Chapter 1

Introduction

Abstract

This chapter summarises a general account of epoxy resins, their properties, various curing agents and fillers used for their modification. Epoxy resins are very important class of thermosetting polymers that often exhibit good mechanical properties, excellent chemical and corrosion resistance and good dimensional stability. In the cured state these are extremely brittle materials having low impact and fracture strengths. Hence toughening of epoxy resin has been the subject of intense investigation throughout the world. Elastomers, thermoplastics, nano fillers, liquid rubbers etc. are employed as toughening agents. Epoxy resins are most successfully toughened by dispersing rubber particles as a distinct phase of microscopic particles in the epoxy matrix. Various mechanisms involved in toughening are discussed in detail. Finally the main objectives of the present work are summarized towards the end of this chapter.

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1. Introduction

1.1 Polymer blends

Alloying and blending technology is a dynamic arena in the present century. Because of the reproducible properties and cost effectiveness of polymeric materials, much of the easy substitution for traditional materials has already been accomplished. Alloys and blends of polymers represent inexpensive routes to satisfy both the end-user material requirements and supplier’s desires for competitive differentiation. Property profiles of polymer blends are superior to those of component homopolymers. Blending technology also provides opportunities for reuse and recycling of polymer wastes. Alloy and blend development, therefore, is typically market driven and requires an ongoing dialogue between supplier and customer to ensure commercial success [1]. The ability to combine existing polymers into new compositions with commercialisable properties offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a particular property profile. Additionally, scale-up and commercialization of these materials entails much less capital investment. Moreover, property profiles which may not be feasible with a single polymer can often be achieved through polymer blending. It is no surprise that polymer blends represent a leading field of research in polymer science.

1.2 Blending

Mixing two polymers together in order to get a material with properties somewhere between those of the two polymers mixed is a versatile technique in the development of polymer products. Materials made from two polymers mixed together are called blends. A successful blending is based on the level of compatibility between the components and the resulting effects of physical and mechanical properties. Some level of compatibility is necessary between their components in all polymer combinations to achieve
the required properties. Beyond this level of compatibility, greater attractive forces between constituents serve to enhance the resultant property profile. Many authors used the term compatibility to describe good adhesion between constituents, average mechanical properties and ease of blending. Compatibility is often used to describe whether the desired or beneficial result occurs when two materials are combined together.

Blending of immiscible polymers is a very useful technical process to obtain materials with improved properties. The increasing use of polymer blends over the last few decades has encouraged many researchers to study different aspects of these materials mainly concerning their structure-property relationship [1-2]. The final properties of such incompatible blends strongly depend on their morphology, which is determined from the flow conditions during the blending and processing steps. Thus polymer blend, polymer alloy, or polymer mixture is a member of a class of materials analogous to metal alloys, in which two or more polymers are blended together to create a new material with different physical properties [1]. Polymer blends can be broadly divided into three categories: miscible, partially miscible and immiscible blends. The third one is by far the most populous group.

A method for blending multiple immiscible polymers resulting in a fine morphology with good interfacial adhesion include melt compounding more than two immiscible polymers with different viscosities in the presence of more than one compatibilizer. The immiscible polymers may be chosen from a wide range of materials including but not limited to thermoplastics, elastomers, thermoplastic elastomers, or thermosets. The compatibilizers may take the form of block copolymers, graft copolymers, random copolymers or other polymers known to reduce the interfacial tension of the immiscible polymers present in the blend [3]. The compatibilizers may be
functionalized to further reduce the size of the domains in the final morphology of the new polymer alloy. This method has been found to be advantageous in recycling commingled plastic wastes.

When we try to mix polymers we get phase-separated mixtures in most cases which often turn out to be rather nifty and useful. These are immiscible blends. An immiscible blend made from two amorphous polymers has two glass transition temperatures ($T_g$s). Since the two components are phase separated, they retain their separate glass transition temperatures. In fact, scientists often measure the $T_g$ of a blend to find out if it is miscible or immiscible. If two $T_g$s are found, then the blend is immiscible. If only one $T_g$ is observed, then the blend is likely to be miscible.

Most of the polymer blends are heterogeneous systems having multiphase structure. The morphology of a blend is a function of the nature of the blend components (both their mutual compatibility and the rheological properties) and of the method employed to produce the blend. It is necessary to distinguish between compatible blends and ones that are truly miscible. The former is homogeneous on a macroscopic scale but miscible only in a technological sense; that is, the polymers can be mixed together and processed to give a useful product.

The objective of an industrial mixing process is production of material having desired properties. For multipurpose polymer systems, this does not necessarily correspond to any equilibrium or steady-state morphology, although such a structure could probably be most reproducibly generated. Blending of thermoset-elastomers can be done by a variety of means [4]; including

1. Solution blending  
2. Melt blending

The principal functions of the mixing operation in preparing epoxy-rubber blends are essentially identical to those associated with the incorporation
of fillers, curatives, etc. into epoxy matrix. The conventional method of preparing epoxy-rubber blends is melt mixing. In solution blending the two polymers are dissolved in a common solvent followed by solvent evaporation, freeze drying, or polymer co-precipitation.

1.3 Miscibility of blends
The question of whether two polymers are miscible is of paramount interest [5]. The level of molecular mixing existing in polymer blends that exhibit macroscopic properties, indicative of single-phase behaviour, is commanding considerable attention. Miscible blends are most commonly formed from polymers of similar three dimensional solubility parameters. Miscible blends of elastomers are also formed with a preferential interaction between components. The compatibility of two polymers depends on the forces acting between the groups in the chains of the same material as well as between the groups in the chains of two different materials. In non-polar or weakly polar polymers, the physical forces acting are principally dispersion forces.

1.4 Morphology generation by phase separation of initially miscible polymer blend system
1.4.1 Thermally induced phase separation
Thermally induced phase separation is generally used to express all techniques where phase separation results from temperature changes. The occurrence and shape of the phase diagram depend strongly on the interaction parameter, which is specific for each system. The interaction parameter does not have a constant value, but it depends on temperature [6], composition [7], and pressure [8]. Several experimental methods exist to determine the interaction parameter. These are based on techniques like either light- or neutron scattering and osmometry for high dilutions, or inverse gas chromatography near the polymer melt [6, 9]. Two types of phase diagrams, which are of great technological importance, derive from
the simplification that the interaction parameter varies linearly with the inverse of temperature:

$$\chi = \frac{a}{bT}$$  \hspace{1cm} 1.1

This relationship, which is most widely used to take into account the temperature dependence of the interaction parameter, was first confirmed experimentally by Huggins [10].

An upper critical solution temperature (UCST) behavior follows Eq. (1.1) if the value of \( \chi \) is positive and increases linearly with \( 1/T \) [11]. The resulting phase diagram is schematically represented in Fig. 1.1 a [12]. If \( \chi \) is negative and decreases linearly with \( 1/T \), the system displays a lower critical solution temperature (LCST) behavior, as shown in Fig. 1.1 b.

![Schematic phase diagrams displaying: (a) upper critical solution temperature (UCST) (b) lower critical solution temperature (LCST).](Ref 12: Joachim Kiefer, James L. Hedrick, Jöns G. Hilborn Advances in Polymer Science 147,175, 1999)

The inner line is called the spinodal line and the outer line the binodal line. The binodal line results from the free energy curve by interconnecting all the
points having a common tangent as a function of the temperature. Hence this represents the equilibrium or coexistence curve. Entering the metastable region, which is limited by the spinodal and binodal line, will initiate phase separation which will proceed via a nucleation and growth mechanism. Similar to the construction of the binodal line, the spinodal line results from the summation of inflection points of free energy curves as a function of temperature. If the area enclosed by the spinodal line is entered, phase separation will take place via spinodal decomposition. Such schematic phase diagrams derived from the Flory-Huggins equation are very useful to explain the morphology development.

The area outside the binodal line is called the stable region. Here the two components are completely miscible. Starting from the stable region, phase separation is achieved, if the temperature is lowered (UCST) or raised (LCST) in such a manner that the metastable region or the domain for spinodal decomposition is entered. The transition from one area of the phase diagram into another is called quench. Any technique where a phase separation results from a temperature quench is therefore known as thermally induced phase separation (TIPS).

The phase separation mechanism and the final morphology depend on the region that is entered during the temperature quench. However, it is difficult to reconstruct these phase diagrams, as this requires an accurate description of the interaction parameter as a function of temperature, composition, and molecular weight of the polymer [13]. TIPS technique is largely applied to yield a wide variety of morphologies deriving from UCST or LCST behaviour and has also proven to be useful for the preparation of porous thermoplastic polymers by the use of a phase separating solvent [14-16].
1.4.2 Reaction induced phase separation

In chemically induced phase separation that involves a reactive polymer precursor and a solvent, phase separation is driven by the change in free energy of the system, given by changes in enthalpy and entropy. Guidelines based on the components’ molecular structure are given for the prediction and verification of phase behavior and hence the final porous morphology. There are two main procedures for dispersing rubbery particles: phase separation during polymerization of an initial homogeneous solution (reaction-induced phase separation), and a two phase initial formulation by either dispersing elastomeric particles (usually the core-shell type) in the mixture of monomers or by emulsification in epoxy monomer [17].

The phase separation method was started with the work of Mc Garry and his colleagues [18-20]. Epoxies based on diglycidyl ether of bisphenol A (DGEBA) were toughened by adding low molecular weight, liquid, carboxyl terminated poly (butadiene-acrylonitrile) copolymers (CTBN). Rubbery domains precipitated in-situ during cure, yielding toughened epoxy materials. Preparing rubber-modified epoxies from reaction-induced phase separation has the advantage of processing initial homogeneous solution with relatively low viscosity. Phase separation in polymer blends occurs via nucleation and growth or spinodal decomposition mechanisms, depending on whether the homogeneous polymer mixture is in the metastable or the unstable state.

1.4.2.1 Nucleation and growth mechanism

On the basis of LCST and UCST phase diagrams; there are two regions of phase separation for a binary or quasi-binary system: the metastable region (i.e. the region between binodal and spinodal curves) and the unstable region where nucleation and growth and spinodal decomposition are both expected to occur; the phase separation process is determined by the phase
diagram and the ratio between fluctuation growth rate of phase structure and disentanglement rate of polymer chain whatever be the phase separation mechanisms [21]. Reaction induced phase separation (RIPS) proceeds isothermally but differently from the phase separation in non-reactive binary blends. Verchere et al. [22] have speculated that low values of interfacial tensions and polymerization rates favour nucleation and growth in most cases. The initial modifier concentration also expected to have a strong effect on the phase separation mechanism [23].

In nucleation and growth, small concentration fluctuations will not cause the system to phase separate, as a thermodynamic barrier to phase growth needs to be overcome with a large concentration fluctuation. This fluctuation is called a nucleus; once nucleus is formed it grows by a normal diffusion process [24]. Starting from initially homogeneous mixtures of a liquid resin and a thermoplastic polymer, most systems will transform into a phase-separated structure due to the increasing molar mass and network formation of the resin upon sufficient curing. Upon reaching the gel point, the morphology is largely set and does not change much with further curing. In reaction induced phase separation, the morphology develops during curing and a variety of structures can be generated in the final material, which cannot be produced by preformed particles.

