Studies on Mechanical, Thermal, and Morphology of Diglycidylether-Terminated Polydimethylsiloxane-Modified Epoxy–Bismaleimide Matrices

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ABSTRACT: An epoxy matrix system modified by diglycidylether-terminated polydimethylsiloxane (DGETPDMS) and bismaleimide (BMI) was developed. Epoxy systems modified with 4, 8, and 12% (by wt) of DGETPDMS were made using epoxy resin and DGETPDMS, with diaminodiphenylmethane as the curing agent. The DGETPDMS-toughened epoxy systems were further modified with 4, 8, and 12% (by wt) of BMI, namely (*N,N'*-bismaleimido-4,4'-diphenylmethane). DGETPDMS/BMI/epoxy matrices were characterized using differential scanning calorimetry, thermogravimetric analysis, and heat deflection temperature analysis. The matrices, in the form of castings, were characterized for their mechanical properties, viz. tensile strength, flexural strength, and impact test, as per ASTM methods. Mechanical studies indicate that the introduction of DGETPDMS into epoxy resin improves the impact strength, with reduction in tensile strength, flexural strength, and glass transition temperature, whereas the incorporation of BMI into epoxy resin enhances the mechanical and thermal properties according to its percentage content. However, the introduction of both DGETPDMS and BMI enhances the values of thermomechanical properties according to their percentage content. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 668–674, 2006

Key words: epoxy resin; bismaleimide; diglycidylether-terminated polydimethylsiloxane; tensile strength; glass transition temperature

INTRODUCTION

Epoxy resins, based on diglycidyl ethers of bisphenol-A (DGEBAs), have been used extensively as thermosetting matrices in the development of high-performance, light-weight, fiber-reinforced composites. Epoxy resin exhibits many desirable properties, such as high strength and modulus, low shrinkage in cure, excellent chemical and solvent resistance, good thermal and electrical properties, outstanding adhesion to various substrates, and easy processability under various conditions.[1–6] However, products from epoxy resins generally exhibit brittle behavior in addition to inferior weathering resistance, which restrict their utility for advanced industrial and engineering applications.

The toughening of epoxy resin received much attention for the development of materials with high performance character, to utilize them for advanced applications. The toughness of epoxy resins has been increased by blending with rubber, such as amino- and carboxyl-terminated butadiene, acrylonitrile elastomers, or terminally functionalized engineering thermoplastics. However, modification of epoxy resins with elastomers improved its impact characteristics, but they lead to a decrease in the physical properties of the cured epoxy in the high temperature region.[7]

Hence, suitable polymeric material is needed to improve the impact resistance and enhanced strain, to fracture with retaining stiffness and thermal stability of epoxy system. To achieve this, development of an interpenetrating polymer network (IPN) having flexible and rigid molecular segments can be considered as an attractive method. Since IPN mechanism provides matrix materials with a single glass transition temperature, IPNs of thermoset–thermoset blends have been extensively studied because of their enhanced mechanical properties.

Among the different materials used for the modification epoxy resins, diglycidylether-terminated polydimethylsiloxane (DGETPDMS) is expected to be the best material because of its versatile behavior, such as flexibility, high thermal stability, heat resistance, dielectric nature, low water absorption, excellent weathering, and chemical resistance.[8–15] It is observed that the introduction of DGETPDMS into epoxy improves the impact strength and thermal stability, but reduces the stress–strain properties and glass transition temperature. To prevent the loss of stress–strain properties and glass transition temperature, modification of DGETPDMS–epoxy system, with rigid materials like
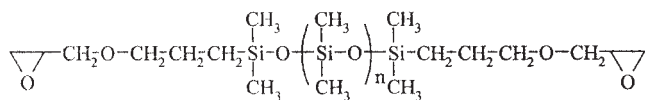
Structure 1 Diglycidylether terminated polydimethylsiloxane.

