1
Introduction

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1.1
Epoxy Resin – Introduction

Epoxy resin belongs to the principal polymer under the term *thermosetting resins*, which covers a wide range of cross-linking polymers including unsaturated polyester resins, phenol-formaldehyde resins, and amino resins. Thermosetting polymers form an infusible and insoluble mass on heating, due to the formation of a covalently cross-linked and thermally stable network structure. They are generally amorphous and possess various desirable properties such as high tensile strength and modulus, easy processing, good thermal and chemical resistance, and dimensional stability. The term *epoxy resin* is applied to both prepolymers and to cured resins; the former is characterized by a three-membered ring known as the *epoxy*, *epoxide*, *oxirane*, or *ethoxyline group*. The epoxy group is shown in Figure 1.1.

1.2
Cure Reactions

In the cured resin all reactive groups may have reacted, so that although they no longer contain epoxy groups, the cured resins are still called *epoxy resins*. Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones. The capability of the epoxy ring to react with a variety of substrates imparts versatility to the resins. Treatment with curing agents gives insoluble and intractable thermoset polymers. In order to facilitate processing and modify cured resin properties, other constituents may be included in the composition: fillers, solvents, diluents, plasticizers, and accelerators.

Epoxy resins are highly reactive, presumably due to the strained three-membered ring structures, and react with many nucleophilic and electrophilic reagents. Therefore, a wide variety of organic compounds having active hydrogen atoms can be used as curatives. Those include amines (both aliphatic/aromatic and primary/secondary), phenols, carboxylic acids, thiols, anhydrides, and so on. The
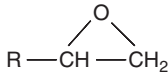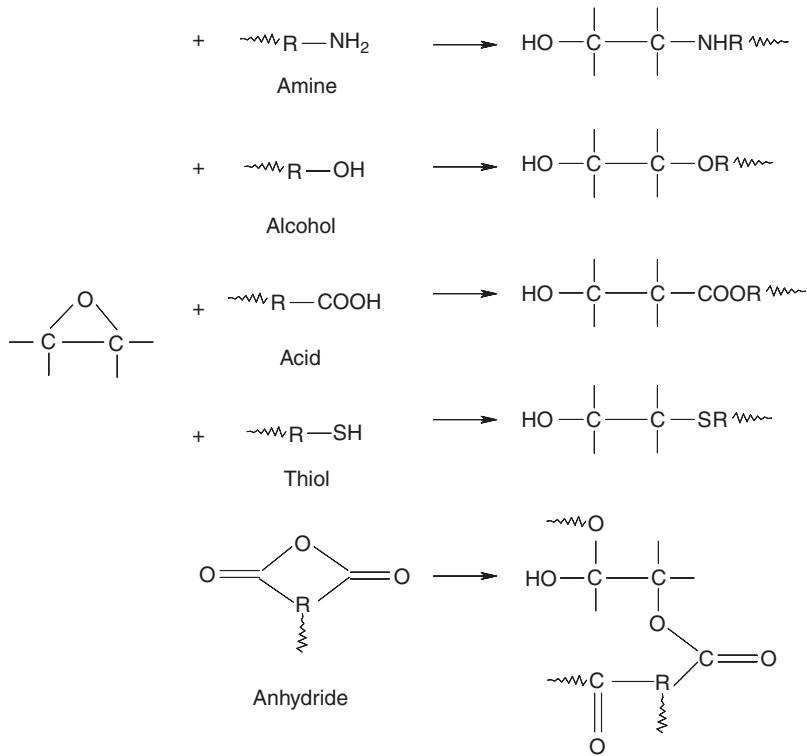
Figure 1.1 Epoxy group.

Scheme 1.1 Reactions between epoxy and different curing agents.

general reactions of the epoxy resin with these compounds are represented in Scheme 1.1.

1.3
Curing Agents

Optimum performance properties are attained by cross-linking an epoxy resin with a curing agent or hardener so as to form a three-dimensional insoluble and infusible network. The choice of curing agents depends on the application and on the handling characteristics such as viscosity, pot life, and gel time; use of properties such as mechanical, chemical, thermal, electrical, and environmental limitations and cost. Curing agents are either catalytic or co-reactive.

1.3.1
Catalytic Cure

Catalytic curing agents function as initiators for epoxy resin homopolymerization. Catalytic cures are initiated by Lewis acids and bases such as boron trihalides and tertiary amines, respectively. Catalytic curing agents can be used for homopolymerization, as supplemental curing agents with polyamines, or as accelerators for anhydrides-cured systems. Catalytic curing agents have high-temperature resistance capacity and long pot lives. However, they have long cure cycles at high temperature. The materials are used as adhesives and for electrical encapsulation purposes.

1.3.2
Co-reactive Cure

On the other hand, the co-reactive curing agents act as a comonomer in the polymerization process. Among this are a wide variety of compounds such as amines (both primary and secondary), mercaptans, isocyanates, carboxylic acids, acid anhydrides, and so on.

1.3.2.1 Primary and Secondary Amines

These are the most widely employed curing agents in epoxy resin chemistry. As a result of the reaction between the epoxy group and the primary amine, a secondary alcohol and amine are generated. The reaction is depicted in Scheme 1.2. The secondary amine, in turn, reacts with the epoxy group to give a tertiary amine and two secondary hydroxyl groups [1].
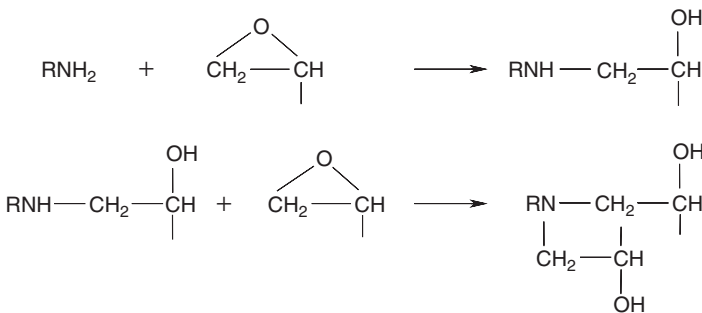
Scheme 1.2 Reactions between epoxy and primary amine.

In general, hydroxyl groups accelerate the rate of curing of amines, among which polyfunctional alcohols are the best accelerators. A mechanism has been proposed [1] in which the hydrogen atom of the hydroxyl group partially protonates the oxygen atom on the epoxy group, rendering the methylene group more susceptible to attack by the nucleophilic amine. The reaction is represented in Scheme 1.3.
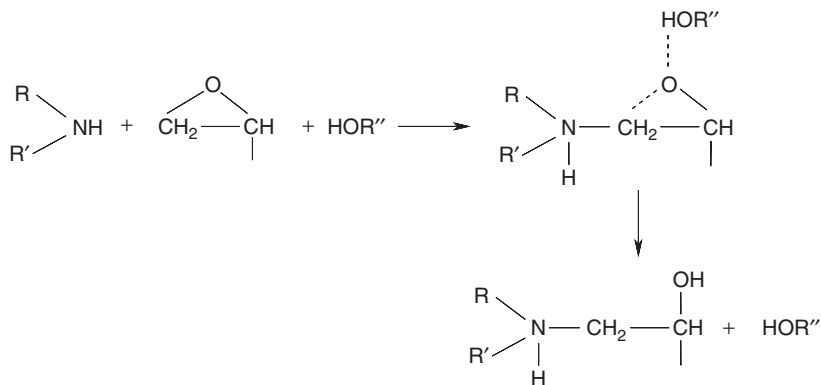
Scheme 1.3 Mechanism of the reaction between epoxy and amine.