### 1.4.2.2 Spinodal decomposition mechanism

When the phase separation mechanism is spinodal decomposition (Fig. 1.2) a highly interconnected two-phase morphology with uniform domain size ("modulated structure") develops [25]. In the early stages of this process the wavelength (domain size) remains constant while the amplitude (concentration difference) of the composition fluctuation increases. In the intermediate stage both the wavelength and the amplitude increases with time. In the final stages the concentration difference between the two
phases reaches its final value while the domains continue to coarsen [26]. The final morphology cannot be distinguished from one resulting from a nucleation and growth process. However if the developing crosslinking network has the ability to “freeze”, the phase separated domains form a co-continuous structure prior to spinodal decomposition.

When a polymer blend is brought from an initially homogeneous state into an unstable spinodal region, various modes of concentration fluctuation develop and are amplified in the mean time by virtue of thermal fluctuations. If thermal fluctuation is fully suppressed, a single selective mode grows predominantly so that the structure becomes more regular, and a spinodal ring may be observed by light scattering. But for the case of reaction induced phase separation, the driving force of the system is the progressive increase of molecular weight of the polymerizing monomers. A nucleation and growth mechanism may take place in RIPS simultaneously with spinodal decomposition [27].

![Figure 1.2](image)

**Figure 1.2** Various strategies of the chemically induced phase separation technique to generate different types of morphologies (Ref. 12: Joachim K., James L., Hedrick J., Hilborn G., and Adv.in Polym. Sci., 147, 175, 1999)
1.4.3 Secondary phase separation

Recent studies have shown that secondary phase separation plays a significant role in the morphological aspects of binary systems with epoxy. According to Flory Huggins mean field theory, as average molecular weight of epoxy resin is reached, epoxy/thermoplastic system will be no longer homogeneous. Different phase morphologies can be obtained, depending on the composition, thermodynamics, kinetics of phase separation and chemical reaction in the binary mixture. These factors are strongly influenced by curing condition, composition, and molecular weight of the toughner [28]. Secondary phase separation was known since 1980. Tanaka [29-33] reported that phase separation is caused by asymmetric molecular dynamics. The origin of dynamic asymmetry is due to \( T_g \) difference between the components in polymer blends. In these cases the domains of the fast dynamic phase appear in the slow dynamic phase matrix, and then grow and result in a co-continuous structure and finally the slow dynamic phase developed into the dispersed phase by shrinkage.

Tanaka and Araki [34] proposed that the quick hydrodynamic reduction of the interface area might spontaneously destabilize the phase separated macroscopic domains and induce secondary phase separation. Zhou et al. [35] recently reported that volume shrinkage and phase inversion are caused by diffusional asymmetry of the consistent molecules. The double phase separation is due to unusual fast growth of domains in the matrix [36]. Huo et al. [37] suggested that double phase separation occurs due to hydrodynamic flow and chemical reaction between the binary mixtures.
Figure 1.3 SEM micrographs of various epoxy-DDS/SAN-15% blends after 7 h of isothermal curing at 160 °C and 10 MPa from PVT analysis blend showing secondary phase separation (Ref. 39 : J Jose, K Joseph, J Pionteck, and S Thomas J. Phys. Chem. B 112, 14793, 2008.)

Pascault and co-workers [38] investigated double phase separation in ternary blends of epoxies with polystyrene (PS) and poly(methyl methacrylate) (PMMA). Jose et al. [39] reported that in-situ volume shrinkage behavior, determined by the pressure-volume-temperature analysis of poly(styrene-co-acrylonitrile)-modified epoxy thermosets has been shown to be governed by the viscoelastic phase separation kinetics during polymerization. Scanning electron micrograph of various epoxy-DDS/SAN-15% blends from PVT analysis blend showing secondary phase separation is represented in Fig. 1.3. Zucchi et al. [40] reported double phase separation in epoxy modified PS/PMMA blends. Both PS and PMMA were initially miscible in the stichometric mixture of DGEBA/m-xylendediamine (MXDA) at 80°C, get phase separated upon curing. Solutions containing 5 wt% of each one of both linear polymers exhibited a double phase separation in which SEM micrographs reveal separate dispersion of PS and PMMA. Pagnoulle and Jerome [41] reported a particle in particle morphology for the dispersed phase formed in the reactive compatibilisation of SAN/poly(ethylene-co-propylene-co-diene
(EPDM) blends. Qin et al. [42] reported double phase separation in polyimide/silica hybrid films. Tang et al. [43] explained the hydrodynamic effect on secondary phase separation in epoxy matrix modified with poly(ether sulfone) (PES). In a dynamic asymmetric system, the diffusion of the fast dynamic phase is prevented by the slow dynamic phase, and hence the growth of fast dynamic phase gets retarded due to slow dynamic phase. The growth of fast dynamic phase will be slow in high viscosity blends and hence diffusion of fast dynamic phase can follow geometrical growth and can establish local concentration equilibrium and hence no double phase separation. In the case of low viscosity blends the growth of fast dynamic phase turns fast and hence diffusion of fast dynamic phase cannot follow geometrical growth and cannot establish local concentration equilibrium and hence double phase separation takes place. The above results indicate that double phase separation will occur spontaneously in the case of low viscosity blends [44]. But it should be noted that in the case of epoxy/thermoplastic blends phase separation phenomena is very complicated since phase separation in thermoset/thermoplastic blends is coupled with polymerisation, gelation and vitrification and hence a realistic description of phase separation is not possible. Double phase separation is a usual observation in modified thermosetting polymers [45]. Jyothishkumar et al. [46] reported that complex substructure formation in dynamic asymmetric blends is due to the combined effect of hydrodynamics and viscoelasticity in epoxy system containing diglycidyl ether of bisphenol A and 4,4′-diaminodiphenyl sulfone modified with poly(acrylonitrile-butadiene-styrene) (ABS). Secondary phase separation in 80/20 cross-linked epoxy resin/ABS blends is given in Fig. 1.4. The phase separation in these binary blends is very complicated; the system can decompose into single, double or ternary phases.
1.5 Factors affecting the morphology

The morphology of modified thermosetting blends is generally characterized by the size and concentration of the dispersed phase particles. They are controlled by many factors, such as miscibility, concentration and molar mass of the modifier, curing conditions, reaction rate and the presence of emulsifier. The crucial factor controlling the generated morphologies is the location of the initial blend composition with respect to the critical composition.

The competition between the rates of curing and of phase separation determines the mechanism of reaction induced phase separation, i.e., nucleation and growth or spinodal demixing [47-51]. The control of this mechanism is crucial for the final morphology and thus the resulting mechanical properties of thermoplastic/epoxy networks.

The influence of parameters, such as composition and cure temperature, on the final morphology has been investigated by several researchers [52-54]. Girard-Reydet et al. [54] demonstrated that for amounts of the
thermoplastic polymer located in the critical composition range, phase separation during the epoxy/amine reaction proceeds by spinodal demixing.

The reaction induced phase separation process in a rubber or thermoplastic-modified thermosetting polymer is caused by the increase in the average molar mass of the polymer superimposed by possible variations of the interaction parameter, $\chi$, with conversion [55-56]. This secondary effect may favour mixing or demixing, depending on whether $\chi$ decreases or increases, respectively, with conversion. Scanning electron microscopy studies of the cured blends revealed a two-phase morphology. A sea-island morphology in which the thermoplastic was dispersed in a continuous matrix of epoxy resin was observed and phase separation occurred by a nucleation and growth mechanism. Similar trend was observed by Francis et al. [57-59] when diglycidyl ether of bisphenol A epoxy resin was toughened with hydroxyl terminated poly(ether ether ketone) (PEEKTOHs) having different molecular weights using DDS as curing agent. All the blends showed two-phase morphology in which PEEKTOH rich domains are dispersed in a continuous epoxy matrix.

1.6 Thermosetting polymers

Thermosetting or network polymers are widely used commercially because cross-linked structures sometimes have improved toughness and strength. They are normally produced in two stages. The first is a prepolymer, which may be either liquid or solid, containing molecules with low molar mass. The polymer will flow to fill a mould in this form and the material is then usually cured to give a heavily cross-linked product. Once these are cured, thermosetting polymers cannot be remelted and tend to decompose on heating.
The most important thermosetting resins include epoxy resins, unsaturated polyester resins, urethanes and the alkyds. Among these, epoxy resins are the most versatile in the sense that a wide range processing, cure and property characteristics can be achieved [60].

1.6.1 Epoxy Resins

Epoxy resins constitute a class of polymeric materials that are of significant technical relevance and are widely used in the microelectronics industry as the workhouse encapsulant and underfill agent in the mounting of chip assemblies to the printed circuit board. Thermosetting epoxies possess many desirable properties such as high tensile strength and modulus, excellent chemical and solvent resistance, dimensional and thermal stability and fatigue properties. These characteristics make them ideal candidate for many important application including adhesives, electronic encapsulant and as matrices for fiber-reinforced composites.

The term epoxy refers to a chemical group consisting of an oxygen atom bonded with two carbon already united in some other way. The simplest epoxy is a three membered ring, to which the term $\varnothing$-epoxy or 1, 2 epoxy is applied and is represented in Fig. 1.5.

![Ethylene Oxide (Oxirane)](image)

**Figure 1.5** Structure of Epoxy group

An epoxy resin is defined as any molecule containing more than one $\varnothing$ epoxy group (whether situated internally, terminally or a cyclic structure) capable of being converted to a useful thermoset form. The term is used
to indicate the resins in both uncured cured state. The ‘oxirane’ group in epoxy resins is highly reactive and further reacts with curing agents to yield high performance thermosetting resins. They have gained wide acceptance in protective coatings, and structural and electrical application because of their exceptional combination of properties such as toughness, adhesion, chemical resistance and superior electrical properties.

1.6.2 Preparation and curing

The epoxy resin used most widely is made by condensing epichlorohydrin with bisphenol A. An excess of epichlorohydrin is used to leave epoxy groups on each end of the low molecular weight (900-3000) polymer.

Depending on molecular weight, the polymer is a viscous liquid or a brittle high melting solid other hydroxyl containing compounds, including resorcinol, hydroquinone, glycols and glycerol can replace bisphenol A. No epoxides, other than epichlorohydrin are available at attractive prices. The structure of bisphenol A based epoxy resin is shown in Fig.1.6.

![Figure 1.6 Diglycidyl ether of bisphenol A epoxy resin.](image)

Cross-linking in certain polymers can also be effected through what are known as cure reaction. The uncross-linked linear polymers contain either reactive functional groups or double bonds in their molecules. They are usually not very high molecular weight and are hence in the form of liquid resins. Such liquid polymers possessing reactive functional groups or double bonds are referred to as ‘pre polymers’. When these prepolymeres are reacted with low molecular weight or polymeric
substances containing appropriate functional groups capable of reacting with active groups of the prepolymer, curing takes place resulting in a cross-linked solid polymeric mass. The low molecular weight or the polymeric material used to bring about the cure reaction is called the curative or curing agent.

Curing is an irreversible change. Cure can be slowed down, stopped or speeded up but it cannot be reversed. In practice cure is brought about simply by mixing the resin and curing agent, the two materials being dissolved in a suitable solvent. Some curing agent will react with the resin at room temperature or below while others require heat to effect polymerization. The curing reaction is exothermic.

