

CHAPTER 8

SUMMARY AND CONCLUSION

The development and importance of composites, the roles of matrix resin systems viz. epoxy resins, silicones and bismaleimides and fabrication of composites have been reviewed in Chapter 1.

The aim of the present work is the development and characterization of siliconized epoxy-bismaleimides matrix systems using hydroxyl-terminated polydimethylsiloxane and bismaleimides namely N,N'-bis(maleimido) 4,4'-diphenylmethane (BMI-1), 1,3-bis(maleimido)benzene (BMI-2), 1,2- bis(maleimido)ethane (BMI-3) and 1,6- bis(maleimido) hexane (BMI-4) as chemical modifiers for epoxy resin with γ -aminopropyltriethoxysilane as crosslinking agent and dibutyltindilaurate as catalyst.

Synthesis of hydroxyl-terminated polydimethylsiloxane prepolymer from octamethylcyclotetrasiloxane through controlled equilibration reaction using alkaline catalyst have been discussed. Preparation of siliconized epoxy prepolymer from epoxy resin and hydroxyl-terminated polydimethylsiloxane (HTPDMS) using γ -APS as crosslinking agent and dibutyltindilaurate as catalyst is explained in Chapter 2. The procedure for the preparation of BMI-1, BMI-2, BMI-3 and BMI-4 and preparation of siliconized epoxy bismaleimides blends are also discussed in Chapter-2. In addition, the experimental procedures

for the studies of physico-chemical, mechanical, electrical, thermal and morphological properties of matrix systems and composites are presented in Chapter 2.

The formation of siliconized epoxy graft IPN has been ascertained from FTIR spectra. The increase in viscosity of epoxy resin with increasing siloxane (HTPDMS) content further confirms the influence of the effect of siloxane incorporation into epoxy resin.

The homopolymerization of bismaleimides (BMIs) in the presence of epoxy resin occurs at much lower temperature (130-140°C) and is confirmed by FTIR spectra. The reason may be due to the formation of zwitter ion adduct between the oxirane ring of epoxy resin and the electron deficient BMI double bond which anionically induce the homopolymerization reaction of bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) at lower temperature in the presence of epoxy resin. Normally the same homopolymerization reaction of bismaleimides (in the absence of epoxy resin) occurs at very high temperature. For example, the temperature required for the homopolymerization reaction of BMI-1, BMI-2, BMI-3 and BMI-4 are 180°C, 202°C, 198°C and 227°C respectively. This observation is well in agreement with Musto *et al.* (1998). However, in the case of BMI-4, the rate of homopolymerization reaction is somewhat lower than that of other bismaleimides (BMI-1, BMI-2 and BMI-3). This may be due to higher activation energy required for homopolymerization reaction of BMI-4 and it occurs only at 227°C and this temperature is very high compared to the temperature required for the polymerization of other bismaleimides (BMI-1, BMI-2 and BMI-3). Hence epoxy resin effectively aids the homopolymerization reaction in the cases of bismaleimides BMI-1, BMI-2 and BMI-3 at lower temperature.

The mechanical properties of unmodified epoxy, siliconized epoxy and bismaleimides modified epoxy and siliconized epoxy matrix materials and composites have been studied as per ASTM standards. The study reveals that the siloxane incorporation into epoxy resin decreases the tensile and flexural properties. This may be explained due to the presence of flexible -Si-O-Si- linkage and weak interface boundary between HTPDMS and epoxy resin.

The tensile and flexural properties of both epoxy and siliconized epoxy systems are increased with incorporation of bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) according to their nature and percentage concentrations. This is due to the formation of intercrosslinking network between bismaleimides and epoxy systems, which in turn enhances crosslinking density and rigidity. Among the bismaleimides modified epoxy and siliconized epoxy systems, the aromatic bismaleimides (BMI-1 and BMI-2) modified systems show higher improvement in both tensile and flexural properties than aliphatic bismaleimides modified systems. This is due to the presence of rigid phenyl ring in the former. Among the aromatic bismaleimides (BMI-1 and BMI-2) modified epoxy and siliconized epoxy systems, the BMI-2 modified systems exhibit higher improvement in both tensile and flexural properties. This observation may be due to the higher number of reactive molecules present in BMI-2 modified systems than that of same percentage of BMI-1 modified systems because, molecular weight of BMI-2 is lower than that of BMI-1, which in turn increases the crosslink density and rigidity. Further the presence of methylene spacer group between the two-phenyl rings impart flexibility to the BMI-1 modified systems. Similarly, the BMI-3 modified systems show higher improvement in both tensile and flexural properties than BMI-4 modified systems, due to the presence of higher number of reactive molecules.

Further, the presence of long aliphatic chain in BMI-4 reduces the crosslink density, and hence lesser improvement in tensile and flexural properties is observed for BMI-4 modified systems.

