Chapter 11

Conclusions and Future Scope

The major conclusions that are drawn from the present study are summarized in this chapter. Future scope and possible applications are also mentioned herewith.
Polymer blends are high performance multicomponent systems, so depend on the physical and chemical properties of the components, they can be arranged into a variety of morphologies using different processing conditions. Many important properties of polymer blends such as thermal stability, chemical resistance, elastic modulus and fracture toughness depend critically on the nature of microscopical arrangement. A well-designed and controlled morphology can result in polymer blends with property combinations that cannot be easily achieved by a homogeneous polymer. Such polymer blends are extensively used for a wide range of applications. A wide range of blends such as thermoplastic/thermoplastic, thermoplastic/rubber, rubber/rubber, thermoset/rubber and thermoset/thermoplastic are available for various applications. Thermoset materials are important base matrix for many blend materials and composites. Epoxy resin is an important class of thermosetting polymer which can be used in both molding and laminating techniques to make glass fiber-reinforced articles with better mechanical strength, chemical resistance and electrical insulating properties. Besides, they are used for a variety of applications in aerospace, military and automobile industry. But the inherent brittleness of epoxy resins necessitates toughening the material for structural applications. High performance engineering thermoplastics as well as liquid rubbers are employed for toughening epoxy resins. The present work is devoted to the toughening studies of diglycidyl ether of biphenol-A (DGEBA) based epoxy resin cured with an anhydride hardener. The liquid rubbers used for modifying the resin were carboxyl terminated copolymer of butadiene and acrylonitrile (CTBN) and hydroxyl terminated polybutadiene (HTPB).

Epoxy-CTBN/HTPB blends were prepared by stirring stoichiometric amount of epoxy resin and hardener for 10 to 15 min so as to ensure proper dispersion of hardener. Varying weights of CTBN or HTPB were added
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followed by accelerator and stirred again for 20 min. The mixture was then degassed to remove any issuing gases. Blend samples were prepared by pouring the mixture into a greased steel mould. It was then pre-cured under ambient conditions for 30 min at 100°C and then post cured for 2 h at 200°C.

Since the ultimate aim of the study was to toughen the epoxy matrix for many end-use applications, all techniques to check the enhancement of toughness characteristics have been performed. Moreover, since the microstructural aspects of the blend system influence the macroscopic properties, efforts have been taken to study the structure-property relationship in modified epoxies using available techniques.

Small angle laser light scattering (SALLS) was employed to analyze the miscibility aspects and phase separation phenomenon in epoxy-CTBN blends. The analysis was supported by scanning techniques such as optical microscopy (OM) and scanning electron microscope (SEM). These techniques were used to follow the resultant phase morphology development. Light scattering measurements were performed at dynamic as well as isothermal curing conditions for epoxy-CTBN systems having CTBN concentration in the range of 5-25 phr (weight %). The dynamic light scattering studies were able to identify miscibility as well as cloud point temperatures. The intensity profile was used to calculate the correlation length at different temperatures of curing. The early stage of demixing process was explained by Cahn-Hilliard theory. The nature of isothermal light scattering profile together with the bi-continuous development of morphology, from OM, during cure, threw light on the possible spinodal demixing mechanism. Further, SALLS technique was employed to compute the size of phase separated particles which increased with increase in weight content of elastomer. Epoxy-CTBN system showed UCST behavior. The elastomer was found to be miscible in the resin above ambient temperature and thereafter phase separated. Finally, a phase
diagram has been computed using Flory-Huggins equation. Since the elastomer, HTPB is immiscible in epoxy resin; there was no possibility for light scattering studies in this system.

Pressure-Volume-Temperature (PVT) analyzes were done to monitor the specific volume change and cure shrinkage during the cure reaction of epoxy-elastomer blends with varying weight content of elastomers. The conversion of neat epoxy at different curing temperatures proved the reaction as a thermally catalyzed one. A decreasing trend in cure shrinkage with increase in initial weight content of elastomer was observed. Since the size of phase separated elastomer domains increases with the loadings of rubber, cure shrinkage was related to the morphology of the epoxy network. The formation of bigger elastomer domains in epoxy-HTPB systems, due to its immiscible behavior, caused less cure shrinkage as compared to their CTBN counter parts. Experimental and theoretical conversions were delayed by the inclusion of elastomer. Furthermore, pressure influenced the cure reaction by decreasing specific volume and conversion. Finally, the data from PVT analysis were utilized to compute coefficient of isothermal compressibility (α) and coefficient of volume thermal expansivity (β). The coefficient of isothermal compressibility increased with increasing elastomer content. The coefficient of thermal expansivity also increased with the addition of rubber in the uncured state.

