

A Comparative Study on the Preparation and Characterization of Aromatic and Aliphatic Bismaleimides-Modified Polyurethane–Epoxy Interpenetrating Polymer Network Matrices

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ABSTRACT: Interpenetrating polymer networks of bismaleimide-modified polyurethane–epoxy systems were prepared using the aliphatic and aromatic bismaleimides and polyurethane-modified epoxy and cured in the presence of 4,4'-diaminodiphenylmethane. Infrared spectral analysis was used to confirm the polyurethane-crosslinked epoxy (PU–EP). The matrices developed were characterized by mechanical, thermal, electrical, and morphological studies. The results obtained from the mechanical studies indicate that the incorporation of polyurethane and bismaleimides into epoxy increased the tensile strength, flexural strength, and impact strength, according to their nature and percentage concentration. The results obtained from the thermal and electrical studies indicate that the incorporation of polyurethane into epoxy decreased the thermal properties (glass transition temperature, heat distortion temperature (HDT), thermal stability) and electrical properties (dielectric

strength, volume and surface resistivity, and arc resistance). The incorporation of aromatic bismaleimide into the polyurethane-modified epoxy system increased the glass transition temperature, thermal stability, and electrical properties. Decreased values of glass transition and HDT were obtained in the case of aliphatic bismaleimide-modified polyurethane–epoxy system. Surface morphology of modified epoxy systems was studied using scanning electron microscopy, and it was found that the polyurethane-modified epoxy systems exhibited heterogeneous morphology and bismaleimides-modified epoxy systems showed a homogeneous morphology. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3592–3602, 2006

Key words: epoxy resin; bismaleimides; polyurethane; glass transition temperature; electrical properties; morphology

INTRODUCTION

Epoxy resins based on diglycidyl ether of bisphenol-A have been used extensively as thermosetting matrices in the development of high-performance light-weight fiber-reinforced composites.^{1–7} Epoxy resins exhibit many desirable properties required for number of industrial and engineering applications. However, epoxy resins are generally brittle materials and also exhibit inferior weathering resistance. In the recent past, many efforts have been made to improve the toughness of the cured epoxy resin, using conventional rubbery materials, but they failed to improve the physical properties of the cured epoxy resin in the high temperature region to the desired level.^{8,9} In this context, in the present study, an attempt has been made to improve the properties of epoxy resin, i.e., toughness, thermal stability, resistance to moisture absorption and weather, and enhanced strain to fracture, using a

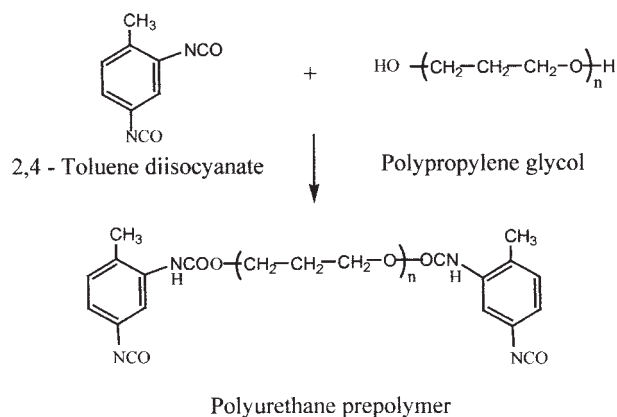
polyurethane prepolymer and rigid bismaleimides into epoxy resin. The incorporation of polyurethane prepolymer and bismaleimides into epoxy resin led to the formation of an intercrosslinked hybrid polymer network having flexible and rigid molecular segments.^{10–17} The modified epoxy resins are characterized for their mechanical, thermal, and electrical behavior for possible utilization in the fabrication of composite components for different industrial and engineering applications.

EXPERIMENTAL

Materials

Commercially available diglycidylether of bisphenol-A-based (DGEBA) epoxy resin LY-556 (Ciba-Geigy), having epoxy equivalent weight about 180–190, and 4,4'-diaminodiphenylmethane HT-972 (Ciba-Geigy) were used as base resin and curative, respectively. 2,4-Toluene diisocyanate, polypropylene glycol, having molecular weight 1000, and dibutyl tin dilaurate were used for the preparation of polyurethane prepolymer. Aromatic and aliphatic bismaleimides were prepared using a procedure reported elsewhere.¹⁸

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Scheme 1 Preparation of polyurethane prepolymer.

Preparation of polyurethane–epoxy prepolymer

An intercrosslinked network system of polyurethane–epoxy was developed in two stages. In the first stage, the isocyanate-terminated polyurethane prepolymer was prepared by reacting 2 mol of 2,4-toluene diisocyanate and 1 mol of polypropylene glycol, at 70°C, using dibutyl tindilaurate catalyst, with continuous stirring for 3 h, under the nitrogen atmosphere (Scheme 1). In the second stage, the varying ratios of polyurethane prepolymer were reacted with epoxy resin at 80°C in presence of dibutyl tindilaurate catalyst, with continuous stirring for 30 min under nitrogen atmosphere. The entire mixture was degassed to remove the entrapped air in the resin mixture (Scheme 2).

Preparation of aromatic and aliphatic bismaleimides

Aromatic bismaleimide (1,3-bis(maleimido) benzene) (BMI-1) was prepared by reacting *m*-phenylenedi-

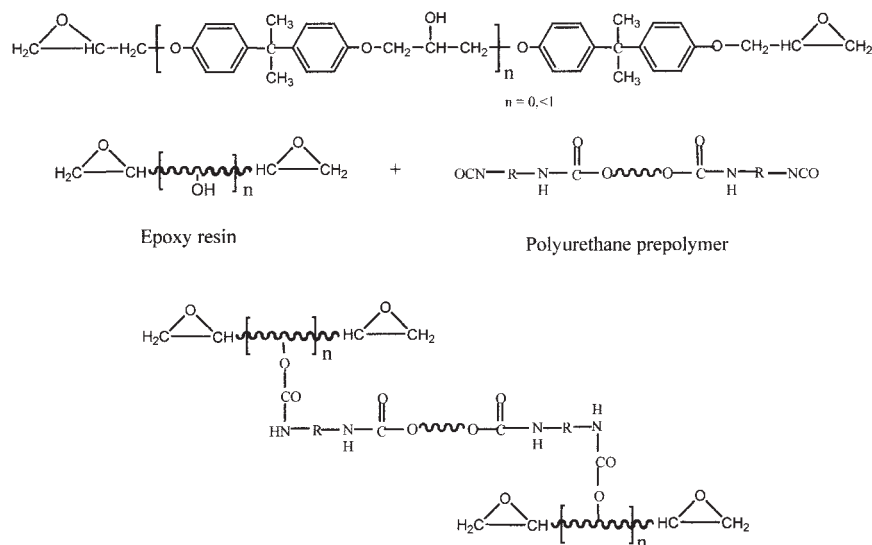
amine and maleic anhydride, using acetic anhydride as the dehydrating agent, with nickel acetate and triethylamine as catalysts.¹⁸ Aliphatic bismaleimide (1,6-bis(maleimido) hexane) (BMI-2) was also prepared by reacting appropriate chemicals, using the same procedure adopted for the preparation of aromatic bismaleimide (Scheme 3).