Amine-cured products, in general, have good elevated temperature performance, chemical resistance, long pot life, and low moisture absorption. Low compatibility with epoxy resins, toxicity, and long cure cycles are certain disadvantages. Amine curators are highly applicable for high-performance composites and coatings, filament winding, and for electrical encapsulation purposes. A few examples of amine curatives are listed in Figure 1.2a−e.
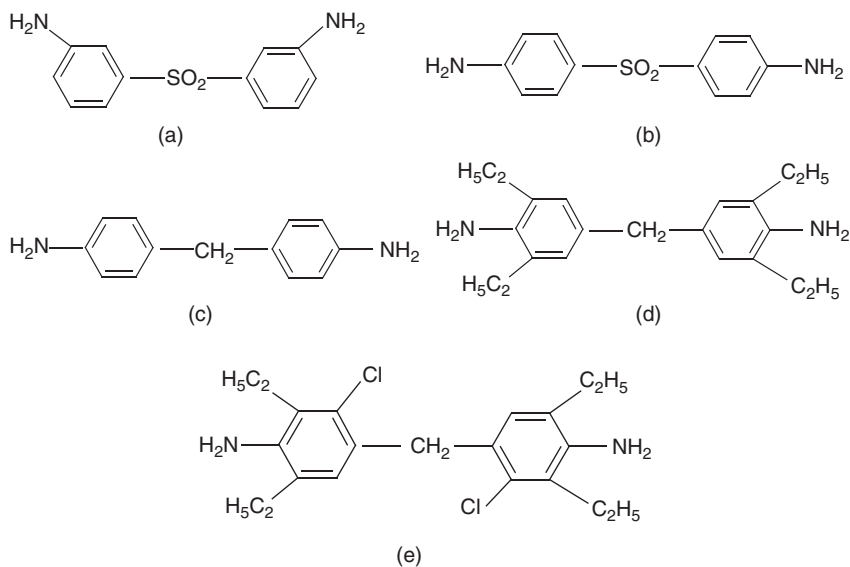
Figure 1.2 Structure of amine curatives. (a) 3,3′-Diaminodiphenylsulfone, (b) 4,4′-diaminodiphenylsulfone, (c) 4,4′-methylenedianiline, (d) 4,4′-methylenebis(2,6-diethylaniline), and (e) 4,4′-methylenebis (3-chloro-2,6-diethylaniline).

1.3.2.2 Mercaptans

The epoxy-mercaptan reaction is faster than the epoxy-amine reaction, especially at low temperatures; the reaction is accelerated by primary and secondary amines (Scheme 1.4).

$$RSH \ + \ CH_2—CH \overset{O}{\diagup} \longrightarrow RS—CH_2—CH \overset{OH}{|}$$
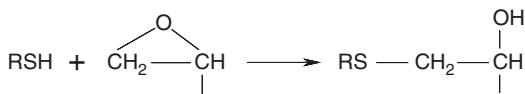
Scheme 1.4 Reaction between epoxy and thiol.

1.3.2.3 Isocyanates

Epoxy groups react with isocyanates or with hydroxyl groups to produce oxazolidone structures or a urethane linkage, respectively, which are depicted in Scheme 1.5. The main advantages are fast curing at low temperature, good flexibility, and solvent resistance. Moisture sensitivity and toxicity limit its application to power coatings and maintenance coatings.

$$R—N=C=O \ + \ CH_2—CH \longrightarrow$$
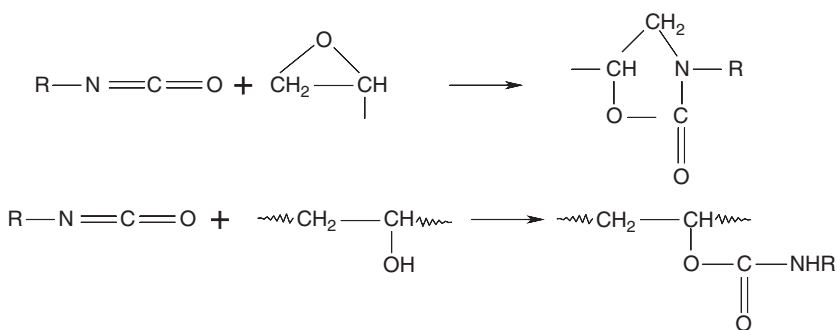
Scheme 1.5 Reactions between epoxy and isocyanate.

1.3.2.4 Carboxylic Acids

Carboxylic acids react with epoxy groups to form β-hydroxy propyl ester, which, in turn, reacts with another carboxylic acid to yield a diester. The hydroxyl ester can also undergo polymerization by the reaction of the secondary hydroxyl group with the epoxy. The possible reactions are summarized in Scheme 1.6.

1.3.2.5 Acid Anhydrides

Acid anhydrides react slowly with epoxy resins even at 200 °C [2, 3]. Both esterification and etherification reactions occur during the reaction. Secondary alcohols from the epoxy backbone react with the anhydride to form a half ester, which reacts with an epoxy group to give the diester. Esterification also occurs as a competing reaction between the secondary alcohol and epoxy group to form β-hydroxy ether. Basic catalysts favor esterification.

RCOOH + CH₂—CH—CH₂— ⟶ RCOO—CH₂CHCH₂—
(with epoxide O bridge on CH₂—CH, and OH below the product)

RCOOH + RCOO—CH₂CHCH₂— (OH) ⟶ RCOO—CH₂CHCH₂— (OOCR) + OH₂

RCOO—CH₂CHCH₂— (OH) + CH₂—CH—CH₂— (epoxide O) ⟶ RCOO—CH₂CHCH₂— (OCH₂CHCH₂—, OH)
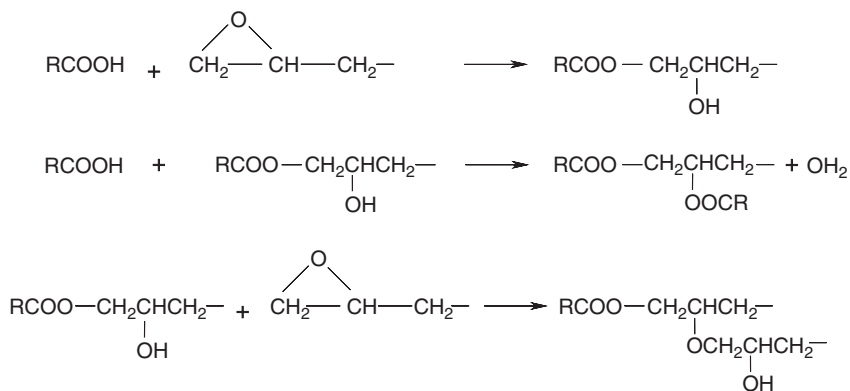
Scheme 1.6 Reactions between epoxy and carboxylic acid.

Other mechanisms are also reported [4–6]. Among this is a theory [7] based on the initiation by reaction of the tertiary amine with the epoxy group, giving rise to a zwitter ion that contains a quaternary nitrogen atom and an alkoxide anion. The anion reacts with the anhydride group to obtain a quaternary salt, the anion of which reacts fi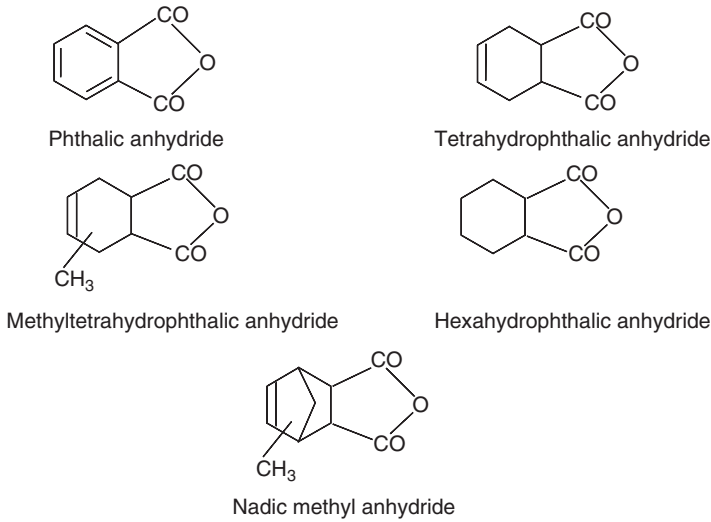rst with the epoxy group and then with the anhydride. Consequently, a diester is formed and the carboxyl anion is regenerated to reinitiate the cycle. The reactions are represented in Scheme 1.7.

