EPOXY THERMOSETS AND THEIR APPLICATIONS I: CHEMICAL STRUCTURES AND APPLICATIONS

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ABSTRACT

Epoxies are the most common and widely used thermosets. They have a very wide application range from dental fillings to rocket casings. The characteristics, which provide such a diversity of applications are explained by the chemistry of the epoxide functional group as well as the curing reaction. In addition to the numerous other uses, epoxies are particularly well suited for fiber-reinforced composites and have been instrumental in the current success of these materials. This overview of epoxies is presented in the context of a general course in Materials Science and Engineering to supplement the need by students in this field.

Keywords: *Epoxies, Thermosets, Epoxy Curing, Prepregs, Crosslinking, Fiber-Reinforced Composites, Aerospace, Encapsulants, Coatings, Adhesives, Sheathing*

USES OF EPOXIES

Epoxy resins represent an important class of polymers primarily due to their versatility.[1, 2] Despite this, epoxies are hardly covered in Materials Science and Engineering textbooks - leaving students unprepared for the extensive applications of these materials. This paper is an attempt to provide a basic understanding of how epoxies react and the diversity of uses. The techniques used to characterize the curing reaction and the models used to describe the kinetics will be provided in future papers in this series.

High degree of crosslinking and the nature of the interchain bonds give cured epoxies many desirable characteristics. These characteristics include excellent adhesion to many substrates, high strength (tensile, compressive and flexural), chemical resistance, fatigue resistance, corrosion resistance and electrical resistance. In addition, processing is simplified by the low shrinkage and lack of volatile by-products. Properties of the uncured epoxy resins such as viscosity, which are important in processing as well as final properties of cured epoxies such as strength or electrical resistance can be optimized by appropriate selection of the epoxy monomer and the curing agent or catalyst. Because of the ease of application and desirable properties, epoxies are widely used for coatings, corrosion protectants, electric encapsulants, fiber optic sheathing, flooring and adhesives. Given so many everyday uses, most hardware stores carry a wide variety of epoxy adhesives and coatings.

The properties, e.g., liquid processability and cured strength control, which result in successful adhesives and coatings also made epoxies the obvious choice for matrices in fiber-reinforced composites. Man-made fiber-reinforced composites predate history itself, being seen in the earliest straw-filled mud huts. Even glass fibers, which seem to be a modern technological achievement, date back 3,000 years to the Phoenicians.[3] Commercialization and exploitation of composites began in the Nineteenth Century[4] and has steadily grown in both scale and range. Today glass fiber-reinforced epoxies are commonly the major components in boats, automobiles, aircraft, medical prostheses and sports equipment. Indeed, many developments were only possible using this material, including the Chevrolet Corvette[5] and the Bell/Textron V-22[6] tiltrotor aircraft. Epoxies and fiber-reinforced epoxy composites have greatly influenced sports equipment, specifically in tennis, golf and cycling.

The market for epoxy resins has grown as new epoxies are developed and new applications are found. The worldwide consumption of epoxy resins in 1991 was over one half million tons, with the United States taking about one third.[7] In 1998 the United States consumed 320,000 tons of epoxy resins, representing an overall annual increase of 3 % over the past 10 years.[8]

HISTORY

Epoxy compounds were first synthesized as early as 1891; however, commercialization did not come about for the next 50 years. Two independent researchers, developing separate applications, synthesized the first commercial epoxy resins. Pierre Castan of de Trey Frères in Switzerland, while developing dental restoration materials, discovered the reaction of diglycidylether of bisphenol-A (DGEBA) with pthalic anhydride. The patents were assigned to Ciba AG of Basel, Switzerland (now Ciba-Geigy) in 1942.[9] At the same time, Sylvan Greenlee at DeVoe and Raynolds (later Celanese Chemical Company, and subsequently

Hoechst-Celanese) in America, while developing surface coatings, discovered another DGEBA resin, which differed only in molecular weight. Greenlee's first of many patents was granted in 1948.[10] These DGEBA resins and subsequent derivatives have, and continue to be, the largest product in the epoxy market, primarily in the surface coatings industry for which it was developed. The characteristics which Greenlee and Castan sought and found in DGEBA, including adhesion, hardness, inertness and thermal resistance, are responsible for its popularity.

