Chapter 8

Literature Review of Epoxy Toughening

8.1 Introduction

Epoxy resins were first commercialized in 1946 and are widely used in industry as protective coatings and for structural applications, such as laminates and composites, tooling, molding, casting, bonding and adhesives, and others.[1,2] The ability of the epoxy ring to react with a variety of substrates gives the epoxy resins versatility. Treatment with curing agents gives insoluble and intractable thermoset polymers. Some of the characteristics of epoxy resins are high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, good electrical insulating properties, and the ability to be processed under a variety of conditions. Depending on the specific needs for certain physical and mechanical properties, combinations of choices of epoxy resin and curing agents can usually be formulated to meet the market demands. However, in terms of structural applications, epoxy resins are usually brittle and notch sensitive. As a result, tremendous effort has been focused on toughness improvement during past three decades. Reviews in this area are available.[3,4,5] This chapter gives a brief introduction to epoxy resins and their toughening methods.

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[1] McAdams, L. V.; Gannon, J. A. In *High Performance Polymers and Composites*, Kroschwitz, J. I. ed., John Wiley & Sons, Inc., **1991**, pp 258-318.

[2]. May, C. A.; ed., *Epoxy Resins Chemistry and Technology*, 2nd ed., Marcel Dekker, Inc.: New York, **1988**.

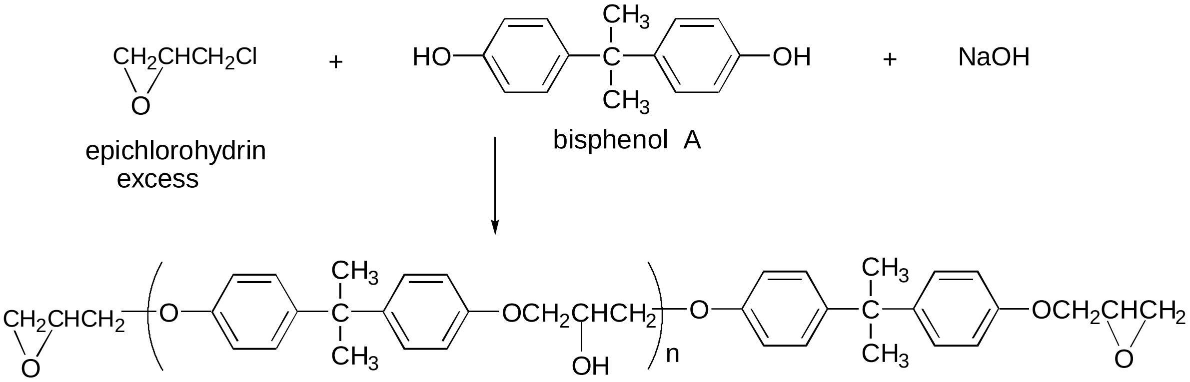
[3] McGarry, F. J. In *Polymer Toughening*, Arends, C. B., ed., Marcel Dekker, Inc.: New York, **1996**, pp 175-188.

8.2 Epoxy Resins

8.2.1 Synthesis

Epoxy resins are compounds containing more than one epoxide group per molecule on average. Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones. They are prepared from either epichlorohydrin or by direct epoxidation of olefins with peracids. The most important intermediate for epoxy resins is the diglycidyl ether of bisphenol A (DGEBA) (**8.1**), which is synthesized from bisphenol A and excess epichlohydrin (Scheme 8.1).

Scheme 8.1



8.1 (diglycidyl ether of bisphenol A, DGEBA, n ~0.2)

Commercial liquid epoxy resins are prepared using different molar ratios of epichlohydrin to bisphenol A to afford different molecular weight products. High molecular weight solid epoxy resins with n values ranging from 2 to 30 are prepared by two process. Lower molecular weight solid resins with n values up to 3.7 are prepared directly from

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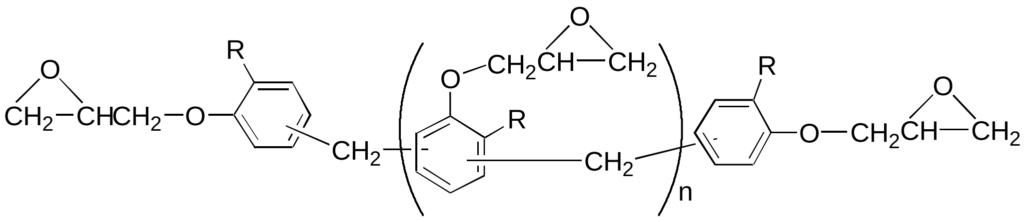
[4] Shaw, S. J. In *Rubber Toughened Engineering Plastics*, Collyer, A. A., ed., Chapman & Hall: London, **1994**, pp 165-209.

