



Studies on thermal and morphological characteristics of bismaleimides modified polysulfone epoxy networks

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ABSTRACT

The effect of incorporation of bismaleimides and bisphenol – A based polysulfone (PSF) into epoxy has been studied. The formulated matrices were characterized in terms of FTIR, DSC, TGA, HDT, thermal ageing characteristics, SEM and water absorption behaviour. The incorporation of both polysulfone and bismaleimide into epoxy resin enhances the glass transition temperature and thermal degradation temperature according to their percentage content. Among the bismaleimides modified polysulfone epoxy systems, BMI-2 modified PS-epoxy systems exhibit better thermal properties than that of other two bismaleimides. SEM analysis showed a homogeneous morphology that would lead to the conclusion of the existence of interpenetrating network. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Epoxy resin;
Polysulfone;
Bismaleimide;
Glass transition temperature;
Thermal stability;
Morphology.

INTRODUCTION

Epoxy resins are a class of thermoset materials widely used for composite applications in industries where properties, such as high modulus, thermal stability, solvent resistance are required^[1-6]. However, the high level of formation of crosslinking during cure imparts brittle behaviour, which limits their application in fields requiring high impact and fracture toughness, such as composites and coatings. Therefore in the last few decades, much attention has been given to improve the thermal and mechanical properties of epoxy resins, especially making them tough.

The modification of epoxy resin with liquid elastomers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN) or crosslinked elastomers has been

investigated as a successful means of enhancing the fracture toughness of brittle epoxy resins^[7-12]. However, toughness improvements in most elastomers modified epoxy systems usually result in a significant decrease in the modulus and glass transition temperature (T_g) of the cured epoxy resins. As an alternate method, engineering thermoplastics have been used to improve fracture properties of epoxy resins^[13], because thermoplastic modifiers are tough, ductile, chemically and thermally stable, and have high T_g . This technology toughens the epoxy resins without affecting their high temperature performance. However, the predominant criteria for achieving optimum toughness enhancement in the thermoplastic toughening of epoxy resins are still not clear from the literature.

On the other hand, attempts have been made to

dissolve the thermoplastics in the epoxy resins homogeneously^[14,15]. It is reported that the incorporation of high performance thermoplastics into thermoset resin systems leads to significant improvement in mechanical properties^[13-21]. Later, this review has focused upon the importance of thermoplastic end groups, the material's morphology and ductility of the matrix and the chemical structure of the thermoplastic modified epoxy systems.

Previously, our research group, has been modified epoxy resin using different chemical and polymeric modifiers namely hydroxyl terminated polydimethylsiloxane^[22], α -aminopropyltriethoxysilane^[23], unsaturated polyester^[23], vinylester^[25], polyurethanes^[26], bismaleimides^[27-29] and the results obtained have been published elsewhere. Bismaleimides represent a class of thermosetting resins, which can be used at elevated temperature (200-230°C). These resins have better thermal stability, flame resistance and retention of mechanical properties at high temperatures than the epoxy resin. In continuation of our earlier studies, an attempt has been made in the present investigation to improve the thermal behaviour of epoxy resin by forming interpenetrating network with bisphenol A polysulfone and three different types of bismaleimides.

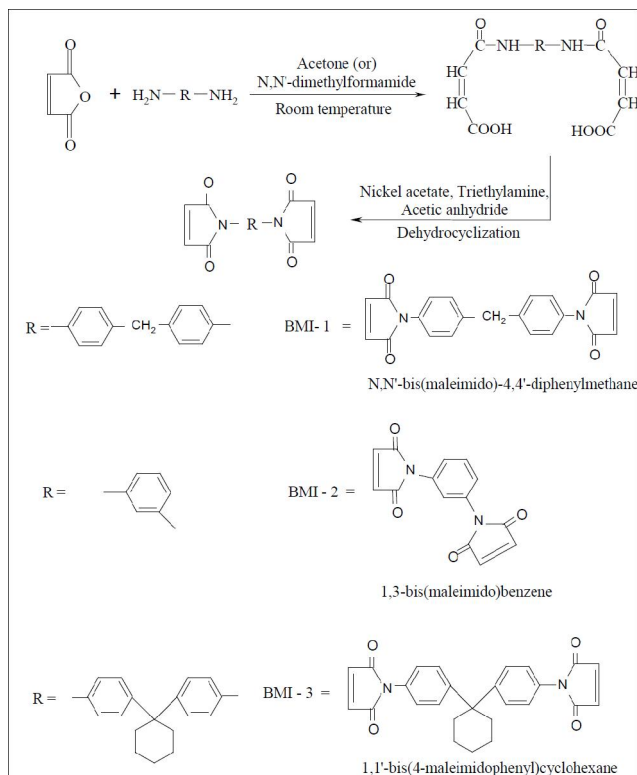
EXPERIMENTAL

Materials

Epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] LY556 (epoxy equivalent about 180–190, viscosity about 10,000 cP) and 4,4'-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy (India). Bismaleimides namely N, N'-bismaleimido-4,4'-diphenylmethane (BMI-1), 1,3-bis (maleimido) benzene (BMI-2) and 1,1'-bis (4-maleimidophenyl) cyclohexane (BMI-3) were prepared by previously reported procedure (Scheme 1)^[30]. Bisphenol A based polysulfone (Mw = 15000g/m, Tg = 195°C) was supplied by Shauguang chemical factory, Shanghai, China was used as received.