Curing is also dependent upon the rate at which polymerization occurs and rate at which the heat evolved is being dissipated to the surroundings. In practice care is taken to ensure that the increase in temperature of the bulk mixture of resin and curing agents is not excessive. In the absence of such control, bubbling, cracking, charring over even complete degradation of the resin could occur in severe cases. The time taken from the initial mixing of the resin and curing agents to the point when the viscosity of the mixture has become so high as compared to render the mixture unusable is called “pot life” of the system. This time is therefore the practical working life of the mixture, during which the material must be applied to the matter of concern.

The simple resin curing agents’ combination alone seldom provides a material with all properties required for use in the given application and other materials must be added so as to modify the properties of the resin or to make it cheaper. The correct choice of the type and amount of the different components of an epoxy formulation is a fairly precise, difficult
task because the final properties and external performance of the system depends upon it [61].

1.6.3 Time-Temperature–Transformation (TTT) diagram

Curing reactions of thermoset materials generate a tridimensional network after chemical reaction of the epoxy resin and the appropriate hardener. During the cure process of a thermoset, the glass-transition temperature of the material increases as a consequence of the increase in both the crosslinking density and the molecular weight [62]. Because of this, there is a decrease in the free volume of both epoxy groups and primary amine not reacted, attributed to the fact that some chains become hindered in an infinite molecular weight network. The transformation from a viscous liquid to an elastic gel is sudden and irreversible and marks the first appearance of the infinite network called the gel point. Gelation is characteristic of thermosets, and it occurs at a well-defined and calculable stage in the course of the reaction, that is, at specific values of conversion and \( T_g \) and is schematically represented in Fig. 1.7 a. One other phenomenon that may occur at any stage during cure is vitrification. This transformation from a viscous liquid or elastic gel to a glass begins to occur as the glass-transition temperature of the system becomes coincidental with the cure temperature. The vitrification point marks a change in the reaction mechanism passing from chemically and kinetically controlled to become diffusion controlled. Samples vitrified during an isothermal curing \( [T_c \text{ (crystallization temperature)}] \) show an endothermic physical aging peak in the vicinity of \( T_g \), [63-64].
Figure 1.7 (a) Schematic Morphology map (Ref 65: LT Manzione and JK Gillham, Journal of Appl. Polym. Sci 26, 889, 1981)
An isothermal time-temperature diagram, Fig.1.7 b can be used to visualize and compare cure of thermosetting systems. These diagrams have been extensively used for epoxy systems. These diagrams mark the four main time events that occur during isothermal cure at various temperatures.

Gelation marks the incipient formation of an infinite molecular network. At this point the systems will no longer flow. The glass transition temperature of the forming polymer rises above the temperature of cure at vitrification. As polymer becomes more and more crosslinked, its glass transition temperature rises. Eventually it reaches the temperature of cure. When this happens, diffusional limitations limit further reaction by hindering molecular mobility. The system becomes rigid at this point. The highest attainable degree of cure is termed full cure. Devitrification is degradation where the glass transition temperature decreases through the isothermal temperature.
1.6.4 Curing agents

Since epoxy resin has a strained three membered ring structure, an epoxy group reacts with nucleophilic reagents. However for the curing of epoxy resin, compounds with active hydrogen atoms are used for their workability and availability. Amines, phenols, alcohols, carboxylic acid and acid anhydrides are examples.

The chemical reactions between epoxy resin and various curing agents are shown below in Fig.1.8.

**Figure 1.7(b)** Time-temperature-transformation diagram (Ref 66: L.V. Mc Adams, J. A. Gannon, Encyclopedia of Polymer Science and Engineering, Vol. 6, 2nd Edn., Wiley Interscience, 1986)
Anhydrides are the principal curing agents for cycloaliphatic and epoxidized olefin resins in electrical casting and potting. The mechanism of anhydride cure is complex and controversial because of the possibility of several competing reactions. The uncatalysed reaction of epoxy resins with acid anhydrides proceeds slowly even at 200°C; both esterification and etherification occur. Secondary alcohols from the epoxy backbone react with the anhydride to give a half ester, which in turn reacts with an epoxy group to give the diester as in Fig. 1.9. A competing reaction is etherification of an epoxy with a secondary alcohol, either on the resin backbone or that formed during the esterification, resulting in a β-hydroxy ether. It has been reported that etherification is a probable reaction since
only 0.85 equivalents of anhydrides are required to obtain optimum crosslinked density and cured properties [67].

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OH} & \quad + \quad \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \\
\text{CO}_2\text{N}^+\text{R}_3 & \quad \rightarrow \quad \text{CO}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

**Figure 1.9** Reaction between epoxy and anhydride

Lewis bases such as tertiary amines and imidazoles are widely used as epoxy-anhydride catalysts. Conflicting mechanisms have been reported for these catalyzed reactions. The most widely accepted mechanism involves the reaction of the basic catalyst with the anhydride in the initiation step to form a betain (internal salt) [68]. The propagation step involves the reaction of the carboxylate anion with the epoxy group,
generating an alkoxide. The alkoxide further reacts with another anhydride, propagating the cycle by generating another carboxylate which reacts with another epoxy group. The end result is the formation of polyester-type linkages. In practice, it has been observed that optimum properties are obtained when stoichiometric equivalents of epoxy and anhydride are used with high temperature cures, which is consistent with this mechanism and does not involve etherification reactions.

At lower anhydride/epoxy ratios (0.5:1) and lower cure temperatures, some etherifications can take place by reaction of the alkoxide with an epoxy group as depicted in Fig. 1.10.

![Figure 1.10 Reaction between epoxy and alkoxide group](image)

Numerous structurally different anhydrides can be used as epoxy curing agents, but the most widely used are liquids for ease of handling. The most important commercial anhydrides are methyl tetrahydro phathalic
anhydride (MTHPA), phthalic anhydride (PA), dodecylsuccinic anhydride (DDSA), benzophenonetetracarboxylic dianhydride (BTDA) etc.

1.7 Modification of epoxy resins
Epoxy resins are normally brittle at room temperature and are toughened to improve their crack resistance and toughness without significantly decreasing other important inherent properties. One of the important and efficient ways to make the epoxy materials tougher is to modify the original epoxy resin, that is, to incorporate a second phase into the continuous matrix of epoxy resin through physical blending or chemical reactions. Unmodified epoxy resins are usually single-phase materials, while the addition of modifiers turns the toughened epoxy resins into multiphase systems. When modifier domains are correctly dispersed in discrete forms throughout the epoxy matrix, the fracture energy or toughness can be greatly improved. The reason for this is that cross-linked epoxy resins have limited ability to deform by shielding and crazing, especially in the tri-axial stress field present inside the sample at the crack tip [69]. However, the addition of a second phase modifier changes this situation and can significantly improve the fracture toughness. Different kinds of modifiers have been used to improve the toughness or ductility of cured epoxy resins; a) engineering thermoplastic modifiers b) liquid rubber modifiers c) reactive diluents d) inorganic and performed particles and e) polyorganic siloxane modifiers.

1.7.1 Thermoplastic modified ER
Thermoplastics can be used for toughening highly crosslinked epoxy resins. It is true that elastomers increase the fracture toughness of epoxy resin, but it often resulted in reduction in high temperature properties and modulus. But thermoplastic modification resulted in enhanced fracture toughness with retention of high temperature properties. Immense
amount of research has been carried out using polyethyleneoxide, poly(ether ether ketone), polysulfone polyetherimide, poly(methyl methacrylate), polyester, poly(acrylonitrile-co-butadiene-co-styrene, polycarbonate and nano particles.

Zhu and coworkers [70] studied the miscibility and mechanical properties of diglycidyl ether of bisphenol A-type of epoxy resin bisphenol A-based polysulfone (PSF) blends. PSF was judged to be miscible with the 4,4’-diaminodiphenylmethane (DDM)-cured epoxy resin as revealed by the means of differential scanning calorimetry, dynamic mechanical analysis and scanning electron microscopy. Morphological investigation of the $K_{IC}$ fracture surface suggests typical characteristics of brittle fracture. A hot-melt processable thermoset was prepared by blending tetraglycidyl-4,4’-diaminodiphenylmethane/ 4,4’-diaminodiphenylsulfone epoxy resin and a high-$T_g$ thermoplastic polyimide by Sillion and co-workers [71]. The consequences of the thermoplastic incorporation (polyimide concentration = 10 wt %) were a slight increase in $T_g$ value ($\Delta T_g = +5^\circ C$) and rather limited improvements in stress at rupture (50%) and strain-energy release rate $G_{IC}$ (27%) compared to the unmodified epoxy matrix.

Pearson and Yee [72] modified diglycidyl ether of bisphenol A with poly(phenylene oxide) (PPO) and cured with piperidine. A two-phase alloy resulted, in which the DGEBA epoxy was the continuous phase. Several PPO loadings were investigated. The tensile yield strengths of these PPO-modified epoxies were found to be independent of PPO content while the fracture toughness improved with PPO content in a linear fashion.

Luo et al [73] investigated curing of epoxy resins/poly (ethylene oxide) (PEO) blends with phthalic anhydride using differential scanning calorimetry and dynamic mechanical analysis. Single glass transition temperatures were
observed for all blends before and after curing, indicating a high degree of miscibility. Fourier transform infrared spectroscopy provided strong evidence that there is a specific interaction between the EP and PEO molecules.

Gomez and Bucknall [74] studied miscibility, phase separation and curing behaviour in blends of poly(methyl methacrylate) (PMMA) with diglycidyl ether of bisphenol A resin and 4,4'-diamino-3,3'-dimethyl dicyclohexyl-methane hardener. Quasi-binary mixtures of PMMA with the resin monomer show complete miscibility over the whole composition range, at all temperatures studied (−25 to 200°C).

Polyether ether ketone (PEEK) is a semicrystalline engineering thermoplastic having a unique combination of properties like toughness, stiffness, thermost oxidative stability, chemical and solvent resistance, electrical performance, flame retardancy and retention of physical properties at high temperature [75]. Functionally terminated PEEK with pendant alkyl groups were used instead of virgin PEEK to modify epoxy resin. All the blends were homogeneous before curing. The cure kinetics of DGEBA epoxy modified with PEEK based on tert-butyl hydroquinone (PEEKT) was found to follow autocatalytic mechanism by Francis et al. [76]. The rate of reaction decreased with the addition of PEEKT to epoxy resin cured with DDS. Reaction rate against time for neat resin and epoxy/PEEKTOH12 blends cured at 150°C is given in Fig. 1.11.
Francis et al. [77] reported the synthesis, processing, thermal and mechanical properties and fracture toughness of epoxy resin formulated with hydroxyl terminated poly (ether ether ketone) with pendant methyl group. Blends of diglycidyl ether of bisphenol-A epoxy resin with hydroxyl terminated poly(ether ether ketones) were prepared by melt mixing. Domain size of the blends increased with increase in PEEKMOH8 in the blends. Phase separation in the blends occurred by nucleation and growth mechanism. The tensile and flexural properties of the blends were comparable to that of neat epoxy resin. The blends exhibited superior fracture toughness compared to unmodified epoxy resin. The increase in fracture toughness was due to local plastic deformation of the matrix, crack path deflection and crack pinning. The thermal stability of amine
cured epoxy resin was not affected by the incorporation of PEEKMOH into the epoxy resin.