Neat epoxy system and rubber-modified blends were subjected to rheology measurements to investigate the physical transformations such as gelation and vitrification taking place during the cure reaction. Viscosity profile indicated the phase separation and network formation in epoxy-elastomer blends. The viscoelastic behavior of the phase separated epoxy-CTBN blend system was analyzed by a two-phase suspension model. Gelation and vitrification during the cure reaction were explained by time-temperature-transformation (TTT) diagram. Inclusion of rubber caused
reduction in the concentration of reacting species as well as changes in the viscosity of the blend systems. This brought about delay in polymerization and gel time. The increase in viscosity was more facile in epoxy-CTBN blends than in epoxy-HTPB, both having the same amount of elastomer. Also, rheology measurements were able to compute the activation energy of the reaction.

Morphology of cured network showed that the phase separated particles in epoxy-HTPB systems were bigger than in epoxy-CTBN having the same amount of rubber. The significant difference in the miscibility of both elastomers in epoxy resin accounted for this. The toughness characteristics of epoxy-CTBN blends were mainly due to plastic deformation and shear yielding of the matrix, crack bridging as well as cavitation of rubber particles. Conversely, shear localization by rubber particles and reduction in cross-linking density were supposed to be responsible for the major toughening behavior in epoxy-HTPB matrices. The percentage of CTBN at the critical composition has been discussed based on Flory Huggins equation of solutions. Finally, AFM technique has also employed to monitor the developed morphology in rubber-epoxy blends.

The in-situ cure reaction and kinetic analysis of blend systems were scrutinized by Fourier transform infra red spectroscopy (FTIR) and differential scanning calorimetric (DSC) technique. The intensity variations in the anhydride (1858 and 1780 cm$^{-1}$) and epoxy bands (913 cm$^{-1}$) during the cure reaction were used to monitor the reaction course. The anhydride bands reduced and a new C=O-band appeared at 1744 cm$^{-1}$ due to ester group formation. DSC measurements proved that the extent of conversion and rate of reaction decreased with the incorporation of more elastomer content and with the decrease of cure temperature. This was accounted to the phase separation of rubber phase from the epoxy phase. CTBN
inclusion decreased the rate and conversion of the reaction to a greater extent than HTPB elastomer. Finally the reaction was analyzed by an autocatalytic model and good correlations were obtained with the experimental data up to the vitrification state. The kinetic parameters such as the order, reaction constants and activation energy of the reaction were computed from the model. Later part of the reaction was explained by a diffusion control mechanism by introducing a diffusion factor.

The viscoelastic behavior of CTBN-modified blends was characterized by noticeable shift in upper and lower $T_g$ values from that of the neat epoxy system. On the other hand such significant shifts in the values of $T_g$ were not observed in HTPB samples. This led to the conclusion that in epoxy-CTBN blends the phase separated rubber domains were not pure unlike in HTPB systems where the phase separated elastomer particles were not mixed up with epoxy resin. This was related to the greater level of miscibility behavior of CTBN in epoxy. The dissolution behaviors in epoxy-CTBN systems were modeled with Fox and Gordon-Taylor equations. Also, schematic models for the phase separated morphology of modified epoxies were presented based on these observations. Significant reduction in cross-link densities was noted in epoxy-HTPB blends compared to CTBN samples which are assigned to the presence of comparatively bigger phase separated elastomer domains in former systems.

Presence of polar functional groups increased dielectric constant in epoxy-CTBN blends. Volume resistivity decreased and electrical conductivity increased with increase in frequency and CTBN loadings. Orientation polarization in epoxy-CTBN samples increased by the presence of polar groups which enhanced the dissipation factor with frequency and elastomer loading.
Thermal degradation behavior of modified samples was investigated by thermogravimetric analysis (TGA). Main degradations observed were the cleavage due to unreacted epoxy and epoxy network. Also, activation energy for the decomposition of neat and rubber incorporated blend samples were computed. Greater cross-linking nature of neat system was responsible for the higher activation energy.

Since the ultimate aim of the incorporation of liquid rubbers in the epoxy matrix was to toughen the matrix for many end use applications, special attention was given to determine the bulk mechanical properties of the cured samples. Neat epoxy samples were distinguished by their brittle nature of failure. While, epoxy-CTBN samples were characterized by ductile failure as well as reduction in tensile strength and modulus. These properties enhanced with the inclusion of more rubber into the epoxy matrix. On the other hand, HTPB-samples underwent almost brittle failure after a certain extent of yield and exhibited comparatively smaller decrease in tensile properties. This was due to the miscibility difference of the elastomers in epoxy. Unlike HTPB, CTBN was miscible in epoxy, and this property has greatly influenced the mechanical performances of cured samples. The incorporation of low modulus elastomer reduced the modulus and tensile properties. The impact strength of epoxy-CTBN samples containing 10-15 weight % of elastomer was greater than HTPB samples having an equivalent concentration of rubber. However, the addition of HTPB up to 10 weight % has improved the impact strength. The higher miscibility of CTBN in epoxy and phase separation of elastomer domains which are well adhered to the matrix rationalized this observation. Flexural properties were also decreased with the incorporation of CTBN. Epoxy-CTBN blends having 10-15 phr CTBN content exhibited more prominent fracture toughness characteristics compared to HTPB samples and was explained by the variation in morphology of these systems. Based on the observations, some of the
toughening mechanisms existing in rubber toughened epoxies were discussed. Further, more prominent reduction in heat deflection temperature and hardness of blend samples were observed in CTBN-modified epoxies.