Plain strain fracture toughness of epoxy resin increases with incorporation of siloxane according to its percentage concentration. This is due to the presence of long flexible and resilient nature of siloxane moiety. The plain strain fracture toughness of epoxy and siliconized epoxy systems decreases with increasing bismaleimides concentration. This can be explained due to the formation of intercrosslinking network between bismaleimides and epoxy systems which in turn increases the crosslink density and rigidity. The reduction in the value of toughness is higher in the case of aliphatic bismaleimides (BMI-3 and BMI-4) modified systems than aromatic bismaleimides modified systems. This is due to the fact that the available free volume in the cases of aliphatic bismaleimides modified systems is lesser than that of aromatic bismaleimide modified systems, because of linear molecular structure, which in turn favours the close packing and hence reduces the molecular relaxation. In the case of aromatic bismaleimide modified systems the complex shapes prevent close packing and more free volume is available for molecular relaxation.

Among the aromatic bismaleimides modified systems the BMI-1 modified systems show lesser reduction in toughness values when compared with the same percentage of BMI-2 modified system, due to the presence of lesser number of reactive molecules. Similarly, in the cases of aliphatic bismaleimides, the BMI-4 modified systems show lesser reduction in toughness than that of BMI-3 modified systems.

The cure reaction behaviour of epoxy-DDM, γ -APS-epoxy-DDM and bismaleimides modified epoxy systems has been studied by DSC. From the results it is ascertained that all the systems follow unimodal reaction behaviour. The increase in the peak maximum temperature with increasing bismaleimides concentration for BMI-1, BMI-2, and BMI-3 modified epoxy systems confirms that the homopolymerization reaction of bismaleimides predominates over Michael addition reaction. In the case of BMI-4 modified systems, the decrease in peak maximum temperature with increasing BMI-4 concentration confirms that the rate of Michael addition reaction is slightly higher than homopolymerization reaction.

Incorporation of HTPDMS into epoxy resin has no significant effect on Tg. However, a slight decreasing trend is observed with increase in HTPDMS concentration. This may be due to the presence of flexible nature and free rotation of -Si-O-Si- linkage. The glass transition temperature (Tg) of epoxy and siliconized epoxy systems increases with the incorporation of BMI-1, BMI-2 and BMI-3, whereas the introduction of BMI-4 decreases the Tg. The reduction in Tg values in the case of BMI-4 modified systems may be explained due to the presence of longer aliphatic chain, which imparts flexibility. Further, the rate of partial Michael addition reaction is slightly higher than that of homopolymerization reaction, since, high temperature (227°C) is required for the homopolymerization reaction of BMI-4. The increase in Tg values for BMI-1, BMI-2 and BMI-3 modified epoxy and siliconized epoxy systems is due to the homopolymerization reaction of bismaleimides rather than Michael addition reaction. Since, Michael addition reaction leads to the formation of thermally weak amine linkage and ultimately reduces the crosslink density due to chain extension. Further the improvement in Tg lends to support to the earlier observation made by Musto *et al.* (1998),

that in the presence of epoxy resin the homopolymerization reaction of bismaleimides starts even below at 130°C. The single T_g value obtained for all the bismaleimides modified epoxy and siliconized epoxy systems confirms the formation of intercrosslinking network.

Incorporation of HTPDMS into epoxy resin improves thermal stability and enhances degradation temperature according to its percentage concentration. The delay in degradation caused by the siloxane moiety may be attributed to its partial ionic nature and high bond energy of -Si-O-Si- linkage that stabilize the epoxy resin. The bismaleimides incorporation into epoxy and siliconized epoxy system enhances thermal degradation temperature and this may be due to the formation of intercrosslinking network between epoxy and bismaleimides and also due to the presence of rigid heterocyclic ring structure.

Among the bismaleimides modified epoxy systems, aromatic bismaleimides modified systems show higher thermal degradation temperature than aliphatic bismaleimides modified systems and this may be due to the presence of aromatic and heterocyclic structure. The thermal stability of bismaleimides modified siliconized epoxy systems is slightly higher than that of bismaleimides modified epoxy and HTPDMS modified epoxy systems. The enhancement is mainly due to synergistic effect of bismaleimides and HTPDMS. Heat distortion temperature of epoxy resin decreases with increasing HTPDMS concentration. However HDT values of bismaleimides (BMI-1, BMI-2 and BMI-3) incorporated epoxy and siliconized epoxy systems increase with enhanced bismaleimides concentration.

SEM micrograph of fractured surface of unmodified epoxy system reveals smooth, glassy and homogeneous microstructure whereas, the fractured

surface of siliconized epoxy systems show heterogeneous morphology. The micrographs of fractured surface of bismaleimides modified epoxy systems are almost similar to that of unmodified epoxy system. This indicates that there are no separate phase domains of the two components involved and also suggests that the formation of homogeneous intercrosslinked network. The fractured surface of the bismaleimides modified siliconized epoxy systems shows heterogeneous morphology.

Siloxane and bismaleimides incorporation into epoxy resin decrease the water absorption behaviour. This may be due to the inherent water-repellent nature of siloxane moiety and negligible water absorption behaviour of bismaleimides.

The electrical properties like dielectric strength, surface resistivity, volume resistivity and arc resistance of epoxy systems increase with the introduction of siloxane and bismaleimides according to their concentration.

Data resulted from different studies reveal that the siliconized epoxy, bismaleimides modified epoxy and bismaleimides modified siliconized epoxy matrix systems can be effectively used for the fabrication of aerospace hardware components, filament wound pressure vessels as well as for high voltage insulating applications under adverse humid environments and high temperature service conditions.