R_3N^+ + CH₂—CH (epoxide O) ⇌ $R_3N^+CH_2CH—O^-$

$R_3N^+CH_2CH—O^-$ + R'C(=O)—O—C(=O)R' ⟶ $R_3N^+CH_2CH—O—C(=O)—R'$ + $R'COO^-$

$R'COO^-$ + CH₂—CH (epoxide O) ⟶ $R'COO—CH_2CH—O^-$

$R'COO—CH_2CH—O^-$ + R'C(=O)—O—C(=O)R' ⟶ $R'COO—CH_2CH—O—C(=O)R'$ + $R'COO^-$
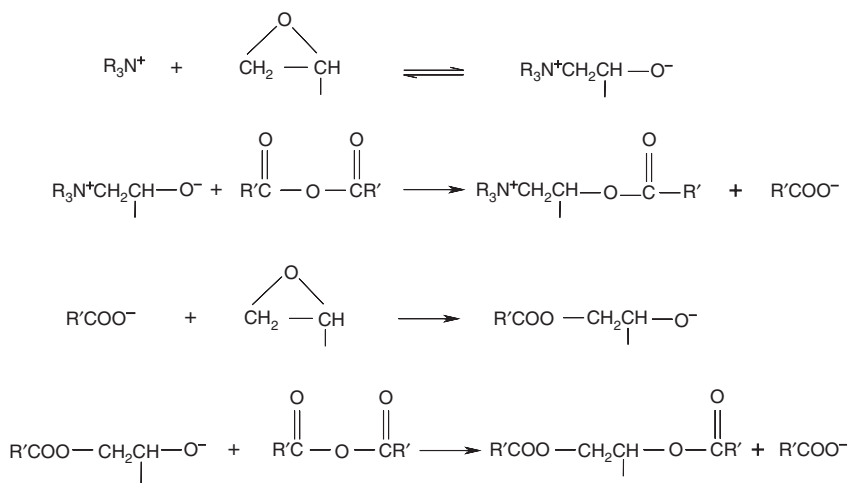
Scheme 1.7 Reactions between epoxy and anhydride the presence of tertiary amine accelerator.

Some of the examples of anhydride curatives are listed along with their structures (Figure 1.3). Good mechanical and electrical properties; low shrinkage; and viscosity, long pot life, and the slight color of anhydride curators supersede certain disadvantages such as long cure cycles at high temperature and brittle nature.

Phthalic anhydride

Tetrahydrophthalic anhydride

Methyltetrahydrophthalic anhydride

Hexahydrophthalic anhydride

Nadic methyl anhydride

Figure 1.3 Structure of anhydride curatives.

1.4
Different Curing Methods

Epoxy resin systems are cured by various methods. These include chemical curing (under ambient or increased temperature as with conventional thermal curing), microwave curing, and radiation curing (electron-beam (EB) and ultraviolet (UV) curing) [8]. The mechanism of curing methods differs in these methods. Thermal curing takes place through a step polymerization mechanism, which follows throughout the curing process, whereas radiation curing leads to chain polymerization involving initiation, propagation, and termination steps. The mechanical characteristics of the cured matrix differ in both cases.

1.4.1
Thermal Curing

In a study by Chekanov *et al*. [9], epoxy resin based on diglycidyl ether of bisphenol F (DGEBF) was cured using an aliphatic amine both frontally and in a batch-cure schedule. Both calorimetric and viscoelastic studies were performed to determine the glass transition temperatures (T_g), storage modulus (E'), and tan delta (tan δ) of cured samples. Tensile properties of both types of cured materials were almost similar. A certain research group [10] have *in situ* analyzed the dielectric properties and infrared (IR) spectroscopy with a view to comparing the reaction mechanism of thermally cured and microwave-cured epoxy resins. Gu *et al*. [11] have investigated the cure reaction of an epoxy system by thermal mode using differential scanning calorimeter (DSC) technology (both dynamic and isothermal) and reported that the curing involved two consecutive reactions. The heat of the cure reaction and

the overall kinetic parameters were determined. The reaction kinetics of two epoxy systems comprising stoichiometric amounts of DGEBA (diglycidyl ether of bisphenol-A)/DDS (diamino diphenyl sulfone) and DGEBA/*m*-PDA (*m*-phenylene diamine) were cured using microwave and thermal energy [12]. In the case of the DGEBA/*m*-PDA system, the rate constants of the primary amine-epoxy reaction were equal to that of the secondary amine-epoxy reaction and the etherification reaction was negligible for both modes of cure. On the other hand, for the DGEBA/DDS system, the reaction constant for the primary amine-epoxy reaction was greater than that of the secondary amine-epoxy reaction. The etherification reaction was negligible only at low cure temperatures for both cure methods. A time-temperature-transformation (TTT) diagram was also computed. At higher isothermal cure temperatures, the vitrification time was shorter for microwave curing.

The influence of a hyperbranched polymer on the thermal and photocuring of DGEBA epoxy resin has been investigated [13]. During thermal curing, the addition of a low amount of water slowed down the reaction, whereas further addition of water accelerated the process. During isothermal photocuring, water decreased the rate of the reaction at low temperatures, whereas it accelerated at high temperatures. Moreover, the addition of water decreased the glass transition temperature in both curing techniques. Thermal curing reactions of two multifunctional epoxy resins using the acetyl esterified calixarene (CA) derivatives as curing agents were analyzed by Xu *et al.* [14]. The glass transition and decomposition temperatures (T_d) were measured by DSC and thermogravimetric analysis (TGA), respectively. They were able to generate cured resins with excellent T_g using the CA derivatives and also concluded that the T_g of the cured resins was strongly affected by the degree of esterification of CA derivatives.

1.4.2
Microwave Curing

Microwave curing can reduce the time of the epoxy resin substantially. The cure times can be reduced to the range of minutes from hours through the use of microwave curing. Nightingale and Day [15] and Zainol *et al.* [16] have significantly reduced the cure time of carbon/epoxy composites and two bismaleimide resins, respectively, by using microwave curing. As the microwave energy is largely concentrated on the sample with greater efficiency, curing is highly economic for commercial manufacturing with shorter cure cycles [17–19]. In a study, Boey and Yap [20] examined the effect of microwave curing on a DGEBA epoxy resin with three different amine hardeners, namely, DDS, diamino diphenyl methane (DDM), and *m*-PDA; all led to faster curing compared to conventional thermal curing. The vitrification time for DGEBA epoxy resin with DDS and *m*-PDA hardeners was much shorter for microwave curing [12].

In a study by Yusoff *et al.* [21], a comparison has been studied between microwave heating and conventional thermal heating in fabricating carbon/epoxy composites by employing two types of epoxy resin systems using the resin transfer molding

(RTM) technique. The curing of the two composites, namely, LY5052-HY5052-carbon and the DGEBA-HY917-DY073-carbon composite systems, were studied at 100 and 120 °C. Better temperature control and faster rate of polymerization were attained with microwave heating for both epoxy systems. Both conventional and microwave heating yielded almost similar glass transition temperatures (120 °C for DGEBA systems and 130 °C for LY/HY5052 systems). In addition, microwave-cured composites had higher void contents than conventionally cured composites. Besides, C-scan traces showed that all composites, regardless of the methods of curing, had minimal defects.

Another interesting study explains the curing of an epoxy resin system using the microwave heating method [22], which also has been cured using the conventional oven method. The cured resins have been compared using a number of techniques. The mechanism of the reaction was found to be slightly different in the two cases. The epoxy-amine reaction occurs to a greater extent than the epoxy-hydroxyl reaction in the microwave-cured resin. This change in the reaction path did not change the dielectric properties for the thermally cured and microwave-cured materials. Owing to the difference in the network structure of the samples cured by the different methods, broadening of the glass transition for microwave-cured epoxy resins was observed.

In their work on low-temperature curing of epoxies with microwaves, Hubbard *et al.* [23] established that the variable frequency microwave (VFM) technology can cure epoxy materials in a wide variety of applications at much faster times (<10%) than that of convection or IR heating. Advantages of curing an epoxy at a low temperature with VFM are reduced shrinkage, reduced stress, and a more uniform film. As the entire adhesive is heated at the same instant with microwave energy, the network formation is uniform throughout the bulk. With convection heating, the outside of the film is heated sooner and to a higher degree than the material on the inside.