Many other monomers and polymers have been subsequently epoxidized to increase the desirable properties of DGEBA and to develop special properties.

CHEMISTRY

Epoxies are characterized by the presence of one or more epoxide functional groups (shown in Figure 1) on or in the polymer chain. The epoxide group is planar, with a three-membered ring composed of one oxygen and two carbon atoms. Due to the high ring strain, similar to that in cyclopropane, the group is very reactive.
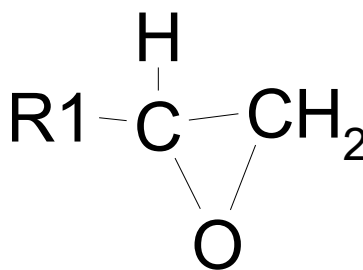
Figure 1: The epoxide functional group, where R1 represents the functionalized molecule.

Although DGEBA (Figure 2) and its derivative resins are still the most common epoxies, especially in the field of coatings, they had limited applications in the structural composites field due to their limited strength and relatively low thermal degradation temperature. The
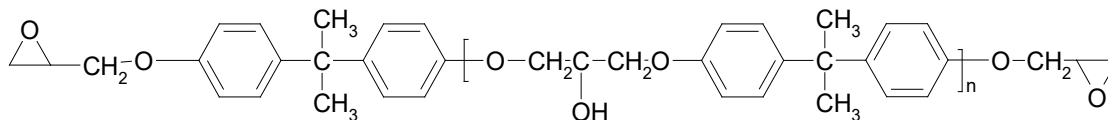
Figure 2: Diglycidylether of Bisphenol-A (DGEBA), n = 0, for the derivatives, n > 0.

demands of the structural composites field spurred development of high performance epoxies. These requirements were met by increasing the functionality (number of epoxide groups per molecule), modifying curing agents, and replacing the thermally weak aliphatic linkages in glycidyl groups with rigid bonds.

The ring-opening polymerization and crosslinking in epoxy resins can be of two general types, catalyzed homopolymerization or bridging reactions incorporating a coreactive crosslinking agent into the network. Homopolymerization, or reactions between epoxy chains, involve elimination reactions on the oxygen atom of the epoxide group using acid or base catalysts, often activated by radiation. The incorporation, or bridging reaction, involves nucleophilic attack on one of the epoxide carbons by an amine (shown in Figure 3) or an anhydride compound. Reviews of curing reactions are available in the literature and terminology[11] has been standardized by the International Union of Pure and Applied Chemistry (IUPAC). An obvious and important difference in the result of the two different curing methods is that in homopolymerization the network is only composed of the cross-linked epoxy monomers, whereas in the bridging reaction the network is composed of a copolymer of both epoxy monomers and a curing agent, as shown in Figure 3. Therefore
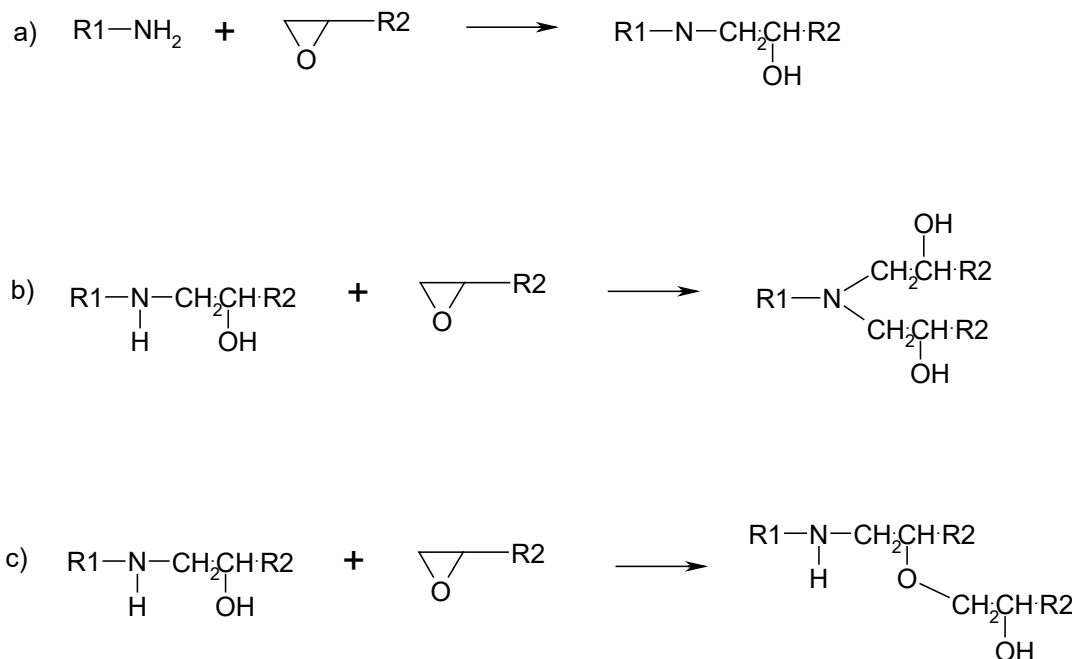