bismaleimides (BMIs), is essential, owing to their superior thermomechanical properties, viz. high thermal stability, high glass transition temperature, high char yield, excellent fire resistance, specific strength and specific modulus, and low water absorption. Hence, in the present study, an attempt has been made to improve the thermomechanical behavior of epoxy resin, using DGETPDMS and BMI as chemical modifiers for epoxy resin.[16–22]

EXPERIMENTAL

Materials

The commercially available epoxy resin, DGEBA LY 556 (having an epoxy equivalent of about 180–190) and 4,4'-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy Ltd., India. DGETPDMS (Structure 1) having an epoxy equivalent of 490 g/mol was purchased from Aldrich chemicals, USA.

Preparation of *n,n'*-bismaleimido-4,4'-diphenylmethane

BMI was prepared as per reported procedure.[23] In a 1-L three-necked flask fitted with a paddle stirrer, reflux condenser, and nitrogen inlet, 600 mL of acetone, 1.0 mol (98.1 g) of maleic anhydride, and 0.5 mol of DDM were added. Rapid formation of precipitate of the bismaleimic acid occurred on mixing the reactants together, and the mixture was allowed to stand for 30 min to complete the reaction. To the reaction vessel were now added 1 g of nickel acetate and 25 mL of triethylamine, and the entire mixture was heated slowly to reflux. Then by means of a pressure equalizing funnel, 117.9 mL of acetic anhydride was added to the refluxing reaction mixture and heating was continued for an additional 3 h. The reaction mixture was diluted with 500 mL water and chilled, to crystallize BMI. The resulting BMI was filtered and recrystallized from toluene. The reaction scheme for the preparation of BMI is given in Scheme 1.

IR (KBr): ν (cm^{-1}) 3097 ($=$C—H); 3467, 1700 (C$=$O); 1385, 1148 (C—N—C). ^{1}H NMR (d_6-DMSO): δ = 7.36 (d, 4H, J = 8.3 Hz, Hb), 7.26 (d, 4H, J = 8.3 Hz, Ha), 7.15 (s, 4H, olefinic-Hc), 4.03 (s, 2H, CH$_2$). ^{13}C NMR (d_6-DMSO): δ = 126.8, 129.1, 129.5, 134.6, 140.6, and 169.9.

Preparation of DGETPDMS–epoxy blends

Fixed amount of epoxy resin, varying amounts of DGETPDMS, and stoichiometric amount of DDM (with respect to epoxy) were thoroughly blended at 100°C for 10 min with constant stirring. The product was then degassed to remove entrapped air, poured into a preheated mold (Teflon-coated Iron mold, with a Teflon spacer of 3 mm thickness) and kept at 120°C for 1 h, and postcured at 200°C for 2 h.

Preparation of DGETPDMS–epoxyBMI blends

N,N'-Bismaleimido-4,4'-diphenylmethane (4 g) was dissolved in an epoxy resin and DGETPDMS mix (100:4) at 120°C, under vigorous stirring. After complete dissolution of BMI, stochiometric of DDM was added. The product was subjected to vacuum to remove trapped air and then cast and cured at 120°C for 1 h. The castings were then postcured at 200°C for 2 h, and finally removed from the mold and characterized.

In an epoxy/DDM/BMI system, several chemical reactions may occur either simultaneously or at different stages of the curing process, depending on the relative reactivity of the components on the process temperature. As far as the epoxy/DDM pair is concerned, there are three main reactions that take place.

Steps 1 and 2 are the primary and secondary amine reactions with the glycidyl ether, and step 3 is an etherification reaction of the glycidyl ether by a pendant hydroxyl group. Reactions 1 and 2 are also catalyzed by the presence of hydroxyl groups, which were created by the amine reaction themselves, and sometimes added in the formulation for acceleration. In the presence of aromatic amine, BMI undergoes two different reactions,[24] which were shown in Scheme 2.