Preparation of epoxy polysulfone/bismaleimide hybrid

The hybrid polysulfone epoxy matrices were prepared by dissolving varying percentages (4, 8, 12 % by



Scheme 1 : Synthesis of bismaleimides

wt) of bisphenol - A based polysulfone and tetra methyl ammonium hydroxide (TMAH) in known amount (100 % by wt) of epoxy resin with continuous stirring at 150 °C for two hours. The hybrid matrix obtained was degassed under vacuum for half an hour and then cooled to 90 °C. The calculated amount of three different types of bismaleimides was also dissolved into polysulfone-epoxy hybrid under vigorous stirring to obtain a homogeneous mixture. A stoichiometric amount of the curing agent 4,42 -diaminodiphenylmethane corresponding to epoxy equivalents was added. The agitation was continued at 100 °C until a homogeneous product was obtained. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120 °C for 3 hours. The castings were then post cured at 180 °C for 2 hours and finally removed from the mould and characterized.

Test methods

The FTIR spectra for unmodified epoxy, polysulfone modified epoxy were recorded on a Perkin-Elmer (Model RX1) FT-IR spectrometer.

Glass transition temperature (Tg) of the samples was determined using NETZSCH DSC 200PC ana-

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TABLE 1 : Percentage water absorption, glass transition temperature and heat distortion temperature of unmodified epoxy, polysulfone modified epoxy, BMIs modified epoxy and BMIs modified polysulfone - epoxy systems

Sample code	Heat Distortion Temperature (°C)	Glass Transition Temperature (°C)	% Water absorption
E ₁₀₀ PS ₀ B ₀	153	165	0.1201
E ₁₀₀ PS ₄ B ₀	152	163	0.1176
E ₁₀₀ PS ₈ B ₀	149	161	0.1102
E ₁₀₀ PS ₁₂ B ₀	146	160	0.1068
E ₁₀₀ PS ₈ B ₁₄	154	167	0.1096
E ₁₀₀ PS ₈ B ₁₈	156	172	0.1021
E ₁₀₀ PS ₈ B ₁₁₂	159	180	0.0967
E ₁₀₀ PS ₈ B ₂₄	165	170	0.0727
E ₁₀₀ PS ₈ B ₂₈	171	178	0.0645
E ₁₀₀ PS ₈ B ₂₁₂	178	184	0.0589
E ₁₀₀ PS ₈ B ₃₄	153	166	0.0734
E ₁₀₀ PS ₈ B ₃₈	157	169	0.0612
E ₁₀₀ PS ₈ B ₃₁₂	163	172	0.0543
E ₁₀₀ PS ₈ B ₁₈	152	165	0.0781
E ₁₀₀ PS ₈ B ₂₈	158	178	0.0723
E ₁₀₀ PS ₈ B ₃₈	155	165	0.0765

E - Epoxy ; PS- Polysulfone; B – Bismaleimide; B1- N, N'-bismaleimido-4,4'-diphenylmethane (BMI-1); B2- 1,3-bis (maleimido) benzene (BMI-2); B3- 1,1'-bis (4-maleimidophenyl) cyclohexane (BMI-3)

lyzer (TA instruments USA) in the temperature range between 50°C and 250°C at a heating rate of 10°C per minute in nitrogen atmosphere.

Thermogravimetric analysis (TGA) was carried out using NETZSCH STA 409PC analyzer (TA instruments USA) at a heating rate of 10°C per minute in air. The heat distortion temperature (HDT) of the samples was tested as per ASTM D 648-72 using HDT apparatus.

Scanning electron microscopy (SEM) JEOL JSM (Model 6360) was used to investigate the morphology of unmodified epoxy, polysulfone modified epoxy and bismaleimide incorporated polysulfone modified epoxy matrix systems. The water absorption property of the samples was determined as per ASTM D 570. The results are presented in TABLE 1 and Figures 1-10.

RESULTS AND DISCUSSION

Formation of polysulfone epoxy IPN

The formation of interpenetrating network of epoxy and polysulfone proceeds through the reaction between bisphenol - A polysulfone (PSF) oligomer with

