Studies on thermal, mechanical and morphological behaviour of caprolactam blocked methylenediphenyl diisocyanate toughened bismaleimide modified epoxy matrices

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ABSTRACT

Diglycidyl ether of bisphenol A epoxy resin (DGEBA, LY 556) was toughened with 5%, 10% and 15% (by wt) of caprolactam blocked methylenediphenyl diisocyanate (CMDI) using 4,4′-diaminodiphenylmethane (DDM) as curing agent. The toughened epoxy resin was further modified with chemical modifier N,N′-bismaleimido-4,4′-diphenylmethane (BMI). Caprolactam blocked methylenediphenyl diisocyanate was synthesized by the reaction of caprolactam with methylenediphenyl diisocyanate in presence of carbon tetrachloride under nitrogen atmosphere. Thermal properties of the developed matrices were characterized by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), heat distortion temperature (HDT) and dynamic mechanical analysis (DMA). Mechanical properties like tensile strength, flexural strength and impact strength were tested as per ASTM standards. The glass transition temperature (T_g) and thermal stability were decreased with increase in the percentage incorporation of CMDI. The thermomechanical properties of caprolactam blocked methylenediphenyl diisocyanate toughened epoxy resin were increased by increasing the percentage incorporation of bismaleimide. The values of impact strength for epoxy resin were increased with increase in the percentage concentration of CMDI. The homogeneous morphology of CMDI toughened epoxy resin and bismaleimide modified CMDI toughened epoxy resin system were ascertained from scanning electron microscope (SEM).

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1. Introduction

Epoxy resin is a versatile and widely accepted matrix material for the fabrication of advanced composites, hardware components, electronic circuit board materials, radomes and missile equipment components because of its excellent bonding, physico-chemical, thermal, mechanical, dielectric and aging characteristics [1–7]. To improve working performance of epoxy resin suitable for advanced engineering applications, the toughening of epoxy resin with appropriate chemical modifiers is essential. The toughness of the epoxy resin has been increased by blending with flexible polymers and elastomers. However, they improved its impact properties with appreciable loss of tensile and thermal properties. Hence, selection of suitable polymeric materials is essential to improve the impact strength with retaining stiffness, glass transition temperature and thermal stability of the epoxy matrix.

In our earlier studies the significant improvement in thermomechanical, dielectric and aging characteristics have been achieved by using siloxane, cyanate ester, unsaturated polyester and polysulphone as chemical modifiers for epoxy resin [8–19].

To make further advancement in this direction the present work is under taken to use caprolactam blocked methylenediphenyl diisocyanate as toughening agent and bismaleimide as chemical modifier for epoxy resin.

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Caprolactam blocked methylenediphenyl diisocyanate is expected to possesses better combinations of thermomechanical properties suitable for the fabrication of polymer composites because of their flexible structure (—NH—CO—) formed during *in situ* reaction of cyclic aliphatic caprolactam with aromatic diisocyanate. Several blocked diisocyanates like ketoxime, dimethylpyrazole and caprolactam blocked aromatic diisocyanates have already been developed and used for the synthesis of chain extended polyurethanes [20–22].

Blocked diisocyanate with flexible linkage (—NH—CO—) is expected to function as the best thermoplastic toughener for epoxy resin, because of its versatile behavior of flexibility. It was observed that the introduction of CMDI into epoxy resin improved its mechanical properties with little loss of glass transition temperature. To retain and to improve the glass transition temperature of CMDI toughened epoxy system to an appreciable extent, bismaleimide is used as a chemical modifier in the present work owing to its superior thermomechanical properties [23–28].

Hence, in the present work an attempt has been made to improve both toughness and thermomechanical behavior of epoxy resin without an appreciable loss in strength properties by forming an inter-crosslinked network of caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system and bismaleimide (4,4′-bismaleimidodiphenylmethane).

2. Experimental

2.1. Materials

The commercially available epoxy resin (diglycidyl ether of bisphenol A, DGEBA) LY 556 having epoxy equivalent about 180–190, 4,4′-diaminodiphenylmethane (DDM) curing agent were obtained from Ciba-Geigy Ltd., India.

Carbon tetrachloride was obtained from SRL Chemicals, India. BMI was synthesized from maleic anhydride and 4,4′-diaminodiphenylmethane (DDM), and recrystallized from acetone [29]. Caprolactam was received from SRF Limited, India. Methylenediphenyl diisocyanate (MDI) was procured from Lancaster Chemicals and were used as received.