Test methods

FTIR spectra were recorded using Perkin–Elmer 781 infrared spectrometer, with KBr pellets, for solid samples. The FTIR spectra for viscous liquid samples were carried out by placing the sample between two KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz NMR spectrometer, with CDCl$_3$ as the solvent.

The tensile (stress–strain) properties were determined using dog-bone-shaped specimens, according to ASTM D 3039 method, using an Instron testing machine (Model 6025 UK), at a crosshead speed of 2 mm/min. The flexural strength was measured as per ASTM D 790. The unnotched Izod impact strength of each sample was tested as per ASTM D 256–88.

Glass transition temperatures (T_g) of the samples were determined using a differential scanning calorimeter (DSC) Netzsch (TA instruments, USA) in the temperature range between 50 and 250°C, at a heating
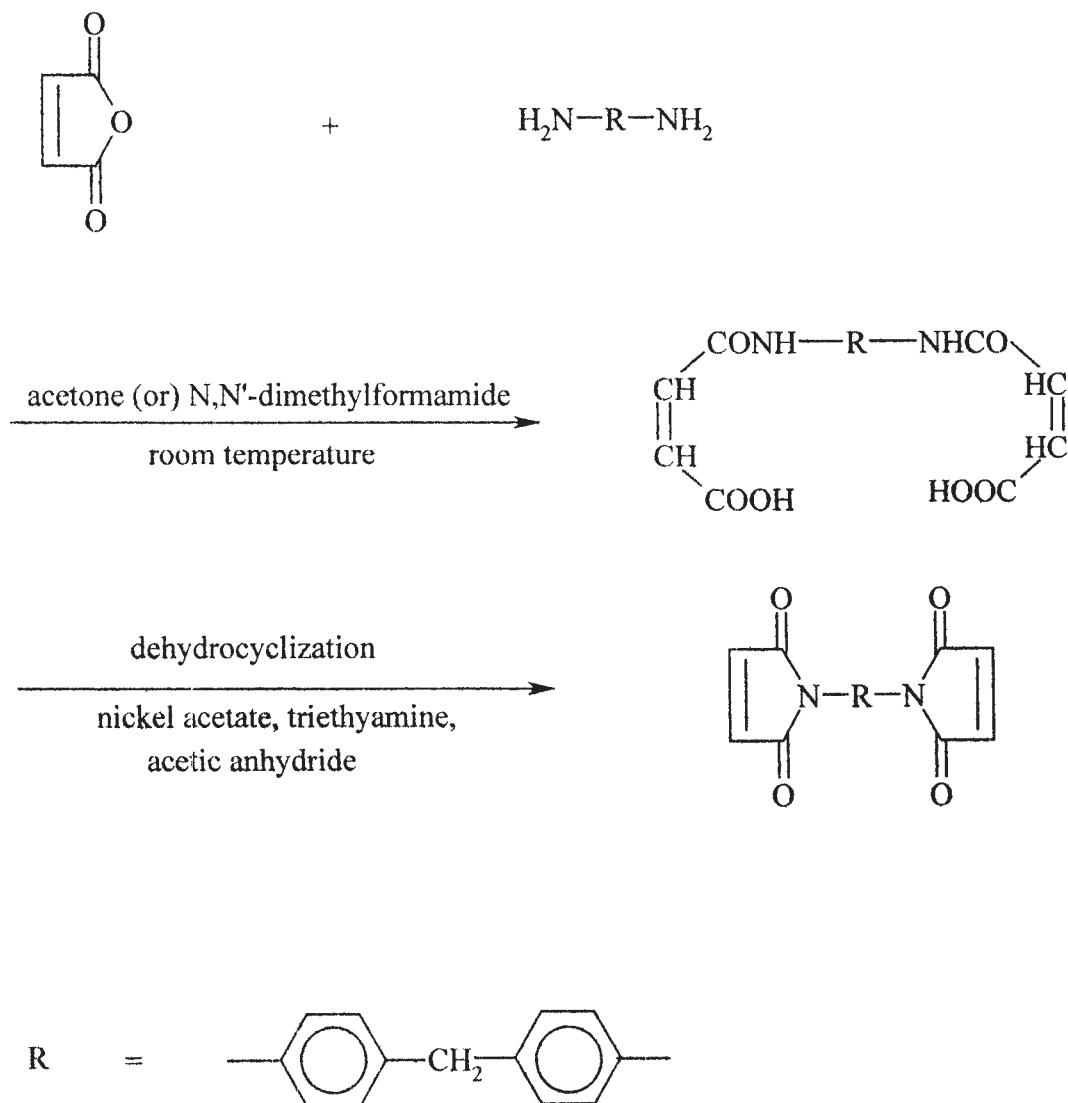
Scheme 1 Synthesis of bismaleimide.