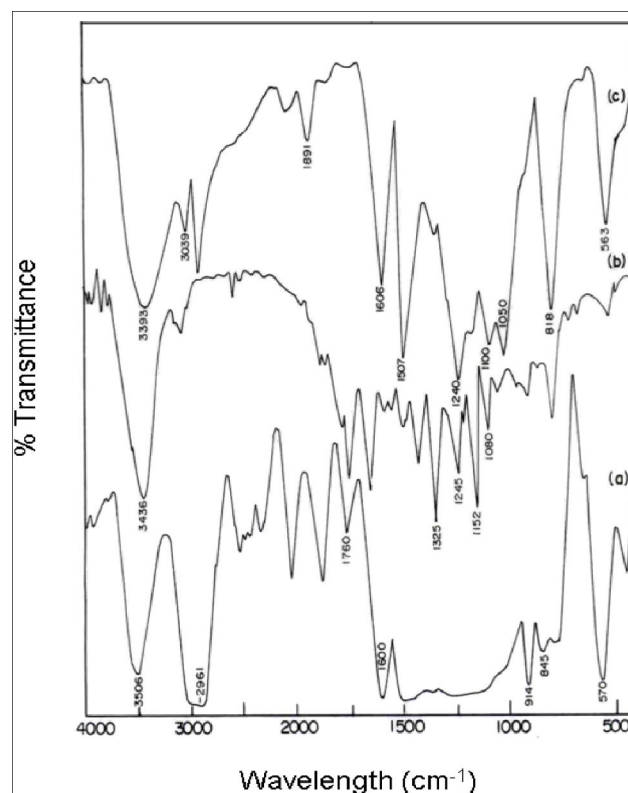
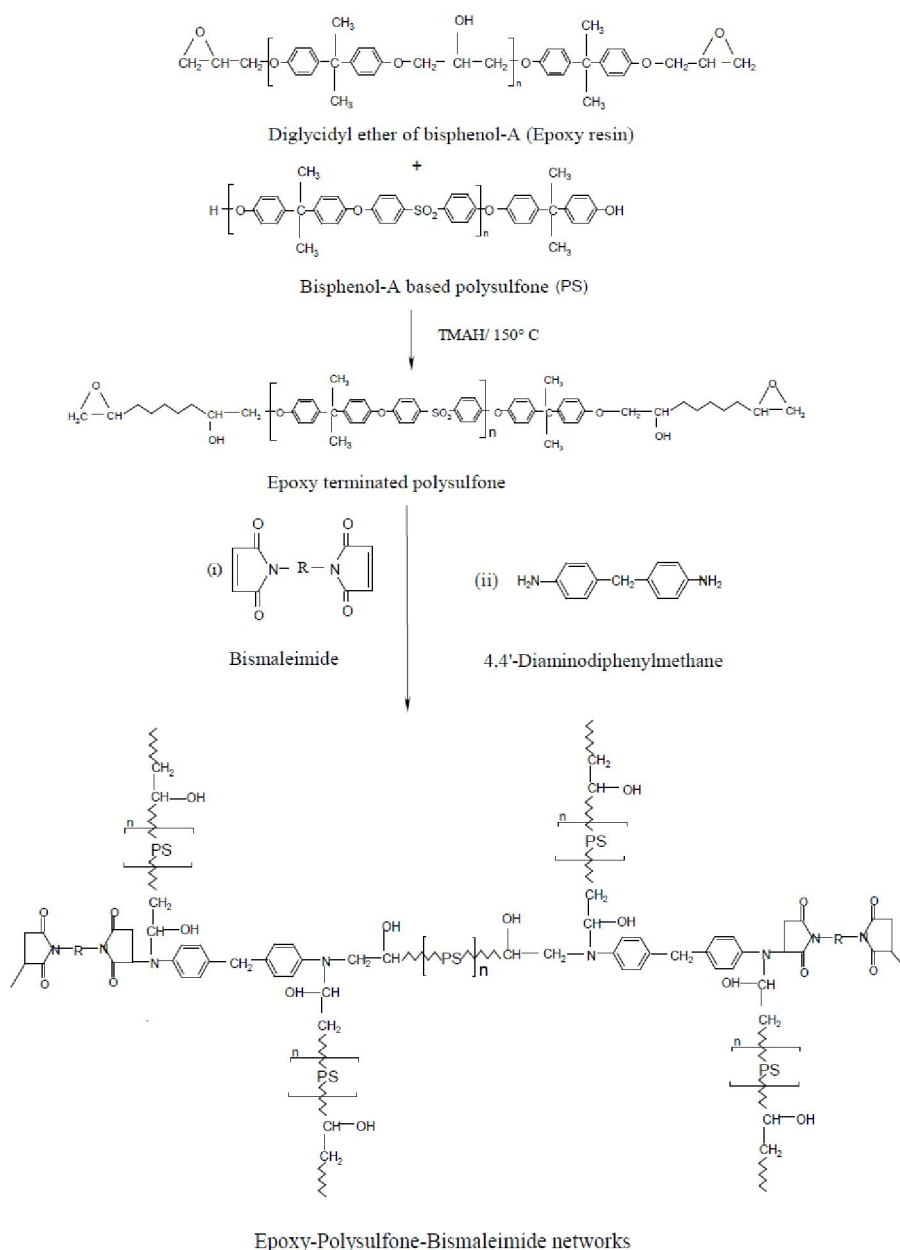


Figure 1 : FTIR spectra of (a) Unmodified epoxy (b) polysulfone prepolymer and (c) polysulfone modified epoxy system cured with DDM



Scheme 2 : Formation of Epoxy-Polysulfone-Bismaleimide Networks

large molar excess of epoxy resin in the presence of a catalyst, tetramethyl ammonium hydroxide (TMAH). The large excess of epoxy resin was used to end cap the polysulfone oligomers which essentially prevents further polymerization^[31]. The disappearance of IR absorption for oxirane ring of epoxy at 914 cm^{-1} was used to ascertain the completion of the reaction. (Figure 1). The intensity of IR absorption peaks observed for oxirane of epoxy (Figure 1a) was very high at the beginning stage of the reaction. The decrease in intensity of the peak for oxirane ring of epoxy confirms the reaction between epoxy and hydroxyl group of polysulfone.