2.2. Synthesis of caprolactam blocked methylenediphenyl diisocyanate (CMDI)

Caprolactam (2.02 mol) was taken in a 1L round bottom flask and was purged with nitrogen gas in order to remove the moisture present in it. Four hundred millilitres of carbon tetrachloride were added to dissolve the caprolactam completely by means of vigorous stirring. 1 mol of methylenediphenyl diisocyanate was added dropwise over a period of 30 min with constant agitation using mechanical stirrer and stirring was continued for another 1 h and slowly heated the mixture to 70 °C. The white solid mass obtained (yield: 92%) was purified, dried and preserved for further use (Scheme 1). FT-IR (KBr): v (cm^{-1}) 3283 (—NH—); 1706, 1658 (C=O). ^{1}H NMR δ = 11.46 (s, 2H, NH), 7.44 (d, 4H, J = 8.4 Hz, ArH), 7.13 (d, 4H, J = 8.4 Hz, ArH), 4.02 (s, 4H, aliphaticH), 3.89 (s, 2H, aliphaticH), 2.75 (d, 4H, J = 6 Hz, aliphaticH), 1.75 (bs, 12H, aliphaticH). ^{13}C NMR (CDCl$_3$-d_6) δ = 179.0 (—C=O present in caprolactam), 151.4 (—C=O present in amide linkage), 136.3, 128.9, 119.8, 114.5 (C aromatic), 42.9, 39.9, 35.84, 29.75, 27.4, 22.7 (C aliphatic) (Figs. 1–3).

2.3. Synthesis of N,N′-bismaleimido-4,4′-diphenylmethane

To a one litre three-necked flask fitted with paddle stirrer, reflux condenser and nitrogen inlet, were added, 600 ml acetone, 0.5 mol (49.05 g) of maleic anhydride
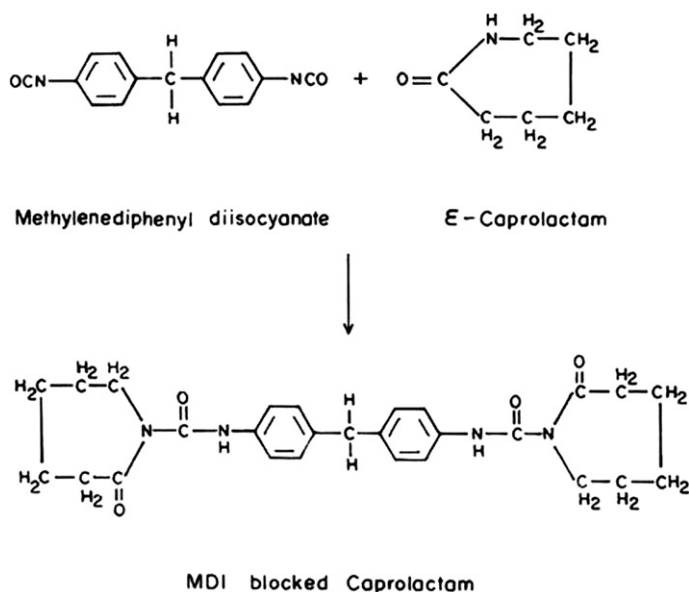
Scheme 1. Synthesis of caprolactam blocked methylenediphenyl diisocyanate.
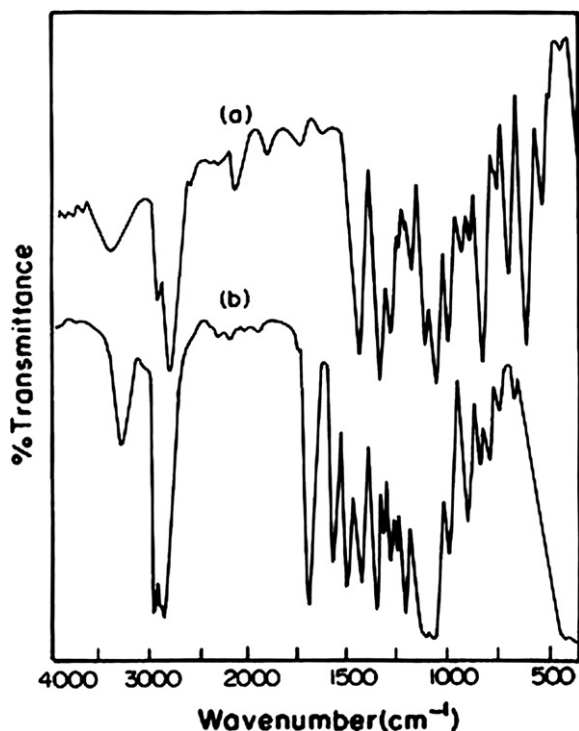
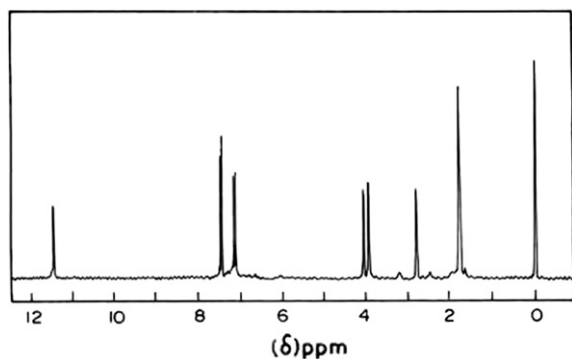**Fig. 1.** FT-IR spectra of (a) unmodified epoxy, (b) caprolactam blocked methylenediphenyl diisocyanate.