Bisphenol A-based epoxy resins were modified with either phenolic hydroxyl or aromatic amine functionally-terminated poly(arylene ether sulphone) oligomers and thermally cured with 4,4′ dianhydrophenyl sulphone by McGrath and co-workers [78]. The resulting networks displayed significantly improved fracture toughness, with little sacrifice in modulus. Despite the two-phase structure, the modified crosslinked systems are nearly transparent, due to a similarity in component refractive index values. The fracture toughness of these modified networks under plain strain conditions improved significantly with minimal sacrifice of the flexural modulus.

The morphologies and tensile properties of an elastomer-modified epoxy (EME)/polycarbonate (PC) binary system and an EME/diglycidyl ether of bisphenol A/PC ternary system were examined by Ohsako et al [79]. In the EME system, a continuous elastomer-rich phase formed, while in the EME/DGEB systems (not blended with PC), a continuous epoxy-rich phase formed. In the EME/PC blend, the tensile elongation reached its maximum value (60 %) at a PC content of approximately 10 phr, with this maximum being approximately one and a half times higher than that of the unblended EME. The improvement in tensile properties was related to blending of the PC which induced a microdispersed structure and improved the elongation of the epoxy resin.

Jayle et al. [80] have blended a ductile thermoplastic, polycarbonate with the diglycidyl ether of bisphenol A epoxy resin to increase the toughness of the resin. Cured epoxy-polycarbonate systems showed no increase in fracture toughness relative to the neat epoxy resin. The binary blends were miscible, single-phase systems.
Chapter 1

1.7.2 Rubber modification of ER

1.7.2.1 Carboxyl-terminated butadiene-co-acrylonitrile rubber

Traditional toughness modifiers such as carboxyl terminated butadiene acrylonitrile copolymer rubbers (CTBN) have been widely used to improve toughness since the frontier work by McGary and Sultan [81-83]. However, such improvements were achieved at the expense of high temperature performance. A binary phase morphology consisting of relatively small (0.1-5 mm) rubbery particles dispersed in and bonded to epoxy is generated. The toughness of the resulting networks was influenced by the properties of the pure epoxy like crosslink density, morphology of the blend, level of interfacial adhesion, the initial composition and properties of the toughener [84]. Significant improvements (10 folds or so) for fracture toughness ($K_{IC}$) have been reported only in the case of lightly cross linked epoxies [85].

Smaller particles were found to deform principally by voiding and induced local shear yielding, and larger particles produced localised yielding in the surrounding matrix, which was facilitated by the presence of smaller particles as reported by Bascom et al. [86]. They used solid and liquid CTBN which provided a dual particle size distribution of 0.5 $\mu$m and 1-2 $\mu$m respectively.

Tripathi and Srivastava [87] modified epoxy resin with varying concentrations of liquid carboxyl-terminated butadiene acrylonitrile copolymer having 27 % acrylonitrile content and cured with aromatic amine. The tensile strength of cured blend samples decreased slightly from 11 to 46 % where as the elongation-at-break showed an increasing trend with increasing rubber content. Toughening of diglycidyl ether of bisphenol-A and 3,4 epoxy cyclohexymethyl, 3',4'-epoxycyclohexane carboxylate, i.e. cycloaliphatic epoxy resin (CAE) with varying weight
ratios (0–25 wt%) of carboxyl terminated butadiene acrylonitrile copolymer have been investigated by Tripathi and Srivastava [88]. Physico-mechanical properties of the prepared samples, e.g. tensile, flexural and impact strengths showed an optimum value for a concentration of CTBN (15 wt %) into epoxy matrix, which offered maximum toughening.

In another study DGEBA involving liquid epoxy resin and CTBN rubber, chemical bond formation between dispersed rubber phase and matrix resin in the presence of piperidine was explained due to the in situ formation of epoxy-CTBN-epoxy adduct [89]. But most of the other curing agents favour either epoxy-epoxy or epoxy-amine reaction and the carboxyl-epoxy reaction is suppressed. Chemical interaction between epoxy cresol novolac resin and CTBN occurred via formation of ester linkage between epoxy groups and the carboxyl groups of CTBN was reported by Mathur and co-workers [90]. Fracture toughness increased with the addition of CTBN.

Calabrese and Valenza [91] analysed the cure kinetics of an epoxy resin matrix, based on diglycid ether of bisphenol A and F (DGEBA–DGEBF), using an anhydride hardener. Calorimetric and rheological analyses clearly indicate that gelation and vitrification take place in a wide range of time. Rheological data shows that the presence of rubbery phase induces a higher rate of gel formation during the early stages of the reactions, confirming the calorimetric results.

Rheo-kinetic behaviour of an epoxy resin, coupled with an anhydride hardener, with different CTBN liquid rubber concentration (0–15 phr), used in fibre reinforced plastics, was analysed by Calabrese and Valenza [92]. Considerable differences in process condition, using different amounts of rubber, are obtained. The numerical modelling of process
conditions shows that the presence of CTBN rubber in the epoxy resin reduces time and temperatures of cure.

Gu and Liang [93] found that epoxy/CTBN blend cured with piperidine possessed high initial degradation temperature and higher activation energy for decomposition both in air and nitrogen atmospheres. This showed better thermal and thermo-oxidative stability of the blends compared to pristine epoxy resin.

The damage zone around the crack tip of 15 phr CTBN modified DGEBA cured with piperidine and 4, 4’-diamine-3, 3’-dimethylidicyclohexylmethane (3DCM) revealed dilatation bands and massive shear yielding in the region close to crack tip in the optical and transmission electron microscopic studies [94]. In 3DCM cured system, a region of cavitated particles without shear deformation was observed.

Karger-Kocsis and Friedrich [95] studied the fracture toughness and fatigue crack propagation (FCP) of plain and modified anhydride-cured epoxy resin at ambient temperature in liquid carboxyl-terminated acrylonitrile-butadiene and silicon rubber toughened epoxy resin. Rubber-induced cavitation and shear yielding of the ER were dominant for CTBN, whereas crack bifurcation and branching controlled the cracking in silicon modified ER. The simultaneous use of both modifiers resulted in a synergistic effect for both the fracture toughness at high deformation rate and the FCP behaviour.
Figure 1.12(a) Fracture toughness versus plate thickness in the neat epoxy. (Ref 96: R Bagheri, R A Pearson Polymer 41, 269, 2000)

Figure 1.12 (b) Fracture energy versus plate thickness in the neat epoxy. (Ref 96: R Bagheri, R A Pearson Polymer 41,269, 2000)
Variation of fracture toughness and fracture energy in carboxyl-terminated butadiene acrylonitrile copolymer modified epoxy is represented in Fig.1.12 (a) and (b) [96]. Thomas et al. [97, 98] investigated the kinetics of the cure reaction and morphology of DGEBA based epoxy-CTBN blend using an anhydride hardener. Isothermal DSC, DMTA, and SEM were mainly employed to monitor the cure reaction and analyses of the morphology. An autocatalytic behavior of the reaction was established where the rate was found to decrease on the addition of elastomer due to dilution and viscosity increase. Large inclusion of elastomer content decreased the cross-linking density of the thermoset matrix.

Morancho and Salla [99] examined the relaxation process at different temperatures in partially cured samples of an epoxy resin and the same resin modified with 11.1 % carboxyl-terminated butadiene acrylonitrile copolymer. In another study, differential scanning calorimetry was used by Morancho and Salla [100] to monitor the degree of cure within epoxy-carboxyl-terminated modifier samples cured at 50 ± 1°C. At this temperature, all samples were found to achieve 80 % of conversion within 1000 min or less. CTBN accelerates the curing process and modifies the cross-linked network. DSC was also used to measure the extent of ‘physical aging’ which took place during the cure process.

Maïstros et al. [101] carried out curing experiments at several temperatures on blends of diglycidyl ether of bisphenol A epoxy resin with 34.4 phr of 4,4′-diamino-3,3′-dimethyldicyclohexitrcymethane hardener and 15 wt% carboxyl terminated poly(butadiene-co-acrylonitrile) rubber. Simultaneous measurements were made of turbidity and of dielectric properties over the frequency range 0.1 to 20 kHz. Changes in viscosity, gel fraction and enthalpy were determined in separate experiments.
Kunz and Beaumont [102] measured fracture energy \(G_{ic}\) values of epoxies modified with CTBN having different percentage of acrylonitrile content in the temperature range of -110 to 20°C. They have noticed that the cured sample containing CTBN (27 % AN) has the small particle size and the highest toughness at room temperature and that generally there was no further reduction in \(G_{ic}\) at temperatures below -80°C.

Pearson and Yee [103] used several varieties of CTBNs and observed that the rubber particle size has influenced the fracture toughness of modified epoxies. The fracture toughness was dependent on particle size where large particles provided only a modest increase in fracture toughness via a particle bridging/crack deflection mechanism. Verchere et al. [104] have observed that the dispersed rubber bonded with the epoxy matrix acted as dissipation center of mechanical energy by cavitation and shear yielding, inducing the increase of crack growth resistance, which ultimately led to excellent fracture properties.

Kinloch and co-workers [105] found that the toughness of CTBN modified thermosets increases with volume fraction of the dispersed rubbery phase, but the modulus and yield strength decrease slightly. Bartlet et al. [106] observed that optimum mechanical properties were achieved with 15 % CTBN; and the toughness is attributed to the presence of small particles with a narrow size distribution.

Egan and Drake [107] employed functional butadiene-acrylonitrile copolymers and polybutadiene homopolymers as effective elastomeric modifiers for formulated epoxy compositions. Adhesive properties, peel and low temperature shear strength accompanying modified epoxy systems are often highlighted in both elevated and ambient temperature cured elastomer modified epoxy adhesives which have excellent durability.
Epoxy resin modified with carboxyl-terminated polybutadiene presented improved impact resistance and outstanding mechanical performance in terms of flexural and tensile properties because of the presence of rubber particles homogeneously dispersed inside the epoxy matrix [108]. This modified system also resulted in an improvement in mechanical properties of the corresponding carbon fiber based composites.

1.7.2.2 Amino-terminated butadiene-co-acrylonitrile rubber (ATBN)

Amino-terminated butadiene-co-acrylonitrile rubber (ATBN) has been used as an effective modifier for epoxy resins. Chikhi et al. [109] modified epoxy resin with liquid amino terminated butadiene acrylo nitrile rubber and found that all reactivity characteristics (gel time and temperature, cure time and exotherm peak) decreased. SEM analysis suggest rubber particle cavitation and localised plastic shear yielding induced by the presence of the dispersed rubber particles within the epoxy matrix as the prevailing toughening mechanisms.

Mechanical properties of ATBN/DGEBA blends of various compositions, cured at different temperatures, have been investigated by Butta and co-workers [110]. Both homogeneous and heterogeneous materials, with different properties, have been obtained. SEM micrographs of impact fractured specimens showed that the moving cracks go through the segregated particles and suggest they lack ductility.

Cure kinetics of epoxy-amine system modified with CTBN and ATBN was examined by Wise et al. [111]. The rate of epoxy-amine reaction increased with the addition of CTBN and decreased with the addition of ATBN.

