Chapter-8

Summary and Conclusions
Scope of the chapter

Major conclusions that are drawn from the present study are summarised in this chapter. Future scope and possible applications are also highlighted.
Summary and Conclusions

Aerospace structural composite applications pose great demand for the development of high performance thermoset matrix resin systems which can outdo the most commonly used epoxy resins in terms of thermal capabilities, toughness and moisture resistance. Despite the emergence of several new generation matrices towards these objectives, epoxies still dominate the aerospace composite market in view of their special qualities like ease of processing, property tailoring etc. The use of specially designed curing agents based on amines, mercaptans, isocyanates, melamine-, urea- and phenol formaldehyde resins, dicarboxylic acids and acid anhydrides which act as a monomer in the polymerization process has been suggested for the formulation of improved quality epoxy matrix formulations. The ultimate properties of the cured product depend on the nature of the curing agent. Though epoxy-phenol systems with good mechanical performances have been reported, their use has been limited by their low thermal capabilities. Diallyl bisphenol-BMI system has successful stories in polymer matrix composites related to aerospace applications. They constitute the toughened BMI matrix with little penalty on thermal resistance. In this backdrop, it was of interest to envisage a thermoset blend system based on epoxy and BMI capable of co-reacting with each other. Such a system is expected to derive the salient features of epoxy (mechanical properties and processability) and bismaleimide (thermal capability). The present work aims at formulating a BMI modified epoxy matrix system wherein, the reaction between the two is ensured by reaction of diallyl bisphenol with each component. Cure optimization was accomplished using techniques such as DSC, infra red spectroscopy, dynamic mechanical analysis and rheological studies. The optimized cure conditions were used for the processing of neat and composite specimens using this new matrix system.

As the first step in the preparation and characterization of the ternary reactive blend, the performance of the epoxy-allyl phenol system was studied in detail. The cure reaction of novolac epoxy-diallyl bisphenol system was monitored by DSC and
rheological analysis to have an understanding of the influence of catalyst and its concentration on the cure behavior. The evaluation of this resin system at the composite level warrants the optimization of its processing conditions. The novolac epoxy –diallyl bisphenol reaction takes place by phenol–epoxy reaction and allyl polymerization. In order to eliminate the excessive resin bleeding during the composite fabrication, the allylphenol-epoxy reaction is to be initiated at a comparatively lower temperature. A suitable catalyst viz: triphenyl phosphine was used for this purpose. The kinetic parameters of the triphenylphosphine catalysed epoxy-phenol reaction was investigated by thermo-analytical techniques based on Ozawa and Kissinger methods, using non-isothermal DSC data. The rate of the phenol- epoxy reaction was found to be very sensitive to the presence of catalyst-TPP. Even 0.5 % of the catalyst was found to cause drastic improvement in the cure reaction rate. The calculated activation parameters varied randomly with the catalyst concentration. The apparent activation energies, normalized to a fixed pre-exponential factor showed a decreasing trend with catalyst concentration and the rate constant, k showed a proportional increasing trend. The kinetic constants obtained using the Kissinger and Ozawa methods agreed well with those reported for epoxies. These kinetic parameters were used for predicting the reaction conditions for the epoxy-phenol reaction in this novolac epoxy-diallyl bisphenol system which enabled the optimization of its cure conditions for composite fabrication.

The optimized cure conditions were used for further studies on novolac epoxy–diallylbisphenol (EP) matrix system. The system was evaluated at neat resin and composite levels to investigate the effect of epoxy / phenol molar ratio on its properties. The epoxy:phenol equivalent ratio was varied from 0.8 to1.1 and its effect on the thermal, physical and mechanical properties was evaluated. Due to the brittle nature of the completely crosslinked matrix, the allyl polymerization in the system was limited to 40% for initial studies by regulating the cure conditions. Under these conditions, the increase of epoxy concentration in the blend resulted in a marginal improvement in mechanical performance of both the neat moldings and glass
laminates. The crosslink density of the system also improved with epoxy-content. As the extent of allyl curing increased, the storage modulus and $T_g$ were found to improve. But their tensile properties were found to be impaired. This was due to the higher cross-linking, which resulted in a more brittle system with consequently poor fracture properties. The utility of the resin system for making composites was examined by processing laminates with plain weave glass cloth. The interlaminar shear strength (ILSS) and flexural strength enhanced as the resin accommodated epoxy beyond the stoichiometric equivalent. The ring-opened epoxy promoted the fiber wetting and enhanced the resin-reinforcement interaction apart from increasing the matrix cohesion. In spite of having improved strength characteristics, the epoxy-phenol system was found to have low glass transition temperature and consequent poor high temperature performance. Hence, matrix modification of the system was attempted so as to improve its high temperature performance.