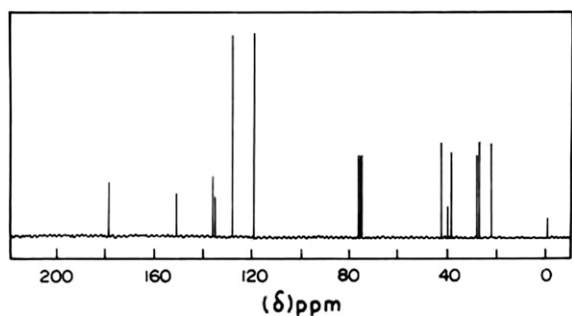**Fig. 2.** ^{1}H NMR spectrum of caprolactam blocked methylenediphenyl diisocyanate.

Fig. 3. ^{13}C NMR spectrum of caprolactam blocked methylenediphenyl diisocyanate.

and 0.25 mol of the desired aromatic diamine. Rapid formation of precipitate of the bismaleiamic acid occurred on mixing the reactants together, and the mixture was allowed to stand for 30 min for the completion of reaction. To the reaction vessel were now added 0.5-g nickel acetate and 12.5 ml triethylamine and the entire mixture was heated slowly to reflux. Then by means of pressure equalizing funnel 59 ml 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 the bismaleimide. The resulting bismaleimide was filtered and recrystallized from toluene. The synthesis route for bismaleimide is presented in Scheme 2. FT-IR (KBr): v (cm^{-1}) 3097 (=C—H); 3467, 1700 (C=O); 1385, 1148 (C—N—C). ^{1}H NMR (DMSO-d_6): δ = 7.36 (d, 2H, J = 8.3 Hz, Hb), 7.26 (d, 2H, J = 8.3 Hz, Ha), 7.15 (s, 4H, olefinic-Hc), 4.03 (s, 2H, CH$_2$). ^{13}C NMR (DMSO-d_6): δ = 126.8, 129.1, 129.5 (C aromatic); 134.6 (C=C); 140.6 (N—C aromatic); 169.9 (C=O).

2.4. Preparation of caprolactam blocked diisocyanate epoxy resin bismaleimide blend

Fixed amount of epoxy resin, varying amounts (5%, 10% and 15%) of caprolactam blocked methylenediphenyl diisocyanate (by wt%) were thoroughly blended at 90 °C for 10 min with constant stirring. The calculated amounts (4%, 8% and 12%) of BMI (by wt%) were dissolved in the above blend at 100 °C under vigorous stirring. After complete dissolution, the stoichiometric amount of diaminodiphenylmethane (with respect to epoxy) was added and the agitation was continued at 90 °C until a homogeneous mixture was obtained. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120 °C for 3 h. The castings were then post cured at 180 °C for 2 h and finally removed from the mold and characterized.
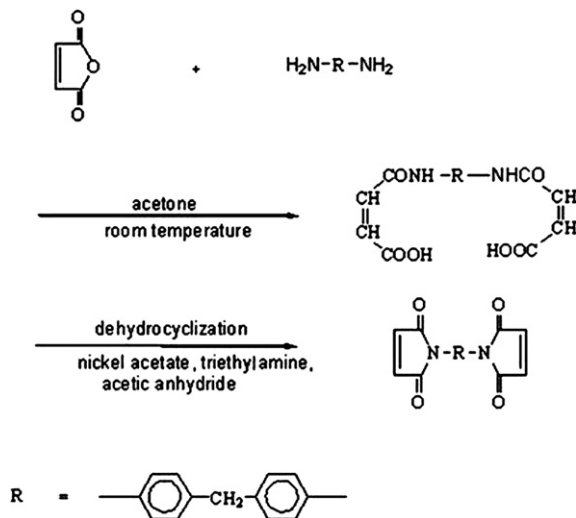
Scheme 2. Synthesis of N,N'- bismaleimido-4,4'-diphenylmethane.

2.5. Test methods

2.5.1. FT-IR spectroscopy

The IR spectra were recorded on a Perkin–Elmer (Model RX1) FT-IR spectrometer, with KBr pellets, for solid samples. For viscous liquid samples, the spectra were carried out by placing the sample between two KBr pellets.

2.5.2. Thermal properties

Glass transition temperature (T_g) of the samples was determined using a DSC Netzsch (TA instruments, USA) in the temperature range between 50 °C and 250 °C at a heating rate of 10 °C per min in nitrogen atmosphere. Thermo-gravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA instruments, USA) at a heating rate of 10 °C per min in nitrogen atmosphere. Dynamic mechanical behavior of the samples was measured using a DMA Netzsch 242 at a heating rate of 10 °C per min from 30 to 300 °C. The heat deflection temperature (HDT) of the samples was tested as per ASTM D 648 - 72.

2.5.3. Mechanical properties

The tensile (stress–strain) properties were determined using INSTRON (Model 6025 UK) as per ASTM D 3039 at 10 mm/min cross-head speed using specimen with a width of 25 mm, length of 200 mm and thickness of 3 mm. The flexural (strength and modulus) properties were measured (INSTRON, Model 6025 UK) as per ASTM D 790 using specimen with dimensions 3 mm in depth, 10 mm in width and 90 mm in length at 10 mm/min cross-head speed. The unnotched Izod impact strength of each sample was studied as per ASTM D 256. Five sample specimens were tested for each analysis.