rate of 10°C/min, under nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA instruments), at a heating rate of 10°C/min, under air atmosphere.

The heat deflection temperatures (HDT) of the samples were tested as per ASTM D 648–72. HDT measures the temperature at which deformation occurs, when the composite specimens, having dimensions 127 mm in length, 13 mm in thickness, and 3 mm in width, were placed in an oil bath under a load of 1.82 MPa and the temperature was raised at the rate of 2°C/min. The temperature at which the specimen deflected by 0.25 mm was noted. The deflection was monitored in a linear variable displacement transducer.

Surface morphology of fractured surface of the samples was performed using scanning electron microscope (SEM; Leica Cambridge, Stereoscan Model 440).

RESULTS AND DISCUSSION

Mechanical properties

The observed values for tensile and flexural properties of epoxy and epoxy systems, modified with DGETP-DMS and BMI, are presented in Table I. The introduction of 4, 8, and 12% DGETPDMS (by weight) into epoxy resin decreases the tensile strength and flexural strength when compared with unmodified epoxy. This may be explained due to the presence of flexible siloxane linkage and free rotation of —Si—O—Si— bond. The incorporation of 4, 8, and 12% (by weight) BMI into the epoxy resin increased the tensile strength and flexural strength (Table I), with increasing concentrations. This may be explained by the incorporation of BMI, increasing the crosslink density and the effective compatibility between the epoxy and BMI networks. Similarly, the introduction of both BMI and
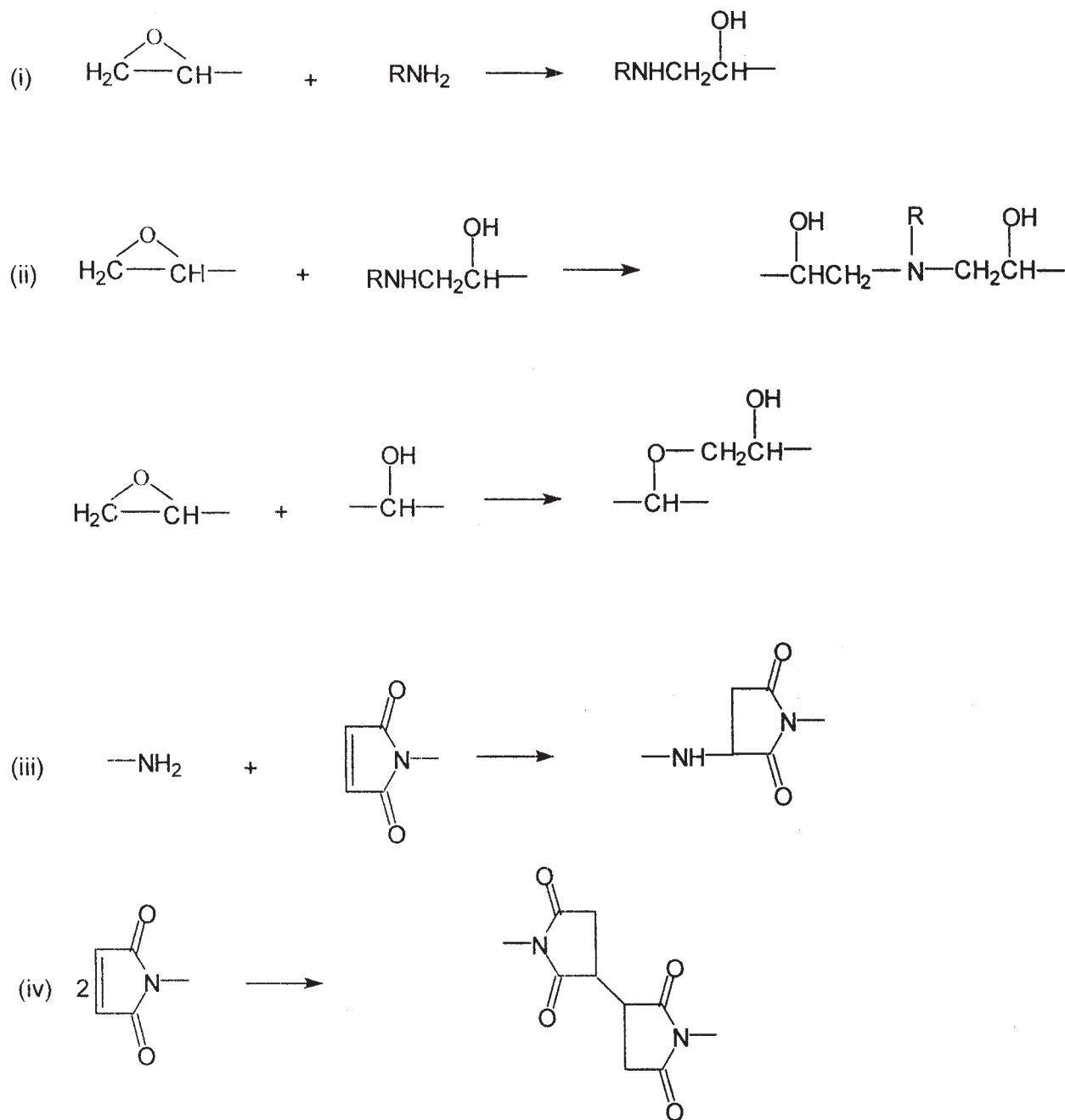
Scheme 2 Reactions involved during the curing process of bismaleimide modified epoxy systems.