The IR absorption peak of epoxy disappeared completely after the completion of the reaction between polysulfone modified epoxy and the curing agent, (DDM). This confirms the reaction between epoxy and polysulfone and the formation of interpenetrating polymer network structure (IPN) (Scheme 2)^[16].

Differential scanning calorimetry

(a) Polysulfone modified epoxy systems

The glass transition temperature of (T_g) unmodified epoxy and polysulfone modified epoxy systems are pre-

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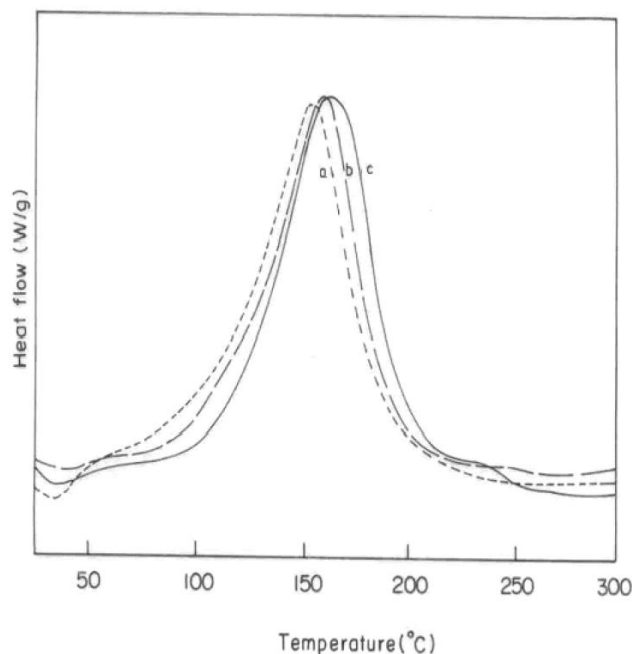


Figure 2 : DSC thermograms of epoxy-polysulfone-DDM systems during cure (a) epoxy-polysulfone (4%) (b) epoxy-polysulfone (8%) and (c) epoxy-polysulfone (12%)

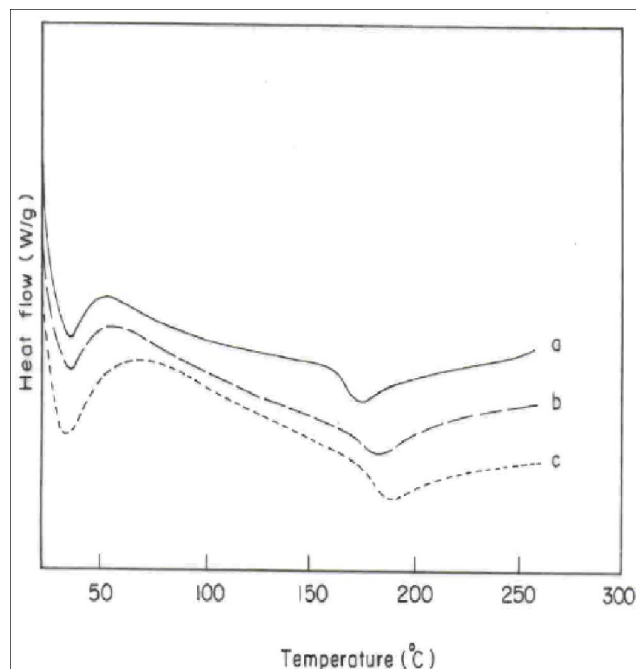


Figure 3 : DSC traces of BMI-1 modified polysulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI-1 modified polysulfone (8%)-epoxy systems

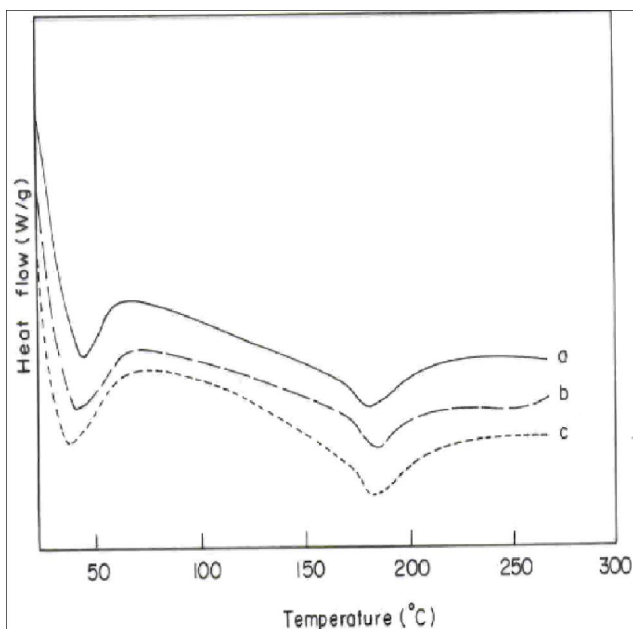


Figure 4 : DSC traces of BMI-2 modified polysulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI-2 modified polysulfone (8%)-epoxy systems

sented in TABLE 1 and Figure 2. The polysulfone modified epoxy hybrids prepared are transparent at ambient temperature and there is no evidence of phase separation is found. Further the single value of T_g observed for polysulfone modified epoxy system suggests that the