Hwang et al. [112] used epoxy terminated butadiene acrylonitrile (ETBN) as well as amine terminated butadiene acrylonitrile to establish the relationship between the microstructural parameters and mechanical
properties. They observed that, $K_{IC}$ and $G_{IC}$ increased while Young’s modulus and yield strength decreased slightly with the incorporation of elastomer.

1.7.2.3 Hydroxy terminated butadiene liquid rubbers

These form yet another class of modifiers for epoxy resins. With small amounts of hydroxy terminated poly butadiene (HTPB), Sanjana and Kupchella [113] got appreciable increase in tensile strength. They observed that HTPB concentration, rubber epoxy compatibility and the changes in amount of curing agent affect the dynamic mechanical properties and fracture toughness of the blends.

Qingyu and co workers [114] proposed toughened epoxy resin with excellent properties by adding organic acid anhydride curing agent and hydroxy-terminated butadiene-acrylonitrile copolymer (HTBN). Zhang et al. [115] studied the bimodal phase separation in DGEBA epoxy modified with HTBN cured with tetrahydrophthalic anhydride (THPA) using time resolved small angle light scattering (SALS), DSC and digital image analysis. The bimodal size distribution was explained qualitatively by nucleation and growth coupled with spinodal decomposition mechanisms and competition between phase separation and polymerisation reaction.

In an attempt to toughen the epoxy resin matrix for fiber-reinforced composite applications, Sankaran and Chanda [116] used a chemical modification procedure of a commercially available bisphenol-A-based epoxy resin using reactive liquid rubber HTBN and toluene diisocyanate (TDI). The progress of the reaction and the structural changes during modification process were studied using IR spectroscopy, viscosity data, and chemical analysis (epoxy value determination).
Thomas et al. [117] modified diglycidyl ether of bisphenol A epoxy resin using varying content of hydroxyl terminated polybutadiene using an anhydride hardener. Chemorheological analysis of the modified network was performed to understand the physical transformations taking place during the cure polymerization reaction. The morphological evolution of the toughened networks was examined by scanning electron microscope, and the observations were used effectively to explain the impact properties of the network having varying content of liquid rubber. Based on acoustic emission results and morphological characteristics, toughening and failure mechanisms were discussed.

Chenze and co-workers [118] investigated the free volume and toughening behavior for epoxy resin/rubber composites in carboxyl-randomized butadiene-acrylonitrile (CRBN) rubber and hydroxyl-terminated butadiene-acrylonitrile rubber modified epoxy resin matrix by positron annihilation.

Ozturk et al. [119] studied the changes in mechanical and thermal properties of diglycidyl ether of bisphenol-A based epoxy resin with hydroxyl terminated polybutadiene (1% and 1.5%). A silane coupling agent (SCA) was also utilized to improve the compatibility of HTPB and epoxy matrix. The changes in storage modulus and glass transition temperatures of all specimens were also evaluated by dynamic mechanical analysis. Fracture surfaces of all specimens were examined by scanning electron microscope. The deformed rubber domains and higher amounts of deformation lines in some specimens indicated the improvement in toughness.

Latha et al. [120] epoxidized hydroxy-terminated polybutadiene using performic acid generated in-situ. Different grades of epoxidized hydroxy-terminated polybutadiene (EHTPB) were prepared by adjusting reaction
conditions such as temperature, time and molar ratios of formic acid and hydrogen peroxide. Lap shear strength and T-peel strength were observed to increase with increasing EHTPB content, pass through a maximum at an EHTPB content of about 10 parts per 100 parts epoxy resin and then decrease. The enhancement of mechanical properties was attributed to the higher toughness produced by the dispersed rubber particles.

Recently, it was found that carboxyl terminated polybutadiene improved the fracture toughness of epoxy cresol novolac resins [121]. 10phr addition gave maximum improvement in flexural strength, tensile strength and impact properties. The change in properties was due to the change in the morphology from homogeneous to heterogeneous due to the addition of rubber. Ramos et al. [122] reported that CTBN and hydroxyl terminated polybutadiene increased the impact strength of DGEBA epoxy resin cured with piperidine. Maximum improvement in impact strength for HTPB was obtained by 3 phr addition.

Various liquid elastomers like HTPB, carboxyl-terminated polybutadiene and isocyanate–terminated polybutadiene (NCOTPB) were used for epoxy modification [123]. More effective interaction was reported for epoxy-CTPB system because of the chemical reactions between carboxyl groups of the elastomer and hydroxyl functionality of epoxy resin. The system exhibited more uniform two-phase morphology suggesting better interactions between phases with narrow particle size distribution. Also, the dielectric relaxation corresponding to this phase was not detected.

1.7.2.4 Epoxy terminated liquid rubbers

Montarnal et al. [124] have reported that phase separation occurred prior to gelation and vitrification in epoxy terminated butadiene acrylonitrile
(ETBN)-modified DGEBA based epoxy resin cured with 4,4’-methyleneedianiline (MDA) and that both gelation and vitrification were delayed in rubber-modified systems. The average diameter of particles increased from 0.5 to 1.1 μm with a nearly constant volume fraction with increase in cure temperature from 27 to 100 °C. Verchere et al. [125,126] found that the domain size was influenced by the nature of the curing agent and curing conditions. In DGEBA/epoxy terminated butadiene acrylonitrile random copolymer blends, the domain size changed with cure temperature and curing agent. 4,4’-diaminodiphenylmethane (DDM) showed maximum size and 4,4′-diamine-3,3′-dimethyl dicyclo hexyl methane showed minimum size for the domains.

Gupta and Latha [127] found epoxidised hydroxyl terminated liquid natural rubber (EHTNR) as an effective modifier for epoxy resin. Lap shear strength and T-peel strength showed noteworthy step up in the vicinity of 10 phr elastomer. The results were explained on the basis of the development of a two-phase microstructure consisting of rubber particles dispersed in the epoxy matrix.

Bussi and Ishida [128] studied the tensile and mechanical properties of blends of DGEBA based epoxy resin and hydroxyl terminated, internally epoxidized polybutadiene rubber. Fracture property measurements showed that pre-reaction of the rubber with the resin was necessary to establish chemical bonding between the rubber and the epoxy matrix. Blends containing 9 to 12 % of pre-reacted rubber exhibited higher fracture properties.

Toughened epoxy networks based on DGEBA prepolymer, 4,4’-diamino diphenyl sulphone curing agent and epoxy-terminated butadiene-acrylonitrile copolymer-2,2′-bis(4-aminophenoxy)phenyl propane (ETBN-BAPP) adduct were prepared using a two-step process by Pascault and
co-workers [129]. The kinetics of the reaction was followed by size exclusion chromatography and differential scanning calorimetry: the extent of reaction was found to be higher at the cloud point and lower at gelation in the two-step process.

The effects of epoxidized natural rubber (ENR) on the curing behaviors and adhesive strengths of an epoxy (diglycidyl ether of bisphenol-A) and dicyandiamide/2-methyl imidazole system are studied by Hong and Chan [130]. SEM micrographs indicate that the particle size of the rubber phase and volume fraction of the separated rubber phase increase with increasing the curing temperature and ENR content.

The dynamic mechanical properties of blends of diglycidyl ether of bisphenol-A based epoxy resin and internally epoxidized polybutadiene rubber have been studied by Bussi and Ishida [131] as a function of initial rubber content, stoichiometry and cure cycle of the epoxy resin. It is shown that both the glass transition temperature of the epoxy-rich continuous phase, \( T_{gE(r)} \), and the apparent enthalpy of activation associated with this transition, \( \Delta H_{aE(r)} \), are sensitive to the state of the rubber in the sample.

Cizravi and Subramanian [132] employed two sets of epoxidised natural rubber ENRs represented as ENR 50 and its liquid version LENR 50 to toughen epoxy matrices. The cured samples showed significant improvement in tensile and impact toughness. The morphological analysis of the fractured surface showed rubber dispersions in the sub micrometer size. Improvement in tensile and impact toughness was 250 % and 125 % respectively.

Chuayjuljit et al. [133] investigated the behaviour of epoxy resin blended with epoxidized natural rubber. It was found that the impact strength of epoxy resin has been improved by blending with ENRs. Tensile strength and Young's modulus were found to be decreased with an increasing
amount of epoxide groups in ENR and also with an increasing amount of ENR in the blends.

1.7.2.5 Acrylic rubbers

Wang and co-workers [134] employed novel polyfunctional acrylate elastomers with medium molecular weight as modifiers of epoxy resin. They observed an optimum functionality for the elastomers to obtain maximum impact resistance and observed that the maximum toughness effect of ETPnBA was attributed to the multiple distributions of particle sizes whereas in CTPnBA, aggregation of particles led to the reduction in toughness.

Cardwell and Yee [135] modified a DGEBA type resin with methacrylate-butadiene-styrene (MBS) rubber and investigated its fracture toughness. These authors observed that the fracture toughness of unmodified epoxy does not depend on the testing conditions while that of the rubber-modified samples increases with a decrease in testing rate or with an increase in temperature.

Yoo et al. [136] investigated the curing reactions of three cycloaliphatic epoxy resins with methyltetrahydrophthalic anhydride (MTHPA) by differential scanning calorimetry at different heating rates. Activation energy was calculated based on Kissinger method and varied in the range of 67–72 kJ/mol depending on sample. The curing kinetic behavior was well described by Sestak–Berggren (SB) model and the order of the curing reaction is observed to be from 0.02 to 2.11.

Ijima et al. [137] studied the effect of cross-link density on the toughness of modified epoxy resins with acrylic elastomers with pendant epoxy groups. The cross-link density of the epoxy matrix was controlled using hybrid hardeners composed of p,p′-diaminodiphenyl sulphone as a
primary diamine and p,p′-(N,N′-dimethyl)-diaminodiphenyl sulphone (MDS) as a secondary diamine. The addition of 20 wt% of the terpolymer led to a 100 % increase in the fracture toughness of the resin cured with the hybrid hardener. The lower the cross-link density, the larger was the fracture toughness and the lower was the glass transition temperature. It is concluded that the ductility of the epoxy matrix contributes greatly to toughening of epoxy resins with acrylic elastomers.

1.7.2.6 Other elastomers

Ratna and Simon [138] synthesized a family of carboxyl randomized poly(2-ethyl hexyl acrylate) (CRPEHA) liquid rubbers with different carboxyl functionality to modify epoxy resin. The effects of functionality of the liquid rubbers and ductility of the matrix on the mechanical properties of the modified networks were investigated. Ratna [139] has reported the study of chemorheology of curing as well as the phase separation behavior of carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) liquid rubber-modified epoxy mixtures by several techniques. The author has explained the flexural and impact properties of modified blends in terms of the generated morphological behavior. The study of CTPEHA as an impact modifier for epoxy resin cured with an ambient temperature hardener has been dealt in other works of the same authors [140-141].

Rubbery epoxy particles were successfully applied as toughening agents for glassy epoxy matrices [142]. Tuning of the final morphology was possible as the size and concentration of the dispersed phase can be chosen independently. The improvement in fracture toughness and morphological features of the fractured surfaces were same as in liquid rubbers.