DGETPDMS into epoxy resin alters the values of tensile strength and flexural strength according to their percentage content The values of tensile strength and flexural strength of DGETPDMS–epoxy increased with increasing BMI content. Like tensile and flexural strength, the values of tensile and flexural modulus also follow a similar trend (Table I).

Incorporation of DGETPDMS into epoxy resin enhances the toughness according to the percentage content of DGETPDMS. This may be because DGETPDMS contains flexible siloxane linkage and aliphatic group (Table I). The incorporation of BMI in both epoxy and

DGETPDMS–epoxy decreases the impact strength, and this is due to increase in crosslinking density and the rigidity imparted by BMI (Table I).

Thermal properties

The glass transition temperature (T_g) of unmodified epoxy and DGETPDMS-modified epoxy systems are presented in Figure 1. The value of the glass transition temperature of the epoxy system was decreased, with increasing concentration of DGETPDMS. This may be

TABLE I
Mechanical Properties of Unmodified Epoxy, DGETPDS-Modified Epoxy, BMI-Modified Epoxy,
and BMI-Modified DGETPDMS-Epoxy Systems

Epoxy/DGETPDMS/BMI composition	Tensile strength (Mpa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})
100/00/00	62.5 ± 6	2751.7 ± 39	112.0 ± 10	1822.9 ± 42	97.3 ± 2
100/04/00	60.2 ± 3	2572.9 ± 30	90.6 ± 6	1735.4 ± 39	105.6 ± 3
100/08/00	57.0 ± 6	2319.9 ± 29	72.3 ± 4	1610.9 ± 28	115.5 ± 3
100/12/00	52.6 ± 5	1899.7 ± 40	59.1 ± 2	1473.4 ± 31	122.2 ± 1
100/04/04	64.4 ± 3	2605.4 ± 25	83.8 ± 3	1854.1 ± 40	101.6 ± 1
100/04/08	68.2 ± 4	2709.4 ± 32	88.8 ± 4	2050.3 ± 25	96.7 ± 3
100/04/12	74.8 ± 2	2938.9 ± 39	101.0 ± 7	2499.3 ± 27	89.4 ± 4
100/08/04	59.3 ± 2	2406.3 ± 42	74.9 ± 3	1795.2 ± 32	108.5 ± 2
100/08/08	66.6 ± 5	2490.2 ± 31	88.0 ± 3	1814.9 ± 29	101.2 ± 3
100/08/12	70.9 ± 3	2550.6 ± 29	96.6 ± 5	2163.9 ± 41	96.0 ± 1
100/12/04	55.6 ± 3	1903.1 ± 27	60.2 ± 4	1514.2 ± 37	120.7 ± 1
100/12/08	59.4 ± 2	2079.7 ± 49	70.7 ± 3	1602.9 ± 27	117.2 ± 3
100/12/12	63.2 ± 5	2177.8 ± 36	75.0 ± 5	2072.6 ± 31	102.1 ± 2