2.5.4. Water absorption

The water absorption behavior of the samples was tested as per ASTM D 570. The cured specimens (dimensions: 60 mm square, 3 mm thickness) were immersed in distilled water for 48 h. Specimens were removed and the surface water was removed using a tissue paper and weighed to an accuracy of 0.001 g.

2.5.5. Morphology

Surface morphology of fractured surface of the samples was performed using scanning electron microscope (SEM; JEOL JSM Model 6360). The fractured surface of the samples was coated with platinum before scanning.

3. Results and discussion

3.1. Spectral analysis

The characteristic IR absorption peak observed for unmodified epoxy and caprolactam blocked methylenediphenyl diisocyanate is shown in Fig. 1. The strong IR absorption for isocyanate group was absent at 2270 cm^{-1} which confirms that the isocyanate is completely blocked with caprolactam (Fig. 1b). The ^{13}C NMR spectra shows the disappearance of signal at 179 ppm and appearance
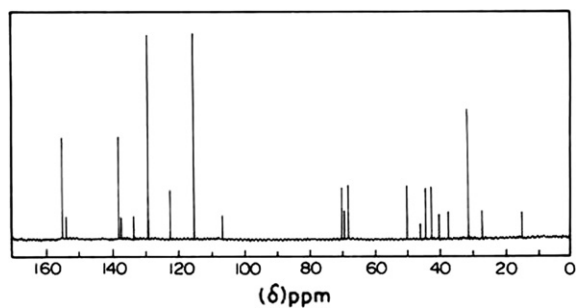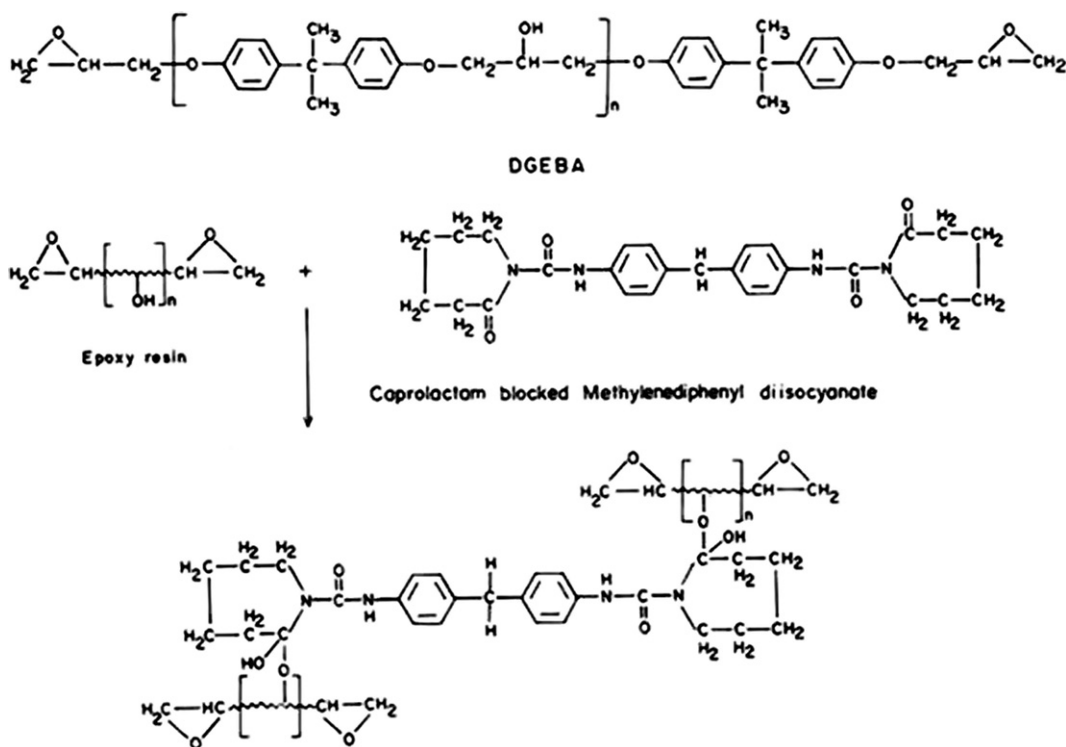

Fig. 4. ^{13}C NMR spectrum of caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system.

of signal at 107 ppm for caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system and is presented in Fig. 4. This confirms that the formation of inter-crosslinked network between epoxy resin and caprolactam blocked methylenediphenyl diisocyanate through the reaction between —C=O group present in caprolactam of CMDI and pendent hydroxyl group of the epoxy resin (Scheme 3).

