PERP Program – Epoxy Resins
New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Epoxy Resins (04/05S11)***. To view the table of contents or order this report, please click on the link below:
http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Introduction

Epoxy resins form a versatile family of generally amorphous thermosetting resins known for their excellent mechanical and electrical properties, dimensional stability, resistance to high temperatures and numerous chemicals, and their strong adhesion to a variety of materials such as glass, metal, fibers, and concrete/masonry. New and growing uses include lithographic inks and photoresists for the electronic industry.

Epoxy resins are characterized by the presence of a three-membered cyclic ether group commonly referred to as an epoxy group, 1,2-epoxide, or oxirane. The most widely used epoxy resins are diglycidyl ethers of bisphenol A derived from bisphenol A and epichlorohydrin. The outstanding performance characteristics of the thermosets derived from bisphenol A epoxies are largely conveyed by the bisphenol A moiety (toughness, rigidity, and elevated temperature performance), the ether linkages (chemical resistance), and the hydroxyl and epoxy groups (adhesion). In addition to bisphenol A, other starting materials such as aliphatic glycols and both phenol and o-cresol novolacs are used to produce specialty resins.

Surface coatings represent the largest application for epoxy resins. Epoxies are employed mainly as primers and high performance non-decorative protective coatings because of their low resistance to degradation from sunlight (UV radiation). They are higher cost that other traditional surface treatments, and are used only where alternatives provide inadequate protection. The main coating categories where epoxies are preferred are:

- Powder coatings – largest and fastest growing outlet for epoxies. Demand for solvent-free, environmentally-friendly products has created a need for powder coatings, and epoxy-based systems provide cost/performance advantages versus other materials. Pure epoxy powder coatings systems compete with polyester and epoxy-polyester and epoxy-acrylate hybrids. Hybrid systems are most widely used: they are less costly than pure epoxy coatings yet retain most of their beneficial properties. Growth in this application area in the early 90s was high, but has decreased to roughly GDP levels as most of the substitution has now occurred. There are a wide range of applications including automotive, industrial equipment, electrical, etc.

- Industrial and marine coatings - epoxy resins' high thermal and corrosion resistance properties have led to broad acceptance in these markets where their cost can be justified.
- Can and coil coating – use of epoxies in can coatings has declined because of current concerns about health risks associated with these coatings, substitution of PET plastic for metal cans, and decreasing demand for canned foods (i.e. consumer preference for other forms of packaging). Demand for consumer durables (appliances) and building cladding remains strong, and epoxies will continue to be widely used as primers in both applications.
- Automotive coatings (e.g. cathodic electrode position primers) - epoxy growth will generally follow industry growth trends in the sector.

Epoxies are used as binders for glass and carbon fiber reinforcing agents in structural composites and laminates for circuit boards, pipes and tanks, sporting goods, and aircraft parts. Epoxy vinyl ester resins offer enhanced resistance to hard-to-hold acids, bases, and organic solvents. Miniaturization in the electronics industry continues to drive the need for new epoxy and hybrid systems with improved temperature, electronic, and flame-resistant properties.

Because of their excellent electrical properties and moderate costs, epoxies are used in casting, potting, and encapsulation of electrical/electronic parts. They exhibit low shrinkage, with minimal cracking or separation of the resins from the parts during cure. Encapsulated parts vary in size from miniature coils and switches that may weigh but a few grams to large motors and insulators that may weigh several pounds. Electronic-grade materials have lower ionic and chloride impurities than standard grades.

Epoxies are used to make patterns, models, core boxes, jigs, fixtures, and templates used in the automotive and machine tool industries.

Epoxy resins are also used in making adhesives. Epoxy-based adhesives are widely used for bonding dissimilar materials like plastics and metal, wood and metal, and ceramics and rubber. Minimum pressure is required to obtain a satisfactory bond. For such applications, epoxy adhesives are available as one- or two-part systems. The one-part system requires curing at elevated temperatures. In two-part systems, curing can take place at room temperature, but better properties result if heat is used.