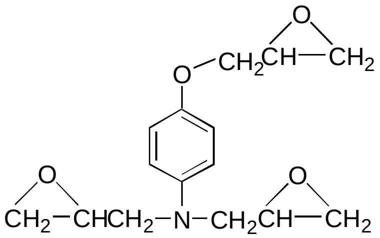
[5] Riew, C. K.; Gillham, J. K., ed., *Rubber Modified Thermoset Resins*, Advances in Chemistry Series No. 208, American Chemical Society, Washington, DC, **1984**.

epichlorohydrin, bisphenol A and a stoichiometric amount of NaOH ("taffy" process). Higher molecular weight solid resins are prepared by chain extension reaction of liquid epoxy resin (crude DGEBA) with bisphenol A using basic inorganic reagents such as NaOH or Na_2CO_3 as catalysts ("advancement" or "fusion" process).

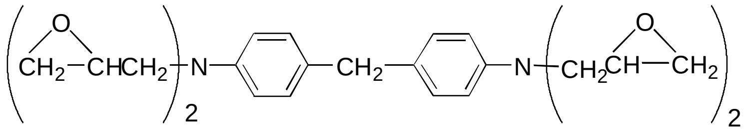
Multifunctional epoxy resins such as aromatic glycidyl ether resins and aromatic glycidyl amine resins are commercially available. Commercially important epoxy phenol Novolac resins (EPN, **8.2a**) and epoxy cresol Novolac resins (CPN, **8.2b**) are prepared from excess epichlohydrin and phenol-formaldehyde or *o*-cresol-formaldehyde resins. The high functionality of the these Novolac resins increases crosslink density and improves thermal stability and chemical resistance. Epoxy resins derived from multifunctional aromatic glycidyl amine resins such as triglycidyl-*p*-aminophenol (**8.3**, ERL 0510, CIBA-GEIGY) and tetreglycidyl-4,4'-diaminodiphenylmethane (**8.4**, TGDDM, Araldite MY 720, CIBA-GEIGY) have excellent elevated temperature properties.



8.2a EPN, R = H
8.2b ECN, R = CH_3

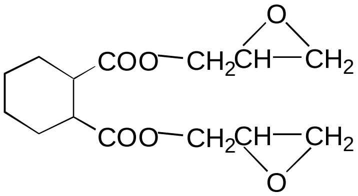


8.3 (triglycidyl-*p*-aminophenol)
ERL 0510 (CIBA-GEIGY)



8.4 (tetraglycidyl-4,4'-diaminodiphenylmethane)
TGDDM, Araldite MY 720 (CIBA-GEIGY)

Glycidyl esters prepared from cycloaliphatic carboxylic acid (**8.5**, CY 184, CIBA-GEIGY) and cycloaliphatic epoxy resins based on the epoxidation of cylcoolefins are also commercially available.



7.5 (diglycidyl ester of hexahydrophthalic acid)

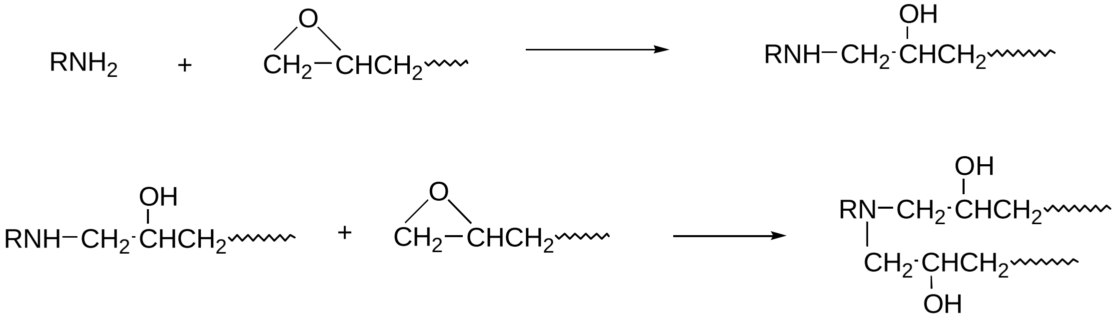
8.2.2 Curing Agents

Treatment of epoxy resins with curing agents or hardeners gives three-dimensional insoluble and infusible networks. Epoxy resins can be cured with a wide variety of curing agents. The choice of curing agents depends on the required physical and chemical properties, processing methods and curing conditions.

