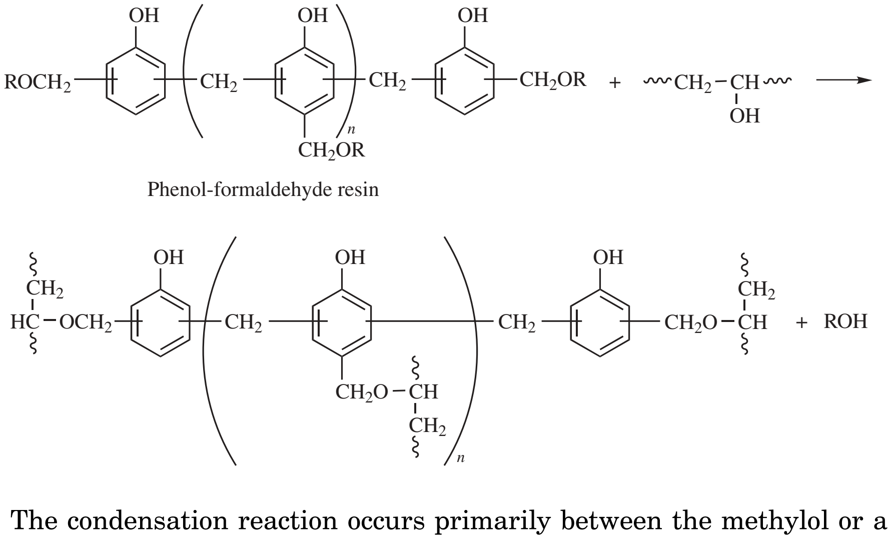
15.4. Melamine–, Urea–, and Phenol–Formaldehyde Resins. Melamine–formaldehyde, urea–formaldehyde, and phenol–formaldehyde resins react with hydroxyl groups of high MW epoxy resins to afford cross-linked networks (72).



Melamine-formaldehyde resin



Urea-formaldehyde resin



Phenol-formaldehyde resin

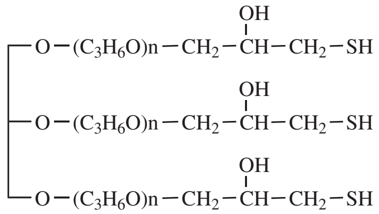
The condensation reaction occurs primarily between the methylol or alkylated methylol group of the formaldehyde resin and the secondary hydroxyl group on the epoxy resin backbone. The high bake temperatures used in these applications drive off the condensation by-products (alcohol or water). Acids such as phosphoric acid and sulfonic acids are often used as catalysts.

There are two types of phenol–formaldehyde condensation polymers: resoles and novolacs (117). Phenol–formaldehyde polymers prepared from the base-catalyzed condensation of phenol and excess formaldehyde are called resoles. In most phenolic resins commonly used with epoxies, the phenolic group is converted into an ether to give improved alkali resistance. At elevated temperatures ($>150\,^{\circ}$C), resole resins react with the hydroxyl groups of the epoxy resins to provide highly cross-linked polymers.

The melamine- and urea–formaldehyde resins are also called amino resins (118). The phenol–formaldehyde resoles are often called phenolic resins, which is rather easily confused with phenolic-terminated cross-linkers such as novolacs and bisphenol A terminated resins.

These formaldehyde-based resins are widely used to cure high MW solid epoxy resins at elevated temperatures (up to 200 °C) for metal can, drum, and coil coatings applications. The resultant coatings have excellent chemical resistance, good mechanical properties, and no effects on taste (adding or taking away taste from packaged foods or drinks). The vast majority of the food and beverage cans produced in the world today are coated internally with epoxy–formaldehyde resin coatings. The phenol–formaldehyde resoles are also used with epoxies in coatings for high temperature service pipes and to protect against hot, corrosive liquids.

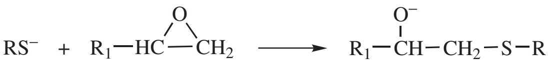
15.5. Mercaptans (Polysulfides and Polymercaptans) Curing Agents. The mercaptan group of curing agents includes polysulfide and polymercaptan compounds which contain terminal thiols.



Polymercaptans

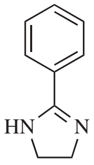
In the language commonly used in this industry, “polysulfides” typically have a functionality of 2, while “polymercaptans” have an average functionality of 3. By itself, the thiol or mercaptan group (SH) reacts very slowly with epoxy resins at ambient temperature. However, when converted by a tertiary amine to a mercaptide ion, they are extremely reactive (119).

$$NR_3 + RSH \longrightarrow RS^- + {}^+NHR_3$$



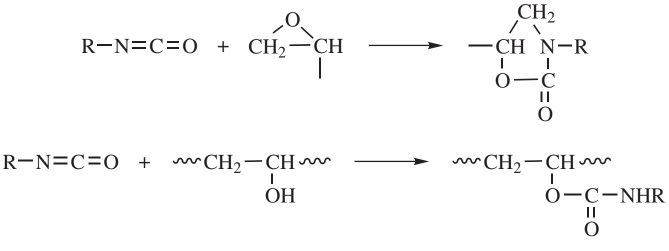
Increasing the basic strength of the amine increases the reaction rate. Polar solvents are also known to speed up these reactions. Fast curing at ambient conditions is the primary attribute of this class of curing agent, lending themselves to applications such as the “5-minutes” consumer adhesives, concrete road repairs, and traffic marker adhesives. In practice, they are often formulated with co-curing agents such as amines or polyamides to achieve a balance of fast cure with improved mechanical properties. The tertiary amine accelerated polymercaptan/epoxy systems exhibit good flexibility and tensile strength at ambient temperature. They are used in high lap-shear adhesion applications such as concrete patch repair adhesives. One disadvantage of polymercatans is their strong odor. Aliphatic amine/polysulfide co-curing agent systems yield improved initial elevated temperature performance and are widely used as building adhesives for their excellent adhesion to both glass and concrete. However, both systems lose some flexibility on aging.

15.6. Cyclic Amidines Curing Agents. Cyclic amidine curing agents are typically used in epoxy powder coating formulations and in decorative epoxy–polyester hybrid powder coatings to produce matte surface for furniture and appliance finishes. 2-Phenyl imidazoline has been used successfully to produce low gloss epoxy powder coatings. It is highly reactive, capable of curing at relatively low temperatures (140 °C) and is suitable for curing of coatings on temperature-sensitive substrates such as wood and plastics. Other curing agents in this group include salts of polycarboxylic acids and cyclic amidines. Their volume is currently small but is expected to grow as the markets for low gloss and low temperature cure powder coatings develop. They can also be used as tertiary amine catalysts similar to imidazoles.

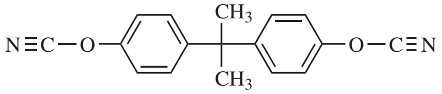


2-Phenyl imidazoline

15.7. Isocyanate Curing Agents. Isocyanates react with epoxy resins via the epoxy group to produce an oxazolidone structure (120,121) or with a hydroxyl group to yield a urethane linkage. The urethane linkage provides improved flexibility, impact, and abrasion resistance. The oxazolidone products have been successfully commercialized in high temperature resistance coating and composite applications. Blocked isocyanates are used as cross-linkers for epoxy in PPG's cathodic electrodeposition (CED) coatings. Isocyanates are also used to cure epoxies in some powder coatings, but their toxicity has limited their use.



15.8. Cyanate Ester Curing Agents. Cyanate esters can be used to cure epoxy resins to produce highly cross-linked thermosets with high modulus and excellent thermal, electrical, and chemical resistance properties. They are used in high performance electrical laminate and composite applications. Cure involves oxazoline formation catalyzed by metal carboxylates in addition to homopolymerization of both cyanate ester and epoxy (122). The high costs of cyanate esters however limit their uses.



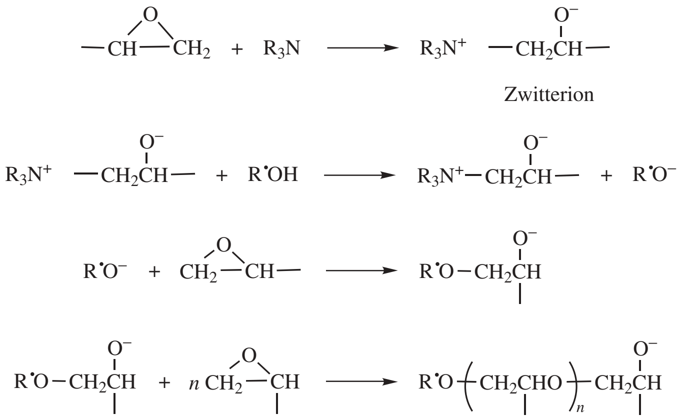
Bisphenol A based dicyanate ester

16. Catalytic Cure

The catalytic curing agents are a group of compounds that promote epoxy reactions without being consumed in the process. In some of the epoxy literature, catalysts are referred to as "accelerators"; the distinction of these two types of additives is discussed in later sections.

16.1. Lewis Bases. Lewis bases contain an unshared pair of electrons in an outer orbital and seek reaction with areas of low electron density. They can function as nucleophilic catalytic curing agents for epoxy homopolymerization; as co-curing agents for primary amines, polyamides, and amidoamines; and as catalysts for anhydrides. Tertiary amines and imidazoles are the most commonly used nucleophilic catalysts. Several different mechanisms are possible:

1. The catalytic curing reactions of tertiary amines with epoxy resins follow two different pathways, depending on the presence or absence of hydrogen donors, such as hydroxyl groups. In the absence of hydrogen donors (123), tertiary amines react with the electron-poor methylene carbon of the epoxy group to form an intermediate zwitterion. The zwitterion then attacks another epoxy group to continue homopolymerization via an anionic mechanism. In the presence of hydrogen donors such as alcohols, the zwitterion abstracts the proton from the alcohol to generate an alkoxide,



Zwitterion

$$-\overset{\overset{O}{\diagup\;\diagdown}}{\mathrm{CH{-}CH_2}} + \mathrm{R_3N} \longrightarrow \mathrm{R_3N^+}\;-\mathrm{CH_2}\overset{O^-}{\mathrm{CH}}-$$

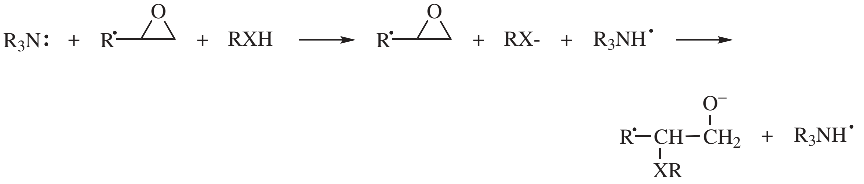
$$\mathrm{R_3N^+}\;-\mathrm{CH_2}\overset{O^-}{\mathrm{CH}}- + \mathrm{R'OH} \longrightarrow \mathrm{R_3N^+{-}CH_2}\overset{O^-}{\mathrm{CH}}- + \mathrm{R'O^-}$$

$$\mathrm{R'O^-} + \overset{\overset{O}{\diagup\;\diagdown}}{\mathrm{CH_2{-}CH}}- \longrightarrow \mathrm{R'O{-}CH_2}\underset{|}{\overset{O^-}{\mathrm{CH}}}$$

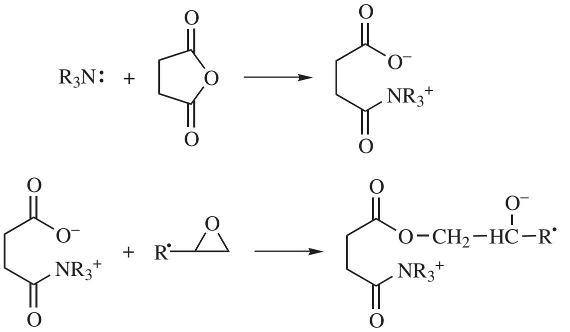
$$\mathrm{R'O{-}CH_2}\underset{|}{\overset{O^-}{\mathrm{CH}}} + n\,\overset{\overset{O}{\diagup\;\diagdown}}{\mathrm{CH_2{-}}\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{R'O}\left(\mathrm{CH_2}\underset{|}{\mathrm{C}}\mathrm{HO}\right)_n\mathrm{CH_2}\underset{|}{\overset{O^-}{\mathrm{CH}}}$$

which further reacts with an epoxide group. Chain propagation continues by way of a polymeric anion mechanism.

2. With more acidic hydrogen donors such as benzyl alcohol, phenols, or mercaptans, the tertiary amine acts as a co-curing agent by first abstracting the proton from the hydrogen donor:



3. With anhydrides, the catalyst facilitates the anhydride ring opening:



Commonly used tertiary amines include 2-dimethylaminomethylphenol (DMAMP) and 2,4,6-tris(dimethylaminomethyl)phenol (TDMAMP, trade name DMP-30 of Rohm and Haas), which contain built-in phenolic hydroxyl groups and can be used as a good catalysts and co-curing agents for room temperature cure of epoxies.

The rate of cure of epoxy resins with tertiary amines depends primarily upon the extent to which the nitrogen is sterically blocked. The homopolymerization reaction depends on the temperature as well as the concentration and type of tertiary amine. Benzyldimethylamine (BDMA) and TDMAMP are mainly used as accelerators for other curing agents, in the curing of anhydride- and dicyandiamide-based systems. Other tertiary amine catalysts include 1,4-diazabicyclo(2,2,2)octane (DABCO) and diazabicycloundecene (DBU).

Imidazoles such as 2-methylimidazole (2-MI) and 2-phenylimidazole (2-PI) contain both a cyclic secondary and a tertiary amine functional groups and are used as catalysts, catalytic curing agents, and accelerators (124,125). They are widely used as catalysts for DICY-cured epoxies in electrical laminates. For powder coatings, 2-MI adducts of LER are often used to facilitate dispersion of the components in powder coating formulations and to enhance shelf-life. Other modified imidazoles are also commercially available. The main advantage of imidazoles is the excellent balance of pot life and fast cure. 2-PI is used to increase T_g and thermal resistance.

Cyclic amidines such as 2-phenylimidazoline have also been used as a catalyst and co-curing agent in epoxy–polyester and epoxy powder coatings.

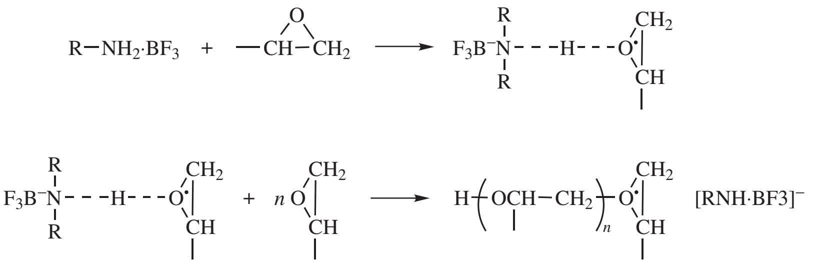
Substituted ureas are another group of epoxy nucleophilic catalytic curing agent, derived by blocking of isocyanates with dimethylamine. They are commonly used as catalysts for DICY cure of epoxies in adhesives, prepregs, and structural laminates. The ureas exhibit outstanding latency at room temperature and are widely used in one-pack adhesives. The catalytic mechanism of ureas is not well understood, but it has been postulated that DICY assists in deblocking of the urea to generate a tertiary amine, which in turns acts as epoxy curing catalyst. Commercially important substituted ureas are 3-phenyl-1,1-dimethyl urea (Amicure UR by Air Products), a reaction product of phenyl isocyanate with dimethylamine; and Amicure UR 2T, a reaction product of toluene diisocyanate (TDI) with dimethylamine.

Quaternary phosphonium salts such as the tetraalkyl and alkyl-triphenylphosphonium halides have been used as fast catalysts for curing of phenolics, carboxylic acid-terminated polyesters, or anhydrides with epoxies (126). Used in powder coatings, they showed good latency and fast cure rates at moderate temperatures.

Air Products is a major epoxy catalyst supplier. Others include Huntsman, Cognis, and SKW Chemicals.

16.2. Lewis Acids. Lewis acids, eg, boron trihalides, contain an empty outer orbital and therefore seek reaction with areas of high electron density. Boron trifluoride, BF_3, a corrosive gas, reacts easily with epoxy resins, causing gelation within a few minutes. Complexation of boron trihalides with amines enhances the curing action. Reasonable pot lives using these complexes can be achieved because elevated temperatures are required for cure. Reactivity is controlled by the choices of the halide and the amine. The amine choice also affects other properties such as solubility in resin and moisture-sensitivity. Boron trifluoride monoethylamine ($BF_3 \cdot NH_2C_2H_5$), a crystalline material which is a commonly used catalyst, cures epoxy resins at 80–100 °C. A chloride version is also commercially available. Other Lewis acids used in epoxy curing include stannic chloride and tin octanate.

Different mechanisms have been proposed for curing epoxy resins with BF_3 complexes or salts. In general, it is assumed that complexation with the oxirane oxygen is involved, facilitating proton transfer and ether formation. Thermal dissociation of the BF_3–amine complex may form a proton that further reacts with the epoxy group to initiate the curing process (127). Another mechanism assumes an amine adduct or salt is solvated by the epoxy groups, resulting in an oxonium ion (128). The curing reaction is initiated and propagated by attack of other epoxy groups on the oxonium ion.



16.3. Photoinitiated Cationic Cure. Photoinitiated cationic curing of epoxy resins is a rapidly growing method for the application of coatings from solvent-free or high solids systems. This technology allows the formulation of epoxy coatings and adhesives with essentially “infinite” shelf life, but almost “instantaneous” cure rates. Cycloaliphatic epoxies are widely cured using photoinitiated cationic initiators.

Photoinitiators used for epoxy curing include aryldiazonium salts ($\mathrm{ArN_2^+X^-}$), diaryliodonium salts ($\mathrm{Ar_2I^+X^-}$), and onium salts of Group VIa elements, especially salts of positively charged sulfur ($\mathrm{Ar_3S^+X^-}$). The anions must be of low nucleophilicity, such as tetrafluoroborates or hexafluorophosphates, to promote polymer chain growth rather than chain termination. Upon UV irradiation, photoinitiators yield a “super” acid, which polymerizes the epoxy resins by a conventional electrophilic mechanism.