The modification of the epoxy-phenol system was effected by co-reacting it with bisphenol A bismaleimide. The cure optimization of the epoxy-allyl phenol-bismaleimide (EPB) system was accomplished with the help of FTIR and DSC analyses and isothermal and non-isothermal rheological studies of the neat system. The study was extended to evaluate the influence of BMI concentration on the chemo-rheology of the blend and the thermo-physical and mechanical properties of the cured ternary blends and their composites. The DSC thermogram of the ternary blend showed the multiple-step curing conforming to epoxy cure and Alder-ene reactions. The non-isothermal rheological analysis indicated the temperatures corresponding to the different stages of the cure reaction in league with DSC profile. The isothermal rheological studies at 250°C of the systems with varying BMI content showed that the absolute modulus and its rate of build up increased with the BMI concentration. The cure stagnation was attained at a lower time scale as the BMI proportion in the system was increased. BMI enhanced the thermal stability of the EPB polymer blend. The dynamic mechanical analysis of these systems with varying BMI concentration
revealed that their tan delta peak shifted to higher temperature with increase in BMI concentration in the blend, indicating a systematic increase in $T_g$.

The mechanical properties of a typical EPB composite showed marginal improvement with the addition of BMI in the system up to the stoichiometric ratio of 1:1:1. A reduction in ILSS, flexural strength and compressive strength was observed for higher BMI concentrations. The higher crosslink density and lower fracture energy of the EPB composite systems at higher BMI concentrations implied that the reduction in mechanical properties at higher BMI concentrations is a consequence of the increased brittleness of the system. The system was toughened using high temperature thermoplastic polymer, polyether sulphone to the extent of 10%. The toughened system was evaluated at composite level. The mechanical properties of the toughened system indicated an improvement over that of the un toughened one, while its dynamic mechanical properties showed marginal decrease in glass transition temperature compared to the virgin EPB system. The thermoplastic- modified system showed an increase in toughness with a nominal penalty on $T_g$.

The high temperature performance of the ternary blend was evaluated indirectly from the adhesive strength of the neat system. Lap shear strength of the neat system and the inter-laminar shear strength of its glass composite at elevated temperatures indicated that the addition of BMI is conducive to enhancing the strength retention of the matrix at high temperature. This is supported by the systematic increase in $T_g$ of the system observed at higher BMI concentrations. The selected EPB matrix was used for composite fabrication using different types of reinforcements. The properties of the laminate composites was tailored by using reinforcements of different types, forms, surface characteristics, stacking sequence and fiber orientation.

The effect of fabric type on the performance of the EPB composite was evaluated using two types of fabrics- plane weave glass cloth and carbon cloth. The mechanical properties such as interlaminar shear strength and flexural strength of the carbon composites were found to be far superior to those of glass composites.
However, the compressive properties of the two systems were comparable. The water absorption of carbon composite was less, compared to glass composite. The coefficient of linear expansion also showed considerable reduction in the case of carbon composites.

The effect of fiber architecture on the performance of the EPB composite was evaluated using composites fabricated using three types of carbon reinforcements—carbon cloth with plane and satin weaving and chopped carbon fiber. The satin weave carbon cloth reinforced EPB-C2 composite was found to have improved inter laminar shear strength, but reduced compressive strength and flexural strength vis-a-vis the plane weave one (EPB-C1). This is attributed to the improved wetting of the fiber by the matrix caused by the reduced crimp in the satin weave compared to that in the plane weave pattern. The properties of performance of the chopped carbon fiber composites (EPB-C3) were found to be minimum among the three carbon composites.