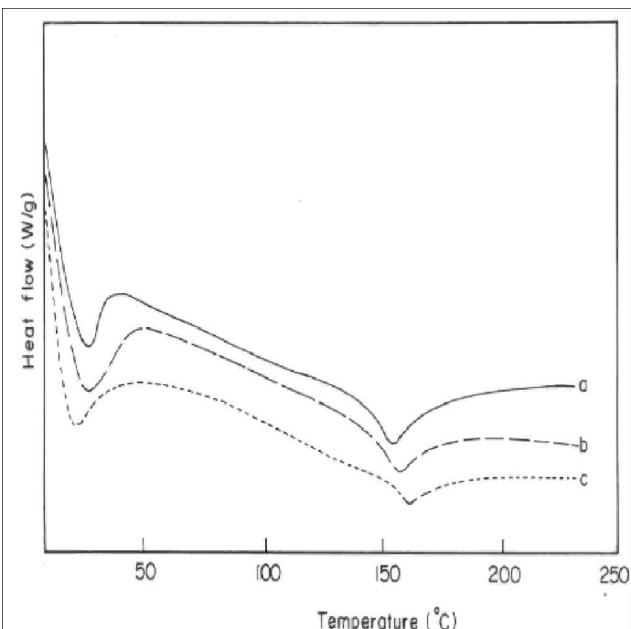


Figure 5 : DSC traces of BMI-3 modified polysulfone-epoxy systems (a) 4%, (b) 8% and (d) 12% BMI-3 modified polysulfone (8%)-epoxy systems

hybrid is chemically bonded homogeneous products of amorphous nature. The value of glass transition temperature of epoxy system is decreased marginally when polysulfone is incorporated.

For example, the values of T_g obtained for 4%, 8%

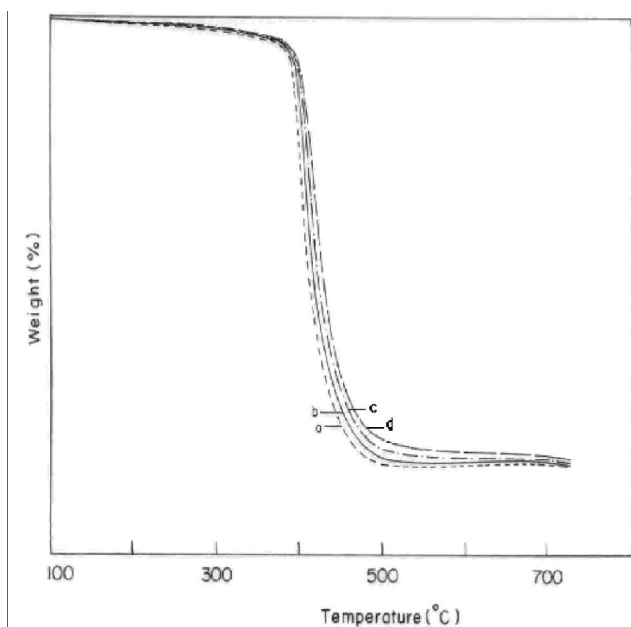


Figure 6 : TGA curves of epoxy and polysulfone-epoxy systems (a) unmodified epoxy, (b) 4%, (c) 8% and (d) 12% polysulfone-epoxy systems

and 12% polysulfone modified epoxy systems are 163°C, 161°C and 160°C respectively, when compared with that of 165°C obtained for unmodified epoxy system. The incorporation of polysulfone raised the viscosity of the system, which could result in an incomplete curing reaction due to the steric hindrance developed under the curing condition^[32]. The thickening effect of polysulfone is also an important factor which gives rise to the reduction in the crosslinking density and consequent chain lengthening of polysulfone skeleton and hence molecular flexibility occurs at low temperature.

(b) Bismaleimides modified polysulfone epoxy systems

The glass transition temperature obtained for unmodified epoxy and bismaleimides modified polysulfone epoxy systems are presented in Figures 3 to 5. The value of glass transition temperature (T_g) are increased with increase in percentage incorporation of bismaleimides^[33,34] into epoxy, polysulfone-epoxy systems.

The rise in T_g when bismaleimides (BMI-1, BMI-2 and BMI-3) are introduced into epoxy and modified epoxy systems confirms the homopolymerisation reaction of bismaleimides which predominates rather than that of Michael addition reaction. In addition,