Preparation of bismaleimides-modified polyurethane–epoxy blend

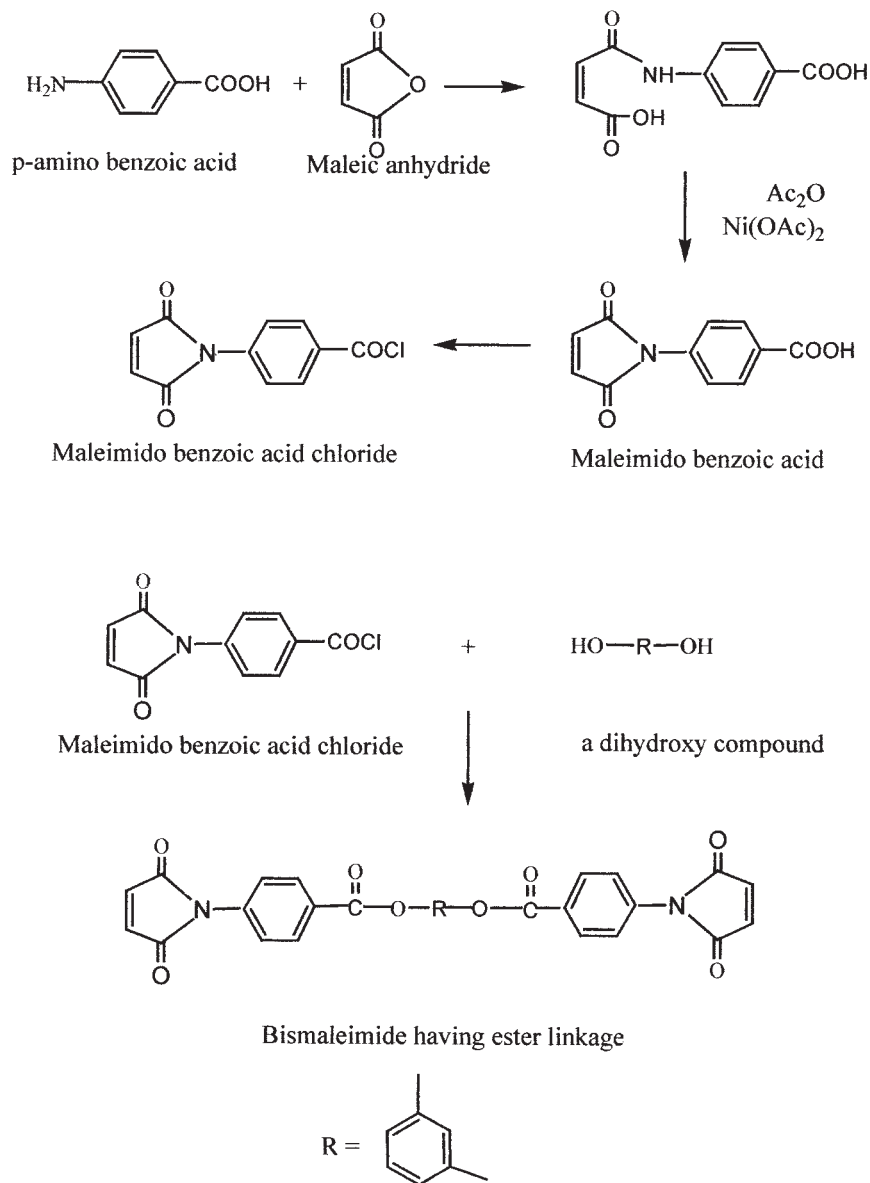
The calculated amounts of aromatic and aliphatic bismaleimides were separately dissolved in polyurethane–epoxy prepolymer, at 120°C, with continuous stirring. After completion of dissolution, the temperature was brought down to 90°C, and then the stoichiometric amount of 4,4-diaminodiphenylmethane was added to the epoxy–polyurethane–bismaleimide prepolymer and vacuum applied to remove the entrapped air. The product was cast in the mold, cured at 120°C for 1 h, and then post cured at 180°C for 2 h.

Test methods

Infrared spectral analysis was recorded on a PerkinElmer 781 (Palo Alto, CA) Infrared spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker 400-MHz NMR spectrometer with dimethylsulfoxide-*d*₆ (DMSO-*d*₆) or CDCl₃ as solvent. Tensile properties were studied, according to ASTM D3039, using Instron testing machine (Model 6025 UK), at 10 mm/min cross-head speed, with a specimen width of 25 mm, length of 200 mm, and thickness of 3 mm. Flexural properties were carried out, according to ASTM D790, with a specimen width of 10 mm, length of 90 mm and thickness of 3 mm. Izod impact strength



Scheme 2 Formation of polyurethane–epoxy intercrosslinked network.



Scheme 3 Synthesis of chain extended bismaleimide having ester linkage.

was studied, according to ASTM D256, using unnotched specimen of 10-mm width, 3-mm thickness, and 63-mm length. Five specimens were tested for each sample. The glass transition temperature of the matrix samples was performed in the temperature range between 50 and 300°C on a DSC 2916 (TA instruments), at a heating rate of 10°C/min. Determination of heat distortion temperature (HDT) was carried out, according to ASTM D648, using HDT apparatus. Thermogravimetric analysis (TGA) of the polymeric matrices was carried out in TGA-Thermal Analyst 2000 (TA Instruments, USA), at a heating rate of 10°C/min in an inert atmosphere. Dielectric strength of matrix samples was determined, according to ASTM D149, in a dielectric strength tester. Arc resistance is measured, according to ASTM D495, and resistivity is

determined using a resistivity meter, according to ASTM D257.