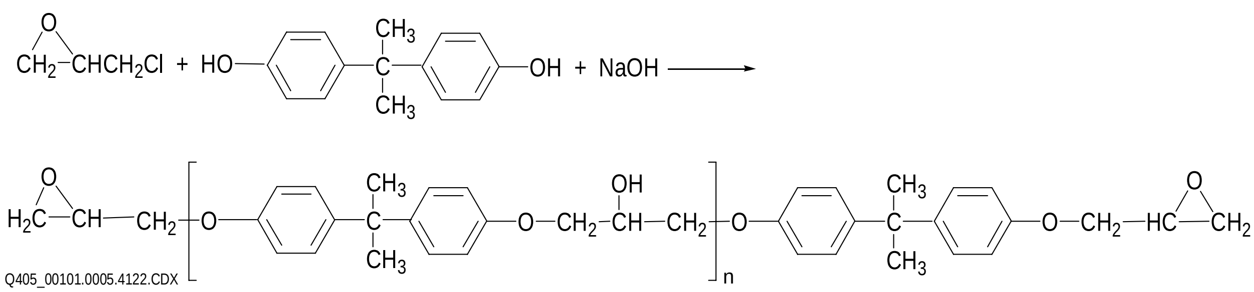
A variety of reagents are employed for converting the liquid and solid epoxy resins to the cured state, which is necessary for the development of the ultimate end-use properties. The curing agents or hardeners are categorized as either catalytic or co-reactive. Catalytic curing agents initiate resin homopolymerization, either cationic or anionic, as a consequence of using a Lewis acid or base in the curing process. Co-reactive curing agents are polyfunctional compounds typically possessing active hydrogens that are employed up to stoichiometric quantities with epoxy resins. The important classes of co-reactive curing agents include multifunctional amines and their amide derivatives, polyphenols, polymeric thiols, polycarboxylic acids, anhydrides, phenol-formaldehyde novolacs and resoles, and amino-formaldehyde resins. This diverse curing chemistry allows formulation of a wide variety of epoxy-based systems, which can be tailored to meet end-use application, performance, and environmental-compliance demands. There is a continuing trend away from low-solids formulations to more environmentally-friendly systems, such as water borne, powder coatings, reactive diluents, high solids, and radiation-cured coatings and adhesives. The driving force is the drastic reduction or elimination of volatile organic compound emissions in the use of epoxy resin systems.

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. Resolution was since acquired by Hexion Specialty Chemicals. 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 specialty epoxy business of Union Carbide became part of the Dow Chemical Company after their merger in the year 2001.

Technology

Resin Production

The most common epoxy resins are made by reacting epichlorohydrin with a polyhydroxy compound such as bisphenol A in the presence of a catalyst. Figure 1 presents a block diagram showing the relationship of bisphenol A and epichlorohydrin (and their feedstocks) to epoxy resin production. Epoxy resins produced from these reactions are known as diglycidyl ethers of bisphenol A (DGEBA). A typical reaction scheme is shown below.



By changing the ratio of epichlorohydrin to bisphenol A, resins ranging from low viscosity liquids to high melting solids can be produced. Liquid epoxy resins can be further reacted with bisphenol A by chain extension to form solid epoxy resins with varying n values. The value of n is determined by the mole ratio of liquid di-epoxide resin to bisphenol A. Each repeat unit contains a pendant hydroxyl group that is a site for curing reactions, along with the terminal epoxy end groups on the overall polymer chain.