100/00/04	66.2 ± 9	2820.4 ± 40	118.3 ± 9	2040.5 ± 41	93.8 ± 2
100/00/08	71.0 ± 4	2876.3 ± 31	127.3 ± 7	2275.9 ± 32	86.9 ± 2
100/00/12	85.4 ± 5	3053.9 ± 37	132.6 ± 5	2596.8 ± 35	81.6 ± 1

explained due to the aliphatic and soft flexible Si—O—Si linkage of DGETPDMS (Fig. 1 and Table II). The incorporation of BMI into both epoxy and DGET-PDMS-modified epoxy systems enhances T_g values. The increases in the values of T_g are due to the homopolymerisation of BMIs rather than Michael addition reaction, which confirmed our earlier studies.[24] Thus, Michael addition reaction reduces the crosslink density due to chain extension.

HDT values for epoxy, DGETPDMS-modified epoxy, BMI-modified epoxy, and BMI-modified DGETPDMS–epoxy systems are presented in Table II. From Table II, it is evident that HDT decreases with increasing DGETPDMS concentration, and this may be explained by the presence of flexible —Si—O—Si— linkage. However, increasing trend in HDT values are observed for BMI-modified epoxy and BMI-modified DGETPDMS–epoxy systems. The enhancement in the values of HDT for BMI-modified systems is due to the high crosslinking and the heterocyclic-aromatic structure imparted by BMI.

Thermogravimetric analysis

Incorporation of DGETPDMS into epoxy resin improves thermal stability and enhances the degradation temperature according to its percentage concentration (Fig. 2). The presence of siloxane skeleton in the epoxy system delays the degradation process, and high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. 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. The thermal degradation temperature of the BMI-modified epoxy systems and BMI-modified DGETPDMS/epoxy systems are raised with increasing BMI concentration. From Figure 2, it is evident that the degradation temperature increases with increasing BMI concentrations, as observed in the case of DGETPDMS-modified systems, and this may be due to the formation of inter-crosslinking network between epoxy and BMIs and the rigid heterocyclic ring structure of BMIs.
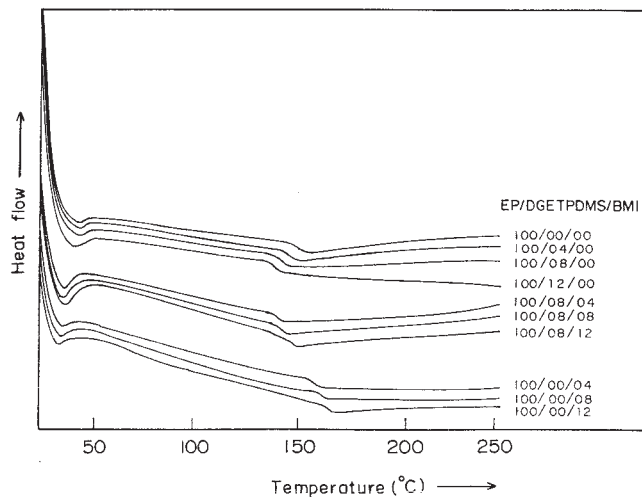