Epoxy resins can be cured with either catalytic or coreactive curing agents. Catalytic curing agents function as initiators for epoxy ring-opening homopolymerization. Epoxy resins can be catalytically cured by Lewis bases such as tertiary amines, or Lewis acids such as boron trifluoride monoethylamine. These catalytic curing agents can be used for homopolymerization, as accelerators or supplemental curing agents for other curing agents such as amines or anhydrides. Photoinitiated cationic curing of epoxy resins has received great attention for the application of coatings from solvent-free or high solid systems.[6]

The epoxide ring can react with chemicals with different structures, especially those that have activated hydrogen atoms such as alcohols, amines, and carboxylic acids, etc. Among them, primary and secondary amines are the most widely used curing agents for epoxy resins. A primary amine reacts with an epoxy group to produce a secondary amine and a secondary alcohol. The secondary amine can further react with an epoxy group to form a tertiary amine (Scheme 8.2). No competitive reaction is detected between an epoxy group and a secondary alcohol when a stoichiometric equivalent or excess amine is used.[7] Aliphatic amines cure epoxy resins at room temperature; aromatic amines are less basic and require elevated temperatures or accelerators to cure epoxy resins.

Scheme 8.2



Other commercially important curing agents are formaldehyde resins and acid anhydrides. Melamine-formaldehyde, urea-formaldehyde and phenol-formaldehyde resins react with hydroxyl groups of high molecular weight epoxy resins to form crosslinked networks. Most commercial anhydride curing agents are based on cycloaliphatic structures.

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[6] Crivello, J. V. Lam, J. H. W. *Macromolecules* **1977**, 10, 1307.

Epoxy-anhydride systems exhibit low viscosity, long pot life and low exothermic heats of reaction. The cured epoxy thermosets have good mechanical and electrical properties.

Other curing agents including carboxylic acids, mecaptans, phenol Novolac resins and isocynates are also commercially available.

The majority of curing agents employed in epoxy systems provide a substantial contribution to the properties of the crosslinked products. Thus the choice of curing agent is very important and needs to be considered very carefully. This is particularly true for modifications of epoxy resins, where the curing agents can influence the curing chemistry, the curing rate, crosslink density, morphology, etc. and eventually affect the fracture toughness of modified epoxy resins.

8.3 Methods for Epoxy Toughening

Toughness is a measure of a material's resistance to failure. It is usually measured as either the critical stress intensity factor or the energy required to fail a specimen under a specific loading condition. For epoxy thermosets, the plane strain critical stress intensity factor (K_{1C}) is usually used to determine the fracture toughness of cured materials.

Various methods are utilized to modify epoxy resins to improve their toughness. Based on the structure-property relationships, the traditional chemistry approaches have been: chemical modification of a given rigid epoxy backbone to a more flexible backbone structure; lowering the crosslink density by increasing the molecular weight of the epoxy monomers and/or decreasing the functionality of the curing agents. The most common approaches are

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[7] O'Neil, L. A.; Cole, C. P. *J. Appl. Chem. London* **1956**, 6, 356.

the incorporation of dispersed toughener phase(s) in the cured epoxy matrix. The second phase includes rubbers, thermoplastics and hard inclusions such as silica, glass beads, etc. Among them, the most successful systems have been the rubber modified epoxy resins.