RESULTS AND DISCUSSION

Spectral analysis

The formation of intercrosslinked network of epoxy and polyurethane proceeds through the reaction between isocyanate groups of polyurethane prepolymer and pendant hydroxyl groups of the epoxy resin. The disappearance of IR absorption for isocyanate groups (2270 cm^{-1}) was used to ascertain the completion of the reaction. The intensity of the IR absorption peaks observed for the isocyanate groups was very high at the beginning stage of the

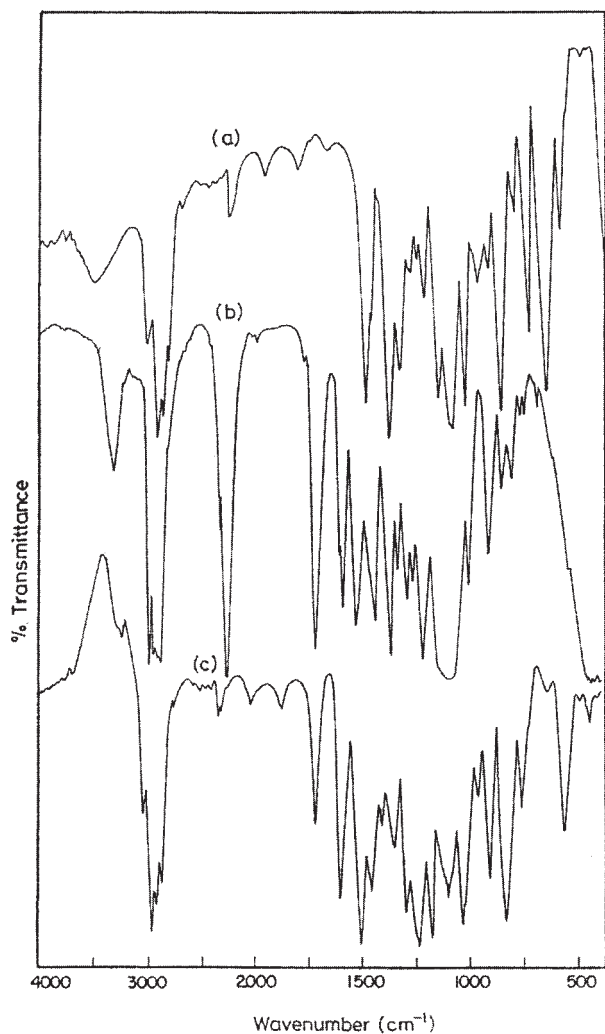


Figure 1 FTIR spectra of (a) unmodified epoxy, (b) polyurethane prepolymer, and (c) polyurethane-modified epoxy.

reaction (Fig. 1). As the reaction proceeds the intensity of the peak for isocyanate groups decreases and then disappears after the completion of the reaction. This confirms the formation of intercrosslinked network structure.

Tensile properties

The values of tensile strength of polyurethane-modified epoxy and aromatic and aliphatic bismaleimide-modified polyurethane-epoxy systems are presented in Table I. The incorporation of polyurethane into the epoxy system enhanced the value of tensile strength when compared with that of unmodified epoxy system, and this may be explained as being due to the formation of an increased degree of the intercrosslinked network between the molecular chains of epoxy and polyurethanes. The bismaleimides-modified epoxy systems enhanced the values of tensile strength, according to their nature and concentration.

For example, the incorporation of 4, 8, and 12% aromatic bismaleimide into this epoxy system enhanced the tensile strength by 7.4%, 16.7%, and 26.4%, respectively, when compared with the unmodified epoxy system, due to the formation of network structure between bismaleimide and epoxy resin, which in turn enhanced the crosslink density. Similarly, when 4, 8, and 12% of aliphatic bismaleimide were incorporated into the epoxy system, the values of tensile strength increased only by 2.4%, 6.1%, and 9.8%, respectively. The reason for lesser improvement in the values of tensile strength may be explained as being due to the occurrence of a Michael addition reaction, which consumes more amino groups of 4,4'-diaminodiphenylmethane (curative for epoxy resin) and leaves less than a stoichiometric amount of amino groups for curing the epoxy resin. Hence, crosslink density is lowered, thus the value of tensile strength are not enhanced, as observed in the case of the aromatic bismaleimide-modified epoxy system.

The incorporation of both aromatic and aliphatic bismaleimide into polyurethane (10%)-epoxy systems increased the values of tensile strength. The values of tensile strength obtained for aromatic bismaleimide-modified polyurethane-epoxy system are higher than that of the aliphatic bismaleimide-modified polyurethane (10%)-epoxy system. The improvement in tensile strength may be explained as being due to the formation of an intercrosslinked network between bismaleimide and polyurethane. In addition, the higher miscibility of bismaleimides with the polar polyurethane domain led to a uniform distribution of bismaleimides in the matrix. For example, the values of tensile strength of the 8% aromatic bismaleimide-modified polyurethane-epoxy system increased by 12.5%, when compared with that of the 10% polyurethane-modified epoxy system. Similarly, in the case of 8% aliphatic bismaleimide-modified polyurethane-epoxy system, the value of tensile strength is increased by 4.5%. The results of tensile modulus follow a similar trend as in the case of tensile strength.

Flexural properties

Flexural strength values of bismaleimides-modified polyurethane-epoxy systems are presented in Table I. The value of flexural strength of epoxy system is increased when polyurethane is incorporated into the epoxy system. For example, the flexural strength value of epoxy systems are increased by 6.7%, 12.8%, 16.9%, and 14.8%, with increasing concentration of polyurethane by 5, 10, 15, and 20%, respectively. This may be explained as being due to the formation of network structure between epoxy and polyurethane molecules. Similarly, the bismaleimides-modified epoxy systems show increased flexural strength, when compared with unmodified epoxy system. For example, the flex-

TABLE I
Mechanical Properties of Unmodified Epoxy, Polyurethane-Modified Epoxy, BMI-1 and BMI-2 Modified Epoxy and Polyurethane-Epoxy Systems