Figure 3: Mechanism of primary amine cure of an epoxy resin, with the epoxide group under nucleophilic attack by a) a primary amine, b) a secondary amine and c) a hydroxyl group generated from reactions a and b, where R1 and R2 are functionalized molecules.

in a bridging reaction the network properties are a function of two components, which allows modifications to be incorporated in either component. Thus, a rigid epoxy with high strength can be used with an impact resistant hardener to yield a desirable network.

In addition, in amine-cured epoxy reactions a side reaction between the products and reactants occurs, as shown in Figure 3c. Epoxy monomers may be attacked by the hydroxyl group of the product of the primary amine opened epoxy, if either the secondary amine is less reactive than the hydroxyl group, or by the hydroxyl group of the final product, in the case of epoxy rich systems or low functionality amines.

PHYSICAL PROPERTIES

The physical properties of uncured epoxy resins vary widely. As with any polymer, the viscosity of the monomers or prepolymers depend on both the molecular weight and the molecular structure. A simple example is DGEBA, already shown in Figure 2. Higher linear molecular weight monomers, i.e. those with higher values of n, exhibit higher viscosities. In addition, molecular structure and types of bonds will greatly affect the viscosity of the resin. Since epoxies are almost always used with catalysts, crosslinking agents, accelerators and various other additives, viscosity effects like plasticization must be considered.

CURING

Epoxy curing involves two phenomena, polymerization and crosslinking. Although each phenomenon is complicated and the two are in competition during the overall curing process, generalizations and simplified models can be made. During the initial stage of curing, polymerization is favored because in the case of catalyzed homopolymerization terminal epoxides are the most reactive, and in the case of coreactive agents primary reactions are more reactive than secondary ones, and the terminal epoxide reactivity already mentioned plays a role too. In most cases the polymerization is an addition reaction, and thus follows a rate equation for addition polymerization. The molecular weight of the growing polymer increases until the molecular weight approaches infinity, so that all monomers are connected by at least one bond and a network is formed. At this point, called the gel point, the polymer possesses high molecular weight and few crosslinks, and thus behaves much like a very high molecular weight thermoplastic. From the gel point, crosslinking becomes the dominant phenomenon due to the lack of free monomers. Crosslinking involves interchain bonding of intrachain reactive sites, either intrachain epoxides or secondary sites on coreactive agents.