Okamatsu and Ochi [143] prepared modified epoxy resins, which have pre-reacted urethane microspheres formed using dynamic vulcanization method in liquid diglycidylether of bisphenol A in order to give toughness
and improve adhesion properties of the cured epoxy system. Fracture energy $G_{1c}$ of the cured system was highly improved. Lap shear strength and peel strength were also improved. These mechanical and adhesion properties do not depend on any curing condition of epoxy resin because of the existing stable particles in the epoxy resin before curing.

1.7.3 Polyorganic siloxane modifiers
Recently, the use of liquid functional polysiloxanes as new modifiers for toughening of epoxy resins is triggering more and more interest. Functionally terminated siloxanes belong to the elastomeric materials.

Yorkgitis et al [144] applied functionally terminated polydimethylsiloxane and its statistical copolymers with either trifluoropropyl (TFP)-siloxane or diphenyl 1,2 siloxane to chemically modified bisphenol A based epoxy resins. They found that the compatibility between the epoxy resin and the siloxane modifiers was enhanced by increasing the percentage of TFP or diphenyl units relative to the dimethylsiloxane content. Also, improved fracture toughness was achieved in epoxy resins modified with polysiloxane copolymers containing 40 % or more TFP content, or 20 % diphenylsiloxane.

Ho and Wang [145] and Ho et al. [146] extensively studied the reduction of stress in thermosetting resins by incorporating organosiloxane moiety into the uncured thermosetting resins, and inducing a phase separation before curing to form small discontinuous rubber particles in the resin matrix. Vinyl or hydrid terminated polydimethyl siloxanes effectively reduced the stress of cured epoxy resins by reducing the flexural modulus and the coefficient of thermal expansion. The dispersed polysiloxane TPU rubbers also effectively reduce the stress of cured epoxy resins by reducing the flexural modulus and the coefficient of thermal expansion, while the $T_g$ is increased because of the formation of the rigid oxazolidone structure. Electronic
devices encapsulated with the dispersed siloxane modified epoxy molding compounds have exhibited excellent resistance to the thermal shock cycling test and have resulted in an extended use life for the devices. In their study, Kasemura et al. [147], showed that aminopropyl-terminated poly(dimethyl siloxane)s (ATPS) were good surface modifiers for epoxy resins because the oil and water repellency could be enhanced by blending the modifiers with epoxy resins. Yilgor and Yilgor [148] investigated the modification of epoxy networks with reactive polydimethylsiloxane (PDMS) oligomers. They used 1,3-bis(-aminopropyl) tetramethyldisiloxane (DSX) as a model curing agent and a modifier in epoxy resins, and attained the expected improvements in tensile and impact strengths of the modified products. But the glass transition temperatures of these materials showed a decrease with an increase in DSX content. Yayun [149] and Meng-huo [150] studied the thermal and mechanical properties of methoxyl-terminated polymethylphenylsiloxane-modified epoxy resins. The thermal stability and the fracture toughness of the modified products have been improved. The $T_g$ and the flexural modulus of the cross-linked epoxy network were not significantly lowered.

1.7.4 Hyperbranched polymers
Curing as well as the phase separation behavior of blends of a hydroxy-functionalized hyperbranched polymer (HBP) and epoxy resin have been studied by Ratna and Simon [151]. HBP strongly enhances the curing rate due to the catalytic effect of hydroxy groups. The impact properties have been discussed in terms of the morphological behavior for an epoxy matrix modified with various amounts of HBP. Dendritic hyperbranched polymers (HBPs) show outstanding performance as tougheners in epoxy resins as observed by Boogh et al. [152]. The critical strain energy
release rate, \( G_{ic} \), of a diglycidyl ether of bisphenol-F (DGEBF) resin was increased by a factor of 6 from 120 J/m\(^2\) to 720 J/m\(^2\) using only a 5% modifier with favourable processability of epoxy resins. By tailoring the HBP’s epoxy functionality and polarity to control reactivity, phase separation, final morphology and phase interactions, this toughening system is potentially applicable to a variety of thermoset resins. A new kind of reactive toughening accelerator for epoxy resin, amine-terminated hyperbranched polymer (H\(_2\)O-NMe\(_2\)) was synthesized by Lu et al. [153] and characterized by FT-IR spectroscopy. The results show that the \( E_a \) at glassy relaxation process of modified system is about 70–80 kJ/mol higher than that of unmodified system, and the high modulus and good thermal properties are still maintained.

1.7.5 Core shell particles

Bagheri and co-workers [154] used core–shell rubber particles and organically modified clay to modify epoxy resin and the changes in mechanical behavior were studied. The yield strength of the organoclay-filled epoxies increased modestly with increasing clay content and the yield strength of the rubber-modified compounds decreased with rubber content. The addition of nanoclay to the rubber-toughened epoxy resulted in a significant decrease in fracture toughness.

Toughened epoxy resin composites have been prepared by resin-transfer moulding using a range of toughening agents by Day et al. [155]. Blends of epoxy-functional preformed toughening particles have a three-layer morphology in which the inner core is crosslinked poly(methyl methacrylate), the intermediate layer is crosslinked poly(butyl acrylate) rubber and the outer layer is a poly[(methyl methacrylate)-co-(ethyl acrylate)-co-(glycidyl methacrylate)]. The presence of glycidyl groups in the outer layer facilitates chemical reaction with the matrix epoxy resin.
during curing. Use of the epoxy-functionalised toughening particles gave rise to superior properties compared with both the non-functionalised acrylic toughening particles and CTBN. A typical coreshell modifier particle is represented in Fig.1.13 [156].

![Figure 1.13](image)

**Figure 1.13** Schematic diagram of the typical acrylonitrile – butadiene-polystyrene (ABS) coreshell modifier particle [Ref 156 : SL Sun, XY Xu, HD Yang, HX Zhang, Polymer 46, 7632, 2005]

The use of structural core/shell latex particles as toughening agents provides a model system which allows independent control of several key factors that influence the fracture toughness of modified plastics. Qian et al. [157] varied the shell composition of poly(butadiene-co-styrene) [P(B-S)] core/poly(methyl methacrylate) (PMMA) shell particles by incorporating acrylonitrile (AN) comonomer into the PMMA shell at various AN/MMA ratios and by crosslinking the shell at various AN/MMA ratios. It was also found that the degree of particle dispersability plays a crucial role on the fracture toughness of the modified epoxies. A microclustered morphology provides a much higher toughness than a uniform particle distribution.

### 1.7.6 Liquid crystalline polymers

In-situ copolymerization of diglycidyl ether of 4,4’-dihydroxybiphenol (DGE-DHBP) with diglycidyl ether of bisphenol F networks using an anhydride curing agent has been investigated by D'Souza and coworkers [158]. DGEB-F is a commercial epoxy while cured DGE-DHBP shows liquid crystal transitions. Cure kinetics was determined using differential
scanning calorimetry. The data were fitted using an autocatalytic curing model for both pure and mixed components.

The effect of coreacting diglycidyl ether of bisphenol F with diglycidyl ether of 4, 4′-dihydroxybiphenol on mechanical properties is investigated by Punchaipetch et al. [159]. DGE-DHBP shows a liquid crystal (LC) transition upon curing. SEM and DMA studies indicate that the mechanical properties of these blended samples are significantly improved at 10–20 % by weight of DGE-DHBP due to the reinforcement provided by the rigid LC component.

1.7.7 Nano structured materials as toughners

1.7.7.1 Nano fillers

Nano-particles are effective tougheners for epoxy matrices than other micro particles and provide good material properties to the system. Wetzel et al. [160] modified epoxy matrix with various amounts of micro- and nano-scale particles of CaSiO₃ (4-15 μm) and alumina (Al₂O₃) (13 nm) and analysed the effect of these particles on the impact energy, flexural strength, and dynamic mechanical thermal properties. Both ductility and modulus were significantly improved in a model system of nanoscale alumina filled bisphenol A based epoxy with two interface conditions done by Zhao et al. [161]. The crack arresting mechanisms included particle matrix debonding, plastic void growth, and in the nanocomposites with a stronger interface, significant plastic deformation of the matrix around the well-bonded nanoparticles.

The tensile and impact properties of amine-cured diglycidyl ether of bisphenol A based nanocomposites reinforced by organomontmorillonite clay nanoplatelets are studied by Miyagawa et al. [162]. The izod impact strength decreased with increasing clay content. The roughness of the failure surface was correlated with the tensile strength.
Zhang et al. [163] determined the electrical properties of nanocomposites by the conductive paths of carbon black and influenced by a "network" of silica. As a non-conductive component, excessive silica will prevent electron flow, giving rise to low conductivity.

Lee et al. [164] mixed carboxyl-terminated butadiene-acrylonitrile with nanoclay to improve the toughness and mechanical strength of bisphenol A type epoxy. The thermogravimetry-derivative thermogravimetry (TG–DTG) curves of the samples showed a rapid decrease as the absorption dose increased and the heating rate decreased.

Miyagawa et al. [165] investigated the tensile and impact properties of amine-cured diglycidyl ether of bisphenol A based nanocomposites reinforced by organomontmorillonite clay nanoplatelets. The sonication processing scheme involved the sonication of the constituent materials in a solvent followed by solvent extraction to generate nanocomposites with homogeneous dispersions of the organoclay nanoplatelets. The microstructure of the clay nanoplatelets in the nanocomposites was observed with transmission electron microscopy, and the clay nanoplatelets were well dispersed and were intercalated and exfoliated. The tensile modulus of epoxy at room temperature, increased approximately 50% with the addition of 10 wt % (6.0 vol %) clay nanoplatelets.

Bakar et al. [166] modified bisphenol-A epoxy resin with a polyamide oligomer and a small amount of montmorillonite and cured with triethylenetetramine. Compositions with different amounts of modifiers were obtained. It was found that the addition of 2 % montmorillonite or 5 % polyamide resulted in the best improvement of impact strength and critical stress intensity factor relative to the unmodified epoxy resin. From scanning electron microscopy and thermal analysis, it appears that the toughening may arise from chemical reactions that have taken place.
between the epoxy resin and the polymeric modifier, which was partially solubilized in the resin matrix.

Pham and co workers [167] modified bisphenol A based epoxy with an amphiphilic poly(ethylene-alt-propylene)–b-poly(ethylene oxide) (PEP–PEO) block copolymer as a toughening agent. PEP–PEO molecules self-assemble into spherical micelles in epoxy with an average diameter of 15 nm and give rise to 180 % improvement in fracture resistance. The toughened epoxy exhibits mechanical properties that are significantly more rate dependent than the neat epoxy material. A higher test rate leads to a more brittle behavior of the material and a lower fracture toughness value. With careful systematic study of their micromechanical deformation processes, the observed strain rate dependence is explained.

Nano structured TiO₂ [168] nano-ZnO [169] and nano-SiO₂ [170] were dispersed in epoxy resin to improve both the mechanical and the thermal properties because of their large specific surface area. Li et al. [171] found the impact strength and thermal properties of epoxy resin improved by forming inter cross-linked networks in epoxy resin with nano-SiO₂. Mirmohseni and Zavareh [172] incorporated both acrylonitrile-butadiene-styrene copolymer and organically modified clay (Cloisite 30B) into epoxy matrix and obtained improved material with enhanced tensile strength, elongation at breaks and impact strength. With incorporation of 2.5 % clay and 4 phr ABS into epoxy matrix, 133 % increase was observed for impact strength. Ternary nanocomposite had impact and tensile strengths greater than that of the binary systems. Exfoliated clay structure was obtained for epoxy/clay and epoxy/ABS/clay nanocomposite.