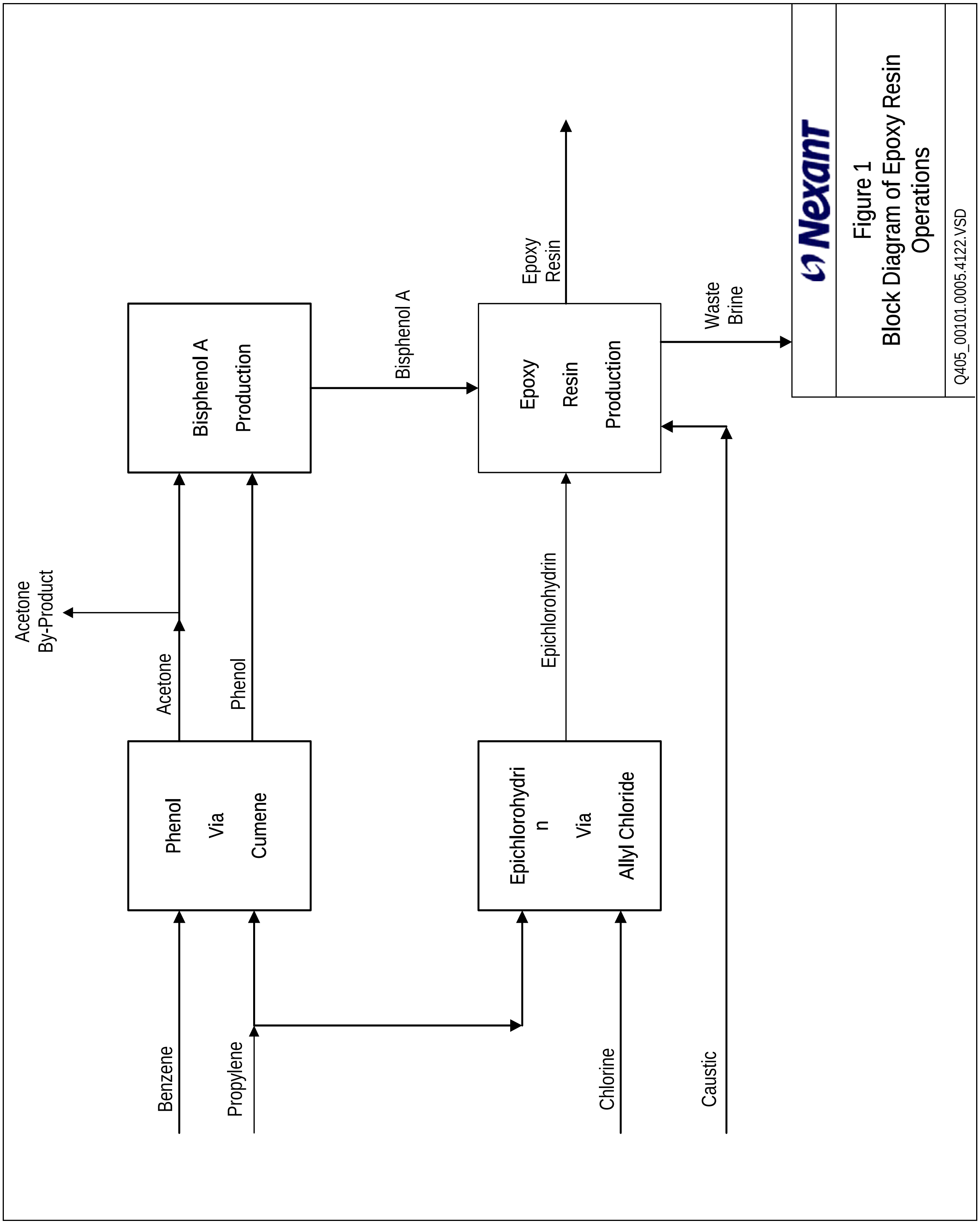


Figure 1
Block Diagram of Epoxy Resin Operations

A wide spectrum of commercial resins is available in which the value of n varies from essentially 0 up to about 30. The selection of the proper molecular weight (n value) is usually determined by the end use application.

Curing

The epoxide group will react readily with a variety of functional groups (e.g. amino, hydroxyl, carboxyl), thus allowing the use of a variety of curing agents that give epoxy resins great versatility. The chemistry of the reactions with curing agents and the use of multifunctional curing agents lead to highly crosslinked polymer networks.