The fiber orientation with respect to the test direction has got profound influence on the performance of the composite. The effect of fiber orientation of the woven glass fabric on the composite property was evaluated using 0/90 and ±45° fiber orientations. The laminate with 0/90 fiber orientation was found to be superior in performance in comparison to that with ±45° fiber orientation. The effect of stacking sequence of the lamina on the EPB composite properties was also studied using three sequential arrangements of lamina. The first one with layers of the plane weave glass pre-preg with fibers in the 0/90 directions [(0/90)ₙ], the second one with all layers of plane weave glass pre-preg with fibers in the ±45° with the test direction[ (±45)ₙ] and the third with each of these two types stacked in such a way as to get [(0/90)₂ / ±45] / [0/90], stacking sequence. The best properties were obtained for the composite with fibers at 0/90 angle, while (±45)₂ₙ stacking sequence resulted in the weakest composite among the three.

The ternary matrix system was evaluated for use in syntactic foam composites. Foam composites with K-37 hollow microballoon (of true density 370
kg/m$^3$) were prepared with microballoon of varying concentrations. These foam composites were characterized for their physical, thermal and mechanical properties. The addition of hollow microballoon to the EPB system resulted in the reduction in strength and modulus of the material in tension, compression and flexure modes but with advantage in reduced density. The mechanical properties and density showed systematic decrease with increase in microballoon concentration in the foam composite. From SEM analysis it was concluded that at lower microballoon concentrations, the failure occurred mainly at filler-resin interphase due to the engulfing of the microballoon by the matrix polymer available in sufficient quantity. At higher microballoon loading, the weak microballoons are not properly protected by the binder matrix, thereby the strength gets reduced. The failure in these syntactic foam composites under compression was crushing failure at the loaded surfaces, while no visual cracks were observed in the other areas of the specimen. The thermo-physical properties of the foam composites were found to vary with the concentration of the microballoon. The specific heat showed a systematic increase with microballoon concentration up to 60 % loading. The coefficient of linear thermal expansion indicated a systematic decrease with increase in microballoon concentration and an increase with rise in temperature for a given composition.

Considering the properties of the foam composites with different types of microballoons, the strength and the corresponding specific strength of the K-37 composites were higher when compared to those with K-25 microballoon system as the latter possessed lower crushing strength, density and shell thickness. Since the breaking strength values are proportional to the shell thickness as well as the crushing strength of the two types of microballoons, the microballoon breakage is confirmed as the cause for the foam failure. The incorporation of mixed filler (K-37 and K-25) resulted in enhancement in mechanical performance of the composite, commensurate with the proportion of the higher strength microballoon in the blend, while the thermo-physical properties did not show any specific compositional dependency.
The influence of structural variations of the components on the properties of the EPB matrix system and its glass composites was studied using two series of EPB systems. In the first system, the nature of epoxy resin in the blend was varied from among di-, tri- and poly-functional, while the nature and molar concentrations of BMI and allyl phenol were maintained constant. In the second system, the structure of the BMI component was varied for a fixed epoxy and diallyl bisphenol molar concentrations. Cure optimisation studies were carried out for all these combinations and their glass composites were fabricated using plane weave glass clothes.

The variation of molecular characteristics of epoxy did not cause any significant difference in the cure pattern. The phenol-epoxy, Enre reaction and Diels-Alder reaction all occurred more or less in the same temperature regions. The curing of the unsaturated groups of the Alder-ene adduct occurred beyond 250°C. The non-isothermal rheograms obtained for the EPB system with different epoxies showed an invariance in the gelation temperatures with change in epoxy type, while those corresponding to the crosslinking were slightly different.

The thermogravimetric analysis of the cured DABA - Epoxy - BMI blends with different types of epoxies showed that the thermal stability (concerning the temperature of initiation of decomposition) is in the order EPB-E3 > EPB-E1 > EPB-E2. The nature of epoxy network was found to have a decisive role on the onset of thermal decomposition. The triepoxy was better than the novolac epoxy in this respect. However, the rate of decomposition was lowest for the system with novolac epoxy and maximum for that with LY-556. This trend was reflected also in the char residue at a given temperature. LY-556 with minimum crosslink density manifested lowest T\textsubscript{i}, minimum residue and a highest decomposition rate.