8.3.1 Rubber Modified Epoxies

The important research work on rubber modified epoxy resins was pioneered by McGarry and his groups at MIT.[8] After that work was published, many investigators started exploring the area in detail. A number of rubbers have been considered and studied as modifiers for epoxy resins. The rubber system that has attracted the most attention is the family of copolymers of butadiene and acrylonitrile; these are commercially available with different acrylonitrile contents ranging from 0%-26%. The low molecular weight (3400-4000 g/mol) butadiene-acrylonitrile rubbers are soluble in liquid DGEBA epoxy resins and can be synthesized with carboxylic acid (CTBN, **8.6**) or amine groups (ATBN) both at the chain ends and pendent along the chain. When a solution of rubber in epoxy is cured, rubber particles precipitate out as a second phase. With just 10 phr (parts per hundred parts resins) rubber modifier, the fracture toughness of modified epoxy resins increases dramatically with only slight reduction in the glass transition temperature and the modulus.

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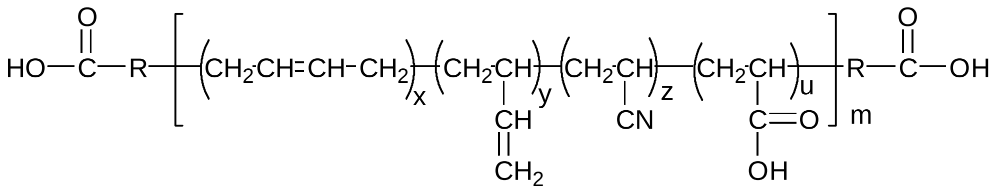
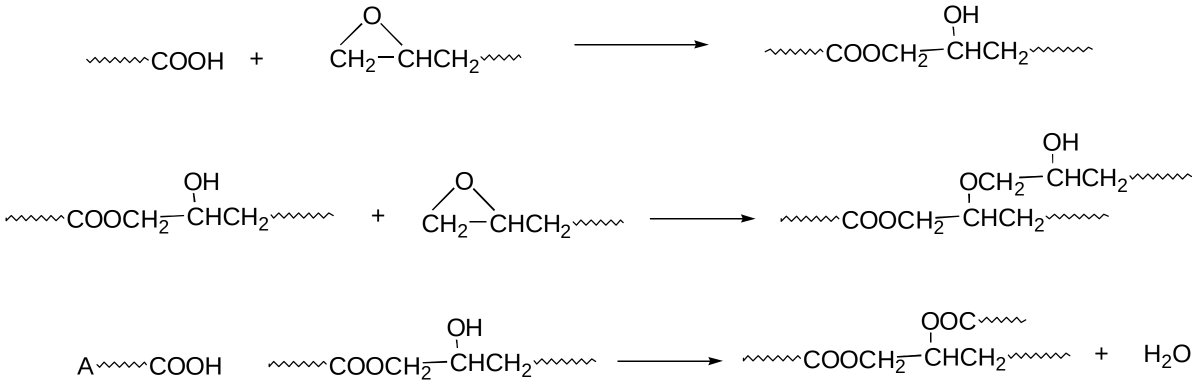
[8] (a) McGarry, F. J.; Willner, A. M.; Sultan, J. N. *Toughening of Glassy Crosslinked Polymer with Elastomeric Inclusions*, Civ. Eng. Dept., Report R69-35, Massachusetts Institute of Technology, Cambridge, **1969**. (b) McGarry, F. J.; Sultan, J. N. *J. Polym. Sci.* **1973**, 13, 29.



8.6 (CTBN)

The reactions between the carboxylic acid groups of CTBN liquid rubbers and epoxies can be considered as chain-extension reactions. Three reactions may occur between CTBN rubbers and DGEBA epoxy resins (Scheme 8.3). The carboxylic acid moiety of CTBN reacts with an epoxy group to form a β-hydroxypropyl ester, which then undergoes polymerization with other epoxy groups. The carboxylic acid may react with the secondary hydroxyl groups to form esters, but in a minor degree, if at all. When the reaction is base catalyzed, the first reaction proceeds until all the carboxylic groups are consumed.[9]

Scheme 8.3



The modified epoxy resins are prepared by a simple additive method or a "prereacted" method.[10] A typical "prereacted" preparation employs about 10 phr CTBN liquid rubber using a catalyst such as triphenylphosphine to promote the reactions between the carboxylic

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[9] Alvey, F. B. *J. Polym. Sci.* **1969**, 7, 2117.

groups and the epoxy groups at relatively low temperature (110 °C), and then further cured with other curing agents (e.g., piperidine). These prereacted formulations provide better control over particle size and composition than the simple additive formulations. The fracture toughness was found to be proportional to rubber content, up to 25 phr rubber. The composition of the formulated system can greatly affect the amount of rubber that phase separates during polymerization. The degree of phase separation and the type of morphology has been shown to depend on curing temperature, the initial molecular weight of the rubber, the butadiene-acrylonitrile ratio, catalyst type, and the vitrification or gelatin rates of the given system.