There are four major classes of curing agents or hardeners used with epoxy resins:

- Amines and amine derivatives
- Acid anhydrides
- Catalytic curing agents
- Melamine-, urea-, or phenol-formaldehyde resins

The curing chemistry for each of these classes is briefly discussed in the report body.

Economics

Economics for epoxy resin production are developed, starting with benzene, propylene, chlorine, and acetone as the primary raw materials, on a U.S. Gulf Coast, first quarter 2005 basis.

The economic section includes graphs that depict the ultimate effect on epoxy resin costs of changes in the prices of the major raw materials: benzene, propylene, chlorine, and acetone.

Commercial Analysis

The broad range of epoxy resin types and their typical applications are surveyed in Table 1.

The markets for epoxy resins are relatively mature, with similar consumption patterns exhibited in each of the major regions. Overall epoxy resin demand is generally a function of macroeconomic activity. Most of the major end markets are sensitive to economic conditions and demand varies accordingly.

The major applications for epoxy resins are:

- Coatings
- Electrical/electronics
- Composites

- Construction
- Adhesives

Table 1
Epoxy Resin Typical Applications

Resin	Applications
Liquid epoxy resins (Diglycidyl ether of bisphenol A, DGEBA	Coatings, castings, tooling, flooring, adhesives, composites
Solid epoxy resins (SER)	Powder coating; epoxy esters for coatings; can, drum, and maintenance coatings
Bisphenol F epoxy	Coatings
Multifunctional	
Phenol epoxy novolac	Castings, coatings, laminates
Cresol epoxy novolac	Electronics encapsultants, powder coatings laminates
Other multifunctional epoxies	Composites, adhesives, laminates, electronics
Cycloaliphatic epoxies	Electrical castings, coatings, electronics
Brominated epoxies	Printed wiring boards, composites
Epoxy vinyl esters	Composites

To meet end-use performance demands (this includes both final properties and mode of application) in a cost effective manner, formulators will employ a variety of additives or modifiers. Modifiers include accelerators, diluents, pigments, fillers, flexibilizers, tougheners, and flame retardants. Diluents can be classified into two categories: reactive or nonreactive. Reactive diluents are generally low molecular weight mono-, di-, or tri-functional glycidyl ethers of aliphatic alcohols or polyols. Use of reactive diluents sharply reduces the viscosity of epoxy resins thus allowing higher filler loadings, easier handling, and better wetting properties. Because these diluents are reactive they become chemically incorporated into the polymer network and contribute to the crosslink density of the final cured system.

Solvents such as toluene, xylene, furfuryl alcohol, dibutyl phthalate, and nonyl phenol are commonly used as non-reactive diluents. While these materials effectively serve to reduce resin viscosity, they do not contain any reactive sites and consequently do not become chemically bound into the epoxy matrix.

Accelerators can be added to epoxy systems to reduce gel time or cure. Of course, use of too much accelerator will reduce pot life to such low levels that the epoxy cures prematurely, not allowing enough application time. Accelerators can be either acidic or basic in nature.

Pigments and dyes can be used with epoxy resins; however, caution must be exercised because of the potential for the pigments or dyes to prematurely initiate cure-out.

Fillers are used in epoxy systems either to alter wet and/or cured-out properties or to lower the cost of a particular formulation. Considerations when choosing the type of filler include loading, resin compatibility, cost, particle size, and properties. Some of the specific properties which can be achieved or altered by using fillers are shrinkage, thermal shock resistance, abrasion resistance machinability, pot life, exotherm, electrical conductivity, viscosity, compressive strength, and adhesive properties. Table 2 lists some of the more common fillers.