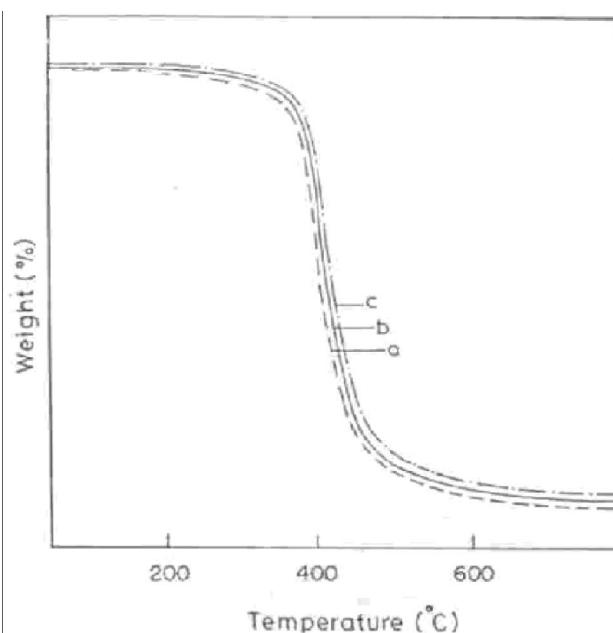


Figure 7 : TGA curves of BMI-1 modified polysulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI-1 modified polysulfone (8%) - epoxy systems

homopolymerization reaction of bismaleimides leads to the formation of thermally stable -C-C- linkage. Further, the improvement in the value of T_g lends support to the earlier observations^[35,36] that in the presence of epoxy resin, homopolymerization reaction of bismaleimides starts even below at 130°C. The single value of T_g obtained for the polysulfone modified epoxy, and bismaleimides modified polysulfone-epoxy systems further confirm the formation of inter-cross linking network.

Among the polysulfone modified epoxy, bismaleimides modified polysulfone-epoxy systems, the BMI-2 modified systems (TABLE 1) show higher improvement in the value of T_g than those of BMI-1 and BMI-3 modified systems due to the formation of higher cross linking density than those obtained from BMI-1 and BMI-3 modified epoxy systems, because of more number of available reactive molecules in the former.

Thermogravimetric analysis

(a) Polysulfone modified epoxy systems

The incorporation of polysulfone into epoxy resin improves the thermal stability and enhances the degradation temperature according to its percentage concentration (Figure 6). The presence of polysulfone skeleton in the epoxy system delays the degradation pro-

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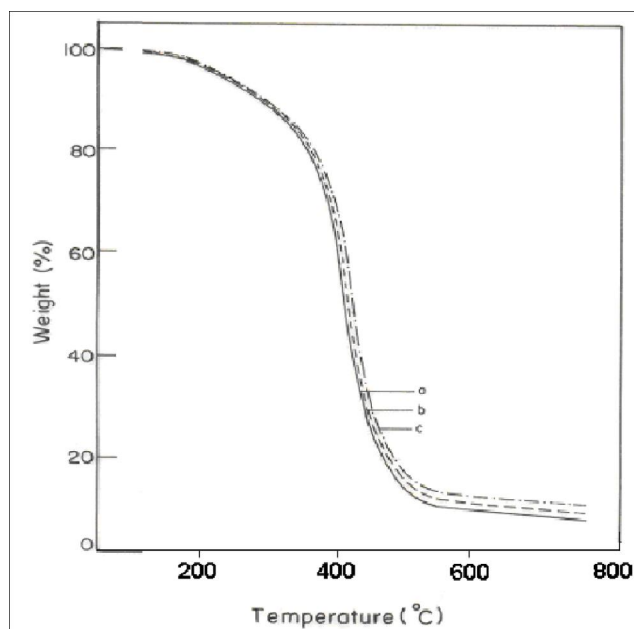


Figure 8 : TGA curves of BMI-2 modified polysulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI-2 modified polysulfone (8%)-epoxy systems

cess and high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. The formation of interpenetrating network between polysulfone and epoxy also delays the degradation temperature of the system. For example, the temperature required for 20%, 40% and 60% weight loss of unmodified epoxy-DDM systems are 376 °C, 386 °C and 402 °C respectively, whereas the temperature required to attain the same percentage weight loss for 12% polysulfone modified epoxy systems are increased to 389 °C, 398 °C and 418 °C respectively (Figure 6).

(b) Bismaleimide modified polysulfone epoxy systems

The thermal degradation temperature of bismaleimides (BMI-1, BMI-2 and BMI-3) modified polysulfone epoxy systems are given in Figures 7-9. It is observed that the thermal degradation temperature of bismaleimides modified polysulfone epoxy systems are increased with increasing bismaleimides concentration due to the formation of intercrosslinking network between epoxy and bismaleimides and rigid heterocyclic ring structure of bismaleimides.

Among the bismaleimides modified epoxy systems, BMI-2 modified systems (Figures 8) show higher thermal degradation temperature when compared with that

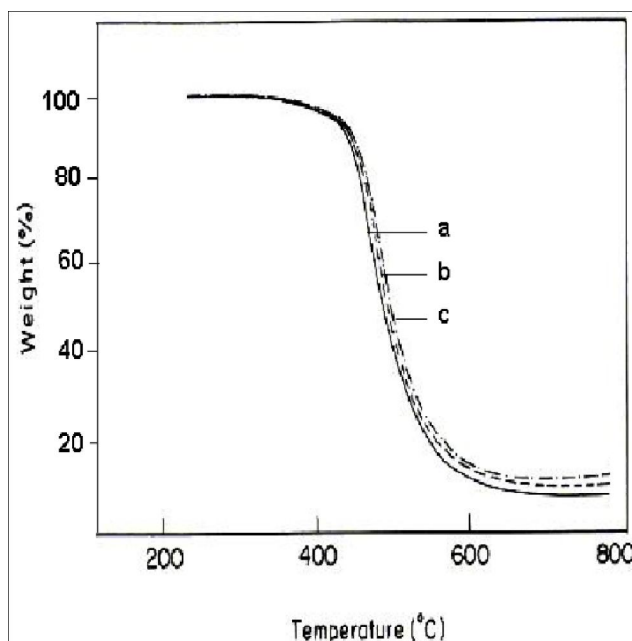


Figure 9 : TGA curves of BMI-3 modified polysulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI-3 modified polysulfone (8%)-epoxy systems

of other bismaleimides (BMI-1 and BMI-3) modified epoxy systems.