Research on butadiene acrylonitrile rubbers and DGEBA epoxy systems was pursued vigorously by a number of researchers. Among them, three researchers at BF Goodrich (Riew, Siebert, and Rowe) contributed greatly to the knowledge of rubber toughened thermosets because of their employment at the producer of reactive liquid rubbers.

It is now well known that the fracture toughness of epoxy resins can be significantly increased by modification with rubbers. However, the actual mechanism of this toughening is still under debate. The main issues are whether the rubber or the matrix absorbs most of the energy, whether the matrix undergoes massive crazing or simple cavitation. Sultan and McGarry[11] attributed the toughening effect mainly to the crazing of the epoxy matrix. Bascom *et al.*[12] accredited the high toughness values of CTBN modified epoxy to an increase

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[10] Riew, C. K.; Rowe, E. H.; Siebert, A. R., In *Toughness and Brittleness of Plastics, ACS Adv. In Chem. Ser.* 1976**,** 154, 361.

[11] McGarry, F. J.; Sultan, J. N. *J. Polym. Sci.* **1973**, 13, 29.

[12] Bascom, W. D.; Cottingham, R. L.; Jones, R. L.; Peyser, P. *J. Appl. Polym. Sci.* **1975**, 19, 2545.

in the plastic zone size. A rubber stretching and tearing mechanism was proposed by Kunz and coworkers[13] as the major toughening mechanism for rubber modified plastics (also known as rubber bridging). A toughening mechanism proposed by Kinloch *et al*.[14] and further developed by Pearson and Yee[15,16,17] is now generally recognized as the most consistent in terms of experimental data and observations. They attribute an order of magnitude increase in toughness to the cavitation of the rubber particles, followed by large scale shear yielding of the epoxy matrix.

The relationships between rubber phase morphology and the mechanical properties of the cured resins have been studied for several systems. However, many of these systems, such as the piperidine cured epoxy resins, are just model systems with limited practical use. Additionally, only the highly toughenable epoxy resins modified with rubber tougheners are known to produce an impressive toughening effect. These highly toughenable ductile epoxy resins usually exhibit rather low glass transition temperatures (usually below 100 °C) and low crosslink densities. They are not suitable for high performance structural applications such as composites or adhesives used in aerospace or electronic markets.

Besides the reactive rubbers, several insoluble, unreactive rubber modifiers, such as core-shell rubbers (CSR) and dispersed acrylic rubbers (DAR), were used to modify the epoxy systems.[18] These preformed dispersions of epoxy insoluble rubbers are particularly useful in

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[13] Kunz-Douglass, S.; Beaumount, P. W. R.; Ashby, M. F. *J. Mater. Sci.* **1981**, 16, 2657.

[14] Kinloch, A. J.; Shaw, S. J.; Tod, D. A.; Hunston, D. L. *Polymer* **1983**, 24, 1341.

[15] Yee, A. F.; Pearson, R. A. *J. Mater. Sci.* **1986**, 21, 2462.

[16] Yee, A. F.; Pearson, R. A. *J. Mater. Sci.* **1989**, 24, 2571.

[17] Yee, A. F.; Pearson, R. A. *J. Mater. Sci.* **1991**, 26, 3828.

[18] Sue, H-J.; Garcia-Meitin, E. I.; Pickelman, D. M. In *Polymer Toughening*, Arends, C. B., ed., Marcel Dekker, Inc.: New York, **1996**, pp 131-174.

many adhesive and composite applications because the rubbery-phase volume of the final product is relatively insensitive to variations in curing conditions.[19] The glass transition temperature does not decrease with increasing rubber content up to a certain level. In addition, the modulus of these modified epoxy systems can be varied independently of the T_g.