A comparative work on the mechanical properties of epoxy–anhydride resins, where the systems were cured by thermal and microwave heating, was reported by Tanrattanakul and SaeTiaw [24]. Two anhydride hardening agents and three types of accelerators were employed. Thermal curing was performed at 150 °C for 20 and 14 min for resins containing 1% and 4% accelerator, respectively. Microwave curing was carried out at a low power (207 or 276 W) for 10, 14, and 20 min. All mechanical characteristics including tensile, impact, and flexural properties, and viscoelastic properties were investigated. Equivalent or better mechanical properties were obtained by microwave curing, in comparison with those obtained by thermal curing. Microwave curing also provided a shorter cure time and an equivalent degree of conversion. The glass transition temperatures (tan δ) of the thermally and microwave-cured resins were comparable, and their activation energies were in the range of 327–521 kJ mol^{-1}.

Chang *et al.* [25] developed two nanocomposites to study the dielectric properties. They developed multiwalled carbon nanotube (MWCNT)/epoxy (EP) composites using microwave curing (m-MWCNT/EP) as well as by thermal curing

(t-MWCNT/EP). Results show that the two types of composites have greatly different dielectric properties. With the same content of MWCNTs, the m-MWCNT/EP composites show a much higher dielectric constant and lower dielectric loss than the t-MWCNT/EP composites because of their different structures. Further study showed that it is possible to control the dispersion and spatial distribution of carbon nanotubes using a different curing technique to obtain high-performance composites with unexpected dielectric properties, especially those with a very high dielectric constant and a low dielectric loss.

1.4.3
Radiation Curing

1.4.3.1 Electron Beam Curing

EB curing of composites is an innovative processing method, begun in the late 1970s, that uses high-energy electrons from an accelerator to initiate polymerization and cross-linking of a matrix resin. Reduced cure time, low-temperature cure, greater design flexibility, and unlimited material shelf life are some of the advantages of this method compared to the conventional thermal curing. As a low-cost and nuisance-free technology, the method has been widely used in recent years [26–28]. The effect of the EB on the fiber and its sizing has been studied by Saunders and Singh [29–31] based on epoxy acrylate composites.

EB curing of filament-wound epoxy acrylates and bismaleimide resin composites has been studied by Béziers since the 1970s [32]. The curing of acrylates, being a vinyl monomer, normally proceeds through a free radical mechanism that is sensitive to oxygen. This leads to high shrinkage and high moisture absorption and ultimately to substandard mechanical properties. The cationic curing of epoxy resin by using appropriate onium salts as initiators [33, 34] were analyzed by Crivello *et al.* In fact, a variety of epoxy resin matrixes have been cured using EB considering its excellent properties and processing characteristics [35–38]. The majority of research studies focus on the development of resin systems and optimization and not on the fundamental theory of EB curing. However, a few studies are related to the mechanism of EB curing and its dependence on materials parameters [39–42]. In this context, the mechanism proposed by Hult and Sundell [43], Ledwith [44], and Crivello *et al.* [36] on EB-induced cationic polymerization in the presence of onium salt photoinitiators is recommendable, in spite of the lack of dependable analysis and validation for the basic reaction process.

In a study by Sui *et al.* [45], the effects of different initiators and diluents on Shell Epon 828 radiation reaction were discussed, and these were also studied by heat treatment. The experimental results proved that cationic photoinitiators can initiate EB radiation curing of epoxy resin, while conventional heat-cured systems are not always suitable for the EB curing. The diluents generally decreased the curing degree of the resin, which was not prominent for reactive diluents. The proposed mechanism was the cationic ring-opening polymerization process followed by the production of protonic acid that can initiate a polyreaction. The characteristics of the cured system consisted of many lamellar structures.

Alessi *et al.* [46] studied the hydrothermal aging of epoxy thermoplastic blends, used as matrices for carbon fiber composites, cured by EB. Irradiation has been carried out at mild temperatures. Radiation-cured epoxy-based matrices have been subjected to a thermal and moisture absorption aging treatment. The vitrification phenomenon specifically characterizes the aging response of the material. Very complex chemical and physical phenomena occur during aging, causing further curing and degradation reactions and plasticization. The mechanical fracture behavior was affected by curing and degradation reactions and has been discussed on the basis of the different curing degree and the developed morphology. A balanced effect between the embrittlement and toughness, which are due to post-curing reactions and separation phase phenomena, respectively, was for the system that showed the best mechanical behavior after aging.

1.4.3.2 Gamma Ray Irradiation

Surface properties of polymeric materials, such as films, fibers, powders, and molded objects [47], can be altered by a new technique using irradiation-induced grafting. This can induce chemical reactions at any temperature without any catalyst in the solid, liquid, and gas phase, and is a safe method against environmental pollution. This technique has been applied to carbon fibers [48]. Epoxy resin and chloroepoxy propane reacted with carbon fibers by a co-irradiation grafting method and acrylic acid was graft-polymerized onto the fiber surface via a pre-irradiation grafting method. The roughness, amount of oxygen-containing functional groups, and surface energy were all found to increase significantly after irradiation grafting. The irradiation grafting, the mechanism of which was proposed by radical reactions, improved marginally the tensile strength of carbon fibers. Moreover, it was reported that the interlaminar shear strength of treated carbon fiber/epoxy was enhanced by at least 17.5%, compared with that of untreated carbon fiber/epoxy. This has been suggested as a method to modify the physicochemical properties of carbon fibers and to improve the interfacial adhesion of composites.

The curing of certain systems, composed of DGEBA and DGEBF as epoxy resins and triarylsulfoniumhexafluoroantimonate (TASHFA), and triarylsulfonium hexafluorophosphate (TASHFP) as initiators, was investigated using EB and γ-ray irradiation [49]. The chemical and mechanical characteristics of irradiated epoxy resins were compared after curing up to 50 kGy in N_2 and air atmosphere. The effect of oxygen on the radiation curing of epoxy resin was established. The chemical structures of cured epoxy were characterized by Fourier transform near-infrared (FTNIR). The gel fraction and the stress at yield of epoxy resins irradiated by E-beam and γ-ray in N_2 atmosphere were also compared with those of epoxy resins irradiated by E-beam and γ-ray in air. The degree of curing of epoxy resins irradiated in N_2 regardless of E-beam and γ-ray was higher than that of epoxy resins irradiated in air. The gel fraction of two epoxy resins increased markedly with the increase in dose, and the values of the gel fraction of DGEBF samples were higher than that of DGEBA. The gel fraction of DGEBF irradiated by γ-ray was higher than that of the epoxy irradiated by E-beam at the same dosage. Therefore, the thermal stability

and stress at yield of epoxy resins irradiated in N_2 were higher than that of epoxy resin irradiated in air.