Heat Distortion Temperature (HDT)

(a) Polysulfone modified epoxy systems

From the heat distortion temperature values of polysulfone modified epoxy systems, it is evident that HDT decreases marginally with increasing polysulfone concentration (TABLE 1) due to the thickening effect of polysulfone which gives rise to the reduction in the crosslinking density and consequent chain lengthening of polysulfone skeleton and hence molecular flexibility occurs at low temperature.

(b) Bismaleimides modified polysulfone epoxy systems

The HDT values of polysulfone modified epoxy and bismaleimides (BMI-1, BMI-2 and BMI-3) modified polysulfone-epoxy systems are increased with increasing concentration of bismaleimides. The enhancement in the heat distortion values of bismaleimides modified polysulfone epoxy systems is due to the rigidity and improved crosslink density imparted by heterocyclic nature of bismaleimides. Among the bismaleimides (BMI-1, BMI-2 and BMI-3) modified polysulfone epoxy systems, the bismaleimide (BMI-2) modified polysulfone epoxy system exhibit higher improvement

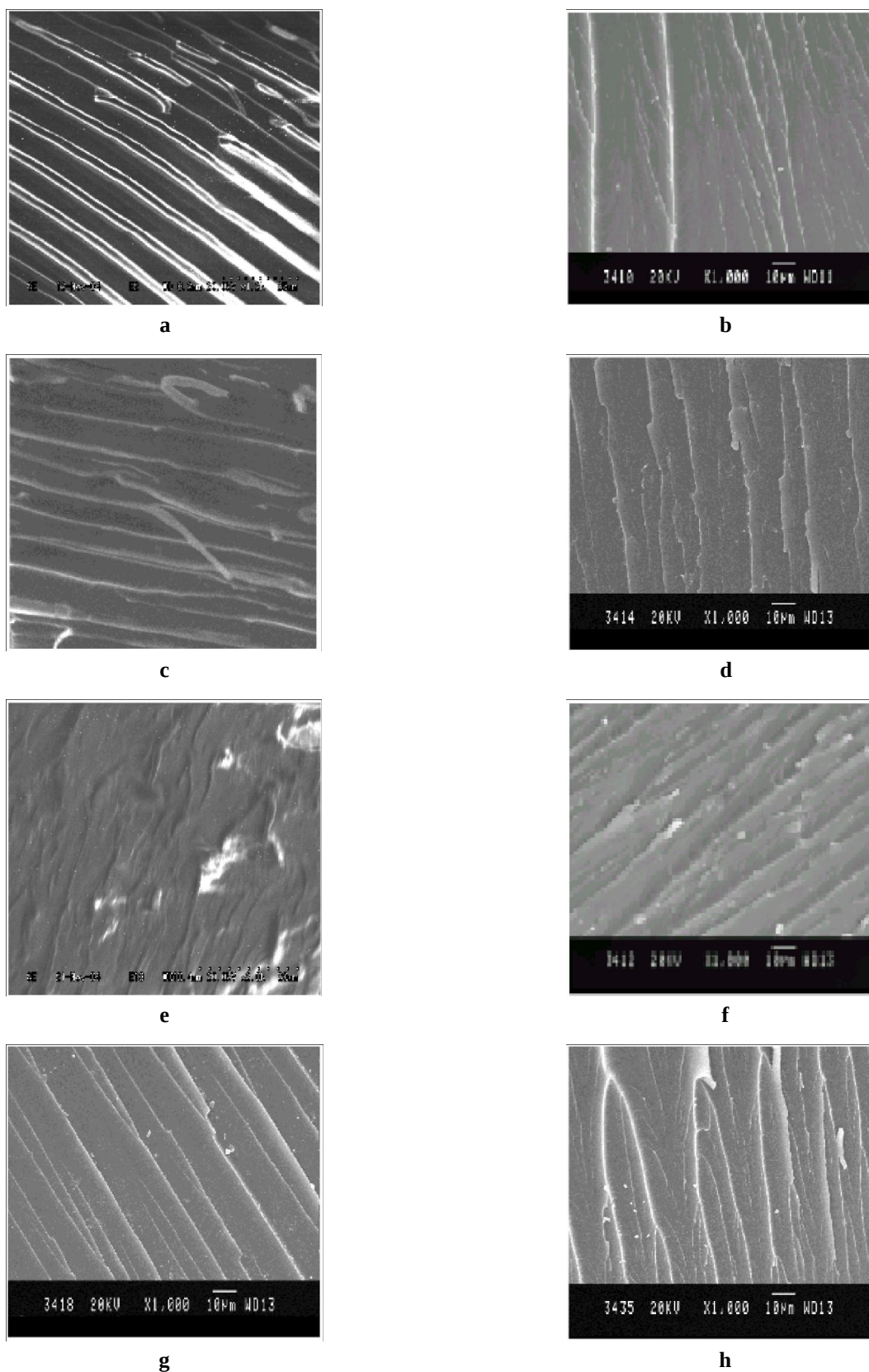


Figure 10 : SEM micrographs of (a) unmodified epoxy, (b) 8 % PSF modified epoxy, (c) 8 % BMI-1 modified epoxy (d) 8% BMI-2 modified epoxy (e) 8 % BMI-3 modified epoxy (f) 8 % BMI-1 modified polysulfone (8 %) epoxy (g) 8 % BMI-2 modified polysulfone (8 %) epoxy (h) (8%) BMI-3 modified polysulfone (8 %) epoxy systems

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TABLE 2 : Retention in tensile properties of bismaleimide modified polysulfone epoxy matrices after thermal ageing

Composition (%)			Retention of tensile strength (%)	Retention of Tensile modulus (%)
Epoxy	PS	BMI-2		
100	0	0	82	80
100	4	0	84	82
100	8	0	86	84
100	12	0	89	85
100	8	4	87	85
100	8	8	89	86
100	8	12	90	88
100	0	4	83	82
100	0	8	85	84
100	0	12	86	87

in the value of heat distortion temperature when compared to that of BMI-1 and BMI-3 modified epoxy systems (TABLE 1).

Thermal ageing characteristics

The changes in mechanical properties such as tensile strength and tensile modulus of the unmodified epoxy, polysulfone modified epoxy, bismaleimide modified polysulfone epoxy hybrid matrices were determined after subjecting the blends at 125°C for 72 hours. The percentage retention of the mechanical properties of the blends after ageing is presented in TABLE 2.

Effect of polysulfone content on thermal ageing

The values of tensile properties of aged matrices are compared with those of unaged blends. The percentage retention of mechanical properties of the blends is increased with increasing percentage incorporation of polysulfone in the modified epoxy matrices. For example the percentage retention of the value of tensile strength of 4%, 8% and 12% polysulfone modified epoxy systems are 84, 86 and 89 (%) respectively. The higher percentage of retention of tensile properties is due to the presence of polysulfone skeleton in the epoxy system which offered better ageing resistance. The formation of interpenetrating network between polysulfone and epoxy also delays the degradation process and retains the mechanical properties appreciably.