Epoxy/PU/BMI (% composition)	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
100/00/00	61.4 ± 3	2714.7 ± 21	103.7 ± 5	1805.4 ± 28	95.7 ± 2
100/05/00	67.3 ± 4	2843.2 ± 29	110.4 ± 2	1825.3 ± 27	102.4 ± 3
100/10/00	74.7 ± 2	2913.5 ± 25	118.5 ± 2	1916.4 ± 27	108.3 ± 3
100/15/00	78.4 ± 3	2985.3 ± 27	124.9 ± 3	1987.7 ± 25	114.9 ± 2
100/20/00	75.2 ± 3	2944.4 ± 27	121.7 ± 5	1956.2 ± 22	119.2 ± 4
Epoxy/PU/BMI-1					
100/00/04	66.3 ± 3	2815.6 ± 29	118.8 ± 7	2939.5 ± 22	90.4 ± 5
100/00/08	73.7 ± 4	2891.4 ± 24	125.2 ± 6	3082.1 ± 24	88.9 ± 4
100/00/12	83.4 ± 4	3019.8 ± 26	131.0 ± 3	3143.3 ± 21	83.5 ± 4
100/10/04	80.7 ± 2	2983.9 ± 24	124.8 ± 4	3157.5 ± 24	103.2 ± 4
100/10/08	85.4 ± 3	3078.7 ± 24	129.5 ± 8	3194.2 ± 26	98.9 ± 3
100/10/12	89.3 ± 3	3195.6 ± 23	133.2 ± 6	3247.6 ± 22	95.4 ± 3
Epoxy/PU/BMI-2					
100/00/04	62.9 ± 5	2734.7 ± 21	109.4 ± 2	1815.0 ± 22	89.3 ± 2
100/00/08	65.4 ± 7	2773.2 ± 20	114.7 ± 3	1892.3 ± 26	85.9 ± 3
100/00/12	68.1 ± 2	2811.5 ± 19	120.9 ± 2	1933.6 ± 26	80.7 ± 4
100/10/04	75.9 ± 6	2930.4 ± 30	122.3 ± 4	1974.1 ± 24	101.9 ± 2
100/10/08	78.3 ± 6	2977.1 ± 26	128.8 ± 6	2022.8 ± 25	97.2 ± 2
100/10/12	80.5 ± 2	2993.3 ± 24	132.5 ± 6	2096.2 ± 25	94.8 ± 3

ural strength values of 4, 8, and 12% aromatic bismaleimide-modified epoxy system enhanced by 6.9%, 12.6%, and 18.1%, and for aliphatic bismaleimide modified systems increased by 3.4%, 7.9%, and 11.3%, respectively, for the same weight percentage. The higher improvement in flexural strength may be explained as due to the enhanced rate of homopolymerization of aromatic bismaleimide, rather than Michael addition reaction, and also the presence of rigid phenyl group, which in turn enhances the crosslinking density and rigidity. The presence of long molecular chains in the case of aliphatic bismaleimide imparts flexibility to the epoxy system and marginally lowers the flexural strength. An observation similar to the flexural strength was also made in case of flexural modulus.

Impact strength

The values of impact strength of unmodified epoxy, polyurethane-modified epoxy, and bismaleimides-modified polyurethane-epoxy systems are presented in Table I. The incorporation of polyurethane into epoxy system improved the impact strength, when compared with unmodified epoxy system. The incorporation of 5, 10, 15, and 20% polyurethane into epoxy system enhanced the values of impact strength by 6.5%, 11.6%, 16.6%, and 19.7%, respectively. The improvement in impact behavior may be explained as due to the influence of long flexible and resilient nature of polyurethane chain. In contrast to the incorporation of polyurethane, the introduction of aromatic

and aliphatic bismaleimides into epoxy system decreased the values of impact strength, when compared with unmodified epoxy system. The decrease in the values of impact strength is based on the nature and concentration of bismaleimides. The restricted chain mobility due to the formation of network structure and reduced free volume may be explained for the cause of lowering of impact strength.

Among the bismaleimide-modified epoxy systems, the lowest reduction in impact strength is observed for the aliphatic bismaleimide-modified epoxy systems, when compared with aromatic bismaleimide-modified epoxy systems. The reason for the lesser reduction with the aliphatic bismaleimide-modified epoxy system may be explained as due to the presence of long flexible molecular chain. For example, the impact strength value of 8% aliphatic bismaleimide-modified epoxy system is decreased by 5.9%, and similarly, for 8% aromatic bismaleimide-modified epoxy system is decreased by 7.1%, when compared with unmodified epoxy system.

Glass transition temperature

The value of glass transition (T_g) temperature of epoxy system decreased when polyurethane is incorporated (Fig. 2 and Table II). For example, the T_g values obtained for 5, 10, and 15% polyurethane-modified epoxy systems are 146, 141, and 138°C, respectively, when compared with the T_g value of 154°C obtained for the unmodified epoxy system. This may be explained as due to the incorporation of a polyurethane

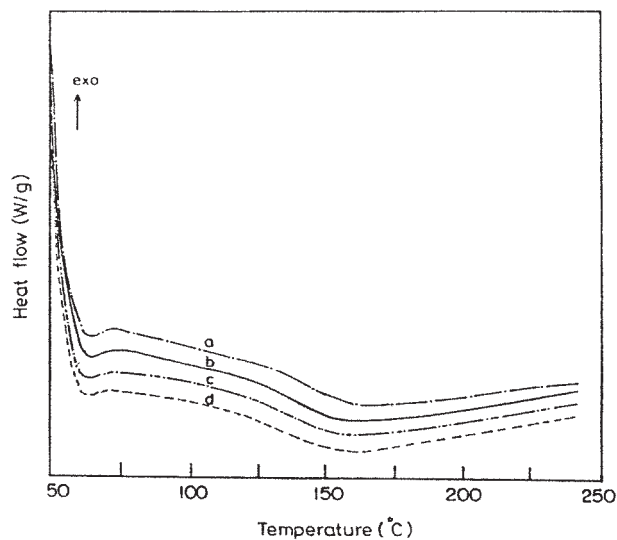


Figure 2 DSC traces of epoxy and polyurethane-modified epoxy systems: (a) unmodified epoxy, (b) 5%, (c) 10%, and (d) 15% polyurethane-modified epoxy systems.

skeleton, which enhances the chain length, and in turn reduces the crosslink density. It also plasticises the epoxy matrix system internally, which in turn creates more available free volume for molecular relaxation and hence lowers the value of T_g .