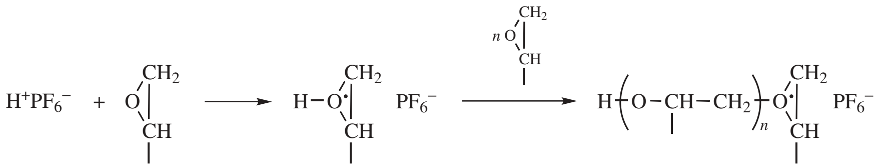
The photolysis of diaryliodonium and triarylsulfonium salts may proceed via formation of a radical cation, which abstracts a hydrogen atom from a suitable donor.

$$\mathrm{Ar_3S^+PF_6^-} \xrightarrow{\mathrm{UV}} \mathrm{Ar_2S^{+\cdot}} + \mathrm{Ar\cdot} + \mathrm{PF_6^-}$$

$$\mathrm{Ar_2S^{+\cdot}} + \mathrm{R{-}H} \longrightarrow \mathrm{Ar_2SH^+} + \mathrm{R\cdot}$$

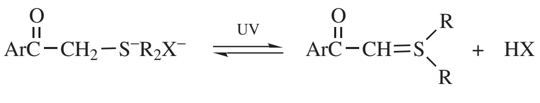
$$\mathrm{Ar_2SH^+} + \mathrm{PF_6^-} \rightleftharpoons \mathrm{Ar_2S} + \mathrm{HPF_6}$$

Subsequent loss of a proton yields the Brønsted acid $\mathrm{HPF_6}$. Catalytic curing of the epoxy resin proceeds through an onium intermediate:



In the presence of triarylsulfonium and diaryliodonium salts, polymerization continues even if UV irradiation is terminated. This phenomenon is called “dark cure” and is due to the “living” nature of the “superacid” generated cation. The cure regime can be thought of as UV-initiated but “thermally cured.” Thermally initiated cationic catalysts are also available (129).

In contrast, dialkylphenacyl sulfonium salts undergo reversible dissociation upon photolysis with formation of an ylid and a Brønsted acid. Cessation of UV activation results in termination of epoxy homopolymerization, since the acid is consumed in a reverse reaction with the ylid.



This type of behavior provides a means of controlling the degree of cure. Dialkylphenacyl sulfonium salts are thermally stable in epoxy resins at room temperature and up to 150 °C for 1–2 h. Significant interest in thermal cationic cure of epoxies, especially cycloaliphatic epoxies, has developed (130).

17. Formulation Development With Epoxy Resins

The most important step in using epoxy resins is to develop the appropriate epoxy formulation since most are used as precursors to a three-dimensional cross-linked network. With the exception of the very high MW phenoxy resins and the epoxy-based thermoplastics, epoxy resin is rarely used by itself. It is usually formulated with modifiers such as fillers and used in composite structures with glass fiber or metal substrates (coatings). To design a successful epoxy formulation that will give optimum *processability* and *performance*, the following factors must be carefully considered:

1. Selection of the proper combination of epoxy resin(s) and curing agent(s) structures
2. Epoxy/Curing agent stoichiometric ratio
3. Selection of catalyst/accelerator
4. Curing/post-curing processes and conditions
5. Formulation modifiers such as fillers, diluents, toughening agents, etc
6. Interactions among the formulation ingredients and with the composite materials (fibers, metals, etc) on the system chemistry, adhesion, rheology, morphology, and performance

The development of an epoxy formulation containing a high number of components can be very resource and time-consuming. Techniques such as design of experiments (DOE) are useful tools to facilitate the formulation development process and to obtain optimum performance (131,132). Future developments should include application of high throughput techniques to epoxy formulation development and optimization.

17.1. Relationship Between Cured Epoxy Resin Structure and Properties. The following diagram illustrates the formation of cured epoxy networks using different ratios of a difunctional epoxy and a tetrafunctional hardener. The structures formed are significantly different, depending on the ratio used. Consequently, it is expected that performance of these networks will be quite different despite the fact that they are derived from identical building blocks (Fig. 5).

The structure between the cross-linking position and the distance between any two of these points are important characteristics. *Molecular weight between cross-links* (M_c) and *cross-link density* are terms developed to describe “distance” between cross-link points. The concept originated with the rubber elasticity theory developed for the lightly cross-linked elastomers and has been adopted for use with epoxy thermosets with mixed success (133,134). The cured epoxy system derives its properties mostly from a combination of cross-link density, monomer structure and the curing process. The two-dimensional schematic network structures do not represent spatial reality but have been devised to help understand

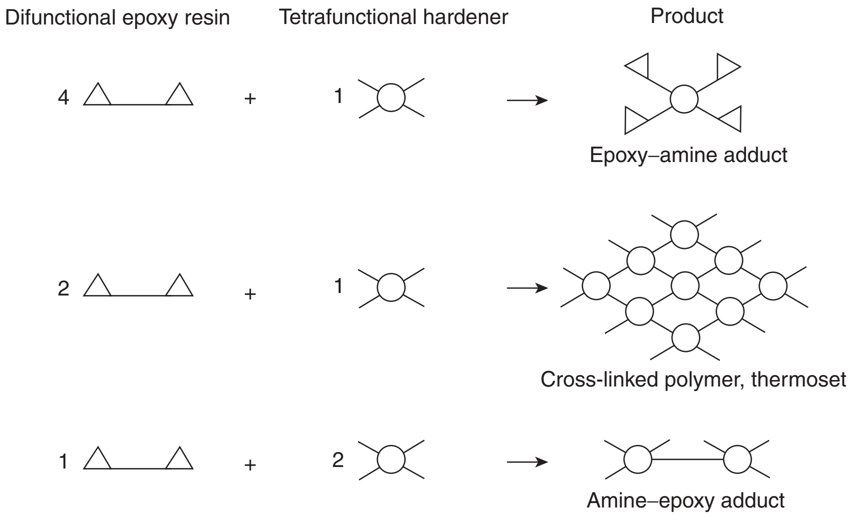


Fig. 5. Formation of resin–hardener networks.

the nature of the various structures (135). A good understanding of the structure/property relationship is critical in designing the appropriate epoxy/curing agent combination. For example, cross-linking with dicarboxylic anhydrides yields polyesters that are resistant to oxidation, but less so to moisture, especially in the presence of basic components. Amine cross-linked systems are resistant to saponification but not to oxidation. There is a large body of specific structure/property relationship knowledge in the epoxy industry and literature, but only a few systematic treatments are available (136–138).

Cross-link density increases with degree of cure up to its limit at full conversion of the (limiting) functional groups. The curing temperature and process strongly influence cross-link density, molecular architecture, network morphology, residual stress, and the ultimate performance. The effects of degree of cure and subsequent cross-link density on the chemical resistance of a cured DGEBA–aromatic polyamine adduct system are depicted in Figure 6. The increase in chemical resistance properties after post-cure also demonstrates the effects of increased cross-link density. The cross-link density of a cured epoxy system can be estimated by a number of different techniques as described in the characterization of cured epoxy section.

17.2. Selection of Epoxy Resins. Successful performance of epoxy-based systems depends on proper selection and formulation of components. The components that have the most significant influences are the epoxy resins and the curing agents. As discussed in earlier sections, there are numerous choices of epoxy resins and curing agents presenting a wide variety of structure and functionality. Figure 7 shows the general attributes of common types of epoxy resins.

Epoxy resins can be used separately or in combination, such that formulations can be designed to take advantage of the desirable characteristics of several

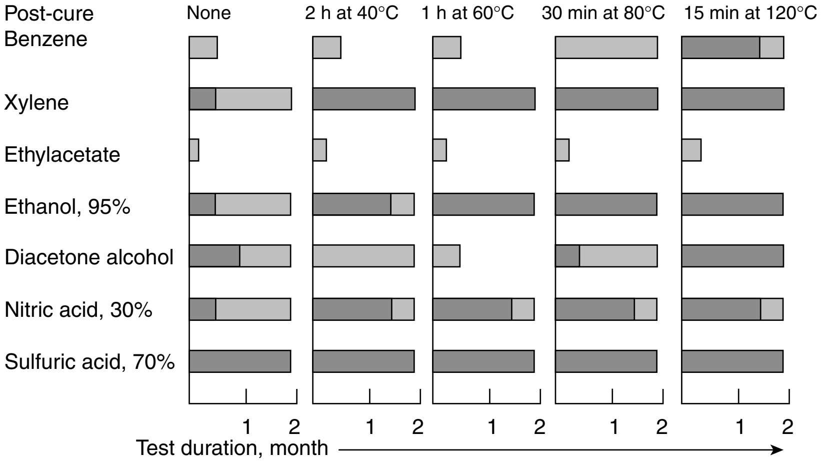


Fig. 6. Chemical resistance of a DGEBA–aromatic polyamine adduct. Post-cured substrate: sandblasted mild steel; film thickness: 300–350 μm; cure: 7 d at 20 °C. ■ Degraded; ▬ resistant.

components. Because combining resins from different families can result in certain trade-offs, a careful balance of components should be investigated to produce optimal performance for specific applications. Table 16 shows effects of different resin backbones on cured properties with formulations based on hexahydrophthalic anhydride as curing agent.

The difunctional DGEBA resins are offered commercially in a wide range of molecular weights. As the molecular weight increases, so does the chain length between the epoxy end groups. Table 5 shows the effects of increasing EEW and MW of bisphenol A based epoxy resins on resin properties. The cross-link density of a difunctional resin cured by way of the epoxy group decreases as the resin

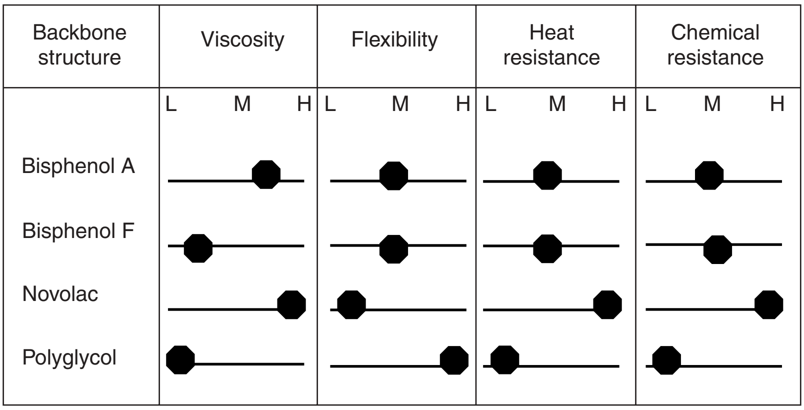


Fig. 7. Comparison of relative properties of common epoxy resins. L, low; M, medium; H, high.

molecular weight increases. High molecular weight resins are frequently cured via the secondary hydroxyl group, chemistry that results in a different set of structure–property relationships.

Multifunctional epoxy resins are available with functionalities ranging from above 2 to about 5. When cured to the same degree using a given curing agent at stoichiometric ratios, they produce a higher cross-link density, higher glass-transition temperature, and better thermal and chemical resistance compared with difunctional epoxy resins.

17.3. Selection of Curing Agents. The selection of curing agents is just as critical as the selection of resins. As discussed in the Curing Agents section, there are numerous types of chemical reagents that can react with epoxy resins. Since coreactive curing agents become part of the network structure, careful consideration must be paid to their contributions. Besides affecting viscosity and reactivity of the formulation, curing agents determine both the types of chemical bonds formed and the functionality of the cross-link junctions that are formed. Table 18 show performance examples of a liquid epoxy resin cured with different curing agents. Several authors have attempted to rationalize the curing agent selection process for different applications (106,139).

The effect of hardener structure on the heat resistance of a cross-linked DGEBA resin is shown in Table 19 (140). Thermal stability is affected by the structure of the hardener. The heat resistance of aliphatic amine cured epoxy is low as measured by TGA. The nitrogen atoms are oxidized by atmospheric oxygen to amine oxides, which attack the polymer backbone. Anhydride systems tend to split off the anhydride at temperatures well below their decomposition point at about 390 °C. The ether segments formed by 2-MI and phenolic cured epoxies have the highest thermal stability.

17.4. Epoxy/Curing Agent Stoichiometric Ratios. In addition to the choices of epoxy resins and curing agents, the stoichiometric ratio of epoxy/curing agent is another factor that has significant effects on the network structure and performance. A variety of products are obtained from different ratios. Network formations for a difunctional epoxy resin and a tetrafunctional amine are illustrated in Figure 5. The products range from an epoxy–amine adduct with excess epoxy to an amine–epoxy adduct with excess amine.

Theoretically, a cross-linked thermoset polymer structure is obtained when equimolar quantities of resin and hardener are combined. However, in practical applications, epoxy formulations are optimized for *performance* rather than to complete stoichiometric cures. This is especially true when curing of high MW epoxy resins through the hydroxyl groups.

In primary and secondary amines cured systems, normally the hardener is used in near stoichiometric ratio. Because the tertiary amine formed in the reaction has a catalytic effect on reactions of epoxy with co-produced secondary alcohols, slightly less than the theoretical amounts should be used. However, if substantially less than the theoretical amount of amine is used, the epoxy resin will not cure completely unless heat is applied (post-cure). The use of excess amine will result in unreacted amine terminated dangling chain ends and reduced cross-linking, yielding a polymer that can be somewhat tougher but which is considerably more susceptible to attack by moisture and chemicals. In formulations containing anhydrides, less than stoichiometric ratios of curing

Table 18. **Typical Properties, Chemical Resistance, and Thermal Degradation of Liquid DGEBA Resin (185 EEW) Cured With Common Hardeners (Dow Chemical Data)**

Curing agent	TETA[a]	MDA[b]	Polyamide[c]	Anhydride[d]	BF$_3$–MEA[e]
		Property			
phr[f]	13	26	43	87.5	3
formulation viscosity, Pa · s[g] (°C)	2.25 (25)	0.110 (70)	1.25 (50)	0.038 (80)	0.040 (100)
cure schedule, h (°C)	16 (25) 3 (100)	16 (55) 2 (125) 2 (175)	16 (25) 3 (100)	4 (100) 4 (165) 16 (200)	4 (100) 16 (150)
heat distortion temperature, °C	111	160	101	156	168
strength, MPa[h]					
compression	112	116	85.6	126	114
flexural	96	93	67	97	100
tensile	79	70.4	57.3	69	39.4
modulus, GPa[i]					
compression	3.05	2.6	2.6	3.04	2.3
flexural	3.05	2.7	2.14	3.05	3.1
textile elongation,%	4.4	4.4	3.9	2.5	1.6
dielectric constant at 10^3 Hz	3.90	4.06	3.19	3.14	3.45
dissipation factor at 10^3 Hz	0.020	0.015	0.0070	0.0054	0.0053
resistivity at 25 °C, 10^{-17} Ω · m					
volume	6.1	12.2	12.2	6.1	8.6
surface	7.8	> 7.9	5.5	> 7.3	> 7.9
		Chemical resistance			
% weight gain after 28 d					
50 % NaOH	0.04	−0.05	0.07	−0.12	−0.02
30 % H$_2$SO$_4$	1.8	1.6	1.9	0.83	1.1
acetone	2.1	4.6	7.3	15.0	1.2
toluene	0.07	0.13	3.7	0.09	0.17
water	0.86	1.1	1.3	0.82	1.2
		Thermal degradation			
% weight loss after 300 h at 210 °C	6.8	5.5	5.0	1.5	4.9

[a] Triethylenetetramine.

[b] 4,4′-Methylenedianiline.

[c] Versamide 140 (Henkel Corp.).

[d] Methylbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride catalyzed with 1.5 phr benzyldimethylamine.

[e] Methylethylamine.

[f] Parts per hundred epoxy resin.

[g] To convert Pa · s to P, multiply by 10.

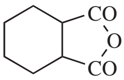
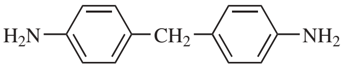
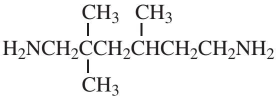
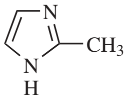
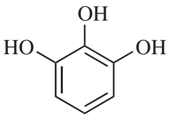
[h] To convert MPa to psi multiply by 145.

[i] To convert GPa to psi, multiply by 145,000.

agents normally are used (0.50 to 0.85 of anhydride to 1 epoxy stoichiometric ratio) because of significant epoxy homopolymerization.

Ladder studies are often conducted varying the stoichiometric ratios and other factors to determine the optimum formulations. Statistical design of experiment (DOE) methodology has been used to efficiently carry out ladder studies (141). Information concerning network structures can be obtained using

Table 19. **Effect of Hardener Structure on Reactivity and Heat Resistance of a Cross-Linked Bisphenol A Diglycidyl Ether**

			TGA, 4 °C/min	
Curing agent	T_{rmax}, °C	E_a, J/mol[a]	Weight loss before decomposition	T_{dec}, °C
 + catalyst	125	92	12	392
	154	50	0	390
 $H_2NCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{C}HCH_2CH_2NH_2$	90	58		320
 + catalyst	126	67	3.2	420
 + catalyst	185	54	2.9	400
 $H_2N\underset{NH}{\underset{\|}{C}}NHCN$	207	125	0	373

[a] To convert J to cal, divide by 4.184.

dynamic mechanical analysis (DMA) (142,143) and chemorheology to guide formulation development (144,145).

17.5. Catalysts. The choice of a catalyst and of its amount is important. As discussed in previous sections, some tertiary amine catalysts can play multiple roles in the curing reaction. Anhydride cure in particular is highly sensitive to catalyst amount. Nucleophilic catalysts, used with acidic curing agents such as anhydrides and novolacs, can greatly reduce the gel time. In the case of anhydrides, a nucleophilic catalyst attacks the anhydride ring, causing the ring to open and promote bonding to the epoxy ring. Figure 8 shows the effect of BDMA and 1-propylimidazole levels on the pot life of a system combining D.E.R. 331 resin and nadic methyl anhydride at 90 °C (194 °F) (146). Imidazoles are more efficient catalysts than tertiary amines; only half the concentration is required to produce the same catalytic effect.