3.2. Thermal properties

The glass transition temperature (T_g) of unmodified epoxy, caprolactam blocked methylenediphenyl diisocyanate toughened epoxy systems and bismaleimide incorporated caprolactam blocked methylenediphenyl diisocyanate toughened epoxy systems are presented in Table 1. The value of the glass transition temperature of the epoxy system is decreased with increasing concentration of caprolactam blocked methylenediphenyl diisocyanate. For example, the T_g values obtained for 5%, 10% and 15% caprolactam blocked methylenediphenyl diisocyanate toughened epoxy systems are 162 °C, 154 °C and 148 °C, respectively, when compared with that of 165 °C obtained for unmodified epoxy system. This may be explained due to the chain lengthening and flexibility behaviour of —NH—CO— linkage formed during the reaction of aliphatic cyclic caprolactam with aromatic diisocyanates, which in turn decreased the effective crosslink density. This creates excess free volume in the matrix system and leads to reduction in the values of T_g, since T_g is associated with mobility of the molecules (Table 1) and which undergo co-operative motions i.e., segmental motion above T_g. The introduction of bismaleimide into caprolactam blocked methylenediphenyl diisocyanate (CMDI) toughened epoxy systems has increased the values of T_g when compared to CMDI toughened epoxy systems. The values of T_g for 4%, 8% and 12% BMI incorporated 10% caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system are increased to 160 °C, 168 °C and 173 °C, respectively (Table 1) when compared with CMDI toughened epoxy system without BMI incorporation. This may be explained due to the homopolymerization of BMIs rather than the Michael addition reaction confirmed from our earlier studies [11], since the Michael addition reaction reduces the crosslink density due to chain extension. The single T_g value obtained for both the BMI modified epoxy and CMDI

DGEBA

Epoxy resin

+

Caprolactam blocked Methylenediphenyl diisocyanate

Scheme 3. Formation of caprolactam blocked methylenediphenyl diisocyanate epoxy inter-crosslinked network.

Table 1
Thermal and water absorption behavior of BMI modified CMDI toughened epoxy hybrid matrices

Epoxy/CMDI/BMI composition	Heat distortion temperature (°C)	Glass transition temperature (°C) from DSC	Glass transition temperature (°C) from DMA	Water absorption (%)
100/00/00	154	165	165	0.1201
100/05/00	150	162	163	0.1222
100/10/00	146	154	154	0.1254
100/15/00	142	148	149	0.1318
100/00/04	157	167	168	0.0836
100/00/08	161	172	171	0.0726
100/00/12	170	180	182	0.0689
100/10/04	151	160	162	0.1190
100/10/08	159	168	170	0.1088
100/10/12	163	173	172	0.0931

toughened epoxy systems confirms the formation of inter-crosslinking network between epoxy and caprolactam. The values of HDT obtained for epoxy, caprolactam blocked methylenediphenyl diisocyanate toughened epoxy systems are presented in Table 1. From Table 1, it is evident that the values of HDT are decreased with increasing caprolactam blocked methylenediphenyl diisocyanate concentration due to lowering crosslink density and in turn reduced the values of heat distortion temperature.

3.3. Thermogravimetric analysis

The incorporation of caprolactam blocked methylenediphenyl diisocyanate into epoxy resin decreased the thermal stability and lowered the degradation temperature according to the rise in percentage concentration (Table 2). For example, the temperature required for 20%, 40% and 60% weight losses of unmodified epoxy system are 375 °C, 393 °C and 422 °C, respectively, whereas the temperatures required to attain the same percentages of weight losses for 10% caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system are decreased to 352 °C, 368 °C and 392 °C, respectively (Table 2). A similar trend is observed for 5% and 15% CMDI toughened epoxy systems. This may be explained due to the presence of thermally weak flexible linkage (—NH—CO—) in the epoxy backbone. The introduction of bismaleimide into caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system increased the degradation temperature. The temperatures required for 20%, 40% and

Table 2
Data on thermal stability BMI modified CMDI toughened epoxy hybrid matrices

Epoxy/CMDI/BMI composition	Initial decomposition temperature (°C)	Temperature at characteristic weight loss (°C)		
		20%	40%	60%
100/00/00	355	375	393	422
100/05/00	348	369	380	408
100/10/00	341	352	368	392
100/15/00	332	343	357	377
100/00/04	364	391	411	428
100/00/08	372	398	421	436
100/00/12	383	408	433	445
100/10/04	349	366	388	407
100/10/08	356	383	413	427
100/10/12	367	394	426	433

60% weight losses of 8% BMI incorporated 10% CMDI toughened epoxy system are increased to 383 °C, 413 °C and 427 °C, respectively, when compared to those of unmodified epoxy resin occurred at 375 °C, 393 °C and 422 °C, respectively (Table 2). This is explained due to the formation of inter-crosslinking network between epoxy resin and bismaleimide and the rigid heterocyclic ring structure of bismaleimide.