8.3.2 Thermoplastic Modified Epoxies

Rubber modified epoxy resins have been proved to be successful with adhesives. However, for high performance epoxy resins, the toughening effect by rubber modification is usually only incremental. Such a disappointing result is attributed to the high crosslink densities of epoxy resins, which greatly reduce the local molecular mobility. Another reason is the low glass transition temperatures of the rubbers that lower the maximum use temperature and the modulus of the epoxy resins. Tough, high performance engineering thermoplastics such as poly(ether sulfone)s, poly(ether ketone)s and poly(ether imide)s were used as toughener for epoxy resins. They are used either as granulated particles or as polymers dissolved in the liquid epoxy and later precipitated out as second phase particles. The major advantage of these thermoplastic modifiers is that their incorporation into epoxy resins does not result in reduction in modulus and glass transition temperature.

Bucknall and Partridge[20] reported modifications of a tetrafunctional epoxy resin **8.4** (TGDDM, Araldite MY 720, CIBA-GEIGY) and a trifunctional epoxy resin **8.3** (ERL 0510, CIBA-GEIGY) with poly(ether sulfone) (PES, Vitrex 100P, ICI). These were cured with

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[19] Hoffman, D. K.; Kolb, G.C.; Arends, C. B.; Stevens, M. G. *Polym. Preprints.* **1985**, 26, 232.

[20] Bucknall, C. B.; Partridge, I. K. *Polymer* **1983**, 24, 639.

either diaminodiphenyl sulfone (DDS) or dicyanodiamide (DICY). No second phase was found and only modest improvement of fracture toughness in the TGDDM/DDS systems modified with PES. However, phase separation was observed in the ERL 0510/DDS/DICY systems modified with PES. Later, Bucknall and Gilbert[21] reported the use of polyimide (Ultem® 1000) as a toughener for TGDDM/DDS epoxy systems. The dispersed polyimide particles were observed and the fracture toughness was found to be related to the content of polyimide.

Similar studies have been conducted by Raghava[22,23] using PES to modify TGDDM epoxy systems cured with aromatic anhydrides. Two phase morphology and modest improvement in fracture toughness were observed.

Hedrick and McGrath[24,25] reported the first studies on the use of purposely functionalized poly(ether sulfone) to modify an epoxy resin. The phenolic terminated bisphenol A based polysulfone was prereacted with an excess of the DGEBA epoxy (EPON 828, Shell Chemical) and then cured with 4,4'-diaminodiphenyl sulfone. Amine terminated poly(ether sulfone)s were also used to modify DGEBA/DDS systems.[26] The cured systems contained polysulfone particles dispersed throughout the matrix. Significant increase in

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[21] Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, 30, 213.

[22] Raghava, R. S. *J. Polym. Sci., Polym. Phys.* **1987**, 25, 1017.

[23] Raghava, R. S. *J. Polym. Sci., Polym. Phys.* **1988**, 26, 65.

[24] Hedrick, J. L.; Yilgor, I.; Jurek, M.; Wilkes, G. L.; McGrath, J. E. *Polym. Bull*. **1985**, 13, 201.

[25] Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. *Polymer*, **1991**, 32, 2020.

[26] Cecere, J. A.; McGrath, J. E. *Polym. Preprints.* **1986**, 27, 299.

fracture toughness was observed and the toughness improvement was found to depend strongly on the molecular weight of the poly(ether sulfone)s.[27]

Cecere and McGrath[26] used amine terminated poly(ether ketone)s as modifiers for the DGEBA/DDS system with modest increase in toughness. It was found that the poly(ether ketone)s were incompatible with the DGEBA epoxy resin.

In comparison with rubber modified systems, the use of tough thermoplastic polymers offers better improvement in fracture toughness for higher crosslink density epoxy systems. The advantages of thermoplastic modified epoxy systems lie in the fact that the modulus and the T_g of the modified epoxy can be maintained, and the fracture toughness can be improved in direct proportion to the amount of thermoplastic added. The use of reactive thermoplastic modifiers provides good adhesion between epoxy and thermoplastic phases via chemical "connections", which allows predictable morphology and chemical resistance of amorphous thermoplastics. Commercial products of epoxy-thermoplastic systems are available and used in some applications. However, in some cases, the processing constraints and cost factors need to be considered.