17.6. Accelerators. Accelerators are commonly added to epoxy systems to speed up curing. This term should be used to describe compounds which

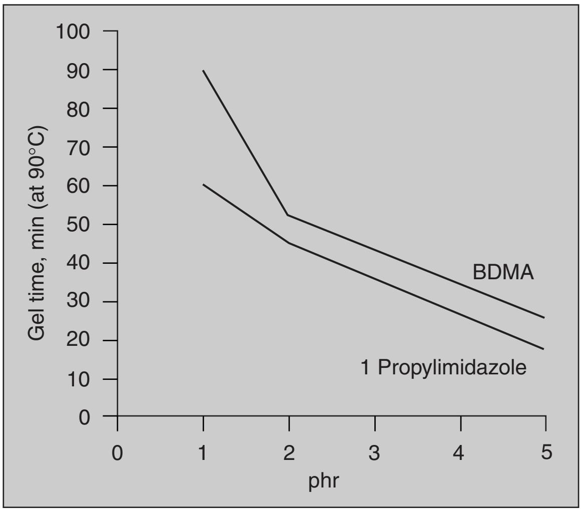


Fig. 8. Effects of catalyst on epoxy/nadic methyl anhydride cure.

increase the rate of catalyzed reactions but which by themselves are not catalysts. However, the term *accelerator* is often used synonymously with *catalyst* in some of the literature. Hydrogen donors such as hydroxyl groups facilitate epoxy reactions via hydrogen bonding or reaction with the oxygen on the epoxide ring. More acidic donors such as phenols and benzyl alcohols increase the rate of acceleration. However, very strong acids can interfere with amine curing agents by protonation of the amine to form an amine salt, resulting in increased pot life. Figure 9 shows the effects of different accelerators on the rate of a DGEBA/triethylenetriamine formulation.

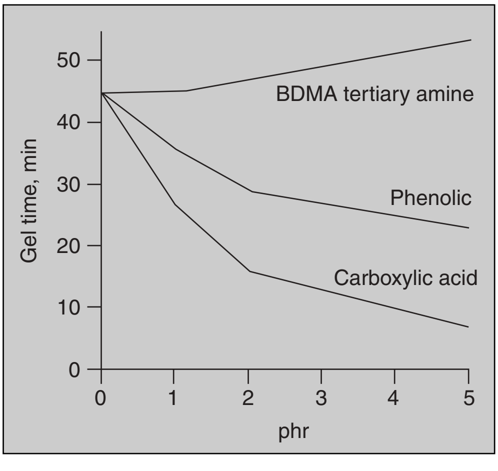


Fig. 9. Effects of accelerator on epoxy/triethylene triamine cure.

18. Epoxy Curing Process

The epoxy curing process is an important factor affecting the cured epoxy performance. Consequently, it is imperative to understand the curing process and its kinetics to design the proper cure schedule to obtain optimum network structure and performance. Excellent reviews on this topic are available in the literature (147,148).

The curing of a thermoset epoxy resin can be expressed in terms of a time–temperature-transformation (TTT) diagram (Fig. 10) (149,150). Later, a CTP (cure-temperature–property) diagram was proposed as a modification of the TTT diagram (151). For nonisothermal cure, the conversion-temperature-transformation (CTT) diagram has been shown to be quite useful (152). In the TTT diagram, the time to gellation and vitrification is plotted as a function of isothermal cure temperature. Important features are the gel point and the onset of vitrification. The gel point is defined as the onset of the formation of insoluble, cross-linked polymer (gel fraction) in the reaction mixture. However, a portion of the sample may still be soluble (sol fraction). The onset of vitrification is when the glass-transition temperature (T_g) of the curing sample approaches the curing temperature T_c. Ideally, a useful structural thermoset would cure until all monomers are built into the network, resulting in no soluble fraction.

The S-shaped vitrification curve and the gelation curve divide the time–temperature plot into four distinct states of the thermosetting-cure process: liquid, gelled rubber, ungelled glass, and gelled glass. T_{g0} is the glass-transition

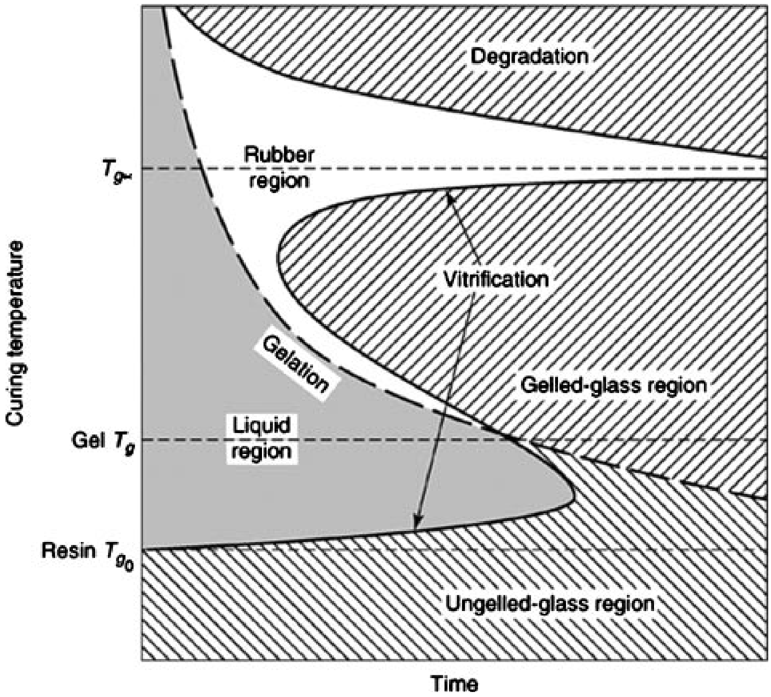


Fig. 10. Time–temperature-transformation diagram.

temperature of the unreacted resin mixture; $T_{g\infty}$ the glass-transition temperature of the fully cured resin; and gel T_g the point where the vitrification and gelation curves intersect.

In the early stages of cure prior to gelation or vitrification, the epoxy curing reactions are kinetically controlled. When vitrification occurs the reaction is diffusion controlled, and the reaction rate is orders of magnitude below that in the liquid region. With further cross-linking of the glass, the reaction rate continues to decrease and is eventually quenched. In the region between gelation and vitrification (rubber region) the reaction can range from kinetic to diffusion control. This competition causes the minimum in vitrification temperature seen in the TTT diagram between gel T_g and $T_{g\infty}$. As the cure temperature is raised the reaction rate increases and the time to vitrification decreases until the decrease in diffusion begins to overcome the increased kinetic reaction rate. Eventually, slower diffusion in the rubbery region decreases the overall reaction rate and thus the increase in time to vitrify is seen. Below $T_{g\infty}$, the reaction does not go to completion. As curing proceeds, the viscosity of the system increases as a result of increasing molecular weight, and the reaction becomes diffusion-controlled and eventually is quenched as the material vitrifies (153). After quenching, the cure conversion can be increased by raising the temperature. This is often practiced as post-cure for certain epoxy systems to achieve maximum cure and performance. Post-cure is only effective at temperatures higher than $T_{g\infty}$. However, it must be noted that at temperatures sufficiently above $T_{g\infty}$, onset of network degradation can also be seen if sufficient time is involved. Thus one must be careful about potential “over-curing.”

The TTT diagram is useful in understanding the cure kinetics, conversion, gelation, and vitrification of the curing thermoset. Gelation and vitrification times can be determined from the intersections of the storage and loss moduli and the maxima in the loss modulus of an isothermal dynamic mechanical spectrum, respectively. Recently, techniques have been developed using rheological and dynamic mechanical analysis instruments to determine the gel point and vitrification (154). Understanding the gelation and vitrification characteristics of an epoxy/curing agent system is critical in developing the proper cure schedule/process to achieve optimum performance.

One important application is the management of cure temperatures (T_c) and heating rate: if T_c is too low, vitrification may occur before gelation and further reactions may not be completed, resulting in an incomplete network structure and poor performance. This is of particular relevance in ambient cures and radiation cures (155). Furthermore, attention must be paid to the relationship between mixing of reactants and gel point. Epoxy resins and curing agents must be thoroughly mixed prior to the gel point since the rapid viscosity buildup at gel point inhibits homogeneous mixing of reactants, resulting in potential network and morphological inhomogeneities and defects (156).

Curing and quenching processes of epoxies have been reported to affect performance of certain epoxy coatings and composites. These effects have been attributed to phenomena known as internal or residual stress and physical aging of cured epoxies (147).

Internal stresses arise mainly because of the diminishing capacity of the cross-linked polymer to expand or contract to the same extent (volume) with the solid substrate to which it is adhered. This phenomenon is caused by mismatches of coefficients of thermal expansion (CTE) of the substrates (metal, glass, etc) and the cross-linked epoxies during nonisothermal cures; and cure shrinkage (solvent loss, cross-linking). The effect often contributes to adhesion failures and is more prominent in metal coatings and large composite parts manufacturing, especially when the T_g of the cross-linking polymer approaches T_c. As discussed previously, while curing of epoxy functional groups via polycondensation reaction results in relatively low shrinkage, failures attributable to internal stresses such as delamination have been observed in certain epoxy coatings of metal substrates, epoxy encapsulants for electronic devices and glass-fiber-reinforced composites (157). The effect can be very severe in the case of photoinitiated curing of epoxy acrylates as well as free-radical curing of epoxy vinyl esters. Shorter bonds are formed during these free-radical curing processes, which result in significant shrinkage. Post-cure with heat is often required to release some of the internal stresses and to improve adhesion. Efforts have been focused on understanding the mechanism of stress development, and stress minimization by modifications of the cure and post-cure cycles (158).

Physical aging is a well-known phenomenon in glassy polymers and has been studied quite extensively in amorphous thermoplastics (see Aging, Physical; Amorphous Polymers) (159). The term *physical aging* refers to the gradual changes in polymer physical properties with time after a glassy polymer is heated above its T_g and rapidly cooled (quenching) to temperatures below T_g. The physical aging process differs from chemical aging processes, in which breakage or formation of chemical bonds are involved such as continuing cure, hydrolytic aging, and photochemical and thermal degradation. The phenomenon has been attributed to the non-equilibrium state of the glassy polymer at temperatures below its T_g, in which the polymer contains excessive free volume as it is quenched. As the polymer recovers gradually over time to approach equilibrium, a reduction in free volume and an increase in density results. Consequently, the term *densification* is sometimes used to describe physical aging. For certain epoxy systems, physical aging has been reported to cause increases in stiffness and decreases of toughness (160,161). Hardening of certain baked epoxy coatings with time and failures of the coatings due to loss of ductility have been observed. However, physical aging has been reported to be reversible (erasable) by post-heating above polymer T_g. Proper selection of the cure and post-cure schedules including quenching cycle is important to minimize the potential detrimental effects of physical aging (162). In some epoxy systems, it is difficult to distinguish physical aging from the effects of residual solvent loss and/or continuing cross-linking. They all can contribute to increases in stiffness of the system.

To develop a proper curing process, it is important to understand the reactivity of different curing agents toward the epoxy structure of interest. The effect of hardener structure on reactivity of a cross-linked DGEBA resin (determined by DSC) is shown in Table 19. Aliphatic amines show a maximum reaction rate, called T_{rmax}, at 90 °C (heating rate 10 °C/min). The same epoxy resin is somewhat less reactive ($T_{\mathrm{rmax}} = 126\,^{\circ}\mathrm{C}$) when homopolymerized via initiators. Aromatic amines and phenols cure considerably more slowly, requiring higher curing temperatures. The highest temperatures are required for dicyandiamide curing, which can, however, be accelerated by basic components.

Relative reaction rates are often expressed in terms of the activation energy E_a (Arrhenius type relationship). E_a allows comparisons of reaction rates at different temperatures and is influenced by the type of chemical reactions involved in the cure. Curing of epoxy resins with phenols or aromatic and aliphatic amines proceeds with a fairly low activation energy of 50–58.5 kJ/mol (12–14 kcal/mol). Activation energies are higher when epoxy compounds having low hydroxyl content are cured alone in the presence of catalysts (92 kJ/mol = 22 kcal/mol) or with dicyandiamide (125.5 kJ/mol = 30 kcal/mol).

18.1. Characterization of Epoxy Curing and Cured Networks. Cured thermoset polymers are more difficult to analyze than thermoplastics since they are insoluble and generally intractable. Their properties are influenced by factors at the molecular level, such as backbone structures of epoxy resin and curing agent; nature of the covalent bond developed between the epoxy resin and the curing agent during cross-linking; and density and extent of cross-linking, i.e., degree of cure.

Epoxy resin formulators are concerned with formulation reactivity and flow during application. Reactivity tests or gel time tests are used to determine the proper reactivity of the formulations. Formulators also developed flow tests to check for the formulation rheology profile. The coatings industry widely uses MEK (methyl ethyl ketone) double rubs as an indication of cure. While the test does give a relative indication of cure for a certain system, caution must be exercised when comparing different systems, which may have very different inherent resistance against MEK. In general, these end-use tests do not provide insights on the structure–property relationship of the system.

Epoxy curing process can be monitored by a number of different techniques:

1. Analysis of the disappearance and/or formation of functional groups
2. Indirect estimation of cure conversion
3. Measurements of changes in thermal, physical, and mechanical properties of the system

Comprehensive reviews of different techniques for epoxy cure monitoring are available (86,94). Wet chemical or physical analysis methods, such as solvent swell (163), titration of functional groups, IR, near IR (164), or NMR spectroscopy, are commonly used to monitor epoxy cure.

The thermal properties of the system reflect the degree of cure, and thermal analysis of polymers (DSC, DMA, TGA) has been used extensively in studies of epoxy resins (156). Correlation between T_g and degree of cure has been well established for many systems.

Viscosity build is observed with increased reaction conversion in epoxy curing. More recently, chemorheology, which utilizes rheological measurement (qv) and thermal analysis such as DSC, has been applied to study epoxy cure (166,167).

Since epoxy curing involves epoxy ring opening and the generation of polar groups, which have a high dipole moment, dielectric measurements have been applied to monitor cures. Dielectric methods (168,169) encompass both macroscopic and microscopic features: the dipoles being oriented during dielectric measurements are on a microscopic scale, whereas the degree and rate of orientation may depend on macroscopic properties such as viscosity and density.

The mechanical properties of a resin system can also be used to estimate the degree of cure (170). The methods range from hardness evaluation to complex static measurements or sensitive dynamic mechanical analysis (DMA). Table 20 gives ASTM standard procedures for measuring the properties of cured or partially cured epoxy resin systems.

Direct measurement of the cross-link density of thermoset polymers including those from epoxy resins remains one of the most difficult analytical challenges in the field. A far too common approach simply relates the rubbery modulus (G_r), the thermoset modulus above T_g, to the molecular weight between

Table 20. **ASTM[a] Procedures for Cured or Partially Cured Epoxy Resin Systems**

Test	ASTM standard
Chemical	
density by displacement	D792
water absorption in plastics	D570
moisture absorption properties in composites	D5229
void content in composites	D2734
Electrical	
volume resistivity	D257
surface resistivity	D257
dielectric strength	D149
dielectric constant and dissipation factor	D150
insulation resistance	D257
Thermal	
heat-deflection temperature	D648
glass-transition temperature	D696
dynamic mechanical properties of plastics	D4065
coefficient of thermal linear expansion	D296
coefficient of linear thermal expansion by thermomechanical analysis	E831
coefficient of thermal conductivity	C177
Mechanical	
tensile strength	D638
compressive strength (plastic)	D695
compressive testing (composite)	D3410
flexural strength	D790
impact strength	D256
fracture strength in cleavage of adhesives in bonded metal joints	D3433
fracture strength in “T” peel of adhesives in bonded joints	D903
fracture testing in 180 ° peel of adhesives	D5528
mode I interlaminar fracture toughness of composites	D2344
apparent interlaminar shear strength of composites	D5045
plane strain fracture toughness of plastics	D4255
on-plane shear response of composites	
hardness, Barcol	D2583
hardness, Rockwell M	D785

[a] From Ref. 171.

cross-links (M_c) using the theory of rubbery elasticity (133,134). Unfortunately thermoset networks have much more complex features than do true elastomers, including non-Gaussian chain behavior, interchain interactions, and entanglements (172). These factors render rubbery elasticity theory inadequate as an absolute measure of M_c from G_r, and doing so can lead to totally erroneous conclusions on the network structure (173). In a given family of thermosets, changes in G_r can be considered to reflect *relative* changes in M_c. Estimates of the expected M_c can be calculated from monomer MW and functionality for stochiometric systems (174). More extensive network structure calculations including M_c are done using statistical relations developed by Miller and Makosco (175).

In many applications, epoxy systems derive their high thermal and mechanical performance of plastics characteristics from highly cross-linked network structures. However, this often results in brittleness of the epoxy thermosets and loss of end-use properties such as impact resistance. Elongation at break (% elongation) has been a popular test used in the industry for many years to measure *toughness*, ability to resist failure under tensile stress. While useful in certain applications, good correlations between elongation at break and end-use properties of cured epoxies are not always possible. The failure envelope concept has been useful in looking at the entire time–temperature failure spectrum of epoxies (176). More recently, progress in the field of fracture mechanics (177,178) has led to advanced fracture toughness tests that are more useful in characterizing cured epoxy performance. Examples of such tests are critical elastic strain release rate (G_{IC}) and critical stress intensity factor (K_{IC}) (179).

Dynamic mechanical analysis (DMA) of cross-linked epoxy resins typically shows, in order of decreasing temperature, an α transition corresponding to T_g, a β transition associated with relaxation of the glyceryl groups, and a γ transition due to methylene group motions (180). Both the β and the γ transitions, which are typically observed at -30 to $-70\,^\circ$C and at about $-140\,^\circ$C, respectively, are attributed to crankshaft motions of the polymer chain segments. The appearance of transitions between the α and β transitions is highly variable and has been attributed to segmental motions due to particular curing agents (181). No definitive correlations between the appearance of sub-T_g relaxations and mechanical properties have been observed (182). Like many other plastics, cross-linked epoxy resins undergo a change in fracture mechanism from brittle to ductile (T_b) with increasing temperature. The window between $\mathrm{T_g}$ and $\mathrm{T_b}$ has been shown to correlate well with the formability of epoxy can coatings in the draw-redraw (DRD) process (183,184).