Figure 1 DSC traces of BMI modified DGETPDMS—epoxy (EP) systems.

TABLE II
Percentage Water Absorption, Glass Transition Temperature Percentage Weight Loss, and Heat Distortion
Temperature of Unmodified Epoxy, DGETPDS-Modified Epoxy, BMI-Modified Epoxy,
and BMI-Modified DGETPDMS–Epoxy Systems

Epoxy/DGETPDMS/BMI composition	Water absorption (%)	Heat distortion temperature (°C)	Glass transition temperature (°C)
100/00/00	0.1262	157	166
100/04/00	0.1182	152	162
100/08/00	0.1098	145	159
100/12/00	0.1006	138	157
100/04/04	0.0965	155	165
100/04/08	0.0889	158	168
100/04/12	0.0748	160	173
100/08/04	0.0702	148	161
100/08/08	0.0666	151	164
100/08/12	0.0570	155	167
100/12/04	0.0855	142	160
100/12/08	0.0712	144	161
100/12/12	0.0632	147	164
100/00/04	0.0822	155	169
100/00/08	0.0781	159	174
100/00/12	0.0698	162	180

Water absorption behavior

The DGETPDMS incorporation into epoxy system and the incorporation of BMI into both epoxy and DGET-PDMS-modified epoxy systems decrease the water absorption behavior by increasing its concentration, and this may due to the hydrophobic behavior of DGET-PDMS and BMI (Table II).

Microscopic investigation

SEM is used to investigate the morphology of matrix systems (Fig. 3). SEM photograph of fractured surfaces of the unmodified epoxy system reveals a smooth, glassy, and homogeneous microstructure

without any plastic deformation. The micrograph of the fractured surface of DGETPDMS-modified epoxy resin systems reveals homogeneous morphology, which indicates that DGETPDMS is compatible with epoxy resin system. The SEM photograph of the fractured surface of BMI-modified epoxy system is almost similar to that of unmodified epoxy system. This indicates that there are no separate phase domains. Further, smooth, fractured surface is observed with increasing BMI content because of the brittle behavior imparted by BMIs.

CONCLUSIONS

DGETPDMS-modified epoxy, BMI-modified epoxy, and BMI-modified DGETPDMS–epoxy composites were developed. The thermal properties, such as glass transition temperature, heat distortion temperature, and thermal stability of BMI-modified epoxy, and DGETPDMS–epoxy systems, have been compared with those of unmodified epoxy systems, and an increasing trend with BMI concentration was observed. The mechanical studies reveal that the incorporation of DGETPDMS into epoxy improves the impact strength, with a reduction in tensile and flexural strength, whereas the incorporation of BMI increases the stress strain properties according to its percentage content, with a reduction in impact strength. The morphology study indicated that BMI- and DGETPDMS-modified epoxy systems showed a homogenous morphology. The matrix systems studied exhibits better thermal stability, mechanical behavior, and good resistant to water absorption properties than that of the
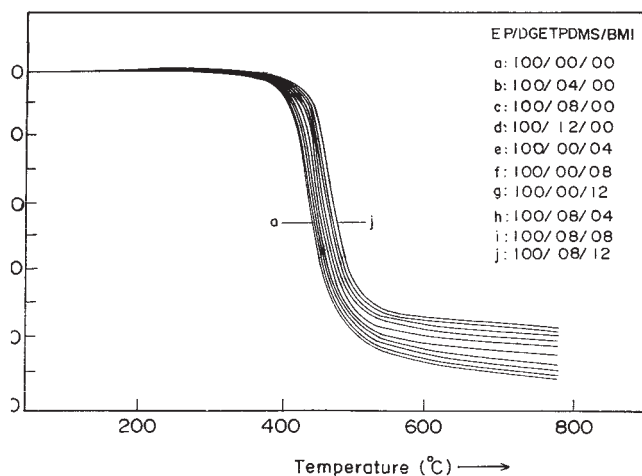