1.5
Curing of Epoxy Resins: Structure–Property Relationship

During curing, epoxy resin is converted into a hard infusible material as a result of cross-linking reactions, which ultimately lead to a network structure. Curing agents or hardeners are widely known to promote curing of epoxy resins. Curing can occur by either homopolymerization initiated by a catalytic curing agent or by a polyaddition/copolymerization reaction with a multifunctional curing agent. Initially, linear growth of the chain occurs followed by branching and finally leads to cross-linking. This irreversible reaction leads to an increase in molecular weight, which results in the physical transformation of the system from a viscous state to an elastic gel. The temperature at which this transformation occurs is known as *gel point*, which is critical in polymer processing as the polymer will not flow beyond this limit, and hence this temperature determines the processability of the system. Gelation mainly depends on the functionality of components, stoichiometry, and reactivity of the system, and does not inhibit the curing reaction. As curing proceeds further, the viscosity of the system increases because of the increase in molecular weight, and the reaction becomes diffusion controlled and eventually quenched as the material vitrifies [50–52]. This is again another physical transformation and occurs during the curing reaction called *vitrification of the growing chain* or *network*. During this conversion, a substantial increase in cross-link density, glass transition temperature (T_g), and ultimate properties takes place. The change in the state of the system from viscous liquid to elastic gel and finally to glassy solid begins to occur as the T_g of the developing network becomes equal to the curing temperature. At the vitrification point, the reaction shifts from chemically controlled to a diffusion-controlled state. The net changes during the curing of the thermoset can be expressed in terms of a TTT diagram. The S-shaped gelation curve and the vitrification 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 temperature of the unreacted resin mixture, T_g, the glass transition temperature of the fully cured resin, gel T_g is the glass transition temperature of the resin at its gel point. The temperature region below the glass transition of the unreacted resin (T_{g0}) represents the solid state and hence the reaction is believed to occur very slowly. This temperature region defines the storage temperature for unreacted resins. The reaction initiates above T_{g0} and continues till the rise in T_g becomes equal to the cure temperature at which vitrification will commence. Thereafter, the reaction becomes diffusion controlled and is eventually quenched when vitrification is complete. In a stage between gel T_g and T_g, gelation precedes vitrification, and a cross-linked rubbery network forms and grows until its T_g coincides with the cure temperature. The reaction will be quenched at this stage. T_g is the minimum cure temperature required

for the completion of cure. Above T_g, the thermoset will remain in the rubbery state, unless other oxidative cross-linking or chain scission occurs. Gelation and vitrification determine the handling, processing, and development of the ultimate properties of the cured resin.

1.6
Toughening of Epoxy Resin

Epoxy resins are characterized by their outstanding properties such as high thermal and corrosion resistance, good thermomechanical properties, and adhesion to various substrates. In spite of these desirable properties, the major disadvantages are their low toughness and poor crack resistance and brittle nature at room temperature. Hence, epoxy materials are to be toughened for many end-use applications. In a broader sense, toughness refers to the measure of the materials' resistance to failure, without much compromise in their enviable thermomechanical properties.

1.6.1
Different Toughening Agents

The most important method for toughening epoxy resins is the incorporation of a dispersed toughener phase in the epoxy matrix. Various important toughener phases are mentioned here, the details of which were described in the preceding sections. The various toughener phases include liquid rubbers, rigid particulates, core–shell particles, and thermoplastics.

1.6.1.1 Liquid Elastomers for Toughening Epoxy Matrices

Reactive liquid rubbers that are initially soluble in the base epoxy resin [53–55] as well as rubbers that are initially immiscible [56, 57] in the resin are used as toughening agents. In the former case, phase separation of rubber takes place during cure, whereas in the latter case the rubber phase will be in the precipitated state. Nevertheless, this type of rubbers generates heterogeneity and hence a very low content is enough for toughening. The former type of rubbers is considered as the best modifiers. On the other hand, rubbers with different functionalities, which permit to form covalent interactions at the epoxy interface, normally serve as the best tougheners. When low-modulus rubber particles are dispersed into the brittle resin matrix, the force that induces and propagates cracks is dissipated by the rubbery phase and prevents the catastrophic failure of the matrices. Significant increase in peel strength, impact properties, and fracture toughness has been achieved without much loss in tensile and thermal properties.

Major liquid rubbers used as tougheners are carboxyl-terminated butadiene-*co*-acrylonitrile (CTBN) [58–66], hydroxyl-terminated polybutadiene (HTPB) liquid rubbers [67–73], epoxy-terminated liquid rubbers [74–78], amine-terminated butadiene acrylonitrile (ATBN) rubbers [78–82], acrylic elastomers [83–87], and other

synthetic elastomers [88–93]. The details of liquid elastomer modifiers are explained in the preceding chapter.

1.6.1.2 Rigid Crystalline Polymers

Epoxies can be toughened using rigid crystalline polymers, even though it is difficult to visualize how such rigid crystalline domains could provide an efficient toughening mechanism. One such possible mechanism could operate by phase transformation, which is well known for ceramic materials [94]. In zirconia-containing ceramics [95–98], the metastable tetragonal phase of zirconia is incorporated into the ceramic, and under the influence of the stress field around the crack tip, this phase transforms to the stable monoclinic phase. Compressive stresses are set up on one of the phases as the monoclinic phase is less dense than the tetragonal phase. This superposes on the tensile stress field ahead of the crack tip producing shear deformations, which result in the increase in critical fracture energy.

1.6.1.3 Hygrothermal Toughening Agents

Functional oligomers for toughening epoxy resins exhibiting low water absorption characteristics and suitable for high-temperature applications are reported by many researchers. Several amine-terminated silicone oligomers were used by Takahashi *et al.* [99] to toughen epoxy resins for its application as encapsulants for semiconductor-integrated circuit devices. Siloxane oligomers offer advantages such as lowering T_g values for the dispersed rubbery particles and good thermal stability. Moreover, siloxane oligomers exhibit good weatherability, oxidative stability, high flexibility, and moisture resistance [100]. Further, siloxane-modified epoxy leads to the formation of a very hydrophobic and chemically bound surface coating [101] and improves the wear properties [102].

1.6.1.4 Core–Shell Particles

Core–shell rubber particles are a type of preformed thermoplastic particles with a glassy shell that can be designed to adhere better with resin and a rubbery core to improve toughness. Reactive core–shell-type hyperbranched block copolymers with onion-like molecular architecture were used as flexibilizers and toughening agents for thermosets. The system was reported to achieve good miscibility, low viscosity, and better interfacial adhesion [103]. Preformed particles will not undergo phase separation and will remain in the shape in which they were added to the neat resin or composite. Consequently, these particles may be developed before the resin formulation and then added to the thermosetting resin or developed *in situ* (during resin formulation) before the resin formulation is catalyzed or cured. An important characteristic of core–shell particles as tougheners for epoxies is the role of the particle/epoxy interface [104]. A discrete interface is generated between the particles and the matrix epoxy by the shell polymer of core–shell particles. However conflicting, there are many studies regarding the effect of shell composition on toughening of epoxies.

1.6.1.5 Nanoparticles for Epoxy Toughening

Nanoparticulate composites are observed to be impact tougheners for epoxy matrices. They showed superior material properties than microscale fillers [105] for toughening. In a noticeable work, Wetzel and coworkers [106] have modified epoxy matrix with various amounts of micro- and nanoscale particles of $CaSiO_3$ (4–15 µm) and alumina (Al_2O_3) (13 nm) for reinforcement purposes. The influence of these particles on the impact energy, flexural strength, and dynamic mechanical thermal properties were investigated. The analyses showed that the stiffness, impact energy, and fracture strain of the epoxy matrix were improved by a low-level addition (1–2 vol%) of alumina particles. Similarly, only 2 vol% of $CaSiO_3$ was enough to improve the flexural modulus and wear resistance of the matrix epoxy.

Many other particles such as nanostructured TiO_2 [107], nano-ZnO [108] and nano-SiO_2 [109], and nanoclay [110] were dispersed in epoxy resin to improve both the mechanical and the thermal properties because of their large specific surface area.

It was found that reinforcement with nanoparticles improved the fracture toughness at room temperature, but decreased the fracture toughness at the cryogenic temperature in spite of their toughening effect.

1.6.1.6 Thermoplastic Modification of Epoxy Resin

Thermoplastics are one of the best toughening agents for thermosetting polymers, particularly for epoxies, as they will not reduce the glass transition of the cured network. Detailed studies have been conducted on mechanical properties, fracture behavior, phase separation, and morphology of polysulfone (PSF)-modified epoxies, and perhaps this is believed to be the most widely studied thermoplastics employed for toughening of epoxy resin [111]. Hedrick *et al.* [112] employed phenolic hydroxyl and amine-terminated PSF oligomers to toughen epoxies and observed an increase in fracture toughness by 100% without any loss in thermal properties. Other researchers [113] have also noticed fracture toughness and fracture energy increase in PSF-modified epoxy resins. Cure kinetics have been analyzed in detail by different analytical techniques [114–116] on PES (poly(ether sulfone)) and PSF-modified epoxy resins cured with DDM hardener and an autocatalytic model was used to explain kinetics. They have also studied rheological changes of PES-modified epoxies and explained the earlier phase separation of PES as due to its higher viscosity compared to that of the resin [117, 118].