Table 2
Typical Epoxy Resin Fillers

Type	Primary Application
Marble flour	General purpose filler
Chalk powder	General purpose filler
Sand	Bulk filler that provides high compression strength and abrasion resistance
Silica flour	Filler for electrical castings that provides abrasion resistance
Mica flour	Improves crack resistance of castings exposed to mechanical and thermal stock
Slate powder	General purpose filler
Vermiculite	Provides low density bulk
Aluminum powder	Provides high thermal conductivity
Chopped glass strand	Improves mechanical strength of edges and thin sections
Hydrated alumina	Improves wet and dry arc-track resistance and flame retardance

Flexibilizers introduce flexible chain segments in an epoxy resin by various means. 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. Flexibilization 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. Some reactive diluents also act as flexibilizers.

Tougheners 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 often comes at the expense of toughness. Toughening approaches for epoxies 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-acrylonitriles) have been popular tougheners for epoxies.

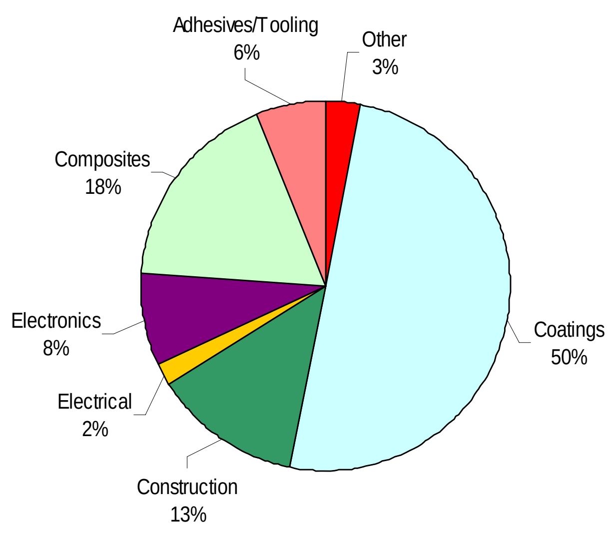
Many applications of epoxy resins require the system to be ignition-resistant, e.g., electrical laminates for PCBs and certain structural composites. A common method of imparting this ignition resistance is the incorporation of tetrabromobisphenol A (TBBA) or the diglycidyl ether of TBBA into the resin formulation. The lower cost brominated epoxies based on TBBA containing ca. 20 wt.

percent Br are extensively employed in the PCB industry. The diglycidyl ether of TBBA (ca. 50 wt. percent 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.

The markets for epoxy resins are relatively mature, with similar consumption patterns exhibited in each of the major regions. Overall epoxy resin demand is generally a function of macroeconomic activity. Most of the major end markets are sensitive to economic conditions and demand varies accordingly.

Global demand for epoxy resins by sector is shown in Figure 2. About half of total demand is attributed to coatings of various types, including powders, water-borne, solvent-borne, radiation-cured, etc. The second largest demand sector is composites for aerospace, process equipment, structural, and other end uses, at about 18 percent of total demand. The construction sector comes in third at 13 percent, while electronics/electrical demand in the aggregate comes in fourth at 10 percent. Combined adhesives/tooling uses account for 6 percent of demand, and the remainder of demand is comprised of a number of miscellaneous uses.

Figure 2
Global Epoxy Resin Demand by Sector



Production of epoxy resins has been dominated in recent years by three major producers: Dow, Resolution Performance Products (RPP), and Huntsman Advanced Materials (formerly Vantico). Dow and RPP have the largest production capacity, and are both fully integrated into the key feedstocks – bisphenol A and epichlorohydrin. These two producers have a clear advantage in commodity resins, while Huntsman is more focused on specialized formulations and applications requiring extensive technical service. Recently, Nan Ya Plastics in Taiwan has developed sizeable production capacity for epoxy resins and feedstocks.

The report presents the historic and forecast global supply/demand balance for epoxy resins for 2001 to 2012. After 2005, operating rates are predicted to improve into the low 80 percent range. Detailed supply/demand data are provided in the report for the United States, Western Europe, and Japan.

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