Among the bismaleimide-modified epoxy systems, the aromatic bismaleimide-modified epoxy system has a higher value of T_g when compared with unmodified epoxy system (Fig. 3 and Table II). For aliphatic bismaleimide-modified epoxy systems, the values of

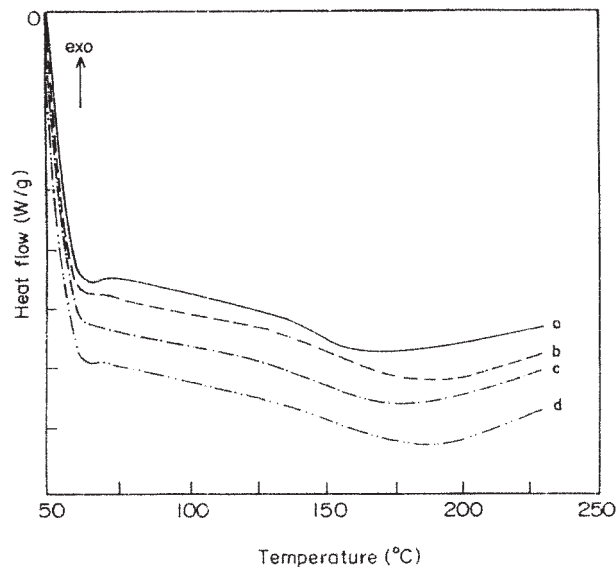


Figure 3 DSC traces of BMI-1 modified epoxy systems: (a) unmodified epoxy, (b) 4%, (c) 8%, and (d) 12% BMI-1 modified epoxy systems.

glass transition temperature is decreased (Fig. 4). The increase in T_g value of aromatic bismaleimide-modified epoxy system may be explained as due to the favored homopolymerization of aromatic bismaleimide rather than Michael addition reaction, whereas, in the cases of aliphatic bismaleimide-modified epoxy system, Michael addition reaction is more favorable than that of homopolymerization reaction, a since the higher temperature is required for homopolymerization of aliphatic bismaleimides.

For example, the value of glass transition temperature obtained for 8% aromatic bismaleimide-modified

TABLE II

Glass Transition Temperature and Heat Distortion Temperature of Unmodified Epoxy, BMI-1 and BMI-2 Modified Epoxy, and Polyurethane-Epoxy Systems

Epoxy/PU/BMI-1 Composition	Glass transition temperature (°C)	Heat distortion temperature (°C)
100/00/00	154	143
100/05/00	146	136
100/10/00	141	130
100/15/00	138	127
Epoxy/PU/BMI-1		
100/00/04	166	158
100/00/08	177	166
100/00/12	181	172
100/10/04	154	143
100/10/08	152	141
100/10/12	150	138
Epoxy/PU/BMI-2		
100/00/04	145	134
100/00/08	142	132
100/00/12	139	128
100/10/04	145	136
100/10/08	141	130
100/10/12	130	127

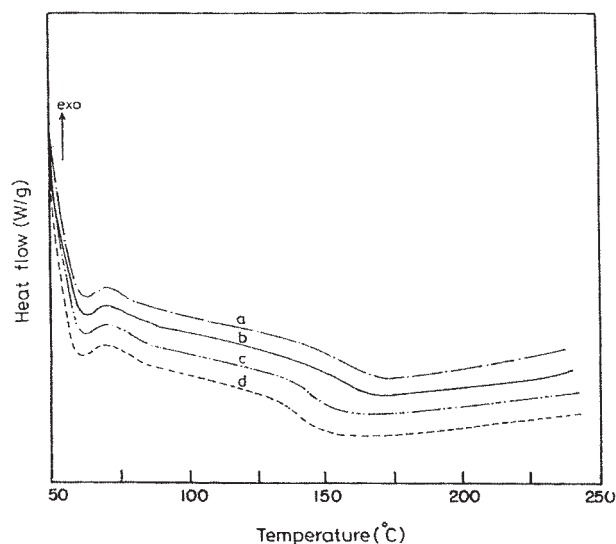


Figure 4 DSC traces of BMI-2 modified epoxy systems: (a) unmodified epoxy, (b) 4%, (c) 8%, and (d) 12% BMI-2 modified epoxy systems.

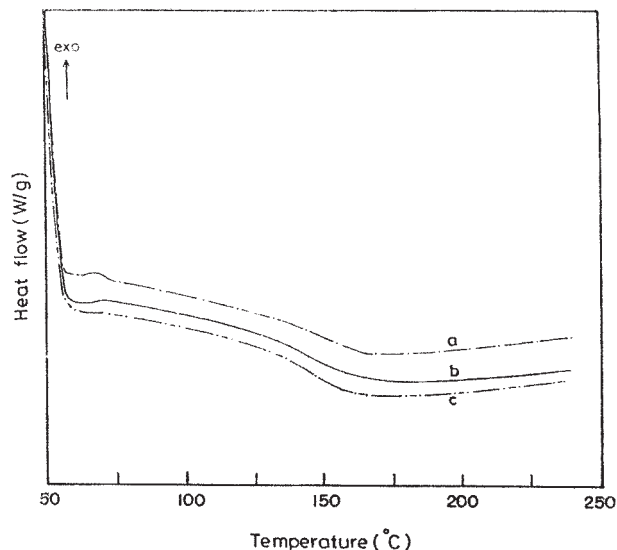


Figure 5 DSC traces of BMI-1 modified polyurethane-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI-1 modified polyurethane (10%)-epoxy systems.

epoxy system was 177°C, whereas the T_g value of 8% aliphatic bismaleimide-modified epoxy system was 142°C. The higher value of T_g obtained for aromatic bismaleimides confirms that the homopolymerization reaction of bismaleimide is predominant rather than Michael addition reaction. Further homopolymerization reaction of aromatic bismaleimide leads to the network formation with thermally stable $-C-C-$ linkage.

The incorporation of bismaleimides into a polyurethane-epoxy system alters the value of T_g , according to their nature and concentration. Among the bismaleimides, the aromatic bismaleimide-modified polyurethane-epoxy system possesses a higher value of T_g than the aliphatic bismaleimide-modified polyurethane-epoxy system (Figs. 5 and 6). For example, for the 12% aromatic bismaleimide-modified polyurethane (10%)-epoxy system, the value of T_g is increased to 150°C, when compared with the polyurethane (10%)-modified epoxy system, whereas in the case of 12% aliphatic bismaleimide-modified polyurethane (10%)-epoxy systems, the value is decreased to 130°C.