Adhesion is an important issue in epoxy applications since epoxy is almost always used as part of a composite system. Examples are epoxy coatings on metal substrates, epoxy adhesives for metal surfaces, and matrix resin in fiber-reinforced composites such as PCB laminates and aerospace composites. Consequently, optimum epoxy adhesion to the substrate is a prerequisite for good system performance in terms of static and dynamic mechanical properties and environmental durability. In rubber-toughened composite systems, it has been reported that a threshold of interfacial adhesion between both phases (rubber and resin matrix) is needed for maximum toughening by promoting the cavitation mechanism and by activating the crack-bridging mechanism (185). Excellent review papers are available on the issue of adhesion of epoxy in composites (186), coatings, and adhesives (187). Effects of internal stresses on coating adhesion failures including the role of coating defects and pigments as potential stress concentrators have been reported (188).

Surface analysis such as dynamic contact angle and surface tension are used to ensure proper wetting of epoxy and the substrate. Microscopic techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), are widely used to study morphology, fracture, and adhesion issues of cured epoxy systems. Chemical analysis techniques, such as micro-IR, X-ray photoelectron spectrometry (XPS), and secondary ion mass spectrometry (SIMS), are useful in providing functional group analysis at the interfaces.

Consumers of products which use epoxy resins have developed increasing expectations for longer and more reliable performance. In automobiles, for example, the coating is expected to maintain its initial “Class A” finish for 10 years and the composite leaf spring is designed to last for the life of the vehicle. To meet these expectations, the long-term durability of epoxy thermosets is a key material-specific and application-specific consideration. The durability of polymeric materials in general depends on phenomena such as physical aging, environmental exposure (such as weathering), and mechanical experience (such as impact and load). A detailed discussion of this topic is beyond the scope of this review; interested readers are referred to a leading reference (189).

In addition, the processing of epoxy formulations into their final thermoset structure and form has a major effect on ultimate performance. Material properties such as rheology and reaction kinetics interplay with processing variables such as temperature and shear rate to affect key properties of extent of cure, orientation, and residual stress. Design of the final form of the material also should incorporate fundamental thermoset properties using finite element analysis methods. Optimization of any given epoxy thermoset application is therefore very specific to formulation, processing conditions, and final form and use of the material, and involves the contributions from chemistry, engineering, and material science disciplines to be fully successful.

19. Formulation Modifiers

The processing behavior (mainly viscosity and substrate wetting) and other properties of an epoxy system can be modified by diluents, fillers, toughening agents, thixotropic agents, etc. Most commercial epoxy resin systems contain modifying agents.

19.1. Diluents.

Diluents affect the properties of the cured resin system and, in particular, lower the viscosity in order to improve handling and wetting characteristics. They are often used in the range of 2–20 wt.% based on the epoxy resin. Diluents can be classified into *reactive* and *nonreactive* types.

The *reactive* diluents are products with low viscosity (1–500 cP at 25 °C) used to lower the viscosity of standard epoxy formulations. The effect of reactive diluents on DGEBA viscosity is illustrated in Figure 11. Lower viscosity allows higher filler loading, lower costs, and/or improved processability. Because of the epoxy functionality, the diluents become part of the cured network. However, the

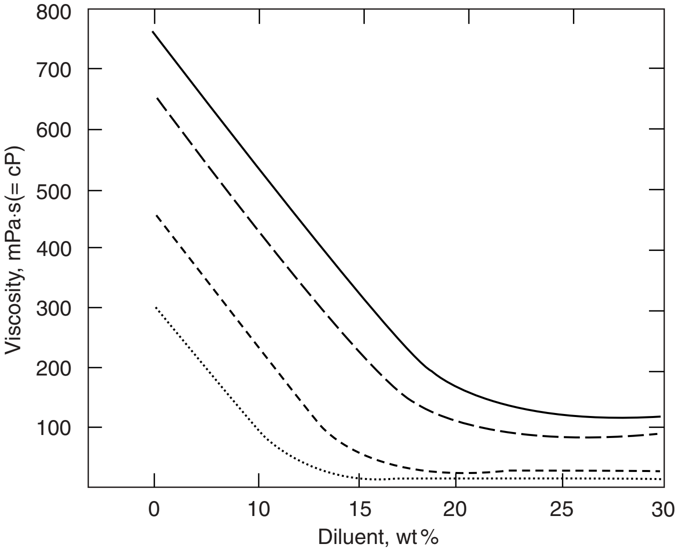


Fig. 11. Reduction of DGEBA viscosity by reactive diluents: ——, *o*-cresol glycidyl ether; – – –, butanediol diglycidyl ether; ---------, C_{12}–C_{14} aliphatic glycidyl ether (Epoxide 8); ··········, *n*-butyl glycidyl ether.

reactive diluents can negatively impact properties, and so balancing of viscosity reduction and property loss is an important consideration. Decreases in tensile strength, glass-transition temperature, chemical resistance, and electrical properties are usually observed. Toxicity is another concern, particularly the aromatic mono glycidyl ethers such as phenyl glycidyl ether (PGE) and *o*-cresol glycidyl ether (CGE). *n*-Butyl glycidyl ether (BGE) is one of the most efficient viscosity reducers, but it has been losing favor because of its volatility and noxiousness. Longer chain alkyls, polyfunctional or aromatic glycidyl ethers such as bisphenol F epoxy, neopentylglycol diglycidyl ether, and triglycidyl ether of propoxylated glycerine are gaining popularity as epoxy reactive diluents. Cycloaliphatic epoxies and glycidyl esters of acids such as neodecanoic acid are also used as reactive diluents.

Acrylics such as 1,6-hexanediol diacrylate and trimethylolpropane triacrylate are nonepoxy multifunctional diluents, which react readily with primary and secondary amines by means of Michael addition of the the amine to the acrylic double bond (190). They have been used to increase cure speed or to lower cure temperature of epoxy–amine systems. Caprolactone acrylates have also been used for this application (191).

Solvents and plasticizers are *nonreactive* diluents. The most common nonreactive diluents are nonyl phenol, furfuryl alcohol, benzyl alcohol, and dibutyl phthalate. These materials have the advantage of being able to add to the amine side of the system to better balance mix ratios. Nonyl phenol and furfuryl alcohol also improve wet-out and accelerate cure slightly. They are also capable of reacting with the epoxy group under high temperature cure conditions. Benzyl alcohol is a popular diluent used with amine-cured systems. In addition to viscosity reduction, it is also known to increase cure speed. Benzyl alcohol can be used up to 10 wt.% level without significant effects on cured properties. Dibutyl phthalate is widely used as a nonreactive diluent for liquid resins. However, performance properties will drop off more quickly with increasing levels of nonreactive diluents than with increasing levels of reactive diluents.

Aromatic hydrocarbons, such as toluene or xylene, significantly reduce the viscosity of liquid DGEBA resins, but their use can be accompanied by a 15–25% decrease in compressive yield strength and a 10–20% reduction in compressive modulus. If the solvent is trapped in the cured system, solvent resistance is reduced and cracks develop if the resin is used in heat-cured castings. The use of solvents and reactive diluents in epoxy systems is reviewed in References 192 and 193.

19.2. Thixotropic Agents. *Thixotropy* is the tendency of certain colloidal gels to flow when subjected to shear, and then to return to a gel when at rest. A thixotropic gel can be produced through the addition of either high surface area fillers such as colloidal silicas and bentonite clays or of chemical additives. Thixotropy is desirable in applications such as encapsulation where the coating is applied by dipping. The resin will wet out and coat the object being dipped, but will not run off when the object is removed from the dipping bath.

19.3. Fillers. Fillers are incorporated in epoxy formulations to enhance or obtain specific desired properties in a system. The type and amount of filler used are determined by the specific properties desired. Fillers can also reduce the cost of epoxy formulations. Inert commercial fillers (qv) can be organic or inorganic, and spheroidal, granular, fibrous, or lamellar in shape. The properties of commercial fillers are given in Table 21, and some effects on epoxy resins are shown in Tables 22 and 23. Some formulations contain up to 90 wt.% fillers. For certain applications, fillers can have significant effects on thermoset morphology, adhesion, and the resulting performance.

Filler loading is often limited for a given application by the maximum viscosity allowable and/or the reduction in some mechanical properties such as tensile and flexural strength in the cured material. Viscosity can be modified by heat or by addition of a reactive diluent; heating is preferred since diluents affect overall system properties. Some of the major property enhancements affected by fillers are described below.

Pot life and exotherm. Fillers can increase pot life and lower exotherm of epoxy systems. Fillers reduce the reactant concentration in the formulation and act as a heat sink. Generally, they have higher heat capacities than the epoxy resins. They are also better heat conductors than the resins, and thus help to dissipate exotherm heat more readily. Commonly used fillers are silica, calcium carbonate, alumina, lithium aluminum silicate, and powdered metals.

Thermal shock resistance. Fillers help to increase thermal shock resistance and to decrease the thermal expansion coefficient of an epoxy system by replacing part of the resin with a material that does not change its volume as significantly with temperature variations. Such fillers are clay, alumina, wood flour, sawdust, silica, and mica. Epoxy molding compounds (EMC)

Table 21. **Typical Properties of Fillers**

Name	Composition	Particle shape	Surface area volume	Bulk density, kg/m^3	Characteristics and main use
Marble flour, dolomitic	Magnesium–calcium carbonate	Granular	Medium	1120–1300	General-purpose fillers, particularly recommended for castings requiring machining
Chalk powder	Precipitated calcium carbonate	Crystalline	High	800–880	
Sand	Quartz, feldspar, and subsidiary minerals	Spheroidal	Low	1500–1700	Bulk filler giving high compressive strength and abrasion resistance; difficult to machine
Silica flour	Ground quartz	Granular	Medium	1100–1150	Standard filler for large electrical castings; high abrasion resistance; difficult to machine
Mica flour	Muscovite[a]	Lamellar	High	300–400	Filler giving high crack resistance to castings exposed to mechanical and thermal shock
Slate powder	Slatea	Mainly lamellar	Medium	700–900	General-purpose filler giving high abrasion resistance; difficult to machine
Vermiculite[b]	Vermiculite[a]	Exfolidated laminae	High	100–150	Fillers giving lightweight bulk in cores or thick backing to increase the rigidity of thin sections
Phenolic microballoons	Phenolic resins	Hollow spheres	Medium	100–150	
Zircon flour	Zircon[a]	Granular	Medium	1700–1900	Filler giving high abrasion resistance; difficult to machine

Table 21 (*Continued*)

Name	Composition	Particle shape	Surface area volume	Bulk density, kg/m^3	Characteristics and main use
Aluminum powder	Metallic aluminum	Granular	Medium	1000–1100	Filler imparting thermal conductivity, eg, to prevent excessive temperature buildup in electrical components or in tools for hot-forming plastics
Chopped glass strand[c]	Low alkali glass	Fibrous	Medium	100–250	Fillers improving the mechanical strength of prominent edges and thin sections
Hydrated aluminum oxide	Alumina trihydrate	Granular	Medium	700–1300	Filler improving wet and dry arc-track resistance and flame retardance

[a] Silicate.

[b] Grain size = 0.15–0.32 cm.

[c] Length = 0.60 cm.

Table 22. **Effect of Fillers**

Advantages	Disadvantages
Lower cost of product	Increased weight[a]
Reduced shrinkage upon curing	Loss of transparency
Decreased exothermic temperature rise on curing[a]	Tendency to entrap air
Increased thermal conductivity[a]	Difficulty of machining hard fillers
Reduced expansion and contraction with temperature change	Decreased impact and tensile strengths
Higher deflection temperature	Increased dielectric constanta and power factor[a]
Improved heat-aging properties[a]	
Reduced water absorption[a]	
Improved abrasion resistance[a]	
Increased surface hardness[a]	
Increased compressive strength[a] and Young's modulus[a]	
Increased electric strength[a]	

[a] Certain fillers, such as vermiculite and phenolic microballoons, have the reverse effect.

Table 23. **Influence of Filler on Epoxy Resin Properties**[a]

Filler	Ease of dispersion	Antisettling	Coast	Shrinkage	Exotherm	Termal conductivity	Coefficient of expansion	Deflection	Weight	Machinability	Abrasion resistance	Impact strength
Marble flour, dolomitic	P	N	-	-	-	+	-	+	+	O	O	-
Chalk powder	N	·	-	-	-	+	-	O	+	O	O	-·
Sand	P	N	–	-	-	+	–	+	+	-	++	-
Silica flour	·	N	-	-	-	+	–	+	+	-	++	-
Mica flour	N	·	-	-	-	+	-	+	+	-	+	+
Slate powder	P	N	-	-	-	+	-	+	+	-	++	-
Vermiculite	N	P	–	O	+	-	O	O	–	+	–	-·
Phenolic microballoons	P	P	–	O	+	-	O	O	–	++	–	-·
Zircon flour	P	N	-	-	-	+	–	+	++	–	++	-
Aluminum powder	P	N	O	-	-	++	-	+	+	+	-	
Chopped glass strand	N	P	O	-	-	+	-	+	+	-	+	+
Hydrated aluminum oxide	N	P	-	-	-	+	-	+	+	O	O	-·

[a] Key: P = positive effect; N = negative effect; – = no significant effect; - = significant decrease; - - = large decrease; + = significant increase; + + = large increase; · = fillers taken for arbitrary standard for comparison of dispersibility and setting.

[b] Porosity of filler reduces protection provided by resin.

can contain up to 90% of fused silica to manage the thermal stress experienced by encapsulated semiconductors. Powdered metals are used when bonding metals together to better match the coefficient of thermal expansion of the bond with that of the metal, thus minimizing thermal stress.

Shrinkage. Using fillers as a partial replacement for a reactive resin that shrinks on curing can reduce shrinkage of the system. Any inert filler will decrease shrinkage, but the most commonly used are silica, calcium carbonate, alumina talc, powdered metals, and lithium aluminum silicate.

Machinability and abrasion resistance. The addition of fillers can increase the machinability and abrasion resistance of an epoxy resin system by increasing the hardness of the thermoset. Greater hardness leads to a higher energy required to scratch but cleaner cuts upon machining. Fillers used for this purpose are powdered metals, wood flour, calcium carbonate, sawdust, clay, and talc.

Electrical conductivity. In certain applications, conducting fillers are added to epoxy formulations to reduce the good insulating properties of the epoxy systems. The most commonly used fillers are graphite and powdered metals.

Other properties that can be affected with the proper choice of fillers for a specific application include compressive strength, adhesion, arc and tracking resistance, density, and self-lubricating properties.

19.4. Epoxy Nanocomposites. Significant recent developments in polymer property enhancement involve polymer nanocomposites. This is a special class of fillers (mostly clay derivatives) in which the nanoscale, highly oriented particles are formed in the polymer matrix through monomer intercalation and particle aggregate exfoliation (see Nanocomposites, Polymer–Clay) (194,195). The objective is to combine the performance attributes of both hard inorganic and plastic materials. Significant efforts have been dedicated to develop epoxy nanocomposites in the past decade. Improvements in electrical and mechanical properties, chemical resistance, high temperature performance, and flame retardancy have been reported. Other silica-based organic hybrids have been developed (196) for military and aerospace applications.

The emerging field of nanotechnology has produced new materials such as the carbon nanotubes, which are filaments of carbon with atomic dimensions. Recent publications claimed exceptional property enhancement from nanotube-laced epoxy (hardness, electrical and heat-conducting properties) (197). However, cost remains a barrier for commercialization.

19.5. Toughening Agents and Flexiblizers. Some cross-linked, unmodified epoxy systems exhibit brittleness, poor flexibility, and low impact strength and fracture resistance. Modifiers can be used to remedy these shortcomings. However, there usually will be some sacrifices of properties. In general, there are two approaches used to modify epoxies to improve these features.

1. *Flexiblization.* Aliphatic diepoxide reactive diluents enhance the flexibility or elongation by providing chain segments with greater free rotation between cross-links. Polyaminoamide hardeners, based on aliphatic polyamines and dimerized fatty acids, perform similarly. Liquid polysulfide

polymers possessing terminal mercaptan functionality improve impact properties in conjunction with polyamine hardeners.

Flexible chain segments are incorporated in an epoxy resin by many means (189). One approach is the incorporation of oligomeric aliphatic polyesters containing carboxylic acid end groups, forming an epoxy resin adduct. This is one of the reasons that epoxy–polyester hybrid powder coatings have become very popular. The effects of flexiblizers are shown in Table 24. Flexiblization can enhance elongation of the system but is often accompanied by a reduction of glass-transition temperature, yield stress, and elastic modulus. Other properties (eg water absorption and thermal and chemical resistance) may also be affected.

2. *Toughening* refers to the ability to increase resistance to failure under mechanical stress. Epoxies derive their modulus, chemical, and thermal resistance properties from cross-link density and chain rigidity. Increasing cross-link density to meet higher thermal requirements (T_g) often comes at the expense of toughness. Toughening approaches for epoxies (199–202) include the dispersion of preformed elastomer particles into the epoxy matrix and reaction-induced phase separation of elastomers or thermoplastic particles during cure.

   Elastomers such as carboxyl-terminated poly(butadiene-*co*-acrylonitrile)s (CTBN) have been popular tougheners for epoxies. Toughening by elastomers can be attributed to the incorporation of a small amount of elastic material as a discrete phase of microscopic particles embedded in the continuous rigid resin matrix. The rubbery particles promote absorption of strain energy by interactions involving craze formation and shear deformation. Craze formation is promoted by particles of 1–5 μm size, and shear deformation by particles > 0.5 μm. Systems possessing both small and large particles, i.e., bimodal distribution, provide maximum toughness (203). The rubber is incorporated in the epoxy resin in a ratio of 1:8 in the presence of an esterification catalyst. The product is an epoxy ester capped with epoxy

Table 24. **Effect of Flexiblizers**

Flexiblizers	Concentration, %	Advantages	Disadvantages
Poly(propylene glycol) diglycidyl ether	10–60	Low viscosity, good flexibility	Poor water resistance fair impact resistance
Polyaminoamides	30–70	Good abrasion resistance, good flexibility	Fair chemical resistance
Liquid polysulfides	10–50	Good corrosion resistance, excellent flexibility	Odor
			Poor heat resistance tendency to cold flow
Aliphatic polyester adducts	10–30	Good water resistance Fair flexibility over a range of temperatures	High viscosity

> groups. The adduct is then formulated with unmodified resin and cured with standard hardeners and accelerators. Phase separation, of the adduct occurs during the curing process, resulting in the formation of segregated domains of elastomer-like particles covalently bound to the epoxy resin matrix. Optimum particle size and particle-size distribution, phase separation, and phase morphology are crucial for the development of desirable properties of the system. If the elastomer remains soluble in the epoxy matrix, it serves as a flexiblizer and reduces the glass-transition temperature significantly. Some reductions in T_g and modulus are typical of CTBN-modified epoxies. Amine-terminated poly(butadiene-*co*-acrylonitrile)s (ATBN) are also available (68).