The localized mechanical properties of elastomer-modified samples were investigated by nanoindentation technique. Reduction in modulus and hardness were more prominent in CTBN-modified epoxies which are accredited to the higher interaction of the elastomer with the resin matrix. A methodology based on the comparison of the ratio of indentation modulus and hardness, \( \frac{E}{H} \), with impact strength was used to evaluate the fracture behavior of modified epoxies. Both properties showed maximum for samples in the range of 10-15 phr CTBN and for 10 phr HTPB concentration proving the fracture toughness property of these samples.

Thermophysical properties such as thermal conductivity and diffusivity of elastomer-modified epoxies were determined using a periodical method. The noticeable shift in thermal conductivity of the modified epoxies was correlated with the continuous nature of morphological development upon the inclusion of higher weight content of elastomers. CTBN influenced on the thermophysical properties of the epoxy system more than HTPB due to its higher polar character. Theoretical prediction models (series conduction, parallel conduction and Hatta and Taya model) were used to compare the thermal conductivity results. For epoxy-HTPB blends, good harmony between experimental and theoretical data was obtained.

Positive annihilation lifetime spectroscopy (PALS) technique has been employed to find free volume present in neat and elastomer-modified epoxies. The relative fractional free volume in HTPB-modified epoxies was higher than in CTBN-modified epoxies due to the occupancy of bigger HTPB elastomer domains in the epoxy network matrix. Thus, the free volume is related to the morphology of the cured network.
The failure mechanisms reigning in epoxy-CTBN/HTPB blends were investigated by acoustic emission (AE) spectral technique. The results were correlated with the initial miscibility behavior and generated morphology of cured blends. Lower acoustic hits generated during the measurements of CTBN-modified samples were due to the energy transference through phase separated and smaller CTBN elastomeric domains having more interfacial adhesion with the epoxy matrix. HTPB samples created large acoustic events and this was explained to the presence of comparatively bigger elastomeric domains in HTPB-epoxy blends. The failure behavior in HTPB-modified blends was described by an “elastomer pull-out” mechanism. The energy dissipation mechanism in CTBN-epoxy blends occurred through the phase separated elastomeric domains. On the contradictory, in HTPB blend systems it took place through elastomer- matrix interface which created interfacial separation and ultimate failure of the matrix.

11.1 Scope for future research

The present work focuses on the toughening studies of epoxy resin modified with CTBN and HTPB liquid rubbers. Several techniques have been employed to analyze the in-situ phase separation behavior and phase morphology development during curing. Mechanical, fracture toughness, thermal, as well as thermophysical properties of cured blends were also analyzed and correlated with the developed morphology. Detailed investigations have also been made to explain the fracture mechanisms prevailing in the toughened matrices.

However, various other analytical methodologies can also be employed to explore various issues in a more detailed manner. The in-situ cure reaction and the corresponding phase separation mechanisms can be probed by small angle neutron scattering or small angle X-ray scattering technique. In-situ dielectric spectroscopy can also be employed for the detailed cure
reaction analyzes. Spectroscopic techniques such as NMR and Raman can also be utilized to give more insight on the phase separation behavior. Phase separation analysis by transmission electron microscopy (TEM) is an advantageous technique that can supplement evidences for the structural features of the phase separated blends studied by other methods. TEM can also be utilized to investigate the phase separation behavior during the early stages of cure. More detailed features such as interfacial thickness can be estimated by this technique. The adhesive properties of the blends can be investigated in detail, which is more significant for its use as structural adhesives. Further, the influence of modifiers on the cure reaction mechanism and the subsequent development in phase morphology can be studied by using different curatives.

The miscibility character of the HTPB elastomer in epoxy can be improved by introducing either epoxy or urethane linkage or by incorporating some coupling agents, thereby expanding the dimensionality of the modified network with epoxy. This may probably leads to generate high performance epoxies with excellent damping characteristics.

Further, the application of the modified networks in aerospace industry can be appraised by fabricating and monitoring the properties of its composites. It is also important to study the low temperature properties and the fracture toughness characteristics of the blends and composites for possible applications at cryogenic conditions. Similarly, the high temperature applications of the blends and composites are to be evaluated so as to anticipate its potential at maximum possible high temperature applications such as components of high performance satellite structures.