Effect of bismaleimide on thermal ageing

The percentage retention of mechanical properties such as tensile strength and tensile modulus is increased with increasing percentage incorporation of bismaleimide in the epoxy system. The values are presented in TABLE 2. It is observed that the bismaleimide modified epoxy system having 12 % composition of bismaleimide possess better retention of mechanical properties after ageing. This can be explained as due to the presence of network structure and thermally stable rigid heterocyclic ring structure of bismaleimides.

Effect of bismaleimide and polysulfone content on thermal ageing

The introduction of bismaleimides and polysulfone into epoxy systems improved the percentage retention of mechanical properties, when compared with unmodified epoxy systems due to the synergistic effect offered by the bismaleimides and polysulfones (TABLE 2).

Morphology

The SEM micrographs of fractured surfaces of the unmodified epoxy, polysulfone modified epoxy and bismaleimide incorporated polysulfone epoxy systems revealed smooth and homogeneous microstructures [Figure 10]. The homogeneous morphology confirms that the hybrid product is in the form of single chemical entity. Further this observation lends support the results obtained from DSC analysis. The efficient interaction between polysulfone and epoxy resin and consequent IPN formation is the cause for the develop-

ment of homogeneous morphology (Figures 10 and 11).

The fractured surface of the bismaleimides (BMI-1, BMI-2 and BMI-3) modified polysulfone-epoxy system also indicates a smooth surface similar to bismaleimide modified epoxy systems (Figure 10).

Water absorption behavior

Data obtained from the water absorption studies indicate that the incorporation of polysulfone into epoxy system and the incorporation of BMIs into both epoxy resin and polysulfone modified epoxy systems were decreased the water absorption behavior, due to the hydrophobic behaviour imparted by polysulfone and enhanced cross linking density induced by bismaleimides (TABLE 1).

CONCLUSION

The polysulfone modified epoxy and BMI modified polysulfone-epoxy intercrosslinked network having varied concentrations of BMI and polysulfone were prepared. The results obtained from thermal studies indicate that the incorporation of polysulfone into epoxy resin marginally lowers the values of T_g and HDT, where as the incorporation of bismaleimides into epoxy and polysulfone modified epoxy enhances the values of T_g and HDT to an appreciable extent. SEM micrographs confirm the homogeneity of the modified hybrid epoxy systems. The modification and hybridization of epoxy with polysulfone and bismaleimides improved the resistance to water absorption behaviour. From the results observed, it is concluded that the modified hybrid epoxy matrix system can be conveniently utilized in the form of adhesives, coatings and composites for better performance and longevity.

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