Thermogravimetric analysis

TGA is used to assess the thermal stabilities and thermal degradation temperatures of unmodified epoxy, polyurethane-modified epoxy, bismaleimides (aliphatic and aromatic) modified epoxy, and bismaleimides (aliphatic and aromatic) modified polyurethane-epoxy systems, and their thermograms are presented in Figures 7–10. The incorporation of polyurethane into the unmodified epoxy system decreased the thermal stability and degradation temperature because of

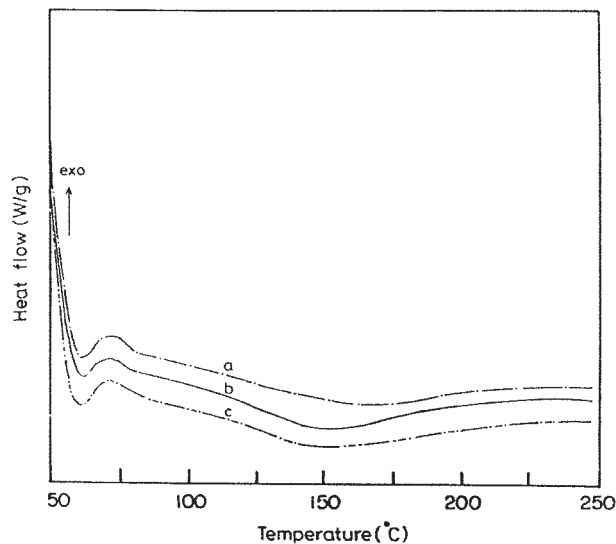


Figure 6 DSC trace of BMI-2 modified polyurethane-epoxy systems: (a) 4%, (b) 8%, and (c) 12% BMI-2 modified polyurethane (10%)-epoxy systems.

the presence of thermally weak urethane linkages in the epoxy backbone. Both aliphatic and aromatic bismaleimide-modified epoxy and bismaleimide-modified polyurethane-epoxy systems showed improved the thermal stability and degradation temperature, according to their concentration. The delay in degradation may be explained as being due to the presence of rigid phenyl groups with the heterocyclic ring structure of bismaleimide.

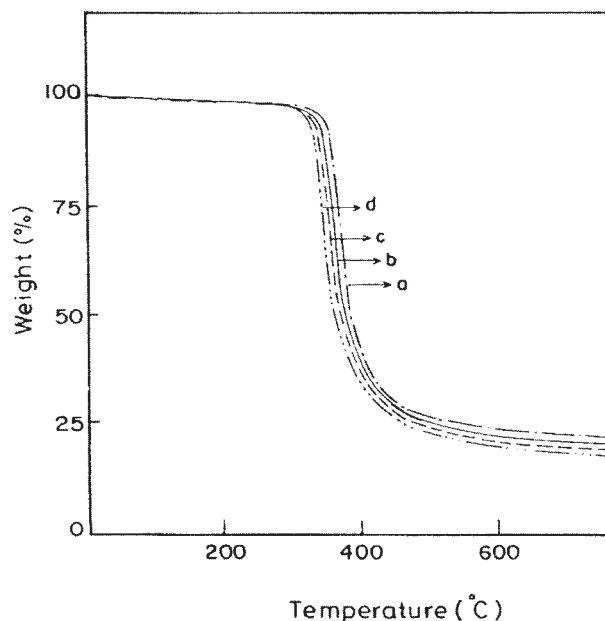
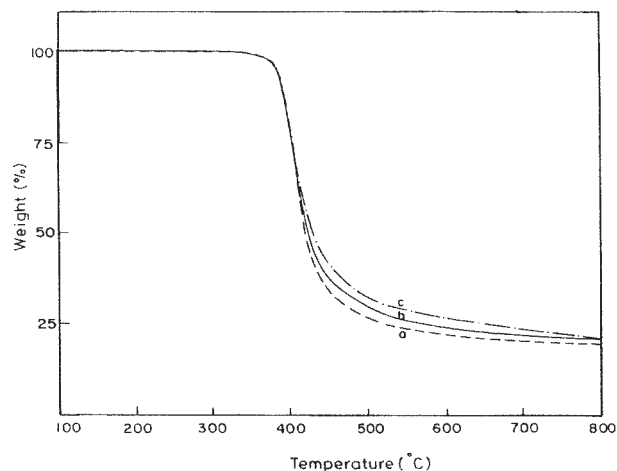


Figure 7 TGA curves of polyurethane-modified epoxy systems: (a) unmodified epoxy, (b) 5%, (c) 10%, and (d) 15% polyurethane-modified epoxy systems.



Figures 8 TGA curves of BMI-1 modified epoxy systems: (a) 4%, (b) 8%, and (c) 12% polyurethane-modified epoxy systems.

Heat distortion temperature

HDT is determined to assess the thermo mechanical behavior of matrix systems. The incorporation of polyurethane into the epoxy system decreases the values of HDT (Table II). The incorporation of polyurethane into epoxy system lowers the crosslink density, rigidity, and T_g , which in turn reduces the values of HDT.

Among the bismaleimide-modified epoxy and bismaleimide-modified polyurethane-epoxy systems, the aromatic bismaleimide-modified epoxy and polyurethane-epoxy systems possess higher values of HDT, when compared with unmodified epoxy system and aliphatic bismaleimide-modified epoxy and polyurethane-epoxy systems. The reason for the higher improvement in the values of HDT is due to the higher thermal stability in association with the rigid molecular structure of aromatic bismaleimide. The presence of long flexible aliphatic chains in the case of aliphatic

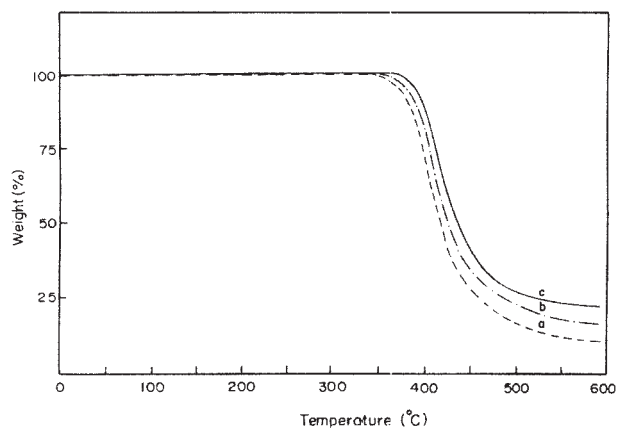


Figure 9 TGA curves of BMI-2 modified epoxy systems (a) 4%, (b) 8%, and (c) 12% BMI-2 modified epoxy systems.