1.7.7.2 Nano structured blends

Xu and Zheng [173] synthesized poly(ε-caprolactone)-block-poly dimethyl siloxane-block-poly(ε-caprolactone) triblock copolymer (PCL-b-PDMS-b-
PCL) via the ring-opening polymerization of \(\varepsilon\)-caprolactone with dihydroxypropyl-terminated PDMS (HTPDMS) as the initiator. The triblock copolymer was incorporated to prepare nanostructured thermosetting blends. The formation of the nanostructures in the thermosetting composites was judged to follow the self-assembly mechanism in terms of the difference in miscibility of PDMS and PCL sub chains with epoxy resin after and before curing reaction.

Zheng and co workers [174] synthesized poly(\(\varepsilon\)-caprolactone)-block-poly (butadiene-co-acrylonitrile)-block-poly(\(\varepsilon\)-caprolactone) triblock copolymer via the ring-opening polymerization of \(\varepsilon\)-caprolactone with dihydroxyl-terminated butadiene-co-acrylonitrile random copolymer. The amphiphilic block copolymer was used to toughen epoxy thermosets via the formation of nanostructures. The fracture toughness of the thermosets was evaluated in terms of the measurement of critical stress field intensity factor. It is noted that at the identical composition the nanostructured blends significantly displayed higher fracture toughness than the ternary blends.

Kim et al. [175] attempted to enhance the crack resistance of a carbon/epoxy composite by adding multi-walled carbon nanotubes (MWNTs) into the epoxy resin formulation. Prior to assessing the effect of MWNTs, the effect of a toughened epoxy resin on the interlaminar fracture toughness was investigated at \(-150\) °C using double cantilever beam (DCB) specimens. It was found that the degree of fracture toughness enhancement obtained from application of the toughened epoxy at cryogenic temperature was less than that at room temperature, due to embrittlement of the epoxy resin.
Material systems blended with 0.2 wt% and 0.7 wt% of MWNTs showed enhanced fracture toughness and low crack density at the cryogenic temperature.

1.8 Toughening mechanisms

In recent years, many advances have taken place in the theoretical understanding of the toughening mechanisms for both rubber and thermoplastic toughened epoxy resins. The relationships between microstructure and fracture behavior of toughened thermoset have been illustrated quantitatively. Several reviews have given detailed descriptions of the existing toughening mechanisms proposed to explain the improved toughness for both rubber and thermoplastic toughened epoxy resins. Sultan et al. [20] were among the first to investigate the behavior of rubber toughened EP and suggested the toughening mechanism involving generation of crazes and shear banding in the vicinity of rubber particles. Some important aspects of these toughening mechanisms are summarized below:

1.8.1 Crack-pinning mechanism

This theory states that as the crack begins to propagate through the resin, the crack front bows out between the filler particles but remains pinned at the particles [176]. A schematic diagram of the crack-pinning mechanism is shown in Fig.1.14. This mechanism is based on the function of small particles as toughening agents [177]. Because this mechanism operates mainly with inorganic fillers that resist fracture during failure of the epoxy matrix resin, it is generally less important in ductile matrix materials.
Figure 1.14 Schematic diagram showing the crack-pinning mechanism: (a) An opening crack pinned by the second phase particles and (b) successive stages of a crack initiating with and passing through a row of second phase particles (Ref 177: F.U.Zengli and S.Yishi, Chinese J Polym. Sci. 7, 4, 367, 1989)

1.8.2 Microcracking mechanism

A schematic diagram of the microcracking mechanism is shown in Fig. 1.15. Microcracks due to rubber particles cause tensile yielding and, thus, a large tensile deformation [178]. Voids result when the microcracks open, and these voids permit large strains. Debonding or microcracking effectively lowers the modulus in the frontal process zone around the
crack tip, and thus effectively reduces the stress intensity there. But this theory could not explain many phenomena such as stress-whitening, the large amount of plastic deformations, higher fracture toughness at high temperature and the fact that nonreactive rigid thermoplastic particles also toughen some systems [179].

![Figure 1.15](image_url) Schematic diagrams showing the crack-pinning mechanism (Ref180: R.A. Pearson, A. F. Yee, J.Mater.Sci. 24, 2571, 1989)

1.8.3 Formation of plastic zone in the matrix

Rubber particles increase the size of plastic zone ahead of the crack tip and hence increase the fracture toughness. This was attributed to the suppression of microcrack formation in the presence of a highly flexibilised interface. This mechanism suggests that extensive plastic deformation in the matrix is the major energy dissipative process in rubber modified epoxies.

1.8.3.1 Crazing of the matrix

Rubber particles initiate crazes in the surrounding matrix at the same time they act as craze terminators preventing uninhibited craze growth resulting
in premature failure. The multiple crazing processes consume significant amount of energy and hence increase the fracture toughness. This mechanism was proposed on the basis of observations like stress whitening ahead of the crack tip, strong dependence of fracture toughness on particle size and pressure sensitivity of yielding. Transmission electron micrograph (TEM) confirmed that crazes frequently initiate from rubber particles [181-183]. A typical micrograph of multiple crazing mechanisms in high impact poly styrene (HIPS) is depicted in Figure 1.16 [184].

**Figure 1.16** Transmission electron micrograph of a microtomed section of HIPS, stained with osmium tetroxide [Ref.184: Kambour, R.P and Russel D. R., Polymer 12, 237, 1971.]
1.8.4 Localized shear yielding (or shear banding) mechanism

A schematic diagram of the localized shear yielding mechanism is shown in Fig. 1.17. Beahan et al. [185] suggested that the rubber-tear mechanism only makes a secondary contribution to toughening, but it does not represent the major toughening mechanism. They proposed a mechanism that involves dilatational deformation of the matrix, and cavitation of the rubber particles in response to the triaxial stresses near the crack tip, combined with shear yielding between the holes formed by the cavitated rubber particles. The stress-whitening was attributed to light scattering by these holes, and the major energy absorption mechanism was suggested to be the plastic deformation of the matrix. Plastic deformation blunts the crack tip, which reduces the local stress concentration and allows the material to support higher loads before failure occurs.

Figure 1.17  Schematic diagrams showing plastic deformation (Ref 185: Beahan P, Thomas A, Bevis M. J Mater Sci. 11, 1207, 1976)

Generally plastic deformation is localized through the postyield strain softening of the epoxy matrix and the shear deformations that initiate at one particle but terminate at another. Enhanced plastic deformation in the
multiphase material is evident by comparing Fig.1.18A and 1.18B and observing the greatly increased surface roughness and drawn ridges of epoxy polymer in Fig.1.18B [186]. Further, the localized nature of the plastic shear bands, visible as furrows running at right angles of approximately 45° to the principal tensile stress (i.e., in the direction of maximum shear stress) is illustrated in Fig.1.19 [187].

Figure 1.18 Scanning electron micrographs of fracture surfaces (test temperature, 23°C). A: Unmodified epoxy polymer; B: Rubber-toughened epoxy polymer [volume fraction of rubber phase=0.14] [Ref 186: Chan LC, Gillham JK, Kinloch AJ, Shaw SJ. In Rubber-Modified Thermoset Resins. Riew CK, Gillham JK Eds. Advances in Chemistry 208, ACS, Washington, DC, 1984, 261]
1.8.5 Rubber particle cavitation and induced shear deformation in the matrix

Rubber particle cavitation is the primary toughening mechanism in rubber modified epoxies especially in relatively lower crosslink density epoxy resins [188]. Fig.1.22 represents the SEM of fracture surface of rubber toughened epoxy showing cavitated rubber particles. Rubber particles cavitate because of the triaxial tension around the crack tip. This cavitational process relieves the plane strain constraint ahead of the crack tip, allowing the stress concentrations associated cavitated particles to activate extensive shear deformation of the matrix in the form of dilatational void growth as represented in Fig.1.20.
1.8.6 Particle bridging (rigid particles) mechanism

A schematic diagram of the particle-bridging mechanism is shown in Fig. 1.21. In this toughening mechanism, it was proposed that a rigid or ductile particle plays two roles: (i) it acts as a bridging particle that applies compressive traction in the crack wake (ii) the ductile particle deforms plastically in the material surrounding the crack tip, which provides additional crack shielding. Sigl et al [189] also pointed out that the shielding which resulted from yielded particles is negligible, and that the particle bridging provides most of the improvement in toughness. In contrast to the crack-pinning mechanism, the particle-bridging mechanism favors large particles and emphasizes the quantum of energy needed to rupture the ductile phase.

Figure 1.20 Scanning electron micrograph of fracture surface of rubber toughened epoxy showing cavitated rubber particles (Ref.188: AJ Kinloch. American Chemical Society, 67- 72, 1984).
Figure 1.21 Schematic diagrams showing the particle-bridging mechanism (Ref.189: L.S Sigl, P.A Magata, B.I Dageleidh, R.M Mc Meeking, A. G Evans, Acta Metall, 30, 1945, 36, 1988)

Good interfacial adhesion is a prerequisite for this mechanism to operate. Rubber particles span the crack and exert closure tractions on the fracture surfaces. This process effectively reduces the stress intensity at the crack tip. Alternatively, rubber particles are stretched and torn to fracture, which consumes additional fracture energy. This mechanism was proposed on the basis of microscopic observation of the fracture surfaces. This mechanism was considered as a secondary toughening mechanism in rubber modified epoxy resin. However, rubber particle bridging has been shown to be important for highly crosslinked epoxies modified by relatively large particles.

1.8.7 Crack-path deflection mechanism

A schematic diagram of the crack-path deflection mechanism is shown in Fig. 1.22. The crack-path deflection may explain the increase in toughness by stress intensity approach. There are both mode I and mode II characters of the crack opening. Most materials are more resistant to mode II crack opening. The deflection of the crack path decreases the mode I crack opening, but increases the mode II crack opening. Therefore, the materials exhibit a higher apparent toughness. This
mechanism does not need to consider the particle size of modifiers, but it is thought that uneven spacing provides better results than uniform spacing [190].

![Diagram showing crack-path deflection mechanism](image)

**Figure 1.22** A schematic diagram showing crack-path deflection mechanism (Ref.190: K. T Feber and A. G Evans, *J. of Am. Cerom. Soc.*, 67, 255, 1984)

This mechanism was considered to be a secondary toughening mechanism. Rubber particles cause the main crack to fork into many secondary cracks, distributing the local stress intensity of the main crack to multiple cracks and/or deviating the crack off the principal plane of propagation, which increases the area of the crack surface and induces a mixed mode of crack propagation as depicted in Figs. 1.23 and 1.24 [191]. This mechanism is important for highly crosslinked epoxies modified with relatively large particles.

1.8.8 Massive shear-banding mechanism

The crack-tip shielding in rubber-modified epoxy resins occurs due to the reduction in yield stress by the stress concentration of the compliant rubber particles that facilitate shear yielding. Kim and Brown [192] provide evidence to show that shear-yielding also exists in thermoplastic particles modified epoxy system.