The trend in the mechanical properties of these EPB composites were in the order EPB-E1 > EPB-E3 > EPB-E2. The improved strength of the EPB-E1 system containing novolac epoxy is attributed to its higher functionality compared to the other two systems. The mechanical performance of the LY-556 based system was found to
be the lowest because of its lower functionality and resulting reduced number of crosslinks. However, this was conducive to imparting good flexural properties. EPN appeared to have the best combination with BMI-1 and DABA to give a stronger composite.

The thermal cure profiles of the EPB systems with different types of bismaleimides were found to be different. The phenol-epoxy and Diels-Alder reactions occurred almost at the same temperature range in all the three cases. However, there was a difference in the relative enthalpy change in these reactions particularly for EPB-B2. In this case, exothermicity of phenol–epoxy reaction was relatively more dominant and occurred at a slightly higher temperature and the ene reaction peak was not that prominent compared to the other two cases. The non isothermal rheograms of the EPB systems with bismaleimide structural variations showed that increase in modulus due to residual unsaturation is insignificant in EPB-B2 and EPB-B3 in comparison to EPB-B1.

The variations in the thermal stabilities of the EPB matrices with different bismaleimides were very subtle. Though the initial decomposition temperature was a few degree lower for BMI-B1 system (containing BMIP) vis-a-vis the rest, this system manifested a reduced rate of decomposition at higher temperature regime. The thermal stability of EPB-B2 was found to be maximum and that for EPB-B1 was minimum among the three systems studied. The higher crosslink density and lower distance between the maleimide groups in BMI-2 has contributed to the enhanced thermal stability of EPB-B2. The presence of more aliphatic groups and diminished crosslink density in the structure of BMIP are responsible for the diminished thermal stability of EPB-B1 in comparison to EPB-B2 (Containing BMIM) and EPB-B3 (containing BMIE).

The trend in the mechanical properties of the EPB composites with bismaleimide structural variations was in the order EPB-B1> EPB-B2 > EPB-B3. BMI-1 was found to have distinct advantage over the other two. In this case, its moderate crosslink density (large spacing between the imide groups) and better compatibility
with diallylbisphenol (similarity in structure) could lead to a good matrix system. Between BMIM and BMIE, the methylene bridged one (BMIM) performed better.

Based on the above studies, the EPB matrix system with 1:1:1 molar ratio of novolac epoxy, diallylbisphenol and bismaleimide (BMIP) was found to give the optimum properties. The optimal matrix system and its composites are suited for structural applications for moderate temperature environments and are superior to the epoxy system in terms of high temperature performance and to BMI system in terms of its toughness. The matrix properties are tunable by changing the nature of its components. The overall composite properties can be further manipulated by changing the nature and orientation of fibers and also by way of interlaminar and matrix toughening.

**Scope for future study**

For matrix systems with improved high temperature performance, ternary system with higher BMI molar concentration can be envisaged. Such the systems are bound to manifest processing problems and brittleness. The increased brittleness of the system can be obviated by toughening the same using high temperature thermoplastics like PES, PEEK etc without great penalty on their glass transition temperature. Such BMI-Epoxy system could find utility in different areas like high temperature adhesives, matrix for high performance / high temperature composites for satellite structures and matrix for foam composites and light weight sandwich structures for aeroshell of aircraft and space craft structures, where the use of epoxy system is limited due to its inferior high temperature capability. The investigations on the effect of structural variations in diallyl bisphenol on the properties of the ternary blend matrix and their composites give scope for further research in this area. Of particular interest will be the systems like 3 3'-diallyl 4, 4'-dihydroxy biphenyl with liquid crystalline, self reinforcing characteristics. Though syntactic foams have been explored in this thesis, the utility of this co-cured matrix in designing cellular foams for related insulating and damping applications remains to be explored.