Functionally terminated polyether ether ketone (PEEK) is a versatile modifier for epoxy. It is characterized by toughness, stiffness, thermo-oxidative stability, chemical and solvent resistance, electrical performance, flame retardant nature, and retention of physical properties at high temperature [119]. Fracture and thermal properties of DDM-cured phenolphthalein PEEK, and polyetherketone cardo (PEK-C)/epoxy blends showed property reduction with the addition of a modifier, whereas a series of amine-terminated oligomers based on *tert*-butyl hydroquinone (TBHQ) and methyl hydroquinone (MeHQ) exhibited toughness improvement [120]. This was caused by the final morphology, that is, the homogeneous nature in the former case [121] changed to a phase-separated one in the latter case [122–124].

1.6.1.7 **Block Copolymers as Modifiers for Epoxy Resin**

Block-copolymer-modified epoxy resins have generated significant interest because it was demonstrated that the combination could lead to nanostructured thermosets. Amphiphilic block copolymers self-assemble to form a variety of well-defined ordered and disordered microstructure morphologies such as spherical, cylindrical, lamellar, and gyroid phase [125, 126]. Studies show that introduction of block copolymers in epoxy resin can greatly improve mechanical and physical properties including tensile, flexural, impact, wear resistance, thermal resistance, and performance [127, 128]. The fracture toughness, modulus, and other thermomechanical properties of the nanostructured blends prepared using block copolymers are generally higher than that of pristine epoxy resin [129–132]. In addition, with the use of block copolymers as the toughening agents, the size of the resulting features can be controlled and are typically on the order of tens of nanometers.

1.7
Rubber-Modified Epoxy Resin: Factors Influencing Toughening

Liquid rubbers are widely used as potential modifiers for epoxy toughening. Commonly employed liquid rubbers are copolymers of butadiene and acrylonitrile. Rubbers with different functionalities, which permit to form covalent interactions at the epoxy interface, normally serve as the best tougheners. When low-modulus rubber particles are dispersed into the brittle resin matrix, the force that induces and propagates cracks is dissipated by the rubbery phase and prevents the catastrophic failure of the matrices. Significant increase in peel strength, impact properties, and fracture toughness has been achieved without much loss in tensile and thermal properties.

1.7.1
Concentration Effects

Increasing the concentration of the rubber content reduces the tensile strength and the modulus of the brittle matrix. This is due to the plasticization of the matrix by the incorporated rubber. In the case of polyamide (PA)-ethylene-propylene-diene monomer (EPDM) blend, the relationship between Izod impact strength and rubber content is linear up to 30% of rubber and shows a decrease on further inclusion of rubber [133, 134].

1.7.2
Particle Size and Distribution of Rubber

The graph of toughness versus rubber particle size gives a maximum toughness for an optimum particle size [135, 136]. The optimum particle size depends on the entanglement density of the matrix and the nature of rubber [137]. This decreases

as entanglement density increases and the matrix becomes more ductile. Bimodal-sized particles are particularly more successful in the toughening of polymers [138] because of the balance of crazing and yielding that occurs in the fracture of the material [139].

The rubbery phase can act as an effective stress concentrator and enhances both crazing and shear yielding in the matrix. The optimization of the size distribution of the dispersed phase depends on the deformation mechanism of the matrix. Crazing mechanism is better suited to a higher particle size than a shear yielding mechanism. The size distribution depends on the processing conditions. According to Taylor's relationship (Equation 1.1), the dispersion process can be described as

$$d = \left(\frac{\sigma_{i}}{\gamma \eta_{m}} \right) f \left(\frac{\eta_{d}}{\eta_{m}} \right) \tag{1.1}$$

where η_{m} and η_{d} are the viscosities of the matrix and the dispersed phase, respectively. σ_{i} is the interfacial tension, d the diameter of the dispersed phase, and γ the shear rate. The shear rate is inversely proportional to the particle size. Furthermore, related to the particle size, it has been observed that coalescence of the dispersed phase during blending can be prevented only if the interfacial tension between the phases is low [140].

1.7.3
Effect of Temperature

Temperature has a significant effect on impact behavior in rubber-toughened polymers. At very low temperatures, the rubber phase is below its T_{g} and is effectively a rigid filler with little or no effect on the host polymer. The rubber-toughened polymer behaves as a brittle glass. Bucknall [141] was able to prove this in a series of poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) polymers.

1.7.4
Effect of Rubber

The effect of rubber is difficult to evaluate as it depends on the mechanism by which the toughening effect is believed to occur. Oxborough and Bowden [142] estimated the stress concentration factors around low-modulus spheres. They have observed that the maximum stress concentration at the particle–matrix interface occurred when $G_{R}/G_{M} = 0.1$, where G_{R} and G_{M} are the shear moduli of the rubber and matrix, respectively. For $G_{R}/G_{M} < 0.1$, there will be no improvement in toughening. Bucknall [143] stated that cross-linking the rubber is desirable, as this would allow rubber to reach high strains by fibrillations, and the fibrils would have high strength.

1.7.5
Interfacial Adhesion

From the work of Wu [144], in the study of the polyamide matrix, it was evaluated that the minimum surface adhesion necessary for toughening was about 10^3 J m^{-2}, which is typical for van der Waals adhesion. The interfacial adhesion does not influence yield stress and Young's modulus [145]. Wu [146] found that the interfacial energy for adhesion was the same as the tearing strength of the rubber (10^3 J m^{-2}), which meant that during fracture the rubber failed by cavitation rather than by debonding. The latter occurred only in the unreactive polyamide-rubber blends.

1.8
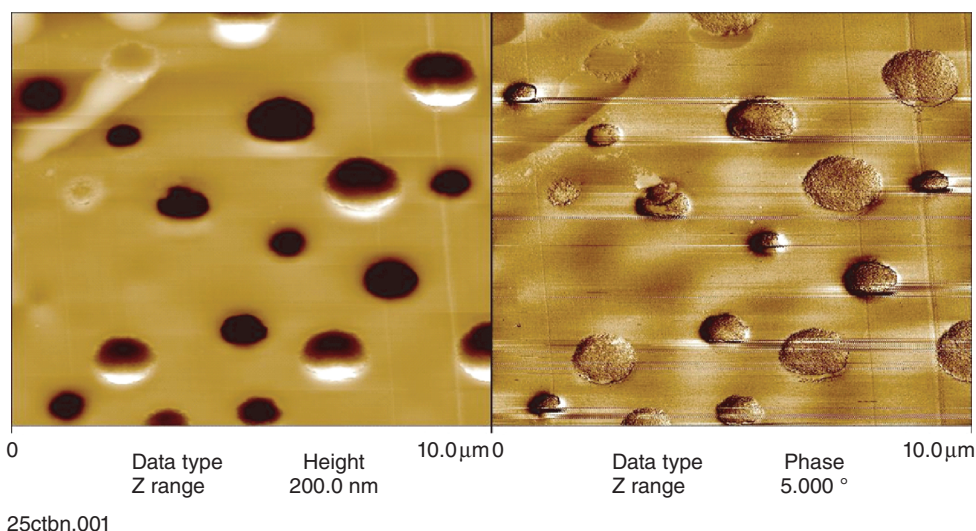## Toughening Mechanisms in Elastomer-Modified Epoxy Resins

This section deals with different energy dissipation mechanisms that contribute to the enhanced crack resistance of elastomer-toughened epoxies.

1.8.1
Particle Deformation

Merz *et al.* [50] are the pioneers who proposed a theory of the mechanism of toughening in rubber-modified plastics. They observed that in high-impact polystyrene (HIPS) an increase in volume and a marked increase in whiteness or opacity accompanied elongation of the material, which is associated with the production of a multiplicity of tiny cracks. They suggested that the function of the rubber particles is to bridge the cracks and thus prevent the cracks from growing to a catastrophic size. Later, Beaumont and coworkers [51, 147] proposed a toughening mechanism that emphasizes the role of deformation and fracture of rubber particles and a model similar to Merz *et al.* [50]. The underlying principle of the theory is that the rubber particles bridge cracks as they propagate through the material. The increase in toughness of the material is due to the amount of elastic energy stored in the rubber particles during stretching, which is dissipated irreversibly when the particles rupture. Nevertheless, this mechanism could not explain the phenomenon of stress whitening in rubber-modified epoxies [148–151].