Elastomer-modified epoxy resins are used in composites and structural adhesives, coatings, and electronic applications. A similar approach to toughen epoxy vinyl esters using other elastomeric materials has been reported (204). Other elastomer-modified epoxies include epoxy-terminated urethane prepolymers, epoxy-terminated polysulfide, epoxy–acrylated urethane, and epoxidized polybutadiene. Preformed dispersions of epoxy-insoluble elastomers have been developed and reported to achieve toughening without T_g reduction (205,206).

Other epoxy toughening approaches include chemical modifications of the system either through the epoxy backbone and/or crosss-linker. Dow Chemical developed a cross-linkable epoxy thermoplastic system (CET) (207). The concept involves introducing stiffer polymer segments into the network structure to maintain the glass-transition temperature while allowing cross-link density reduction to improve toughness. Thermoplastics, core-shell rubbers (CSR), and liquid crystal polymers (LCP) have also been used. Semi-interpenetrating network (IPN) approaches involve formation of a dispersed, cross-linked epoxy second phase in a thermoplastic matrix. The systems were reported to have good combinations of toughness, high T_g, high modulus, and processability.

Incorporation of block copolymers has been shown to improve toughness of certain epoxy systems (208). More recently, nanocomposites and self-healing epoxy systems (209) represent new approaches to develop more damage-tolerant epoxies.

Through the proper selection of resin, curing agent, and modifiers, the cured epoxy resin system can be tailored to specific performance characteristics. The choice depends on cost, processing and performance requirements. Cure is possible at ambient and elevated temperatures. Cured epoxies exhibit good combinations of outstanding properties and versatility at moderate cost: excellent adhesion to a variety of substrates; outstanding chemical and corrosion resistance; excellent electrical insulation; high tensile, flexural, and compressive strengths; good thermal stability; relatively low moisture absorption; and low shrinkage upon cure. Consequently, epoxies are used in diverse applications.

20. Coatings Applications

Commercial uses of epoxy resins can be generally divided into two major categories: protective coatings and structural applications. U.S. consumption of epoxy resins is given in Figure 12. The largest single use is in coatings (> 50 %), followed by structural composites. Among the structural composite applications, electrical laminates contribute the largest epoxy consumption. A similar trend is observed for the European market, but the Asian consumption is heavily tilted toward electrical laminate and electronic encapsulant applications (210). Electrical and electronic applications account for the largest consumption of epoxy resins in Japan (> 40 %). In 2000, it is estimated that the Asia-Pacific region consumed up to 70 % of all epoxies used in electrical laminate production worldwide. While the overall epoxy markets continue to grow at a steady pace over the past two decades, more rapid growth has occurred in powder coatings, electrical laminates, electronic encapsulants, adhesives, and radiation-curable epoxies.

The majority of epoxy coatings are based on DGEBA or modifications of DGEBA. Chemical and corrosion-resistant films are obtained by curing at ambient and/or elevated temperatures. Ambient temperature cured coatings primarily involve cross-linking of the epoxy groups in mostly two-package systems, while elevated temperature cured coatings in one-package systems take advantage of the reactivity of both the epoxy and the secondary hydroxyl groups. As a class, epoxy coatings exhibit superior adhesion (both to substrates and to other coatings), chemical and corrosion resistance, and toughness. However, epoxy coatings have been employed mainly as primers or undercoats because of their tendency to yellow and chalk on exposure to sunlight.

Epoxy-based coatings are the preferred and dominant choices for cathodic electrodeposition of automotive primers, marine and industrial maintenance coatings, and metal container interior coatings. Use of epoxy flooring for institutions and industrial buildings has been growing at a steady rate as the industry becomes more aware of its benefits.

Solvents are commonly used to facilitate dissolution of resins, cross-linkers, and other components, and for ease of handling and application. Although most of the epoxy coatings sold in the 1970s were solvent-borne types, they made up only 40 % of epoxy coating consumption in 2001 (211). Economic and ecological pressures to lower the volatile organic content (VOC) of solvent-borne coatings have stimulated the development of high solids, solvent-free systems (powder and liquid), and waterborne and radiation-curable epoxy coatings technologies (212). These environmentally friendly coating technologies have experienced

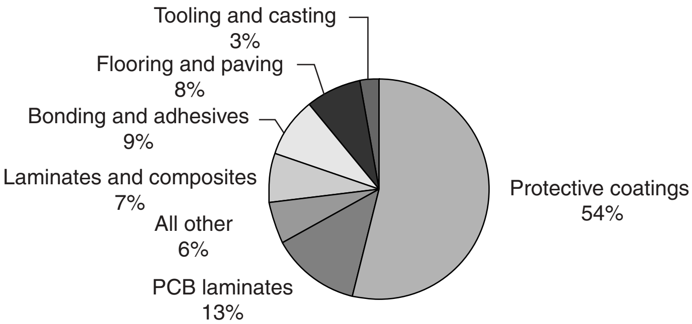


Fig. 12. End-use markets of epoxy resins (U.S. data, 2000).

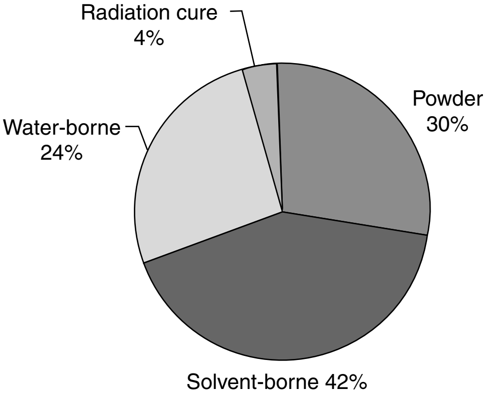


Fig. 13. Global epoxy coating application technologies (211).

rapid growth in the past decade. For example, epoxy powder coatings have been growing at rates exceeding those of other coating technologies as new applications such as automotive primer-surfacer and low temperature cure coatings for heat-sensitive substrates are developed. Radiation-curable liquid coatings based on epoxy acrylates and cycloaliphatic epoxies have also been growing significantly over the last decade. The current distribution of coating technologies is summarized in Figure 13.

20.1. Coatings Application Technologies. *Low Solids Solvent-Borne Coatings.* These traditional low solids coatings contain less than 60 % solids by volume (typically 40 %). Their advantages include established application equipment and experience, fast drying and cure at ambient temperatures and excellent film formation at extremely fast cure conditions like those used in coil coatings (<30 s, >200 °C). However, because of stricter VOC regulations, solvent-based coatings have been losing market share steadily to more environmentally friendly technologies.

High Solids Solvent-Borne Coatings. High solids coatings contain 60–85 % by volume of solids. They are mostly based on standard LERs or low molecular weight SERs modified by reactive diluents, low viscosity multifunctional aliphatic epoxies, or bisphenol F epoxy resins. High film build is one key advantage of high solids coatings. Examples include the coal-tar epoxy coatings that contain up to 85 % solids used in industrial protective coatings.

Solvent-Free Coatings (100 % Solids). Ecological concerns have led to increasing uses of these materials. Low viscosity LERs based on bisphenol A and bisphenol F epoxies are often used in combination with reactive diluents. The advantages include high buildup in a single application, minimization of surface defects owing to the absence of solvents, excellent heat and chemical resistance, and lower overall application costs. Disadvantages include high viscosity, difficulties to apply and produce thin films, poor impact resistance and flexiblity, short pot life, and increased sensitivity to humidity. Weatherable cycloaliphatic epoxies can be used to formulate solvent-free thermally curable coatings because of their low viscosities (213).

Waterborne Coatings. In the switch from solvent-borne to waterborne systems, epoxies are successfully bridging the gap largely by adaptation of conventional resins. Waterborne coatings accounted for almost 25 % of epoxy coating consumption in 2001.

In addition to the waterborne epoxy dispersions which are typically supplied by epoxy resin producers, significant advances in waterborne coatings have been made by coatings producers such as PPG Industries, ICI Paint, and others utilizing modified epoxies. PPG coatings are used in cathodic electrodeposition systems that are widely accepted for automobile primers. Many patents have been issued for this important technology (214). The Glidden Co. (now ICI Paint) developed a waterborne system for container coatings based on a graft copolymerization of an advanced epoxy resin and acrylic monomers (215). These two waterborne epoxy coatings were significant breakthroughs in the coatings industry in the 1970s and are still widely used today.

For ambient temperature cure applications such as industrial maintenance and marine coatings, LERs or low molecular weight SERs (type 1 resin) are dispersed in water with a surfactant package and small amounts of co-solvents (216). Some producers offer waterborne curing agents that, typically, are salts of polyamines or polyamides. Key disadvantages include higher costs, slow cure at ambient and humid conditions, and tendency to cause flash rush. In addition, expensive stainless steel equipment are required for application. Recent developments include the elimination of co-solvents in some epoxy dispersions (217). Custom synthesized acrylic latexes have shown promise when thermally cured with cycloaliphatic epoxies (218). While the overall volume is still relatively modest (estimated at $< 20,000$ MT in 2000 for the global market), it is expected that future growth rate for this segment will be much higher than standard epoxy resins, particularly in Europe where environmental pressures are stronger.

Powder Coatings. Epoxy-based powder coatings exhibit useful properties such as excellent adhesion, abrasion resistance, hardness, and corrosion and chemical resistance. The application possibilities are diverse, including metal finishing, appliances, structural rebars, pipes, machinery and equipment, furnitures, and automotive coatings. Together, these applications accounted for 30% of epoxy coatings (Fig. 13) and 17% of epoxy resin consumption globally in 2001 (Fig. 14). This is a high growth segment of epoxy coatings (see Coating Methods, Powder Technology).

The development of highly reactive powder systems which cure using low energy (150 °C) and the possibility of economical thin films (30–40 μm) have made powder coatings competitive with waterborne and high solids systems. Powder coatings can be applied by fluidized-bed (thick films, 50–150 μm) or electrostatic spray (thin films, 30–40 μm).

In powder coatings, epoxies are continuing to grow at rates exceeding other technology segments mainly because of the 100 % solids feature, improved coverage, and recyclability of overspray materials. Pipeline projects, important because of worldwide energy problems, are significant consumers of epoxy powder coatings. The value of improved service life is being increasingly accepted even at the somewhat higher material cost of epoxy systems. Four types of epoxy resin systems are commonly used as powder coatings.

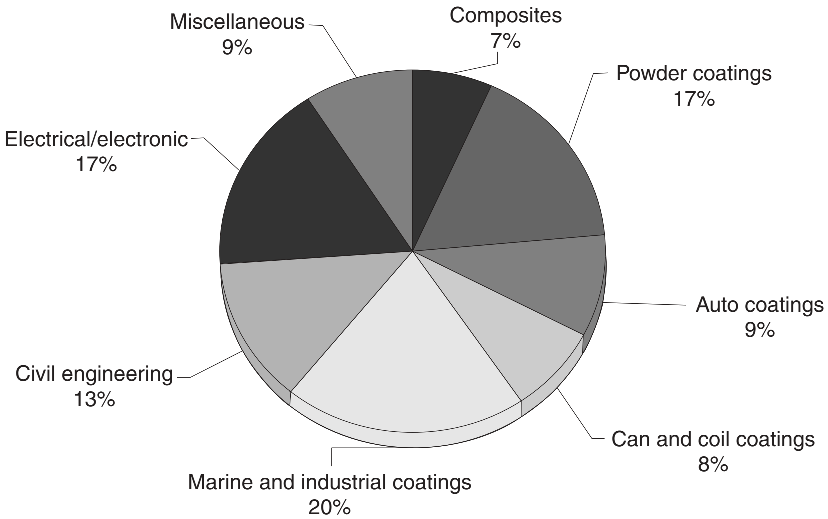


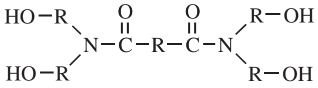
Fig. 14. Major global epoxy resin markets (Dow Chemical data, 2001).

1. *Epoxy powder coatings* are based on SERs of intermediate molecular weight (800–2000 EEW). They provide good flow and reactive terminal epoxy functionality. The properties of these thermoset coatings depend on the curing agents, which are friable solids such as dicyandiamide (DICY), phenol-terminated epoxy hardener, and anhydrides. Epoxy powder coatings are generally employed for interior or undercoat uses. Functional epoxy powder coatings are thick films (0.1–0.5 mm, 5–20 mil) used to protect automotive and truck parts, pipe, and concrete reinforcing bars. Fusion-bonded-epoxies (FBE), first developed by 3M Co., are epoxy powder coatings used to protect oil and gas pipelines where long-term corrosion protection under adverse conditions (for example, the Alaska oil and North Sea underwater pipelines) is critical. The performance requirements for FBEs are challenging as the hard, cross-linked coatings are expected to survive the pipe bending/unwinding processes and handling abuses in the field. FBEs are also used to protect rebars embedded in critical concrete structures such as bridges, tunnels, and highways. Their primary function is to extend the lifetime of the concrete structures (5–10 years when built with uncoated rebars) to 20–30 years, reducing maintenance and repair costs. Epoxy powder coatings also serve as electrical insulation for bus bars, motor armatures, and similar articles. Decorative epoxy coatings are applied as a thin film (0.02–0.1 mm, 1–5 mil) and used mainly in appliance and general metal product applications. Coating for heat-sensitive substrates is an emerging market for epoxy powders.
2. *Epoxy–polyester hybrids* are mixtures of solid epoxy resins based on bisphenol A and acid-terminated polyester solid resin (25–85 acid equivalent weight). These hybrids are typically less expensive than the epoxy-based powder coatings and offer improved weatherability, and better resistance

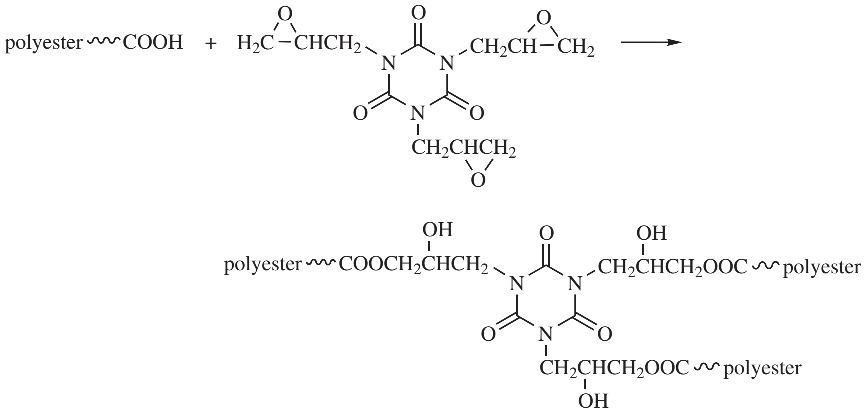
to overbake yellowing while retaining many of the properties of the standard epoxies. Corrosion resistance is equivalent to epoxy powders in most cases, although solvent and alkali resistance is inferior. One significant new application of the epoxy–polyester hybrids is the primer-surfacer coating for automobiles. Primer-surfacer coatings based on epoxy–polyester hybrid is applied in between the epoxy primer and the topcoats. Its functions are to provide intercoat adhesion and to improve the chip resistance properties of the coatings. Automakers have also found that the epoxy–polyester hybrid primer-surfacer give a smoother surface under the top coats, resulting in a better quality appearance (219). Epoxy–polyester hybrids have experienced exceptional growth in the global market in the past decade.

3. *Polyester–TGIC*, a third type of epoxy powder coating, is based on a mixture of polyester polycarboxylic acids (18–37 acid equivalent mass) and triglycidyl isocyanurate (TGIC). The TGIC-cured powder coatings have excellent UV resistance, good gloss and color retention, as well as good adhesion and mechanical properties. They were originally developed in Europe for coating metal window frames and buildings, exterior siding, outdoor hardware, high quality outdoor furniture, and other articles requiring superior outdoor durability. These polyester–TGIC powder coatings have gained popularity worldwide.

   In recent years, there have been concerns over toxicity of TGIC, and a number of potential replacement compounds have been developed. Among these, β- hydroxyalkylamide (HAA), trade named Primid by EMS-Chemie is gaining in popularity, particularly in Northern Europe.



Hydroxy alkylamide (HAA)



Reaction scheme of TGIC with carboxylic-terminated polyesters

4. *Glycidyl methacrylate–acrylic.* These powder coatings are based on copolymers of glycidyl methacrylate (GMA) and acrylic monomers. They are often

thermally cured with dodecanedioic acid (DDDA) and are used in automotive primer-surfacer and clear coats of luxury automobiles such as BMW (220,221).

Recent developments in powder coatings based on epoxy include UV-curable GMA–acrylic coating for automotive parts; lower temperature cure coatings for heat-sensitive substrates such as wood (222,223) and plastics; and dual cure (thermal/UV) systems.

Radiation-Curable Coatings. UV and electron beam (EB) radiation curable coatings (74) is a fast-growing segment of epoxy coatings, increasing at 8–10% annual growth rate. The technology is environmental-friendly. No solvent is used, and volatile emission is essentially eliminated. Cure is highly effective and energy-efficient at ambient temperatures, lending the technology highly applicable to heat-sensitive substrates such as wood, plastics, and paper. Capital cost requirements are low especially when compared to new thermal ovens for solvent-borne and waterborne coatings. EB cure is a relatively new technology which initiates cure via highly energetic electron beams, and unlike UV cure, no photoinitiator is needed. However, EB capital cost is higher.