3.4. Mechanical properties

The observed values for tensile and flexural properties of unmodified epoxy, caprolactam blocked methylenediphenyl diisocyanate toughened epoxy are presented in Table 3. The introduction of 5%, 10% and 15% caprolactam blocked methylenediphenyl diisocyanate (by wt%) into epoxy resin enhanced the values of tensile strength by 3%, 12%, 20%, respectively, when compared with that of unmodified epoxy resin. Similarly the values of flexural strength of 5%, 10% and 15% of CMDI blocked epoxy resin systems are increased to 4%, 13% and 20%, respectively, when compared with that of unmodified epoxy system, due to the formation of an interpenetrating network between the molecular chains of epoxy and caprolactam blocked methylenediphenyl diisocyanate. Further, the incorporation of 4%, 8%, 12% bismaleimide into 10% CMDI

toughened epoxy resin increased the values of tensile strength by 18%, 27%, 33%, respectively, and flexural strength by 18%, 24%, 32%, respectively, when compared with that of unmodified epoxy system due to the formation of the network structure between bismaleimide and epoxy resin. A trend similar to this was observed in the cases of tensile modulus and flexural modulus (Table 3).

The incorporation of 5%, 10% and 15% of CMDI into the epoxy system improved the impact strength to an appreciable extent by 23%, 59%, 74%, respectively, when compared with that of unmodified epoxy system (Fig. 5). The improvement in impact behaviour may be explained due to the influence of long molecular chain with flexible group (—NH—CO—) present in the caprolactam blocked methylenediphenyl diisocyanate skeleton. In contrast, the incorporation of bismaleimide in both epoxy and caprolactam blocked methylenediphenyl diisocyanate toughened epoxy resin decreased the values of impact strength when compared with that of unmodified epoxy system and 10% CMDI toughened epoxy resin. The decrease in the values of impact strength is due to the restricted chain mobility resulted from the formation of network structure and consequent reduction in free volume (Fig. 5). However, a significant improvement in the values of impact strength (51%, 46% and 36%) is observed for 10% CMDI toughened epoxy system incorporated with 4%, 8% and 12% BMI when

Table 3
Mechanical properties of BMI modified CMDI toughened epoxy hybrid matrices

| Epoxy/CMDI/BMI composition	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
100/00/00	66 ± 6	2753 ± 39	115 ± 4	1984 ± 31	105 ± 3
100/05/00	68 ± 4	2770 ± 28	120 ± 6	2071 ± 22	129 ± 5
100/10/00	74 ± 7	2863 ± 21	130 ± 2	2162 ± 18	167 ± 4
100/15/00	79 ± 3	2912 ± 23	138 ± 7	2210 ± 26	183 ± 2
100/05/04	73 ± 3	2974 ± 23	128 ± 3	2143 ± 23	126 ± 4
100/05/08	80 ± 4	3088 ± 14	137 ± 1	2247 ± 18	121 ± 2
100/05/12	85 ± 7	3194 ± 27	147 ± 7	2335 ± 44	115 ± 7
100/10/04	78 ± 2	3053 ± 33	136 ± 3	2198 ± 19	159 ± 4
100/10/08	84 ± 4	3164 ± 24	143 ± 4	2283 ± 27	153 ± 2
100/10/12	88 ± 7	3260 ± 28	152 ± 2	2386 ± 12	143 ± 7
100/15/04	81 ± 3	3117 ± 23	144 ± 3	2237 ± 33	177 ± 4
100/15/08	86 ± 6	3221 ± 14	150 ± 5	2318 ± 14	169 ± 2
100/15/12	91 ± 2	3314 ± 18	157 ± 2	2424 ± 28	160 ± 7
100/00/04	71 ± 5	2920 ± 17	123 ± 3	2091 ± 14	96 ± 6
100/00/08	77 ± 8	3026 ± 22	131 ± 2	2206 ± 23	91 ± 4
100/00/12	83 ± 3	3144 ± 27	143 ± 4	2307 ± 29	86 ± 7
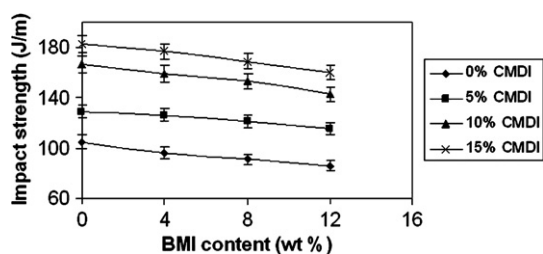
Fig. 5. Effect of bismaleimide content on impact strength of caprolactam blocked methylenediphenyl diisocyanate toughened epoxy systems.

compared with that of unmodified epoxy system (Table 3). The mechanical properties of epoxy-BMI modified with different modifiers (DGTPDMS, PS and PES) are compared with BMI modified CMDI toughened epoxy system (Table 4a, b and c).

3.5. Dynamic mechanical analysis

The ability of a polymeric material to withstand load at elevated temperatures is one of the key aspects of thermo-

Table 4a
Epoxy modifications using different modifiers – a comparison

Polymer systems (100/10/12)	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/m)
Epoxy/CMDI/BMI	88 ± 7	152 ± 2	143 ± 7
Epoxy/DGTPDMS/ BMI	71 ± 3	97 ± 5	96 ± 1
Epoxy/PS/BMI	70 ± 4	124 ± 5	119 ± 3
Epoxy/PES/BMI	70 ± 5	119 ± 5	120 ± 7

CMDI – Caprolactam blocked methylenediphenyl diisocyanate.
DGTPDMS – Diglycidyl ether terminated poly(dimethyl siloxane).
PS – Polysulfone.
PES – Polyethersulfone.