Thus, while ligaments of rubber spanning a crack must reduce the stress concentration at the crack tip and their fracture involves some energy dissipation, it appears that this mechanism is usually only of secondary importance in increasing the toughness of such multiphase polymers. The deformation mechanisms in the matrix, enhanced by the presence of the second phase improve toughness. Figure 1.4 illustrates the transmission electron micrograph of the multiphase microstructure of a rubber-modified epoxy. The rubber employed is CTBN (15 phr).

| 0 | Data type
Z range | Height
200.0 nm | 10.0 µm | 0 | Data type
Z range | Phase
5.000 ° | 10.0 µm |

25ctbn.001

Figure 1.4 Transmission electron micrograph of a thin section of a rubber-modified epoxy polymer [152].

1.8.2
Shear Yielding

Extensive shear yielding accompanying the fracture process is a major toughening mechanism in many tough single-phase polymers, and this mechanism may be greatly enhanced in many brittle polymers by the presence of a second particulate phase, especially when it is rubbery in character. The initial evidence of the importance of shear yielding mechanisms in multiphase plastics came from mechanical property and optical microscopic studies [153] on certain ABS materials. These studies revealed that in uniaxial tensile tests, shear deformation had occurred and that the matrix had undergone localized plastic deformation around virtually every rubber particle.

According to Newman and Strella [153], the principal function of the rubber particles is to produce sufficient triaxial tension in the matrix to increase the local free volume and hence enable extensive shear yielding and drawing of the matrix to initiate. They identified that spherical voids that have a higher stress concentration at the equator could also initiate shear yielding of the matrix. Later, Petrich [154] supported this mechanism by suggesting that a change in the refractive index of the oriented rubber particles by birefringence is the major cause of stress whitening. Haaf *et al.* [155], from microscopical and light scattering analysis, arrived at the conclusion that the dispersed rubber phase initiated micro shear bands at an angle of 55–64° to the direction of the applied stress, depending on the particle size of the modifier in the blends. They also found that cavities were initiated in the rubber particles and were aligned along the shear bands, an obvious explanation for the

stress whitening. Thus, shear yielding accompanied by initiation of cavities leads to toughening.

Enhanced plastic deformation in the multiphase material is evident by comparing Figure 1.5a,b and observing the greatly increased surface roughness and drawn ridges of epoxy polymer in Figure 1.5b. The ripples in Figure 1.5a are due to the brittle fracture of the network, which accounts for its poor impact strength, as there is no energy dissipation mechanism operating here. Further, the localized nature of the plastic shear bands, visible as furrows running almost parallel to the principal tensile stress (i.e., in the direction of maximum shear stress) is illustrated in Figure 1.5b.

1.8.3
Crazing

Studies on various rubber-toughened polymers using transmission electron microscopy (TEM) confirmed that crazes frequently initiate from rubber particles [156–165]. In rubber-toughened polymers too, under suitable conditions [165], rubber particles contain occlusions of glassy polymer. The addition of 5–10 wt% of rubber generates the occluded structure of rubber particles, which can typically increase the rubber phase volume to 20–30%. This structure also has consequences for the mechanism of crazing. Bucknall and coworkers [166–168] defined the role of rubber particles as initiators and terminators of crazes. Under applied tensile stress, crazes are initiated at points of maximum triaxial stress concentrations, which are near the equator of the rubber particles. The crazes then grow approximately normal to the maximum applied stress, although deviations may occur because of the interactions between the particles. In addition, rubber particles are craze terminators, preventing the growth of very large crazes. Inclusion of rubber particles generates a large number of small crazes, in contrast to the small number of large crazes in the absence of rubber particles in the same polymer. Further studies [169, 170] have optimized the size of particles as 2–5 μm

(a) (b)
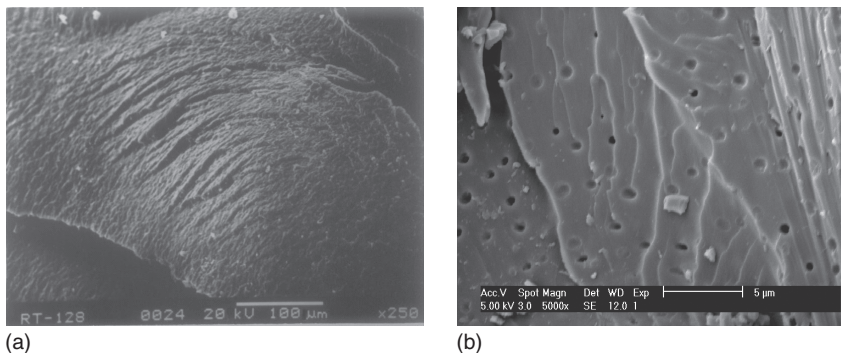
Figure 1.5 Scanning electron micrographs of fracture surfaces (test temperature, 23 °C). (a) Unmodified epoxy polymer and (b) rubber-toughened epoxy polymer (10 phr) [152].
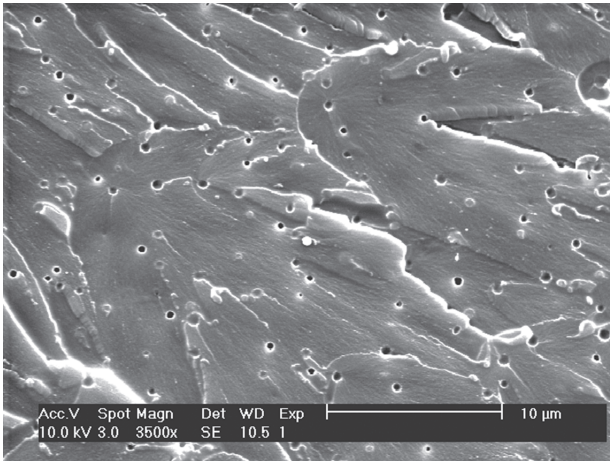
Figure 1.6 Scanning electron microscope (SEM) micrographs of 5 phr CTBN-modified epoxy at $T_{cure} = 140\,°C$ [152].

for maximum toughness. Donald and Kramer [171] suggested that crazes are rarely nucleated from particles smaller than about 1 μm. Figure 1.6 illustrates the crazes developed in a rubber-modified epoxy system cured at 140 °C.

1.8.4
Simultaneous Shear Yielding and Crazing

In many toughened polymers, both shear yielding and crazing mechanisms operate simultaneously, for example, in ABS and rubber-toughened polyvinyl chloride (PVC). In HIPS, crazing is usually the dominant mechanism, while shear yielding is generally the major mechanism in rubber-toughened epoxy resins. However, the microstructural features of the toughened polymers, such as particle size, will affect the balance of the mechanisms, as with the rate and temperature of test.

Bucknall and coworkers [166, 168] observed that shear bands are formed approximately along the planes of maximum resolved shear stress and therefore intersect crazes at an angle of about 45°. This led them to suggest that in addition to increasing the energy absorption, shear bands act as effective terminators for growing crazes. Hence, in those polymers where shear banding occurs in addition to crazing, the necessity for relatively large rubber particles to function as craze terminators is removed and the size of the rubber particle need no longer be increased via subinclusions.

Donald and Kramer [171, 172] believed that relatively large occluded particles can effectively initiate and prevent the premature breakdown of crazes, while small rubber particles can only initiate shear bands. Also, small rubber particles may even assist crack breakdown, especially the crazes formed in the matrix are relatively weak. A complex balance of these factors such as particle sizes and

internal structures determine maximum toughness for various rubber-modified polymers.