Epoxy acrylates are widely used as the base resin in many UV-initiated free-radical cure varnish formulations. Epoxy acrylates provide varnishes with excellent scuff resistance, high gloss, and good adhesion. Major markets are overprint varnishes for papers (books, magazines, cards, labels, etc) and exterior can coatings. Wood furniture and particle board are new but growing markets for this technology. Alternatively, cycloaliphatic epoxies can be UV-cured via a photo-initiated cationic mechanism. They are used in metal container exterior overprint varnish and inks, and high performance electronic applications. While cycloaliphatic epoxies are more expensive than epoxy acrylates, they offer several advantages: better adhesion to metals, fewer hazards in handling, and continued curing in the dark (which is important in certain applications). A related and high value market is inks and resists, where radiation and heat-curable epoxies and epoxy acrylates are used. As discussed in the powder coatings section, radiation-curable epoxy powder coatings are being developed for a number of applications.

20.2. Epoxy Coatings Markets. The major global market segments of epoxies are represented in Figure 14. The marine and industrial protective coating is the largest market for epoxy coatings, followed by powder coatings, automotive, and container coatings.

Marine and Industrial Maintenance Coatings. The combined marine and industrial maintenance coatings application constitutes the largest epoxy coating market segment globally. While the end-use markets and application requirements are different, the basic epoxy systems utilized in these two markets are quite similar. The basic function of these coatings is to protect metal and concrete structures from degradation in aggressive environments for extended periods of time. The long service life of the coating and/or extended intervals between repairs are critical requirements, especially for marine applications because of the high costs of dry-docking of ships for re-painting. The excellent corrosion, abrasion, and chemical resistance properties of epoxy coatings allow their dominant position in these markets. They are used in new construction as well as in maintenance and repair works. Examples are corrosion-resistant coatings for ships, shipping containers, offshore oil rigs and platforms, transportation infrastructures such as bridges, rail car coatings, coatings for industrial storage tanks, and primers for light industrial and agricultural equipment.

Most coatings used in these markets are two-component systems applied and cured at ambient conditions. LERs and low molecular weight SERs based on bisphenol A and bisphenol F epoxies are commonly used (224). Aliphatic polyamines, adducts of epoxy resins with aliphatic and aromatic amines, ketimines, phenalkamines, amidoamide, and polyamide resins are employed as curing agents. The working pot life of the amine–epoxy resin systems depends on the curing agent, solvents, catalysts, and temperature. High solids solvent-borne coatings are most popular. Tighter VOC regulations have facilitated the development of lower VOC, 100 % solids, and waterborne epoxy coating systems. Important types of epoxy coatings in this segment include the following.

1. *Two-component epoxy–amine coatings* are used primarily as a primer or mid-coat over the inorganic zinc-rich primer coating. High solids epoxy mastics can be applied over contaminated substrates and form thick, good barrier coatings. These coatings account for the majority of epoxies used in marine and industrial protective coatings markets.
2. *Organic (epoxy) zinc-rich primers* are used in place or to repair imperfections of the inorganic zinc-rich primer. Their advantages over inorganic zincs include improved adhesion to the epoxy primer coating and better tolerance to poor surface cleaning.
3. *Coal-tar epoxies* are historically some of the most popular high solids epoxy coatings, having excellent water barrier, chemical resistance properties, and low costs. They are typically cured with polyamides and are used as ship bottom or primer coatings for tanks, pipes, and steel pilings. However, their use has been declining or banned in certain countries because of concerns and regulations over the toxicity of coal-tar as a suspected carcinogen.
4. *Epoxy esters* are used as primers in less demanding applications. Their performance is inferior to epoxy–amine systems but their costs are lower.
5. *Waterborne coatings*. These are based on two-component epoxy–polyamine/polyamidoamine or epoxy–acrylic latex hybrids. One limitation of the water-borne systems is their poor cure in high humidity conditions. They have made some penetration in industrial maintenance coatings and are expected to grow more significantly in the future.

Epoxy coatings are known to have poor weatherability and often chalk when exposed to sunlight for long periods of time. Over the years, significant efforts have been dedicated to develop weatherable epoxy resin systems such as hydrogenated bisphenol A epoxy cured with siloxane-modified epoxy curing agent (225), but higher costs and compromises in curing characteristics and performance limited their commercialization. Today, most industrial structures are only coated with epoxy coatings which can last up to 10–15 years. When appearance is critical, epoxy primers are often top-coated with aliphatic isocyanate based polyurethane coatings. Marine coatings have very diverse requirements depending on the specific functions of the parts of the ship being coated. For example, ship decks are coated with antislip, abrasion- and corrosion-resistant epoxy coatings; the cargo tanks require highly chemical-resistant coatings; ship exteriors above the water line are coated with epoxy primers followed by urethane top coats for appearance; underwater ship bottoms are coated with multilayer coatings including a zinc-rich or epoxy primer, epoxy intermediate coats and antifouling top coats based on vinyls or acrylates.

Concerns over the safety of large tankers have led to regulations and construction of double-hull ships, increasing epoxy coatings consumption. While Japan was the center of the ship-building industry since the 1980s, Korea and China have emerged as major players in this market because of their low cost advantages. According to data from the Japanese Ship Building Industry Association, Korea has overtaken Japan as the global leader in ship building in the year 2000. The combined market shares of these three Asian countries now account for more than 80% of the global ship-building business. In addition, China already owns 80% of the world shipping container construction business.

The migration of ship building yards to Korea and China has led to significant increases in marine epoxy coatings consumption in that region, and has resulted in increased demands for lower temperature cure (LTC) epoxy systems. Traditional ambient-cure epoxy coatings do not cure well at temperatures below 10 °C (50 ° F). They often require excessive cure time, affecting productivity and performance, and shorten the painting season in colder climates such as in Korea. A number of LTC epoxy coating technologies have been developed. Uses of accelerators such as tertiary amines, organic acids or alkyl-substituted phenols have allowed cures at 4.45 °C (40 ° F) temperature range. However, shorter pot-life is a limitation of these systems. Newer epoxy coatings utilizing cycloaliphatic amines, phenalkamines as curing agents can cure at temperatures of about 0 °C (30 °F). For industrial protective coatings, systems developed by Ameron International (Amerlock 400) and ICI-Devoe (Bar-Rust 235) are claimed to achieve LTC down to −18 °C (0 °F).

Other new technology developments in this market segment include surface-tolerant epoxy coatings for aged or marginally-prepared surfaces, interval-free epoxy coatings to extend coating service life, mineral spirit-soluble epoxy coatings for shipping containers repairs, and styrene-free coatings to replace foul-smelling and regulated organic solvents such as toluene and xylene in coatings for new shipping containers.

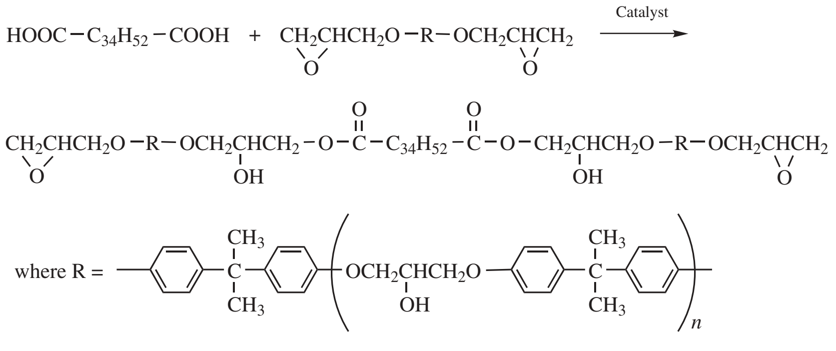
Metal Container and Coil Coatings. Metal container and coil coatings represent a major outlet for epoxy resins considering there are more than 100 billion beverage cans and 30 billion food cans produced annually in the United States. Globally, the metal can market is estimated at over 300 billion cans. While the majority of metal containers coated with epoxy coatings are aluminum and steel food and beverage cans, coatings for drums, pails, and aerosol spray cans are included in this market segment. Coil coating is a highly efficient, automated coating process used to produce precoated metal coils, which are subsequently stamped and fabricated to parts. The majority of epoxy coil coatings are used to produce metal can ends and can bodies with smaller amounts going to building products, appliance panels, transportation, and metal furniture applications.

Higher molecular weight SERs (EEW = 2000–4000), which contain predominantly secondary hydroxyl groups, are used in these coatings where maximum resistance to chemicals, good flexibility, freedom from off-taste, good thermal stability, blush (hydrolysis) resistance, and the ability to hold corrosive foods and beverages are needed. In addition, compliance with food regulations such as the Food and Drugs Administration (FDA) rules is required for food and beverage interior can coatings. This application is where the unique combination of properties of epoxy resins stand out.

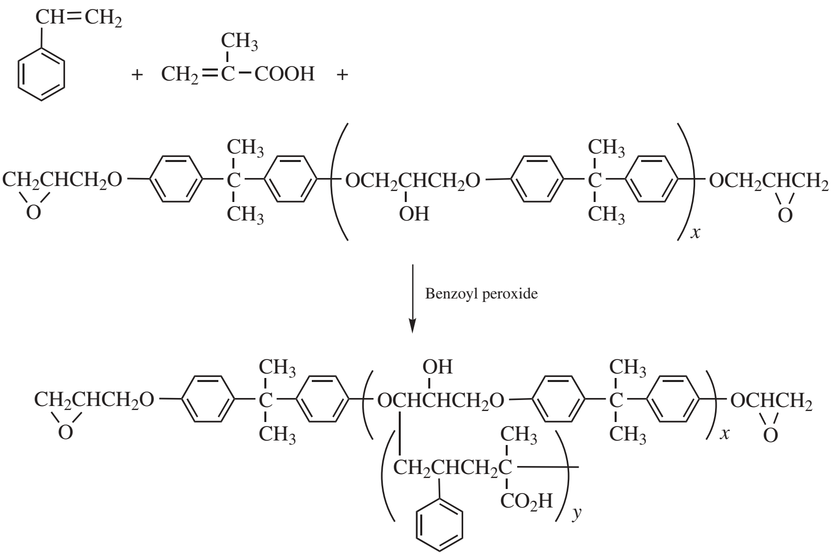
The can and coil coatings, generally, are cross-linked with phenol, melamine, or urea–formaldehyde condensation products at elevated temperatures (150–200 °C) with acid catalysts. Normal epoxy–amino resin weight ratios are epoxy–urea, 70:30; epoxy–benzoguanamine, 70:30; epoxy–melamine, 80:20 and 90:10. Increasing cross-linker levels give improved thermal and chemical resistance at the sacrifice of coating flexibility and adhesion.

Phenol–formaldehyde resole cured epoxies have excellent chemical resistance and hardness and are the popular choices for drum coatings. Their golden color is affecting their uses in food can coatings because of the increasing popularity of the water-white coatings based on melamine–formaldehyde resins, which are perceived to be “cleaner” by the consumers and the food industry. Melamine–formaldehyde resins are the primary cross-linker for beer and beverage interior can coatings. Urea–formaldehyde resins can be cured at lower temperatures and faster speed than phenol and melamine–formaldehyde resins and are widely used in the coil coatings industry where cure schedules are extremely short. However, their use has been declining because of concerns over the release of formaldehyde fumes. Recently, there have been regulatory issues in the can industry concerning worker exposure to volatile formaldehyde emissins from the formaldehyde resins. A number of new, formaldehyde-free coating formulations have been introduced by coating suppliers (226).

High solids binders for metal can coatings have been developed on the basis of dimer acid modification of epoxy resins, whereby a flexible C_{34} difunctional acid is used to esterify a conventional diepoxide resin (227). The resultant epoxy ester possesses a sufficiently lower viscosity to provide binders with solids contents > 70 vol. %. Curing is accomplished by a melamine–formaldehyde resin (Cymel 303, from Cytec) in conjunction with phosphoric acid catalyst.



In the 1970s, a waterborne coating system for aluminum beverage can coatings was developed by the Glidden Company (ICI Packaging Coatings) on the basis of a graft copolymerization of an advanced epoxy resin and acrylic monomers (228,229). The acrylic–vinyl monomers are grafted onto preformed epoxy resins in the presence of a free-radical initiator; grafting occurs mainly at the methylene group of the aliphatic backbone on the epoxy resin:



The polymeric product is a mixture of methacrylic acid–styrene copolymer, SER, and graft copolymer of the unsaturated monomers onto the epoxy resin backbone. It is dispersible in water upon neutralization with an amine, and cured with an amino–formaldehyde resin. The technology revolutionized the can coatings industry in the 1970s which was primarily based on low solids, solvent-borne coatings. This waterborne epoxy coating system and its variations continue to be the dominant choices for interior beer and beverage can coatings globally today. They are also formulated with phenol–formaldehyde resole and used as interior coatings in the new two-piece food can plants in the United States.

UV-curable coatings based on cycloaliphatic epoxies are used on the exterior of some beer, beverage, and food cans, as well as food and composite can ends. The technology is environmentally friendly and energy-efficient.

Coil coatings have been gaining in the appliance market. More OEMs have turned to precoated metal coils as an efficient manufacturing alternative to produce appliance panels, eliminating the needs for post-formed coating processes. PVC organosol (copolymers of vinyl chloride and vinyl acetate) coatings for coil-coated can ends and bodies have been under environmental pressures and epoxy has been gaining as PVC coatings are replaced (230).

The growth of can coatings has been steady globally because of the expansion of new can plants in Asia-Pacific and South America in the 1980s and early 1990s, which made up for the stagnant growth of the U.S. market. However, growth of plastic bottles based on PET [poly(ethylene terphthalate)] has recently eroded the metal can position in beverage packaging, affecting epoxy can coatings growth. In addition, new can fabrication technologies utilizing other polymers are being developed which may challenge the dominant position of epoxy coatings in metal cans.

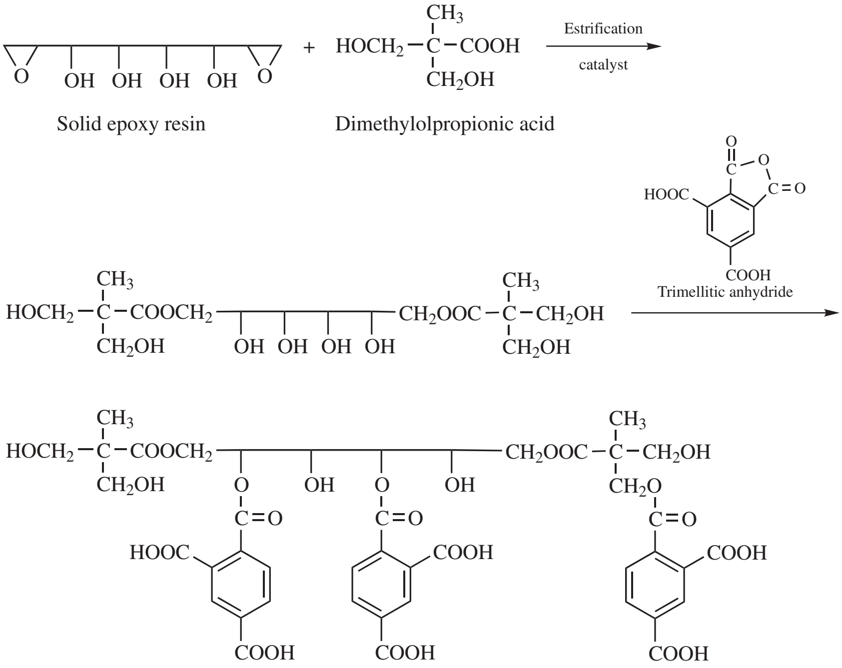
In the 1980s, Toyo Seikan Co. of Japan successfully developed and commercialized TULC (Toyo Ultimate Laminate Cans), a revolutionary technology in which cans are fabricated using a deep draw process from metal coils laminated with thermoplastic polyester films (231,232). No epoxy coating is used in this technology. Special polyester film combinations were used (in a much higher thickness than typical epoxy coatings) to facilitate the demanding deep draw process while maintaining all of the other requirements of can coatings. This technology is a significant breakthrough with claimed benefits such as no solvent emission, lower energy and water usage, and excellent quality cans. The costs however are significantly higher than those of conventional cans, and the technology has found widespread application only in Japan where higher packaging costs are acceptable. Other companies such as British Steel have been actively promoting laminated cans as a way to produce differentiable packaging like shaped cans with very limited success. Higher cost is the biggest barrier to their broad commercialization. Recent developments include attempts to fabricate can ends and bodies from extrusion-coated metals by companies such as Alcoa. Thermoplastics like modified polyesters are providing challenges to epoxies in these new technologies due to their excellent formability. However, their resistance against aggressive drinks, foods, and retort are inferior to those of epoxies.

More recently in the United States, Campbell Soup Co. has successfully launched a new line of microwaveable, ready-to-eat plastic cans. These cans are constructed from a molded thermoplastic can body (polypropylene, high density polyethylene) and an easy-open-end (EOE) of coated metal. In addition, flexible pouches have made inroad as an alternative for metal cans in certain markets such as packaged tuna fish.

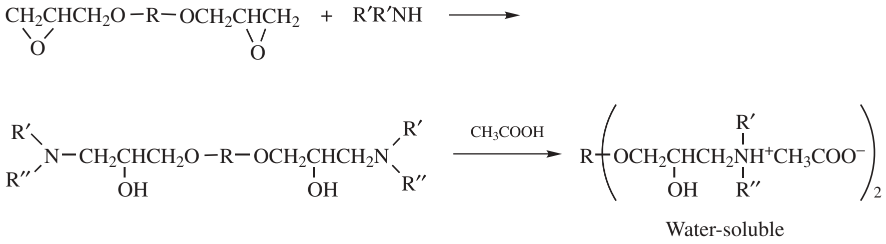
Recently, there have been debates in the can coatings industry concerning the potential health effects of residual bisphenol A and DGEBA in epoxy can coatings. The resin suppliers, can coatings producers, and can makers have jointly formed an industry group to coordinate a number of studies on this issue. Results indicated that epoxy can coatings, when properly formulated and cured, are safe and in compliance with global food contact regulations. Current regulatory guidelines such as the Specific Migration Levels for Europe set extractable limits of 1 mg/kg for DGEBA and 3 mg/kg for bisphenol A. Additional information is available in the references (233,234). Some polyester coatings have been developed as epoxy coating alternatives, but high costs and inferior pasteurization-resistance limit their uses (235).