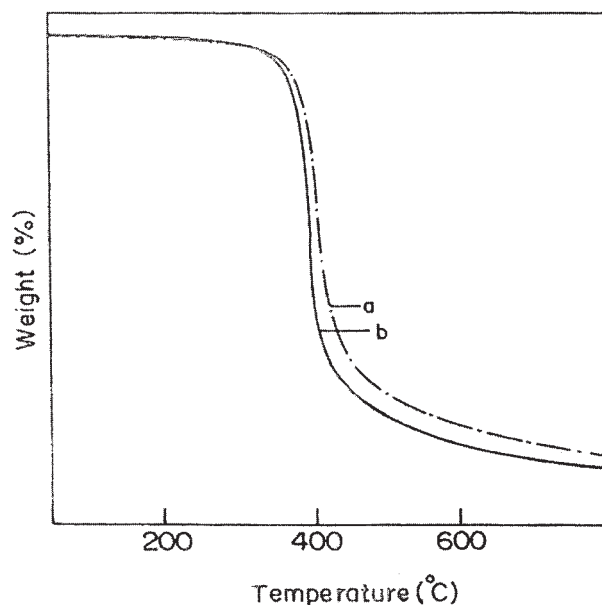


Figure 10 TGA curves bismaleimide-modified polyurethane (10%)-epoxy systems: (a) BMI-1, (b) BMI-2 modified polyurethane (10%)-epoxy systems.

bismaleimide weakens the secondary forces between the molecular chains and thus lowers the values of HDT.

Dielectric strength

The values of dielectric strength of epoxy and polyurethane-modified epoxy systems are presented in Table III. The incorporation of polyurethane into these epoxy system decreases the values of dielectric strength. The values of dielectric strength of the unmodified epoxy system is 18.4 kV/mm, whereas the values of dielectric strength of 5, 10, and 15% polyurethane-modified epoxy systems are 17.6, 16.9, and 16.1 kV/mm, respectively. This may be explained as being due to the polar and hydrophilic nature of urethane linkage. The incorporation of bismaleimides into unmodified epoxy and polyurethane-modified epoxy systems enhances the value of dielectric strength, according to their nature and concentration. The improved tendency to resist moisture absorption is imparted by bismaleimides and also contributes to the better dielectric behavior of bismaleimides-modified polyurethane-epoxy systems.

Among the bismaleimides-modified epoxy and bismaleimides-modified polyurethane-epoxy systems, the aromatic bismaleimide-modified epoxy system exhibits better dielectric behavior than the aliphatic bismaleimide because of the presence of the rigid hydrophobic phenyl ring in aromatic bismaleimide. For example, the values of dielectric strength of 8% aromatic and aliphatic bismaleimides-modified epoxy systems

TABLE III
Electrical Properties of Unmodified Epoxy, Polyurethane-Modified Epoxy, BMI-1 and BMI-2 Modified Epoxy, and Polyurethane-Epoxy Systems

Epoxy/PU/BMI (% Composition)	Dielectric strength (kV/mm)	Surface resistivity (Ω)	Arc resistance (s)
100/00/00	18.4	4.28×10^{12}	86
100/05/00	17.6	3.92×10^{12}	82
100/10/00	16.9	3.13×10^{12}	77
100/15/00	16.1	2.65×10^{12}	72
Epoxy/PU/BMI-1			
100/00/04	23.6	2.82×10^{14}	98
100/00/08	24.9	4.26×10^{14}	105
100/00/12	26.1	6.7×10^{14}	113
100/10/04	20.7	9.13×10^{12}	89
100/10/08	22.2	4.57×10^{13}	96
100/10/12	23.4	9.82×10^{13}	103
Epoxy/PU/BMI-2			
100/00/04	19.3	2.35×10^{13}	89
100/00/08	20.1	4.98×10^{13}	91
100/00/12	21.7	6.87×10^{13}	94
100/10/04	17.8	4.97×10^{12}	79
100/10/08	18.5	6.32×10^{12}	83
100/10/12	19.3	9.83×10^{12}	87

were 24.9 and 20.1 kV/mm, respectively. This may be explained as due to the presence of more number of reactive sites in aromatic bismaleimide, which in turn enhances the crosslinking density and rigidity, when compared with aliphatic bismaleimides. A trend similar to this behavior is also observed in the cases of bismaleimide-modified polyurethane-epoxy systems.

Surface resistivity

The values of surface resistivity of these polyurethane-modified epoxy system are presented in Table III. The value of surface resistivity decreases with increasing concentration of polyurethane into the epoxy system. The values of surface resistivity of 5, 10, and 15% of polyurethane-modified epoxy systems are decreased to 3.92×10^{12} , 3.13×10^{12} , and $2.65 \times 10^{12} \Omega$, respectively. This may be due to the enhanced moisture absorption behavior imparted by polar ether and urethane linkages present in the polyurethane, when compared with unmodified epoxy system.

The values of surface resistivity are increased with increasing the concentration of bismaleimides in the epoxy and polyurethane-epoxy systems. Among the bismaleimide-modified epoxy and bismaleimide-modified polyurethane-epoxy systems, the aromatic bismaleimide-modified epoxy system exhibits higher values of surface resistivity than the aliphatic bismaleimide-incorporated epoxy systems. For example, the value of surface resistivity of the 8% aromatic bismaleimide-modified epoxy system was $4.36 \times 10^{14} \Omega$, and that for the 8% aliphatic bismaleimide-modified

epoxy system was $4.98 \times 10^{13} \Omega$. A similar trend is observed in the cases of bismaleimide-modified polyurethane-epoxy systems.

Volume resistivity

The values of volume resistivity of epoxy and polyurethane-epoxy systems are increased with incorporation of bismaleimides: the increase is based on the nature and concentration of the bismaleimide. The values of volume resistivity obtained for bismaleimide-modified epoxy and bismaleimide-modified polyurethane-epoxy systems are above the order of $10^{14} \Omega$.

Arc resistance

The values of arc resistance of polyurethane-modified epoxy systems are presented in Table III. The incorporation of polyurethane into the epoxy system lowers the values of arc resistance. The values of arc resistance decreased with increasing concentration of polyurethane in the epoxy system. For example, the values of 5, 10, and 15% polyurethane-modified epoxy systems are 82, 77, and 72 s, respectively, due to the formation of a conducting path influenced by the polar urethane linkages.

The incorporation of bismaleimide into epoxy and polyurethane-epoxy systems increases the values of arc resistance, according to their nature and concentration. Among the bismaleimide-modified systems, the aromatic bismaleimide-modified polyurethane-epoxy system exhibits higher values of arc resistance than aliphatic bismaleimide-modified epoxy systems. The value of arc resistance of the 8% aromatic bismaleimide-modified epoxy system is increased to 105 s, when compared with the value of 85 s obtained for the unmodified epoxy system. Similarly, for the 8% aliphatic bismaleimide-modified epoxy systems the values of arc resistance obtained was 91 s. A trend similar to this observation is also noticed in the cases of bismaleimide-modified polyurethane-epoxy systems because of the improved stability imparted by aromatic and heterocyclic skeletons of the bismaleimides.