1.8.5
Crack Pinning

Lange and Radford [173] reported that fracture energy of thermosetting epoxy could be increased by rigid particulate fillers and the toughness enhancement depends on both volume fraction and particle size of the filler; they proposed [174] crack pinning as the major toughness mechanism. This arises from interactions between the moving crack front and second phase dispersion. Lange, from fractographic studies, was able to show that as a moving crack front interacts with inhomogeneities present in the brittle matrix, tails, or steps, are formed at the rear of the inclusion as a result of the meeting of the two arms of the crack front from different fracture planes.

It is important to note that this mechanism is more suited for increasing the toughness of relatively brittle polymers containing rigid particulate fillers.

1.8.6
Cavitation and Rumples

The occurrence of cavitation in the presence of shear yielding has been observed in rubber-toughened amorphous and crystalline polymers [149, 150, 175–177], whereas it is absent in untoughened matrices. Shear yielding is not accompanied by expansion of the matrix, but in rubber-toughened blends the presence of the rubber gives rise to volume increase if the strain rate is sufficiently high [178]. This expansion is caused by the cavitation of the rubber particles [179]. The rubber particles dissipate the bulk strain energy by cavitation, leading to a reduction in local hydrostatic stress and a reduction in the yield stress of the blend. Thus, shear band formation is enhanced by voids in the matrix caused by the cavitated rubber particles [180, 181].

In the presence of a sharp crack, a triaxial stress exists ahead of the crack tip, giving rise to rapid cavitation and growth of the resulting voids [178, 179]. A zone of voids and shear bands is formed ahead of the crack tip on the opening up of the crack faces. This void zone blunts the crack tip and further tension causes an even larger plastic zone to form. The increasing size of this large plastic zone acts as the principal toughening mechanism [178, 179]. The rubber particles toughen by acting as stress concentrators by enhancing shear yielding. The cavitation of rubber particles gives rise to more shear yielding. Also, cavitation stress depends on the modulus of the rubber [182]. Further, the occurrence of a rumpled surface was observed in many modified polymers [183, 184].

The cavitation mechanism of the rubbery particles is responsible for the apparent holes in the scanning electron micrographs. Such features are particularly pronounced at higher test temperatures when plastic deformation of the matrix can occur more easily and the rubber particles more readily cavitate. The higher magnification (Figure 1.7) confirms that the holes are filled with rubber [54]; in
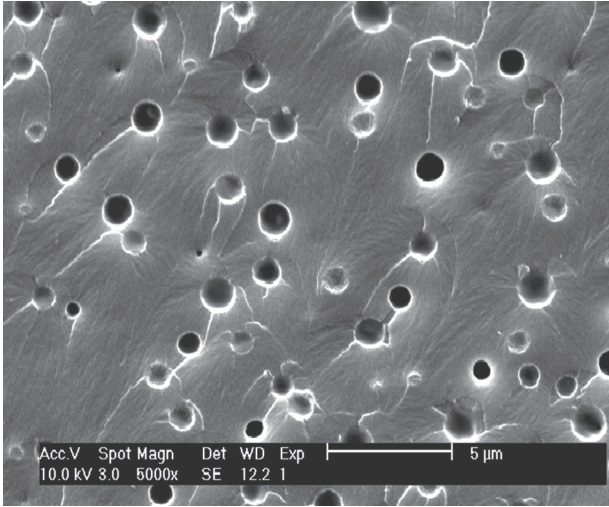
Figure 1.7 SEM micrographs of 15 phr CTBN-modified epoxy at $T_{cure} = 140\,°C$ [152].

some instances, an internal void or tear in the rubbery particle can be seen clearly. The initiation and growth of voids in the rubbery particles gives rise to the stress whitening, which is often observed before the crack tip and on the fracture surfaces.

1.9
Quantitative Assessment of Toughening Mechanisms

According to Kunz-Douglas *et al.* [51] toughness enhancement due to rubber particles primarily depend on the degree of elastic energy stored in them during loading of the two-phase system. A quantitative model has been proposed, which can be expressed mathematically as

$$G_{1C} = G_{1ce}(1 - V_p) + \left(1 - \frac{6}{\lambda_t^2 + \lambda_t + 4}\right) 4\gamma_t V_p \tag{1.2}$$

where V_p is the volume fraction of the rubber particles, γ_t is the particle tear energy, λ_t is the rubber particle extension ratio at failure, and G_{1ce} is the fracture energy of the epoxy matrix. According to this mechanism, the enhancement of toughness is solely due to elastomeric particles and any interaction between elastomeric phase and matrix is not considered.

Lange [174] proposed a model expression for fracture energy (G_{1C}) for the crack-pinning mechanism, which normally occurs in the thermoset matrix with particulate fillers. As the crack begins to propagate within the material, the crack front bows out between the second phase dispersion while still remaining pinned at all the positions where it has encountered the filler particles. During the initial stage of crack propagation, a new fracture surface is formed and the length of

the crack front is increased because of its change of shape between the pinning positions. The fractional increase in crack front length depends on the particle spacing. Using the crack growth criterion, Lange [174] proposed an expression for fracture energy (G_{1C}) as

$$G_{1C} = G_{1C}(\text{matrix}) + 2\frac{T_L}{d_p} \tag{1.3}$$

where G_{1C} is the fracture energy of the filled material, $G_{1C}(\text{matrix})$ is that of the unfilled matrix, T_L is the line energy per unit length of the crack front, and d_p is the distance between the particles. Thus, the fracture energy will increase as particle spacing decreases.

1.10
Introduction of Chapters

Chapter 2 discusses various functionalized liquid rubbers employed to toughen epoxy resins.

Reactive liquid rubbers may be initially soluble or partially soluble in the base epoxy resin. However, as the cure reaction progresses, the molecular weight increases, and the rubber is no longer soluble in the resin. This necessitates phase separation at some stage of the cure reaction. Rubbers that are not completely miscible in the resin initially are also used as toughening agents. Nevertheless, this type of rubbers generates heterogeneity and hence a lower content is enough for toughening. The former type of rubbers is considered as the best modifiers.

Chapter 3 introduces nanostructured epoxy blends, their methods of preparation, nanostructure formation by self-assembly, and properties with special reference to morphology characteristics. Various methodologies adopted for the preparation of epoxy resin-liquid rubber blends are discussed in Chapter 4. The cure details and measurements of cure kinetics of epoxy – rubber systems are discussed in Chapter 5. Chapter 6 is devoted exclusively to discuss different theoretical modeling of cure process. The thermodynamics of phase separation behavior and different aspects of the same are discussed in Chapter 7. Various microscopic techniques to analyze the details of demixing phenomenon and *in situ* phase growth of epoxy-rubber blends are also discussed in-depth.

Chapter 8 is devoted to a discussion on various techniques to follow the generated morphology in the modified matrix of epoxies. Chapter 9 is dedicated to the role of pressure–volume–temperature (PVT) analysis in modified epoxies to follow the phase growth behavior. Chemorheological aspects and physical transformations during the curing of elastomer-incorporated epoxies are discussed in Chapter 10.

A comprehensive coverage of the viscoelastic behaviors of rubber-modified epoxies are analyzed in Chapter 11. Analysis of miscibility aspects and phase separation behavior characteristics using scattering techniques are explained in Chapter 12. The variation in mechanical properties including the fracture toughness characteristics and interpretation with respect to the developed morphology are

included in Chapter 13. Thermal behavior of modified epoxies is covered in Chapter 14. Chapter 15 discusses the dielectric properties of elastomer-modified epoxies. Chapter 16 explains various spectroscopy analyses to follow the chemical structures and type of interactions in modified blends. Various applications of elastomer-incorporated epoxies in diverse fields are discussed in Chapter 17. The comparison of epoxy/rubber blends with other toughening strategies such as thermoplastic and hyperbranched polymers are presented in Chapter 18. This is analyzed in terms of the mechanical and thermal performances of resulting blend systems. Recent developments in the field of toughening strategies for liquid molding technologies are also focused on in this chapter. Chapter 19 discusses the effects of different environmental parameters on the properties of elastomer-modified epoxies. Analysis of different failure modes on rubber-modified epoxy systems is updated in Chapter 20. Finally, Chapter 21 explains the life cycle analysis of rubber-modified epoxy systems.

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