Automotive Coatings. Automotive coatings are another major application for epoxy resins. The excellent adhesion and corrosion resistance properties of epoxies make them the overwhelming choice for automotive primers. One new, growing application is the use of epoxy–polyester or acrylic–GMA powders in primer-surfacer coatings. In addition, glycidyl methacrylate (GMA) is used as a comonomer in etch-resistant liquid top coats containing acrylic acid/anhydride (236) and in GMA-acrylic powder coatings for clear coats and automotive parts (220). Epoxy powder coatings for automobiles are expected to grow significantly in the near future.

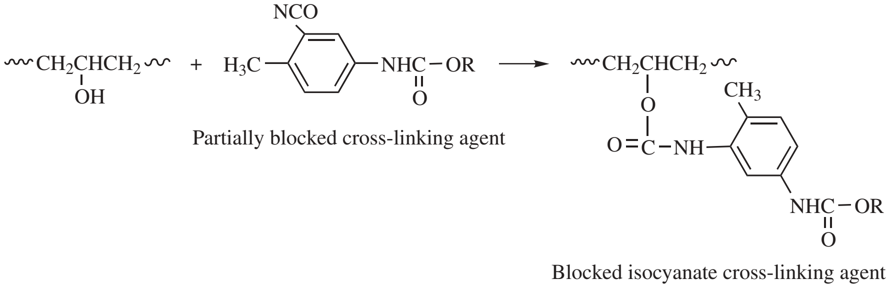
Electrodeposition processes using epoxy-based automotive primers were developed for anodic and cathodic systems. Anodic systems (AED) employ carboxylated epoxy resins neutralized with an amine. A typical binder is prepared by the esterification of the terminal epoxy groups of a solid resin (EEW = 500) with stoichiometric quantities of dimethylolpropionic acid to form a hydroxyl-rich resin. This intermediate is subsequently treated with a cyclic anhydride to form an acid functionalized polymer, which is then neutralized with the amine.



Significant advances in waterborne automotive coatings have been made by PPG Industries and others utilizing epoxies as co-resins in the 1970s. These coatings are used in cathodic electrodeposited (CED) systems, which are widely accepted for automobile primers. Many patents have been issued for this important technology (214). Cathodic systems, which have superior corrosion resistance, have replaced anodic systems. A typical epoxy binder for cathodic electrodeposition is prepared by first forming a tertiary amine adduct from an epoxy resin and a secondary amine, followed by neutralization with an acid to form a water-soluble salt:



Cross-linking is achieved by reaction of the hydroxyl groups with a blocked isocyanate, which is stable at ambient temperature.



where R = 2-ethylhexanol

The ability of the CED coating system to thoroughly coat all metal surfaces of the car and the resultant superior corrosion resistance was a significant breakthrough, enabling its dominant position in the global automotive industry.

PPG has continued to develop new generations of improved CED epoxy coatings (237). Dupont, BASF, and a number of Japanese coating companies such as Nippon Paint and Kansai Paint have contributed to the epoxy primer coating technology by developing advanced coating systems to meet higher performance and regulatory requirements of the automotive industry (238–240). The popular pigment systems based on heavy metals such as lead and chromium in primer coatings have been recently banned in certain countries, leading to efforts to develop new formulations with improved corrosion resistance. Nippon Paint has proposed pigment-free CED systems (241).

Epoxy–polyester and acrylic–GMA powder coatings have made significant advances recently in the area of primer-surfacer coatings. They offer better adhesion to topcoats and significantly improve chip resistance compared to the traditional liquid polyester and epoxy ester coatings. This translates to warranty cost reductions, leading many car manufacturers to convert to the powder coating technologies.

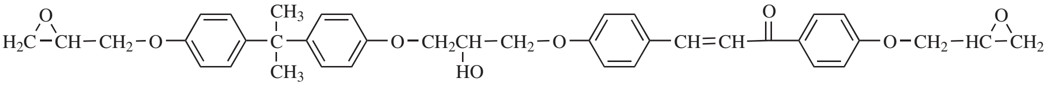
While epoxy coatings based on DGEBA and other aromatic epoxies are limited to undercoats and under-the-hood applications because of their poor UV resistance, GMA-based coatings have been developed for improved acid-etch performance automotive top coats. They compete with traditional acrylic polyol–melamine topcoats that are highly susceptible to acid rain-induced hydrolysis, and offer better mar resistance and less worker exposures than isocyanate-based topcoats (242,243). BMW has coverted to a GMA–acrylic powder clear coat developed by PPG.

20.3. Inks and Resists. Inks and resists comprise a relatively small but high value and growing market for epoxies and epoxy derivatives. In 2001, there were an estimated of 6800 MT of epoxies and epoxy derivatives used in this market to produce ink and resist formulations worth almost $400 million in the U.S. market. Epoxies are often used with other resins such as polyester acrylates and urethane acrylates in these formulations. The largest applications are lithographic and flexographic inks followed by electronic inks and resists.

Resist technology is widely used in the electronics industry to manufacture printed circuits (see LITHOGRAPHIC RESISTS). The resist (a coating or ink) is applied over a conducting substrate such as copper in a pattern to protect its surface during etching, plating, or soldering. Cure is either by radiation or heat. The uncured coating (or ink) is removed later by solvents. Solder masks perform similar functions in the manufacturing of printed circuit boards. The growth of the computer and electronics industries has fueled growth of epoxy-based inks and resists. The market is projected to grow at 10% annually.

The primary resins used in this market are the radiation-curable epoxy acrylates, accounting for 60 % of the resins used. A small amount of cycloaliphatic epoxies are also used in UV-curable inks and resists. Phenol and cresol epoxy novolacs, and bisphenol A based epoxies are used in thermally cured formulations. The epoxy novolacs are used where higher heat resistance is needed such as in solder masks. Both free-radical and cationic-curable UV inks and colored base coats have grown rapidly because of the needs for higher line speeds, faster cleanup or line turnaround, less energy consumption, less capital for a new line, and fewer emissions.

A unique epoxy (epoxy chalcone) produced by Huntsman can be used for dual cure (244):



Radiation-initiated free-radical cure is possible via the double bonds, while the epoxy groups are available for thermal cure. Epoxy chalcone is used as a photopolymerizable solder mask and in photoresists.

21. Structural Applications

Next to coatings, structural applications account for the second largest share of epoxy resin consumption (~40 %). Epoxy resins in structural applications can be divided into three major areas: fiber-reinforced composites and electrical laminates; casting, encapsulation, and tooling; and adhesives. Within this segment, the largest applications are electrical laminates for PCB and composites made of epoxy and epoxy vinyl ester for structural applications.

21.1. Structural Composites. Epoxy resins and epoxy vinyl ester resins are well suited as fiber-reinforcing materials because they exhibit excellent adhesion to reinforcement, cure with low shrinkage, provide good dimensional stability, and possess good mechanical, electrical, thermal, chemical, fatigue, and moisture-resistance properties. Epoxy composites are formed by aligning strong, continuous fibers in an epoxy resin-curing agent matrix. Processes currently used to fabricate epoxy composites include hand lay-up, spray-up, compression molding, vacuum bag compression molding, filament winding, resin transfer molding reaction, injection molding, and pultrusion (see Composites, Fabrication).

Important fiber materials are surface-treated glass, boron, graphite (carbon), and aromatic polyaramides (eg. DuPont's Kevlar). In most composites the reinforcement constitutes ca. 65 % of the final mass. Orientation of the fibers is important in establishing the properties of the laminate. Unidirectional, bidirectional, and random orientations are possible. The characteristics of the cured resin system are extremely important since it must transmit the applied stresses to each fiber. A critical region in a composite is the resin–fiber interface. The adhesive properties of epoxy resins make them especially suited for composite applications.

The most important market for epoxy composites is for corrosion-resistant equipment where epoxy vinyl esters is the dominant material of choice. Other smaller markets are automotive, aerospace, sports/recreation, construction, and marine. Because of their higher costs, epoxy and epoxy vinyl esters composites found applications where their higher mechanical strength and chemical and corrosion resistance properties are advantageous.

Epoxy Composites. Composites made with glass fibers usually have a bisphenol A based epoxy resin–diamine matrix and are used in a variety of applications including automotive leaf springs and drive shafts, where mechanical strength is a key requirement. A large and important application is for filament-wound glass-reinforced pipes used in oil fields, chemical plants, water distribution, and as electrical conduits. Low viscosity liquid systems having good mechanical properties when cured are preferred. These are usually cured with liquid anhydride or aromatic–amine hardeners. Similar systems are used for filament-winding pressure bottles and rocket motor casings. Other applications that use fiber-reinforced epoxy composites include sporting equipment, such as tennis racquet frames, fishing rods, and golf clubs, as well as industrial equipment. The wind energy field is emerging as a potential high growth area for epoxy composites, particularly in Europe where a number of new wind energy farms are planned. With windmill blades increasing in lengths (up to 50 m), the strength and fatigue properties of epoxy composites provide benefits over competitive chemistries.

In the aerospace industry, particularly in military aircraft construction, the use of graphite fiber-reinforced composites has been growing because of high strength-to-weight ratios. Some newer commercial airliners now contain up to 10% by weight of composite materials. High performance polyfunctional resins, such as the tetraglycidyl derivative of methylenedianiline in combination with diaminodiphenylsulfone or nadic methyl anhydride, are used to provide good elevated temperature properties and humidity resistance. Handling characteristics are well suited to the autoclave molding technique primarily used in the manufacture of such components. The low viscosity and high T_g of cycloaliphatic epoxies has led to their use in certain aerospace applications. Newer resins such as diglycidyl ether of 9,9′-bis(4-hydroxyphenylfluorene) have been developed.

While the overall growth of composites in the aerospace industry is continuing, epoxy has been facing stiff competition from other materials and the growth rate has been relatively small (2% annually). While epoxies are still used in many exterior aircraft parts, carbon fiber composites based on bismaleimide and cyanate esters have shown better temperature and moisture resistance than epoxies in military aircaft applications. In the commercial aircraft arena, phenolic composites are now preferred for interior applications because of their lower heat release and smoke generation properties during fires. High performance thermoplastics, such as polysulfone, polyimides, and polyetherether ketone (PEEK), have also found some uses in aerospace composites.

Epoxy Vinyl Ester Composites. Epoxy vinyl ester composites are widely used to produce chemically resistant glass-reinforced pipes, stacks, and tanks by contact molding and filament-winding processes. Epoxy vinyl ester resins provide outstanding chemical resistance against aggressive chemicals such as aqueous acids and bases and are materials of choice for demanding applications in petrochemical plants, oil refineries, and paper mills. Epoxy vinyl ester composites are also used in demanding automotive applications such as engine and oil pan covers where high temperature performance is required. Exterior panels and truck boxes are also growth automotive applications for vinyl esters. However, in less demanding automotive applications, cheaper thermoplastics and thermosets such as unsaturated polyesters or furan resins are often used. In general, epoxy vinyl ester is considered to be a premium polyester resin with higher temperature and corrosion resistance properties at higher costs. It is used where the cheaper unsaturated polyesters cannot meet performance requirements. For the same reason, epoxy vinyl ester has not grown significantly in less demanding civil engineering applications. Other uses of epoxy vinyl ester composites include boat hulls, swimming pools, saunas, and hot tubs.

Improved versions of the high performance resin systems continue to be developed (245,246). Toughening of epoxies and epoxy vinyl esters has emerged as an area for investigation (247). Lower styrene content vinyl esters have been developed to reduce worker exposure. Performance enhancements with epoxy and vinyl ester nanocomposites have been reported in the literature, but commercialization has not been yet realized.

Mineral-Filled Composites. Epoxy mineral-filled composites are widely used to manufacture laboratory equipment such as lab bench tops, sinks, hoods, and other laboratory accessories. The excellent chemical and thermal resistance properties of epoxy thermosets make them ideal choices for this application. Typically, liquid epoxy resins of bisphenol A are cured with anhydrides such as phthalic anhydride, which provide good exotherm management and excellent thermal performance. The systems are highly filled with fillers such as silica or sand (up to 70 wt.%). Multifunctional epoxy novolacs can be added when higher chemical and thermal performance is needed.

21.2. Civil Engineering, Flooring, and Construction. Civil engineering is another large application for epoxies, accounting for up to 13% of total global epoxy consumption. This application includes flooring, decorative aggregate, paving, and construction (248). Key attributes of epoxies such as ease of installation, fast ambient cure, good adhesion to many substrates, excellent chemical resistance, low shrinkage, good mechanical strength, and durability make them suitable for this market. In the United States an estimated 20,000 MT of resins were used for flooring applications in 2000. The building boom in China has provided significant growth for this market during the past decade. Epoxy flooring compounds are expected to grow well as the construction industry becomes more aware of their benefits.

Epoxy resins are used for both functional and decorative purposes in monolithic flooring and in factory-produced building panel applications. Products include floor paints, self-leveling floors, trowelable floors, and pebble-finished floors. Epoxy floorings provide wear-resistant and chemical-resistant surfaces for dairies and food processing and chemical plants where acids normally attack concrete. Epoxies are also used in flooring for walk-in freezers, coolers, kitchens, and restaurants because of good thermal properties, slip resistance, and ease of cleanup. In commercial building applications, such as offices and lobbies, terrazzo-like surfaces can be applied in thin layers. Continuous seamless epoxy floors are competitive with ceramic tiles. They are usually applied by trowel over a prepared subfloor. Semiconductive epoxy/carbon black floorings are used in electronics manufacturing plants because of their ability to dissipate electrical charges. Decorative slip-resistant coatings are available for outdoor stair treads, balconies, patios, walkways, and swimming-pool decks. Epoxy aggregates are highly filled systems, containing up to 90% of stones or minerals. They are used for decorative walls, floors, and decks.

Usually, two-component systems consisting of liquid epoxy resin, diluents, fillers (eg sands, stones, aggregates), pigments, thickening agents, and polyamine or polyamide curing agents are employed. Cycloaliphatic amines and their adducts are used when either better low temperature cure or adhesion to wet concrete is desired. The other components of the flooring formulation are as critical as the resin and hardener. Typical filler and pigment levels are 10% for paving, 30% for flooring, and 40% or higher for decorative aggregates. Self-leveling floors consist of resin-hardener mixtures with low filler content or unfilled compositions with high gloss. In epoxy terrazzo floors, an epoxy binder replaces the cement matrix in a marble aggregate flooring, providing impact resistance, mechanical strength, and adhesion.

Epoxy systems for roads, tunnels and bridges are effective barriers to moisture, chemicals, oils, and grease. They are used in new construction as well as in repair and maintenance applications. Typical formulations consist of liquid epoxy resins extended with coal tar and diethylenetriamine curing agent. Epoxy resins are widely used in bridge expansion joints and to repair concrete cracks in adhesive and grouting (injectable mortar) systems. Epoxy pavings are used to cover concrete bridge decks and parking structures. Formulations of epoxy resins and polysulfide polymers in conjunction with polyamine curing agents are used for bonding concrete to concrete. After cleaning the old surface, the epoxy adhesive is applied and good adhesion between the old and the new concrete is obtained.

Recent developments in the construction and civil engineering industry include the development of “intelligent concrete” with self-healing capability in Japan (249). Some of the systems are based on epoxy resins encapsulated in concrete which when triggered by cracks open and cure to repair the concrete.

21.3. Electrical Laminates. Printed wiring boards (PWB) or printed circuit boards (PCB) are used in all types of electronic equipment. In noncritical applications such as inexpensive consumer electronics, these components are made from paper-reinforced phenolic, melamine, or polyester resins. For more critical applications such as high end consumer electronics, computers, complex telecommunication equipment, etc., higher performance materials are required and epoxy resin-based glass fiber laminates fulfill the requirements at reasonable costs. This application constitutes the single largest volume of epoxies used in structural composites. In 2000, an estimated 200,000 MT of epoxy resins were used globally to manufacture PCB laminates.

Systems are available that meet the National Electrical Manufacturers Association (NEMA) G10, G11, FR3, FR4, FR5, CEM-1, and CEM-3 specifications. Both low viscosity liquid (EEW = 180–200) and high melting solid (EEW = 450–500) epoxy resins are used in printed circuit prepreg manufacture. Currently, the most widely used boards ($> 85\%$) are manufactured to the flame-retardant FR4 specification using epoxy thermosets. Flame retardance is achieved by advancing the liquid DGEBA epoxy resin with tetrabromobisphenol A (TBBA). This relatively low cost resin which contains about 20 wt. % bromine is the workhorse of the PCB industry. Epoxy resins based on diglycidyl ether of TBBA are also available, which allow the preparation of resins with even higher bromine content, up to 50 wt. %. Multifunctional epoxy resins such as epoxy novolacs based on phenol, bisphenol A, and cresol novolacs or the tetraglycidyl ether of tetrakis(4-hydroxyphenyl)ethane are used as modifiers to increase the glass-transition temperature ($T_g > 150\,^\circ$C), thermal decomposition temperature (T_d), and chemical resistance.

The most commonly used curing agent for PWBs is dicyandiamide (DICY) catalyzed with imidazoles such as 2-methylimidazole (2-MI), followed by phenolic novolacs and anhydrides.

The epoxy–DICY systems offer the following advantages:

1. Cost effectiveness (DICY is a low equivalent weight, multifunctional curing agent)
2. Stable formulations
3. Excellent adhesion to copper and glass
4. Good moisture and solder resistance
5. Good processability

The primary disadvantage of the standard epoxy–DICY systems is their relatively low thermal performance ($T_g < 140\,^\circ$C, $T_d = 300\,^\circ$C), which limits their uses in more demanding applications such as the FR-5 boards and other high density circuit boards. Specialty epoxy–DICY systems are available with T_g approaching 190 °C but at higher costs. Alternatively, high temperature epoxy systems are obtained using diaminodiphenyl sulfone (DDS) as curing agent and boron trifluoride monoethylamine (BF_3/MEA) complex, benzyldimethylamine (BDMA), or various imidazoles as catalysts. However, concerns over the toxicity of DDS have led to significant decrease of its use. More recently, higher thermally resistant laminates using novolac curing agents, including bisphenol A based novolacs, have become popular in the industry. However, brittleness is a significant disadvantage of these systems.

