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Synthesis and characterization of siliconized epoxy-1, 3-bis(maleimido)benzene intercrosslinked matrix materials

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Abstract

Intercrosslinked network of siliconized epoxy-1,3-bis(maleimido)benzene matrix systems have been developed. The siliconization of epoxy resin was carried out by using various percentages of (5–15%) hydroxyl-terminated polydimethylsiloxane (HTPDMS) with γ-aminopropyltriethoxysilane (γ-APS) as crosslinking agent and dibutyltindilaurate as catalyst. The siliconized epoxy systems were further modified with various percentages of (5–15%) 1,3-bis(maleimido)benzene (BMI) and cured by using diaminodiphenylmethane (DDM). The neat resin castings prepared were characterized for their mechanical properties. Mechanical studies indicate that the introduction of siloxane into epoxy resin improves the toughness of epoxy resin with reduction in the values of stress–strain properties whereas, incorporation of bismaleimide into epoxy resin improves stress–strain properties with lowering of toughness. However, the introduction of both siloxane and bismaleimide into epoxy resin influences the mechanical properties according to their percentage content. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and measurement of heat distortion temperature were also carried out to assess the thermal behavior of the matrix samples. DSC thermogram of the BMI modified epoxy systems show unimodel reaction exotherms. The glass transition temperature (T_g), thermal degradation temperature and heat distortion temperature of the cured BMI modified epoxy and siliconized epoxy systems increase with increasing BMI content and this may be due to the homopolymerization of BMI rather than Michael addition reaction. The morphology of the BMI modified epoxy and siliconized epoxy systems were also studied by scanning electron microscopy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Bismaleimide; Hydroxyl-terminated polydimethylsiloxane

1. Introduction

The modern technology development needs reliable high performance composite materials of light-weight with excellent thermal and mechanical properties. 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. Epoxy resin exhibits many desirable properties, such as high strength and modulus, excellent chemical and solvent resistance, good thermal, and electrical properties and outstanding adhesion to various substrates, and easy processability under various conditions [1–8]. Epoxy resins are also widely used as molding compounds and encapsulation materials for electronic components. However, cured epoxy resins are generally brittle and they exhibit inferior weathering resistance. These are the major factors, that inhibit further proliferation of epoxy resins into many advanced industrial applications and these have resulted in many studies devoted to toughening them without compromising their stress–strain and thermal properties.

Of late, many efforts have been made to improve the toughness of the cured epoxy resin. Most of the studies on the modification of epoxy resins had been carried out by using CTBN (carboxyl-terminated acrylonitrile-butadiene), ATBN (amine-terminated acrylonitrile-butadiene), HTBN (hydroxyl-terminated acrylonitrile-butadiene) rubbers, functionally terminated acrylates, poly(phenylene oxide) and alkylene oxides [9–11]. Though such modification of epoxy resins with these polymeric materials improved its impact characteristics, it failed to increase the physico-mechanical properties of cured epoxy resin when they were used for high temperature applications.

Hence, suitable polymeric toughening materials are needed to improve impact resistance and enhanced strain to fracture with retaining stiffness and thermal stability of epoxy system. To achieve this, development of an intercrosslinked polymer network having flexible and rigid molecular segments can be considered as an attractive

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method. Since, intercrosslinking network mechanism provides matrix materials with good mechanical properties and single glass transition temperature when compared with polymer blends, which normally exhibit multiple glass transitions due to thermodynamic incompatibility of the components involved. Hydroxyl-terminated polydimethylsiloxane (HTPDMS) and bismaleimides are selected as flexible and rigid segments, respectively, for modification of epoxy resin system.

Among the different elastomeric materials used for toughening of epoxy resin, it is found that the HTPDMS is the most suitable polymer because of it's versatile behavior like flexibility due to –Si–O–Si– linkage, high thermal and thermo-oxidative stability, high moisture resistance, good dielectric properties, excellent UV and chemical resistance [12–20]. In our earlier work, it is observed that the siloxane incorporation into epoxy resin improves impact strength with insignificant change in glass transition behavior but reduces stress–strain properties [21,22].

Though the incorporation of siloxane in to epoxy system improves its impact strength and thermal stability, it reduces the stress–strain properties and glass transition temperature. In order to prevent the loss of stress–strain properties, modification of siliconized epoxy system with rigid materials like bismaleimides is essential owing to their superior thermo-mechanical properties viz. high crosslinking ability, high glass transition temperature, high thermal stability, high char yield, excellent fire resistance, specific strength and specific modulus, and low water absorption [22–28].