Figure 2 TGA curves of BMI modified DGETPDMS—epoxy (EP) systems.
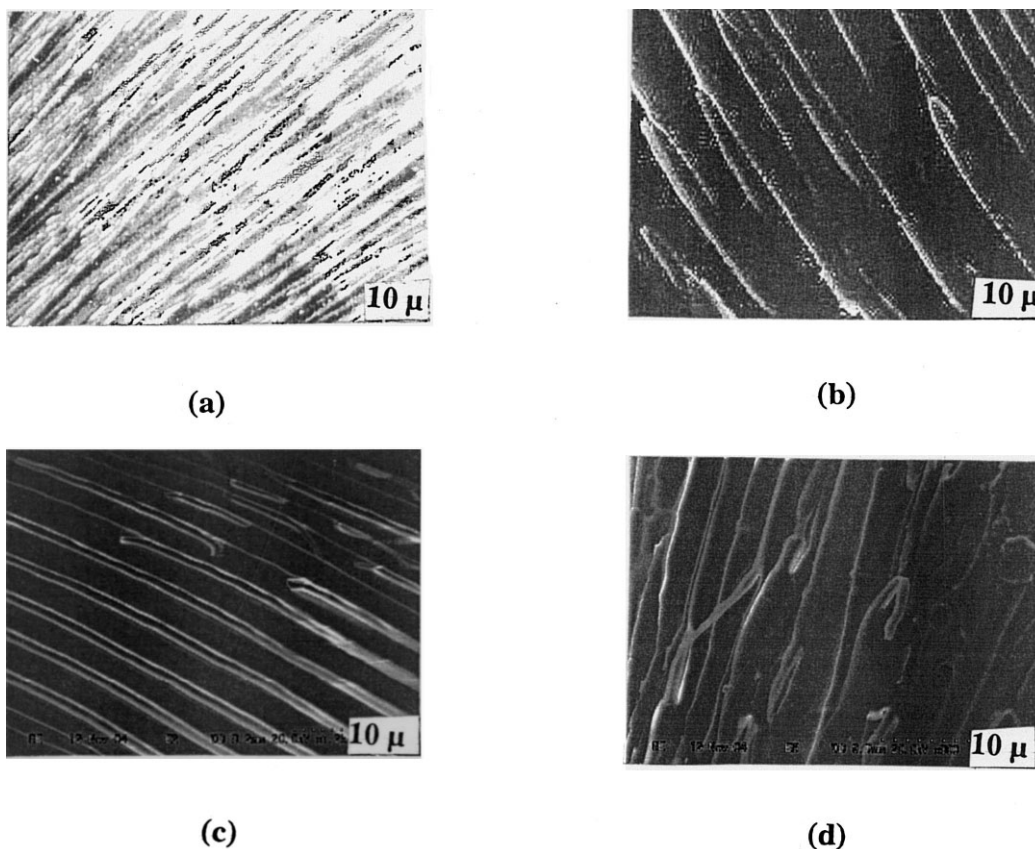
Figure 3 SEM micrographs of BMI modified epoxy and BMI modified DGETPDMS—epoxy (EP) systems: (a) unmodified epoxy, (b) BMI modified epoxy, (c) DGETPDMS—epoxy, (d) BMI modified DGETPDMS—epoxy.

unmodified epoxy system. From the data results from various studies, this matrix system may be used to fabricate advanced composite components for engineering and aerospace applications and for better performance.

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