Table 4b
Epoxy modifications using different modifiers – a comparison

Polymer systems (100/10/12)	Heat Distortion Temperature (°C)	Glass transition temperature (°C)	Water absorption (%)
Epoxy/CMDI/BMI	163	173	0.0931
Epoxy/DGTPDMS/ BMI	155	167	0.0570
Epoxy/PES/BMI	157	179	0.0977

Table 4c
Epoxy modifications using different modifiers – a comparison

Polymer systems (100/10/12)	Initial decomposition temperature (°C)	Temperature at characteristic weight loss (°C)		
		20%	40%	60%
Epoxy/CMDI/BMI	367	394	426	433
Epoxy/DGTPDMS/ BMI	380	414	454	470
Epoxy/PES/BMI	347	378	412	426

CMDI – caprolactam blocked methylenediphenyl diisocyanate.
DGTPDMS – diglycidyl ether terminated poly(dimethyl siloxane).
PS – polysulfone.
PES – polyethersulfone.

mechanical behaviour required for high performance applications to be studied. Dynamic mechanical analysis is a method that measures the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. The loss tangent is a sensitive indicator of crosslinking. At temperatures above T_g, damping behaviour decreases due to increase of crosslinking. Fig. 6 shows the tan δ curves of unmodified epoxy, caprolactam blocked methylenediphenyl diisocyanate toughened epoxy and BMI modified CMDI toughened epoxy systems at a heating rate of 10 °C per min from 30 to 300 °C. The caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system exhibited a higher tan δ maximum value and storage modulus than unmodified epoxy resin. This indicated that the caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system has lesser crosslink density than unmodified epoxy system, where as the incorporation of BMI into epoxy has decreased the tan δ maximum value and storage modulus, due to the increased crosslink density. This further supports the results obtained from thermal studies (T_g) (Fig. 7).

3.6. Water absorption

The incorporation of caprolactam blocked methylenediphenyl diisocyanate into epoxy increased the water absorption (Table 1). The increase in percentage water absorption by the caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system is due to the polar and hydrophilic nature of the flexible linkages (—NH—CO—). The water absorption behaviour of bismaleimide incorporated into the epoxy system was decreased according to their concentration (Table 1). The negligible amount of water absorption in the case of bismaleimide – modified epoxy system is due to the formation of an inter-crosslinking network between epoxy and bismaleimide. Similarly, the water absorption behaviour of the bismaleimide modified CMDI toughened epoxy system was also decreased in comparison with that of caprolactam
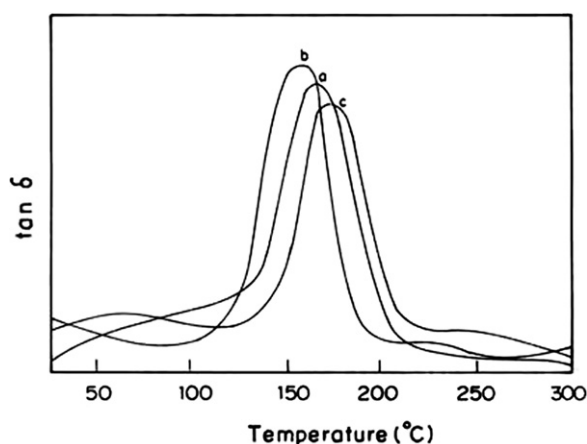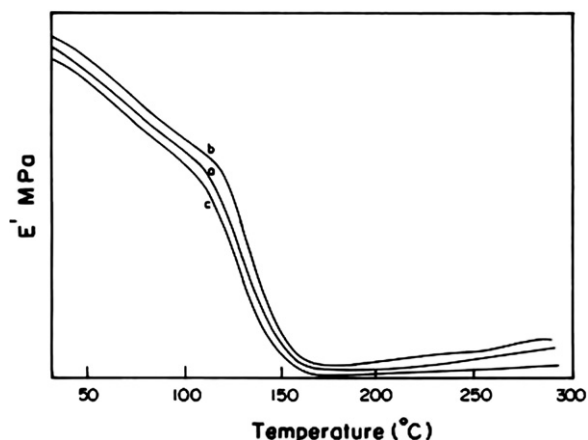

Fig. 6. Variation of tan δ as a function of temperature (a) unmodified epoxy, (b) caprolactam blocked methylenediphenyl diisocyanate (10%) toughened epoxy system and (c) bismaleimide (8%) modified caprolactam blocked methylenediphenyl diisocyanate (10%) toughened epoxy system.

Fig. 7. Variation of storage modulus as a function of temperature (a) unmodified epoxy, (b) caprolactam blocked methylenediphenyl diisocyanate (10%) toughened epoxy system and (c) bismaleimide (8%) modified caprolactam blocked methylenediphenyl diisocyanate (10%) toughened epoxy system.

blocked methylenediphenyl diisocyanate toughened epoxy system (Table 1). This may be explained due to the inherent water repellent character of bismaleimide.