8.3.3 Other methods for Epoxy Toughening

By far the most commonly used materials as second phase for epoxy toughening have been rubber based materials. Other materials are also utilized as epoxy tougheners. It has been shown by several investigators that the incorporation of rigid particle fillers, such as

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[27] Yoon, T. H.; Priddy, D. B.; Lyle, G. D.; McGrath, J. E. *Macromol. Symp.* **1995**, 98, 673.

silica,[28] and alumina trihydrate,[29]can improve the toughness of epoxy resins whilst contributing to a greatly enhanced modulus. Compared with the rubber modified system, although only limited improvement in fracture toughness can be achieved, a substantial modulus increase accompanying the toughness improvement is a major advantage.

Even just voids have been reported by Kinloch[30] to toughen an epoxy matrix. Microvoids created using a urea terminated polyether amine (Jeffamine BuD 2000, Huntsman Corporation) were found to toughen a relatively ductile epoxy system significantly. As expected, the toughening was not as great as that of rubber modified systems because of the absence of some energy absorbing modes of rubber containing systems. The yield stress was reduced, of course, due to the voids.

Fracture toughness of high temperature epoxy systems can be also improved by means of decreasing the crosslink density and increasing the chain stiffness at the same time since the T_g depends on both the crosslink density and the stiffness of the polymer chain. This can be achieved by adjusting the molecular weight between crosslinks using rigid diphenolic compounds as chain extenders. One example is CET resins such as Tactrix 695 (Dow Chemical).[31] CET resins consist of a mixture of epoxy resins that also contain difunctional chain extender materials (typically diphenols), a multifunctional, dual active curing agent that

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[28] Young, R. J.; Beaumount, P. W. R. *J. Mater. Sci.* **1977**, 12, 684.
[29] Lange, F. F.; Radford, K. C. *J. Mater. Sci.* **1971**, 6, 1197.
[30] Kinloch, A. J.; Huang, Y. *Polymer* **1992**, 33, 1330.
[31] Burton, B. L.; Bertram, J. L. In *Polymer Toughening*, Arends, C. B., ed., Marcel Dekker, Inc.: New York, **1996**, pp 339-379.

is capable of linear advancement prior to crosslinking, and an advancement catalyst to promote the reaction of the epoxy with the diphenol.[32,33]

8.4 Summary and Conclusions

New ways to improve fracture toughness while retaining thermomechanical properties have been sought for over twenty years. The rubber modified epoxy systems have received a great deal of attention and developed substantially. Commercial adhesives and laminating resins based on these systems are now widely available. Later, high performance thermoplastics have been successfully used to modify epoxies with higher crosskink density. The behavior of thermoplastic modified systems is still being studied. For composite applications, especially for fiber reinforced composites, the processibility such as the initial viscosity of the thermoset resins, is very important. The materials used to toughen epoxies, such as rubbers and thermoplastics, are linear polymers, which behave as classical chain entangled polymers and often have high viscosities. The focus of this research is to use hyperbranched polymers as modifiers for epoxy resins taking advantages of the unique properties of hyperbranched polymers such as low viscosity, high solubility and high degree of functionality.

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[32] Bertram, J. L.; Walker, L. L.; Berman, J. R.; Clarke, J. A. U. S. Patent 4,594,291 (**1986**).

[33] Bertram, J. L.; Stuart, V. I. W.; Walker, L. L. U. S. Patent 4,725,652 (**1988**).

Chapter 9

Research objectives and Scopes

The objectives of this research are to synthesize hyperbranched polymers, functionalize them with different reactive groups via chemical modifications and then explore the possible applications of these functional hyperbranched polymers for composites and adhesives. Hyperbranched poly(arylene ester)s were chosen for these studies. Chapter 10 describes the synthesis of hyperbranched poly(arylene ester)s and copoly(arylene ester)s, the molecular weight control and the functionalization of hyperbranched poly(arylene estes)s with different reactive groups. To demonstrate the applications of these functional hyperbranched poly(arylene ester)s via taking the advantage of their special properties, such as low viscosity and high solubility, carboxylic acid terminated hyperbranched poly(arylene ester)s were use to modify the inherent brittle epoxy resins. We desired to improve the fracture toughness of hyperbranched modified epoxies and improve the processibility of modified epoxy resins without sacrificing their thermal and other mechanical properties. The modifications of a commercially available DGEBA epoxy resin (EPON 828) with carboxylic acid terminated hyperbranched poly(arylene ester)s are described in Chapter 11. The modified epoxies were characterized by kinetic FTIR, solid state NMR, gel fraction analysis, DMA and fracture toughness K_{1C} measurements.