Even though there are various toughening mechanisms proposed by different researchers, it seems that a single theory is not sufficient to explain every experimental result and phenomenon of toughening. One reason may be the discrepancy of the raw materials chosen by different researchers, because the initial properties of raw materials have significant influence on the final fracture properties of epoxy materials. Another reason lies in the fact that the fracture itself is a complex phenomenon, and a single theory cannot represent every detail. Huang et al. [193] combined the schematic diagrams of several toughening mechanisms and gave a comprehensive schematic diagram to describe the different toughening mechanisms involved in the fracture of rubber-toughened epoxy polymers, as shown in Fig. 1.25.
Thus the toughness of a material is enhanced by introduction of mechanisms for energy absorption in response to the application of stress. The improved toughness of rubber-toughened epoxies has been proposed through the mechanisms; cavitation, crazing, shear banding and elastic deformation of rubber particles. These mechanisms can either act alone, or in combination, to produce toughening effect. Scanning electron microscopy of fracture surfaces indicates cavitation of the rubber particles to be a major deformation mechanism. The fracture surface shows that the cavitated particles generate shear bands. Cavitation relieves the triaxial tension at the crack tip, and shear band formation creates a large plastic zone. So the toughening mechanism of rubber modified epoxy resins may be a combination of the above mechanisms.
1.9 Structure and properties of natural rubber

Natural rubber (NR) is a completely amorphous polymer. Rubber is a member of an important group of polymers called elastomers. Elastomers are amorphous polymers that have the ability to stretch and then return to their original shape at temperatures above $T_g$. At temperatures below $T_g$, elastomers become rigid glassy solids and lose all elasticity. The introduction of relatively large and stiff substituents (such as benzene rings) will interfere with this chain movement, thus increasing $T_g$. The introduction of small molecular compounds called plasticisers into the polymer matrix increases the interchain spacing, allowing chain movement at lower temperatures with a resulting decrease in $T_g$.

Chemically NR is a polymer of isoprene units linked together at 1-4 positions [194-195] and arranged in cis configuration as shown in Fig.1.26.

![Figure 1.26 Structure of natural rubber.](image)

The molecular weight ranges from 3 to 10 lakhs. Due to the presence of a very reactive double bond in the main chain, it is susceptible to attack by oxygen, ozone etc. and has very poor resistance to high temperature.

1.9.1 Liquid natural rubber (LNR)

Liquid NR is the product of the thermal or chemical depolymerisation of NR. It consists of the same monomer (1, 4 cis polyisoprene), contains the same natural components that are responsible for colour, odour, appearance and performance and has the same density, unsaturation and
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glass transition temperature as NR. The difference is found in molecular weight, less than 100,000. The liquid non-volatile material is dark brown and can be used as a premium plasticizer. It is available in several grades. The grades with higher molecular weights have a higher viscosity, from 4000 poise down to 400 poise. When used as a plasticiser it is possible to fill rubber compounds with higher loads of carbon black and still keep good cure characteristics since the LNR vulcanizes together with the NR. The advantages are further reduced risk of scorching, lower energy demand, improved mould flow and lower plasticity.

LNR can be prepared by the mechanical, photochemical or oxidative degradation of natural rubber. Hydroxyl terminated liquid natural rubber (HTNR) was prepared by Gupta et al. [196] by thermal degradation in presence of \( \text{H}_2\text{O}_2 \) as the reagent. Ravindran et al. [197] reported a method for large scale preparation of HTNR by photochemical degradation in presence of \( \text{H}_2\text{O}_2 \).

Compatibility of liquid rubber with epoxy resin can be substantially increased by functionalisation. Epoxidation progressively increases \( T_g \) of rubbers. Epoxy terminated liquid natural rubber (ELNR) exhibits oil resistance and is a better adhesive too. It can be generated from liquid rubber by peracids [198]. As peracids are electrophilic in nature, epoxidation of natural rubber is facilitated by the presence of electron donating methyl groups in isoprene.

Epoxidized natural rubber (ENR) is qualified for the reinforcement of the epoxy resin because of its good reactivity and acceptable compatibility with the epoxy matrix. ENR is usually prepared by epoxidation of natural rubber with peracetic, perbenzoic, and perpthallic acids in solutions [199]. The introduction of the epoxy group lets ENR have a higher glass transition temperature, a better oil resistance, and a higher polarity than
the natural rubber [200]. By varying the degree of epoxidation, ENR with different physical properties, such as $T_g$, resilience, damping, polarity, oil swelling, and compatibility, can be prepared [199-201].

Aziz et al. [202] have studied the cure process and the mechanical properties of liquid polymethylmethacrylate grafted natural rubber (LMG30) modified epoxy. Addition of LMG30 significantly increased the fracture toughness and the impact strength of the epoxy resin. The glass transition temperature however, decreases as the rubber content increases. The SEM analysis shows uniform dispersion of rubber particles within the epoxy matrix with average particle size between 0.4 to 0.8 µm in diameter. The effects of epoxidized natural rubber (ENR) on the curing behaviors and adhesive strengths of an epoxy (diglycidyl ether of bisphenol-A) and dicyandiamide/2-methyl imidazole system are studied with differential thermal calorimetry and scanning electron microscopy by Hong and Chan [203]. The result of SEM indicates that the particle size of the rubber phase increases with increase in the curing temperature and ENR content. The volume fraction of the separated rubber phase also follows the similar trend except at the high curing temperature indicating that the dissolution of epoxy resin in the ENR rubber phase also change with respect to the curing temperature and ENR content. Cizarvi and Subramaniam [204] have investigated thermal and mechanical properties of epoxidized natural rubber modified epoxy matrices. Two sets (A and B) of bisphenol A-diglycidyl ether (DGEBA) based epoxy resin formulations were modified with epoxidized natural rubber (ENR 50) and its liquid version (LENR 50), and cured with amino propoxylate initiator/accelerator at ambient temperatures. Scanning electron micrographs of fractured surfaces show uniform rubber dispersions in the submicrometre size range. Significant improvements in tensile toughness and impact toughness could only be observed for first
set. Diglycidyl ether of bisphenol A type epoxy resin has been modified with maleated depolymerised natural rubber (MDPR) by Kothandaraman and Kumar [205]. MDPR has been developed by grafting maleic anhydride with depolymerised natural rubber. The addition of MDPR to epoxy resin results in an increase in the elongation at break and flexural strain to failure values with some expense in other mechanical properties. The unnotched izod impact strength of epoxy/MDPR blends are higher than that of the unmodified epoxy. Yoksan [206] prepared ENR based adhesives under the concepts of (i) crosslinking at epoxirane rings and/or (ii) curing at \( \cap \)-carbon positions along the rubber chain. The crosslinking at epoxirane rings was accomplished when two crosslinking agent/catalyst systems, i.e., diamine/bisphenol A and anhydride/imidazole were used. However, the crosslinking efficiency of the anhydride/imidazole crosslink system was higher than that of the diamine/bisphenol A crosslink system. Chuayjuljit [207] investigated the behaviour of epoxy resin blended with epoxidized natural rubber (ENR). ENRs were prepared via \textit{in situ} epoxidation method. Scanning electron microscope micrograph of fracture surface suggested that the toughening of epoxy resin was induced by the presence of ENR globular nodules attached to the epoxy matrix. TGA and DSC analysis revealed that thermal decomposition temperature and glass transition temperature of the samples were slightly different.

The focus of the present study is to use both hydroxyl terminated and epoxy terminated liquid natural rubber as modifiers for epoxy resins taking advantages of the ductility of the diglycidyl epoxy resin and bifunctional liquid rubbers.
1.10 Scope and objectives of the work

It is well known that epoxies can be cured rapidly and during cure, no volatile byproducts are formed and are widely used as adhesives, sealants and dripping compounds, flooring and anti skid surfacing etc. But for structural applications modulus and strength decide the suitability of the material. Thus toughness improvement of a material has to be achieved without significant loss in modulus and strength [208].

The outstanding versatility of the resin is due to the great reactivity of the epoxy group that can react with different compounds like aliphatic and aromatic amines, anhydrides, and polyamides. The use of different hardeners produces changes on the macromolecular network of the cross linked epoxy systems and also on the resulting macroscopic physical properties of epoxy-based materials. Most studies have been devoted to different aspects related to epoxy resins cured with amine curing agents. In fact, anhydride-like curing agents are preferred for electrical and electronic applications or when chemical safety has to be taken into account.

From the foregoing discussion, it is understood that a well-dispersed and good chemically bonded rubbery phase with a suitable volume fraction and particle size/distribution can offer the best toughness increase to a specific epoxy system but without the significant loss of the elastic modulus and yield strength. The optimal formulation and curing conditions are dependent on the type of epoxy, curing agent, and rubber used. The structure-property relationship of the modified resin depends on curing conditions, nature of curing agents, and the properties of the toughner employed. Functionalized liquid rubbers are efficiently used as modifiers without much compromise in thermomechanical properties.
From the review on rubber toughened epoxy resins, it was observed that relatively few systematic studies were conducted on liquid natural rubber modified epoxy resins. The relatively less literature on LNR toughened epoxy is due to the difficulty in the synthesis and processing conditions. A bifunctional diglycidyl ether of bisphenol A based epoxy resin was utilized in the present study for blending with liquid natural rubbers due to its less cross link density which leads to greater toughness achievement. The blends were cured with a cyclo aliphatic anhydride, nadic methyl anhydride, which possess good mechanical and electrical properties, low shrinkage and viscosity, long pot life and little color formation. The major objectives of the study are:

(i) To synthesise functionised liquid natural rubbers like hydroxy terminated liquid natural rubber (HTLNR) and epoxy terminated liquid natural rubber (ETLNR) of varying molecular weights.

(ii) To evaluate the structure and properties of the synthesised liquid rubbers using various analytical techniques.

(iii) To analyse the miscibility of HTLNR and ETLNR in epoxy resin using DSC.

(iv) To study the interactions between blend components and the completion of cure through FTIR.

(v) To understand the morphology generation and fracture mechanisms responsible for the enhancement in fracture toughness through scanning electron microscopy.

(vi) To investigate cure kinetics of selected blend systems to understand the cure reaction.
(vii) To study the main physical changes such as gelation and vitrification taking place during the curing of the thermoset resin through chemorheology.

(viii) To investigate the viscoelastic properties of the blends with respect to composition and to model the $T_g$-composition behaviour.

(ix) To study the effect of composition of modifier on the fracture toughness, tensile and flexural properties of the blends.

(x) To investigate the localized mechanical properties like hardness and elastic moduli of the epoxy-rubber blends using nanoindentation technique.

(xi) To investigate the thermal stability of the blends using TGA.

The modification of epoxies by synthetic rubber has been extensively reported but so far no serious attempts have been done using liquid natural rubber. Though photodepolymerisation of natural rubber is a time consuming process, there is scope for getting different molecular weights by varying the experimental conditions. The easy availability of the raw material and its comparatively low cost favour the preparation of the epoxy–liquid natural rubber blends. Its main attraction is cost-effectiveness. In view of this, a detailed investigation has been carried out on the morphology and mechanical and thermomechanical properties of epoxy resin/liquid natural rubber blends.
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