3.7. Morphology

Scanning electron microscope was used to investigate the morphology of matrix systems (Fig. 8). SEM photographs of fractured surfaces of the unmodified epoxy and caprolactam blocked methylenediphenyl diisocyanate toughened epoxy resin systems indicated a smooth, glassy and homogeneous microstructure without any plastic deformation. The homogeneous morphology exhibited by

the CMDI toughened epoxy system is due to the good compatibility and inter-crosslinking reaction between the caprolactam blocked methylenediphenyl diisocyanate and epoxy resin.

The SEM micrograph of the fractured surface of a BMI modified epoxy system is almost similar to that of the unmodified epoxy system. This indicates that there are no separate phase domains. Further, a smooth fractured surface is observed with increasing BMI content due to the brittle behaviour imparted by BMI. The fractured surface of BMI modified CMDI toughened epoxy system showed a homogeneous morphology according to their percentage concentration.

4. Conclusion

Caprolactam blocked methylenediphenyl diisocyanate was synthesized and characterized by IR, ^{1}H and ^{13}C NMR spectra. BMI modified epoxy and caprolactam blocked methylenediphenyl diisocyanate toughened epoxy inter-crosslinked network with various concentrations of BMI and CMDI were developed. Thermal properties such as glass transition temperature, heat distortion temperature and thermal stability of BMI modified epoxy and caprolactam blocked methylenediphenyl diisocyanate toughened epoxy matrices were compared with that of unmodified epoxy system. The caprolactam blocked methylenediphenyl diisocyanate toughened epoxy system possessed decreased thermal stability, glass transition temperature and heat distortion temperature. The incorporation of bismaleimide into caprolactam blocked methylenediphenyl diisocyanate toughened epoxy has increased the thermal properties such as thermal stability, heat distortion temperature and glass transition temperature. From the data obtained from thermal analysis, it was observed that
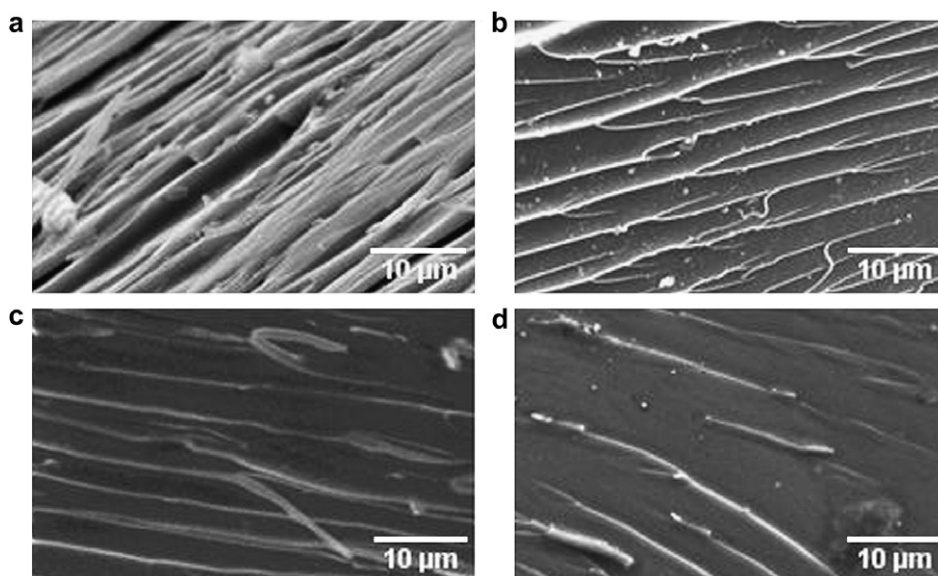
Fig. 8. SEM micrographs of (a) unmodified epoxy, (b) caprolactam blocked methylenediphenyl diisocyanate (10%) toughened epoxy system, (c) bismaleimide (8%) modified epoxy system and (d) bismaleimide (8%) modified caprolactam blocked methylenediphenyl diisocyanate (10%) toughened epoxy system.

the BMI homopolymerization reaction predominates over the Michael addition reaction.

Data resulted from mechanical studies indicated that the incorporation of caprolactam blocked methylenediphenyl diisocyanate into epoxy, improved the tensile and flexural properties with appreciable extent in impact behaviour. Similarly, the incorporation of BMI also increased the tensile and flexural properties according to its percentage content with a little loss in the values of impact strength. The incorporation of CMDI into epoxy increased the water absorption when compared with unmodified epoxy system but decreased in the case of BMI incorporated CMDI toughened epoxy systems. The morphology study indicated that BMI modified epoxy systems showed homogenous microstructure without any plastic deformation. The BMI/CMDI modified epoxy matrix systems possess better thermal stability, dynamic mechanical behaviour and better resistance to water absorption properties than that of the unmodified epoxy system. These toughened epoxy matrix systems could be used to fabricate advanced composite components of improved toughness with better thermomechanical behaviour for engineering applications.

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