Prepreg is commonly prepared by passing the glass cloth through a formulated resin bath followed by heat treatment in a tower to evaporate the solvent and partially cure the resin to an intermediate or B stage. Prepreg sheets are stacked with outer layers of copper foil followed by exposure to heat and high pressure in a laminating press. This structure is cured (C-staged) at high temperature (150–180 °C) and pressure for 30–90 min. Attempts to develop continuous prepreg and laminating processes have only achieved limited commercialization. Laminate boards may be single-sided (circuitry printed on only one side), double-sided, or multilayered (3 to 50 layers) for high density circuitry boards. Electrical connections for mounted components are obtained via drilled holes which are plated with copper.

Table 25. **Reinforcing Material Comparison**[a]

Reinforcing material	D_k (at 1MHz)	D_f (at 1MHz)	Relative cost
E glass	6.5	0.003	1
S-2 glass	5.3	0.002	4
D glass	3.8	0.0005	10
Quartz	3.8	0.0002	30
Aramid	3.8	0.012	10

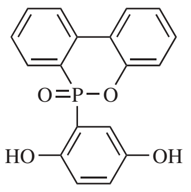
[a] From Ref. 253.

The 1990s witnessed the explosive growth of the personal computer, consumer electronics, and wireless telecommunication industries, resulting in significant demands for PWB based on epoxy resins. The PWB industry trends toward device miniaturization, multilayer laminates, high density circuitries, lead-free solder, and faster signal transmission speeds have resulted in increased performance requirements. For example, lead-free legislation which bans electronics containing lead in the European Union became law in 2003 with an implementation date of 2006. This legislation is expected to speed up the phase-out of lead-based solders globally, forcing the industry to use alternatives such as tin alloys which have much higher soldering temperatures, and thereby drives the need for epoxy systems with higher thermal performance.

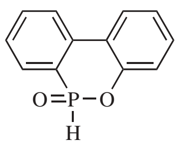
The end-use industries' demands for PCB boards with better heat resistance (250,251), higher glass-transition temperature (T_g), higher thermal decomposition temperatures (T_d), lower water absorption, lower coefficient of thermal expansion (CTE), and better electrical properties (dielectric constant D_k and dissipation factor D_f) have led to the development of new, high performance epoxies and cross-linker systems (252). Toughness is also becoming an issue as electrical connection holes are drilled in the highly cross-linked, high T_g laminates.

Since reinforcing materials make up from 40 to 60 wt.% of the PCB laminates, their contributions to the laminate dielectric properties are significant. The standard reinforcing glass–cloth compositions in electrical laminates are designated E (electrical) glass. Woven E glass is most commonly used, but other reinforcing materials such as nonwoven glass mat, aramid fiber, S-2 glass, and quartz are available. In recent years, the PCB industry has been evaluating materials with better dielectric properties, but they are much more expensive than standard E glass (Table 25).

In recent years, environmental concerns over toxic smoke generation during fire and end-of-life incineration of electronic equipment containing brominated products, particularly in Europe and Japan, have driven development efforts on halogen-free resins. This has resulted in a number of alternative products such as phosphorous additives and phosphor-containing epoxies (254–256). Some examples of these phosphorous compounds are as follows:



9, 10-Dihydro-9-oxa-10-phosphathenanthrene-10-oxide



6H-dibenz(*C*,*H*)(1,2)oxaphosphorin,6-oxide

However, commercialization of phosphor-containing epoxies has been limited because of higher costs and other disadvantages such as poorer moisture resistance and lower thermal performance. In addition, concerns over phosphine gas emission during fires and potential leakage of phosphorous compounds in landfills have raised questions about their long-term viability. Alternatively, the industry has been researching new epoxy resins based on nitrogen, silicon, sulfur-containing compounds, and new phenolic resins as potential halogen-free, phosphor-free replacements. Inorganic fillers such as alumina trihydrate, magnesium hydroxide, and zinc borate have also been evaluated as flame-retardant alternatives in epoxy systems.

While brominated epoxy resin remains the workhorse of the PCB industry (FR-4 boards) because of its good combination of properties and cost, it is facing competition from other thermoset and thermoplastic materials as industry performance requirements increase. Thermosets with higher temperature performance (>180 °C T_g) and lower dielectric properties include polyimides, cyanate esters, and bismaleimide–triazine (BT) resins. They are used alone or as blends with epoxies in high performance chip-packaging boards and military applications. GE's GETEK system is an interpenetrating network of polyphenylene oxide (PPO) in epoxy and has lower dielectric constant than standard epoxies. Polytetrafluoroethylene (PTFE) has a very low dielectric constant (Table 26) and is used primarily in high performance PCBs for military and high frequency (eg radars) applications. While these alternative materials offer certain performance advantages over standard epoxies, they are generally more expensive and more difficult to process. Thermosets such as polyimides, cyanate ester, and BT resins are very brittle and have higher water absorption than epoxies. PTFE has very poor adhesion to substrates, requiring special treatments. Consequently, they are limited to niche, high performance applications (250).

In flexible printed circuits, polyimide and polyester films are the preferred choices over epoxies. Molded interconnects based on heat-resistant thermoplastics such as polyether sulfone, polyether imide, and polyarylate have been developed to replace epoxy-based PCBs in certain applications. However, their uses are limited to special applications.

Table 26. **Base Resin Systems Used in PCB Laminates**

Resin system	T_g, °C	D_k (at 1MHz)	D_f (at 1MHz)	Estimated relative resin cost	Laminate cost
Standard Epoxies	135–140	4.6–4.8	0.015–0.020	1	1
High performance Epoxy	170–180	4.6–4.8	0.015–0.020	1.5–2	1.5
PPO/Epoxy	175–185	3.6–4.2	0.009–0.015	4–6	2–3
BT/Epoxy	170–220	3.9–4.2	0.008–0.013	8–15	2–5
Polyimide	260	3.9–4.4	0.012–0.014	5–16	3–6
Cyanate ester	230–260	3.5–3.7[a]	0.005–0.011[a]	5–16	4–8
Polyester	135–140	3.1–3.2[b]	0.004–0.014[b]	—	7–10
PTFE	NA	2.1–2.5[b]	0.0006–0.0022[b]	40	15–50

[a] Measured at 1GHz.

[b] Measured at 10 GHz.

There has been a significant migration of the PCB laminate manufacturing capacity to Asia (mainly Taiwan and China) in the late 1990s. In 2001, 70% of epoxy resins used in PCB laminates was consumed in the region and the trend is expected to continue in the near future.

21.4. Other Electrical and Electronic Applications. *Casting, Potting, and Encapsulation.* Since the mid-1950s, electrical-equipment manufacturers have taken advantage of the good electrical properties of epoxy and the design freedom afforded by casting techniques to produce switchgear components, transformers, insulators, high voltage cable accessories, and similar devices.

In casting, a resin-curing agent system is charged into a specially designed mold containing the electrical component to be insulated. After cure, the insulated part retains the shape of the mold. In encapsulation, a mounted electronic component such as a transistor or semiconductor in a mold is encased in an epoxy resin based system. Coil windings, laminates, lead wires, etc, are impregnated with the epoxy system. Potting is the same procedure as encapsulation except that the mold is a part of the finished unit. When a component is simply dropped into a resin-curing agent system and cured without a mold, the process is referred to as *dipping*. It provides little or no impregnation and is used mainly for protective coatings.

The choice of epoxy resin, curing agent, fillers, and other ancillary materials depends on factors such as cost, processing conditions, and the environment to which the insulated electrical or electronic component will be exposed.

The type and amount of filler that can be incorporated into the system are very important and depend on the viscosity of the resin at the processing temperature. Filler loading reduces costs, increases pot life, improves heat dissipation, lowers exotherms, increases thermal shock resistance, reduces shrinkage, and improves dimensional stability.

The exotherm generated during the resin cure must be controlled to prevent damage to the electrical or electronic component. The exotherm is easily controlled during the production of small castings, pottings, and encapsulations. In the production of large castings, the excess heat of reaction must be dissipated in order to prevent locked-in thermal stresses. During the 1970s, the pressure gelation casting process was developed (257); this method provides better temperature control and reduces cycle times. The heat generated by polymerization is used to heat the resin mass and is not dissipated in the mold.

Both DGEBA and cycloaliphatic epoxy resins are used in casting systems. Most systems are based on DGEBA resins cured with anhydride hardeners and contain 60–65 wt.% inert fillers. The cycloaliphatic resin systems exhibit good tracking properties and better UV resistance than DGEBA resins, the latter of which causes crazing and surface breakdown. An electrical current is more likely to form a carbonized track in aromatic-based resins than in nonaromatic ones. Their lower viscosity also facilitates device impregnation. The cycloaliphatic epoxies are often used as modifiers for DGEBA resin systems. This application represents a significant outlet for cycloaliphatic epoxies.

Amine curing agents are used in small castings, and anhydrides are used in large castings. Anhydrides are less reactive and have lower exotherms than amines. In addition, their viscosity and shrinkage are low and pot lives are longer.

Transfer Molding. Epoxy molding compounds (EMC) are solid mixtures of epoxy resin, curing agent(s) and catalyst, mold-release compounds, fillers, and other additives. These systems can be formulated by dry mixing or by melt mixing and are relatively stable when stored below room temperature. Molding compounds become fluid at relatively low temperatures (150–200 °C) and can be molded at relatively low pressures (3.5–7.0 MPa) by compression, transfer, or injection molding. Advantages of molding over casting are elimination of the mixing step immediately before use, improved handling and measuring procedures, and suitability for high production quantities. A typical standard EMC formulation contains approximately 30 % epoxies, 60 % filler, and 10 % of curing agents and other additives such as release agent.

An important application of epoxy molding compounds is the encapsulation of electronic components such as semiconductor chips, passive devices, and integrated circuits by transfer molding. Transfer molding is a highly automated, efficient method of encapsulation. High purity phenol and cresol epoxy novolacs and phenol and cresol novolacs and/or anhydride curing agents are used most often in semiconductor applications. For passive device encapsulation, standard epoxy novolacs can be used as blends with bisphenol A based solid resins. The ECN or EPN molding powders can be processed at relatively low pressures and provide insulation for the electronic components. Ionic impurities, i.e., NaCl or KCl, must be kept to a minimum, since trace quantities can cause corrosion and device failure. In addition, residual stress and thermal and mechanical shock resistances are issues that must be managed properly (258).

Efforts have been made to improve the high temperature performance of these systems by replacing the epoxy novolacs with other multifunctional epoxy resins. Hydrocarbon based epoxy novolacs (HEN) were developed to improve the moisture resistance of molding compounds. Crystalline epoxy resins derived from biphenol and dihydroxy naphthalenes were developed for high end semiconductor encapsulants using Surface Mount Technology (SMT). The emergence of SMT as a key semiconductor manufacturing technology requires epoxy molding compounds with a high filler loading capacity (up to 90 wt. %) to enhance solder crack resistance. SMT uses new solder alloys to attach components to the PCB board at high temperatures (215–260 °C). Solder reflow, delamination, and package cracks are problems often encountered with conventional molding compounds based on cresol epoxy novolacs. The high filler content helps lower costs, reduces moisture absorption, and decreases the thermal expansion coefficient of the system. Crystalline products with very low melt viscosity such as biphenyl epoxies facilitate the processing of the high silica filler formulations while maintaining other critical requirements: moisture resistance and electrical, thermal, and mechanical properties (61). The majority of high purity epoxies used in epoxy molding compounds (EMC) for semiconductor encapsulations are supplied by Japanese producers and a few Asian companies.

21.5. Adhesives. Epoxy-based adhesives provide powerful bonds between similar and dissimilar materials such as metals, glass, ceramics, wood, cloth, and many types of plastics. In addition, epoxies offer low shrinkage, low creep, high performance over a wide range of usage temperatures, and no by-products (such as water) release during cure. The epoxy adhesives were originally developed for use in metal bonding in the aircraft industry (259,260). In aircraft wing assemblies, high strength epoxy adhesives are used in place of metal fasteners to avoid corrosion problems inherent with metal fasteners, to reduce weight, and to eliminate "point" distribution by spreading the load over a large area. Today, epoxy is the most versatile engineering/structural adhesive, widely used in many industries including aerospace, electrical/electronic, automotive, construction, transportation, dental, and consumer. The market is of high value, consuming 25,000 MT of epoxies in North America in 2001 worth almost $500 million.

The broad range of epoxy resins and curing agents on the market allows a wide selection of system components to satisfy a particular application. Although the majority of epoxy adhesives are two-pack systems, heat activated one-pack adhesives are also available. Low molecular weight DGEBA liquid resins are the most commonly used. Higher molecular weight (EEW = 250–500) DGEBA epoxy resins improve adhesive strength because of the increased number of hydroxyl groups in the resin backbone. For applications requiring high temperature or improved chemical performance, the multifunctional epoxy phenol novolac and triglycidyl-*p*-aminophenol resins are employed. More recent products include vinyl epoxies. Adhesive systems modified with reactive diluents facilitate wetting of the substrate, allowing more filler to be added and modifying handling characteristics; however, adhesive strength is reduced. Toughened epoxy adhesives are available.

Polyamines or polyamides are the curing agents for ambient or slightly elevated temperature cures, and aromatic polyamines or anhydride hardeners are used for hot cures. These systems provide exceptional bonding strength but slower cure time. Boron trifluoride amine complexes and dicyandiamide are used in one-component adhesives. Polythiols (polysulfides, polymercaptans) are the fast-curing hardeners in "5-min." consumer epoxy formulations. The lap-shear strengths of a DGEBA epoxy cured with different hardeners are given in Table 27.

Cationically cured UV laminating adhesives based on cycloaliphatic epoxies are emerging as an alternative to solvent-based adhesives. The "dark cure" of cationics allows UV exposure and post lamination in line. This process does not require UV exposure "through" the plastic barrier material.

Epoxy adhesives are expected to grow at GDP (3–4 %) over the next decade. Increased usage in the automotive and recreational markets, and replacement of mechanical fasteners help offset the slowdown in the aerospace industry (see also Adhesive Compositions).

21.6. Tooling.

Tools made with epoxy are used for producing prototypes, master models, molds and other parts for aerospace, automotive, foundry, boat building, and various industrial molded items (261). Epoxy tools are less expensive than metal ones and can be modified quickly and cheaply. Epoxy resins are

Table 27. **Epoxy Adhesive Lap-Shear Strengths**

Hardener	Lap-shear strength,[a] MPa[b]
Aliphatic polyamine	19
Polythiol cohardener	18
Aromatic diamine	24

[a] Adhesive strength.

[b] To convert MPa to psi, multiply by 145.

preferred over unsaturated polyesters and other free-radical cured resins because of lower shrinkage, greater interlaminar bond strength and superior dimensional stability.

Most epoxy-based tooling formulations are based on liquid DGEBA resins. Aliphatic polyamines, amidoamines, or modified cycloaliphatic amines are used for ambient temperature cure, and modified aromatic diamines and anhydrides are used for high temperature cure. When high heat resistance is required ($> 350\,^\circ$F) epoxy novolac resins can be employed. Reactive diluents such as aliphatic glycidyl ethers are often employed to permit higher filler load or to reduce the system viscosity for proper application. Fillers, reinforcing fibers, toughening agents, thixotropic agents, and other additives are often used depending on the desired application and final properties.

Tooling production uses four major processing methods: lamination, surface cast, splining, and casting. Lamination is made by alternating layers of glass cloth or fabric and formulated resin, usually on a framework of metal or plastic. Surface cast utilizes a filled resin compound that is applied onto the surface of a mold, which is later filled with a core material that adheres to the casting compound. Splining employs heavily filled formulations that are directly applied to a surface and manually molded or leveled to the desired shape, before or after curing, with the help of proper tools. Lastly, casting compounds are filled formulations that are directly poured or compressed into a mold coated with a release agent.

22. Health and Safety Factors

There have been many investigations of the toxicity of various classes of epoxy-containing materials (glycidyloxy compounds). The use and interpretation of the vast amount of data available has been obscured by two factors: (*1*) proper identification of the epoxy systems in question and (*2*) lack of meaningful classification of the epoxy materials. In general, the toxicity of many of the glycidyloxy derivatives is low, but the diversity of compounds found within this group does not permit broad generalizations for the class. Information on toxicity and safe handling of epoxy compounds are summarized in References 262,263, and 264.

> *Diglycidyl ether of bisphenol A.* Bisphenol A based epoxies are the most commonly used resins. Although unmodified bisphenol A epoxy resins have a very low order of acute toxicity, they should be handled carefully and personal contact should be avoided. Prolonged or repeated skin contact with liquid epoxy resins may lead to skin irritation or sensitization. Susceptibility to skin irritation and sensitization varies from person to person. Skin sensitization decreases with an increase in MW, but the presence of low MW fractions in the advanced resins may present a hazard to skin sensitization. Inhalation toxicity does not present a hazard because of low vapor pressure. DGEBA-based resins have been reported to cause minimal eye irritation. Toxicological studies support the conclusion that bisphenol A based epoxy resins do not present a carcinogenic or mutagenic hazard.

Because of the solvents used, solution of epoxy resins are more hazardous to handle than solid resins alone. Depending on the solvents used, such solutions may cause irritation to the skin and eyes, are more likely to cause sensitization responses, and are hazardous if inhaled.

Epoxy phenol novolac resins. Acute oral studies indicate low toxicity for these resins. Eye studies indicate only minor irritation in animals. The EPN resins have shown weak skin sensitizing potential in humans.

Low MW epoxy diluents, particularly the aromatic monoepoxides such as phenyl glycidyl ether (PGE) are known to have high toxicity and should be handled with care. They are capable of causing skin and eye irritation and sensitization responses in people. They may also present a significant hazard from inhalation.

Curing agents. In general, amine curing agents are much more hazardous to handle than the epoxy resins, particularly at elevated temperatures. Aliphatic amines and anhydrides are capable of serious skin or eye irritation, sensitization, and even burns. Other curing agents possess consideration variation in the degree of health hazards because of the variety of their chemical structures and it is impossible to generalize.

All suppliers provide material safety data sheets (MSDS), which contain the most recent toxicity data. These are the best sources of information and should be consulted before handling the materials.

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