Hence, in the present study an attempt has been made to improve both toughness and thermal behavior of epoxy resin without an appreciable loss in strength properties by forming an intercrosslinked network of siliconized epoxy-bismaleimide using HTPDMS and 1,3-bis(maleimido)benzene (BMI) as chemical modifiers with γ-aminopropyltriethoxysilane (γ-APS) and dibutyltindilaurate as crosslinking agent and catalyst, respectively.

2. Experimental

2.1. Materials

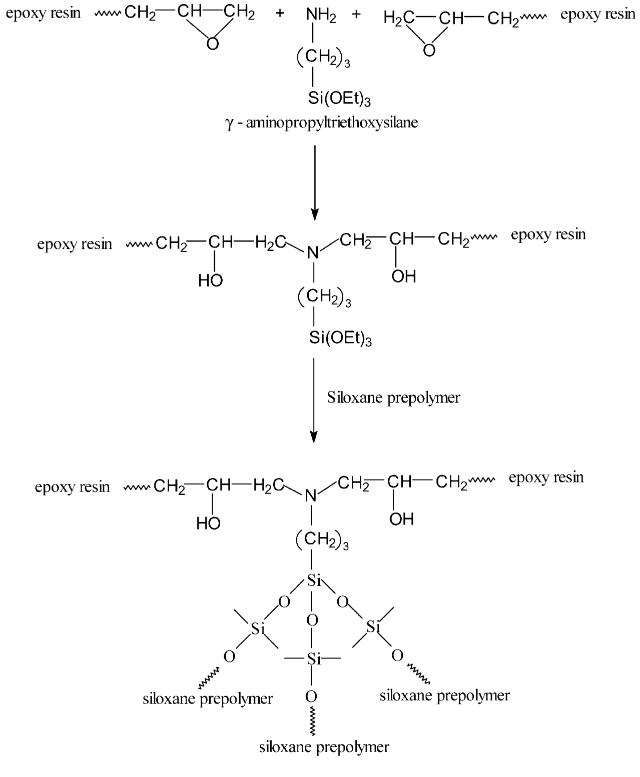
Epoxy resin (Diglycidyl ether of bisphenol A, DGEBA) LY556 having epoxy equivalent of about 180–190, with viscosity about 10,000 cP and 4,4-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy Ltd, India. BMI was synthesized from maleic anhydride and *m*-phenylenediamine, and recrystallized from acetone [29]. HTPDMS having molecular weight 17,000–18,000, viscosity 800–900 cP was prepared from octamethylcyclotetrasiloxane by ring opening polymerization technique [30]. Cross-linking agent γ-APS and dibutyltindilaurate catalyst were obtained from Union Carbide (USA) and Merck (Germany), respectively.

2.2. Preparation of siliconized epoxy prepolymer

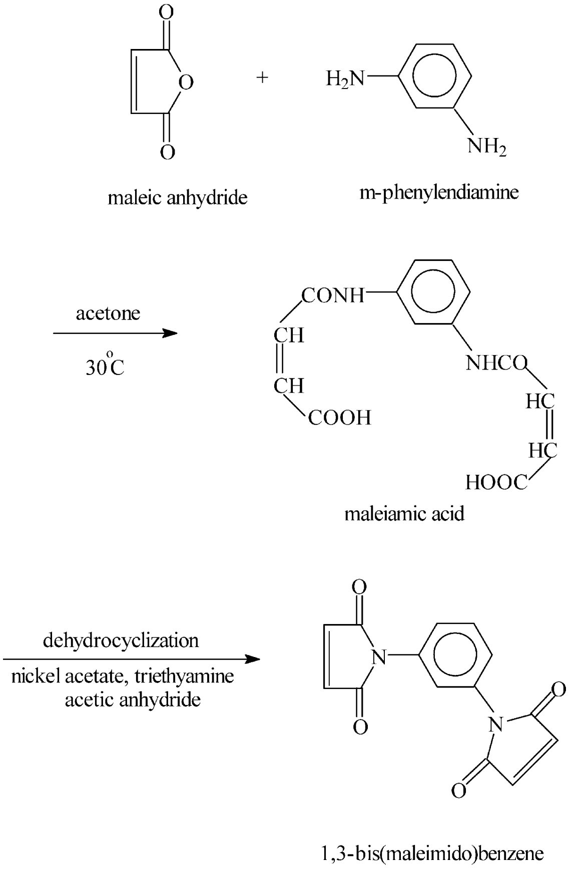
Fixed amount of epoxy resin, varying amounts of hydroxyl-terminated polydimethysiloxane, stoichiometric amount of γ-APS (with respect to hydroxyl groups of HTPDMS) and dibutyltindilaurate catalyst were thoroughly mixed at 90°C for 30 min with constant stirring (Scheme 1 (preparation of siliconized epoxy resin)). The product was then degassed to remove ethanol formed during the condensation reaction between γ-APS and HTPDMS.