Although crosslinking is a different phenomenon, the rate of chemical conversion of the epoxide groups is unaffected in most epoxy systems. The crosslinking reactions produce a growing network and reduce the mobility of the chain segments. The growth of the network results in mechanical and thermal stabilization of the structure, resulting in increasing modulus and glass transition and degradation temperatures. At a certain high degree of crosslinking, the increasing molecular weight of the structure exceeds the molecular weight, which is thermodynamically stable as a rubber, and the material transforms into a glass, a process called vitrification. In a glassy state, the mobility of reactants is severely restricted, reducing the rate of the reaction to a diffusion-controlled reaction, which is much slower. Further conversion is still possible; however, the rate is much slower since the process relies on diffusion rather than mobility to bring the reactants together. When the crosslinking reaction exhausts all the reactive sites available, the resulting structure is hard (high modulus) and insoluble due to a high degree of interchain bonding.
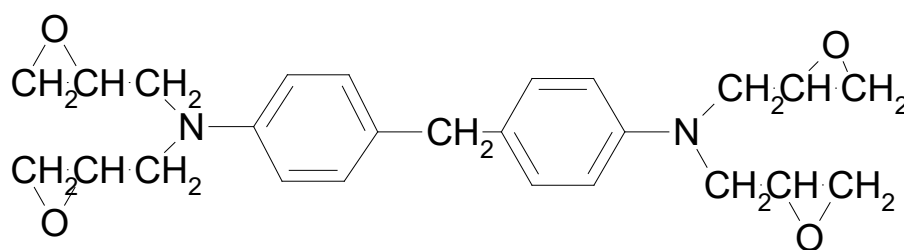
PREPREGS

Since epoxy resins must be mixed with various curing agents, catalysts, modifiers and additives, as well as any reinforcements, many epoxy suppliers provide premixed molding compounds (MCs) and preimpregnated fibers (prepregs). MCs and prepregs have many advantages for manufacturers since all of the careful mixing is done by and ensured by the supplier in large batches. The manufacturer is thus only concerned with the actual processing of the compound. MCs are very popular in high volume industries like automotive and consumer products whereas prepregs are very common in hand and machine layup of high fiber content laminates in aerospace and specialty markets.

A SAMPLE SYSTEM

One material studied by many groups is a premixed epoxy resin and amine curing agent molding compound, designated 8552 by its manufacturer Hercules (Hexcel). The material, illustrated in Figure 4, consists of the tetrafunctional epoxy tetraglycidyl 4,4-

TGDDM
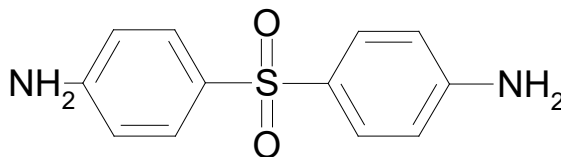
DDS

Figure 4: Chemical structures of the epoxy and amine components in a TGDDM/DDS prepreg.

diaminodiphenyl methane (TGDDM) and the tetrafunctional amine curing agent 4,4'-diaminodiphenylsulfone (DDS), along with an ionic initiator/accelerator and a thermoplastic modifier.[12, 13] This material is common in the aerospace industry and has been the subject of many studies including a comprehensive study of the material using an array of different techniques.[14] Several manufacturers produce similar prepregs with glass or carbon fiber reinforcement. Commercial TGDDM/DDS prepregs are prepared with an epoxy-rich stoichiometry. The present article covers several important aspects of epoxy-based polymers and composites, but even more deserves to be covered in courses in Polymer Science and Engineering as well as taken into account in research and development. We shall discuss other aspects of these materials in future articles.

ABBREVIATIONS AND ACRONYMS

DDS   4,4'-diaminodiphenylsulfone
DGEBA   diglycidylether of bisphenol-A
IUPAC   International Union of Pure and
             Applied Chemistry
MC   molding compound
TGDDM   tetraglycidyl 4,4-
             diaminodiphenyl methane

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