Scanning electron microscope

Surface morphology of the modified epoxy matrix systems was characterized by SEM (Fig. 11). The fractured surface of the unmodified epoxy system showed a smooth, glassy surface and homogeneous microstructures, whereas the fractured surfaces of polyurethane-modified epoxy systems showed the heterogeneous morphology and heterogeneity increased with increasing the concentration of polyurethane.

The SEM micrographs of fractured surfaces of bismaleimides-modified epoxy systems showed a close similarity as that observed for the unmodified epoxy

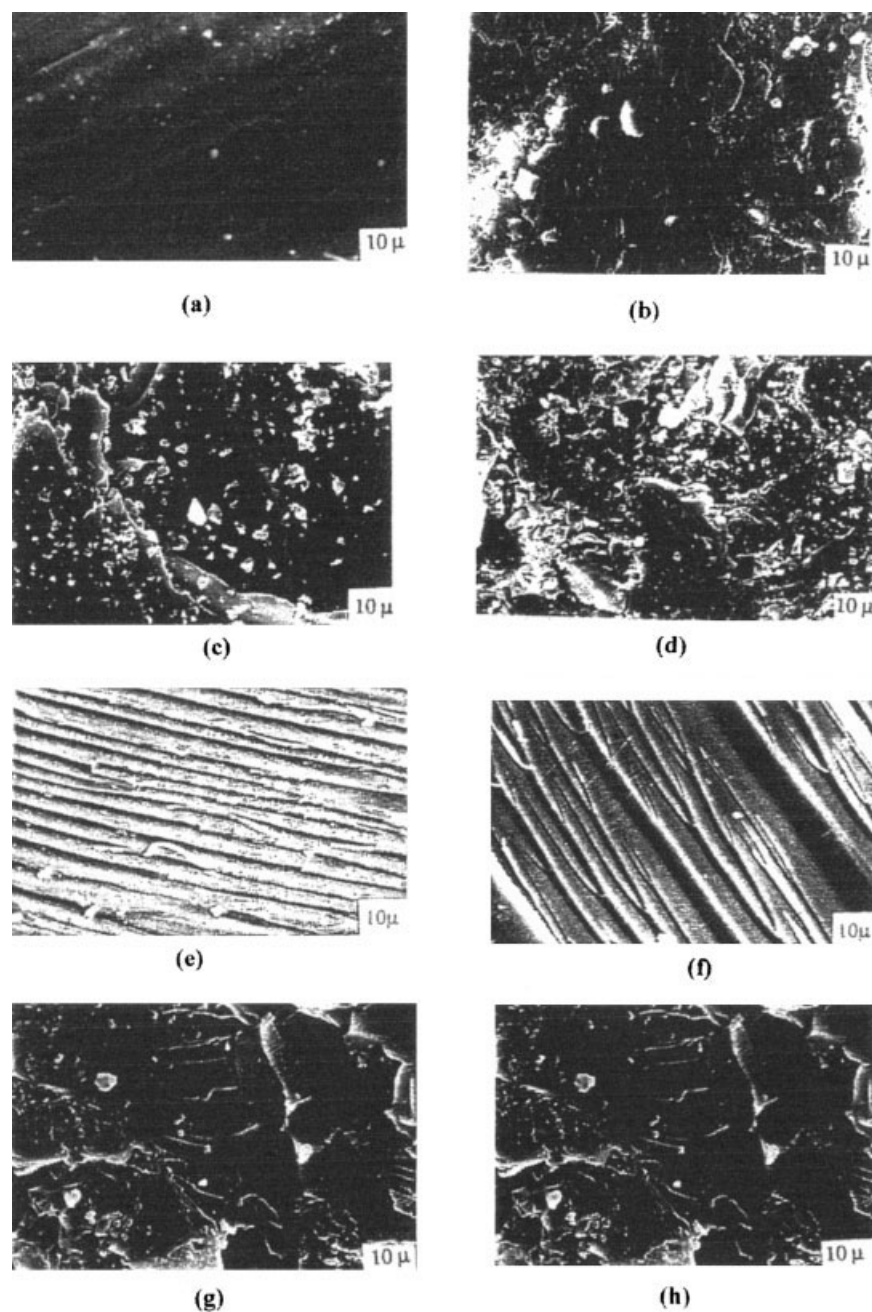


Figure 11 SEM micrographs of (a) unmodified epoxy, (b) 5%, (c) 10%, (d) 15% polyurethane modified epoxy, (e) BMI-1 (8%), (f) BMI-2 (8%) modified epoxy, (g) BMI-1 (8%), and (h) BMI-2 (8%) modified polyurethane (10%)–epoxy systems.

system. These results show that there are no separate phase domains in the cases of bismaleimide-modified epoxy systems and confirm the formation of homogeneous intercrosslinked network structure. The fractured surfaces of bismaleimide-modified polyurethane–epoxy systems showed a heterogeneous morphology, according to their percentage concentration.

CONCLUSIONS

From the data obtained from the experimental studies, it is concluded that the toughness and stress–strain

properties of these epoxy matrix systems increased by forming intercrosslinked network with polyurethane, whereas the glass transition temperature and thermal stability decreased with increasing the concentration of polyurethane. The stress–strain properties of epoxy and polyurethane-modified epoxy systems increased with increasing bismaleimide concentration, whereas the impact strength decreased with increasing concentration of bismaleimide. The glass transition temperature, HDT, thermal stability, and electrical properties of all epoxy decreased with increasing the concentration of polyurethane and increased with increasing

concentration of aromatic bismaleimide. Introduction of aliphatic bismaleimide into epoxy resin lowered the values of glass transition temperature. Surface morphology of fractured surfaces of polyurethane-modified epoxy and bismaleimide-modified polyurethane-epoxy systems showed heterogeneous morphology, according to their concentration, whereas bismaleimide-modified epoxy systems showed a homogeneous morphology. Among the matrix systems studied, it can be concluded that the aromatic bismaleimide-modified polyurethane-epoxy system is the most suitable for the fabrication of composite components for different industrial and engineering applications under adverse environments and high temperature service conditions.

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