2.3. Preparation of 1,3-bis(maleimido)benzene

Bismaleimide was prepared according to the reported procedure with slight modification [29]. In a 1 l three-necked flask fitted with paddle stirrer, reflux condenser and nitrogen inlet, 600 ml of acetone, 1.0 mol (98.1 g) of maleic anhydride and 0.5 mol (54.1 g) of *m*-phenylenediamine were added. Rapid formation of precipitate of bismaleiamic 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 refluxed. By means of pressure equalizing funnel 117.9 ml of acetic anhydride was added to the refluxing mixture and heating was continued for an additional 3 h. The mixture was diluted with 500 ml of water and chilled to crystallize the bismaleimide. The resulting bismaleimide was filtered and recrystallized from acetone. The reaction



Scheme 1.



Scheme 2.

scheme for the preparation of bismaleimide is given in Scheme 2 (synthesis of 1,3-bis(maleimido)benzene).

2.4. Preparation of siliconized epoxy bismaleimide blend

The calculated amount of BMI was dissolved in siliconized epoxy system at 125°C under vigorous stirring. After complete dissolution, the stoichiometric amount of 4,4′-diaminodiphenylmethane 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 1 h. The castings were then post cured at 205°C for 2 h and finally removed from the mold and characterized.

2.5. Test methods

FTIR spectra were recorded using Perkin–Elmer 781 infrared spectrometer with KBr pellets for solid samples. The viscous liquid samples were directly applied by dabbing onto a KBr pellet. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with dimethylsulfoxide-d_6 (DMSO-d_6) as solvent.

Glass transition temperature (T_g) of the samples was determined using DSC 2910(TA instruments USA) in the temperature range between 50 and 250°C at a heating rate of 10°C min^{-1}. Thermogravimetric analysis (TGA) was carried out using Thermal Analyst 2000 (TA instruments USA) at a heating rate of 10°C min^{-1} in an inert atmosphere.

The tensile (stress–strain) properties were determined using dog bone shaped specimens according to the ASTM-D3039 using Instron testing machine (Model 6025 UK), at a crosshead speed of 2 mm min^{-1}. The flexural strength was measured as per ASTM D 790. The fracture toughness of the neat resin castings under conditions of plain strain was evaluated as per ASTM-E399-74. As many as five test pieces were used to generate the data points for the mechanical tests.

To study the morphological behavior, the fractured surfaces were obtained from plain strain fracture toughness tested specimens. Excess material was removed from the other faces of the specimens by razor blade. The fracture surfaces of specimens were coated with gold and examined under a scanning electron microscope (SEM) (Leica Cambridge, Stereoscan Model 440).

3. Results and discussion

3.1. Spectral analysis

^{1}H- and ^{13}C-NMR spectra of the synthesized bismaleimide (BMI) along with the assignment of each proton and carbon is shown in Figs.1 and 2, respectively.

^{1}H-NMR (d_6-DMSO): $\delta = 7.60$ (t, 1H, $J = 8$ Hz, Hc), 7.39 (dd, 2H, $J = 8.0$ and 2.0 Hz, Hb), 7.36 (t, 1H, $J = 2$ Hz, Ha) 7.20 (s, 4H, olefinic-Hd)

^{13}C-NMR (d_6-DMSO): $\delta = 124.8, 126.1, 129.2$ (C_{aromatic}); 132.0 ($N\text{–}C_{\text{aromatic}}$); 134.7 (C=C); 169.7 (C=O).

The formation of siliconized epoxy graft network structure and effectiveness of siliconization were ascertained from IR studies and viscosity measurements, respectively [22].

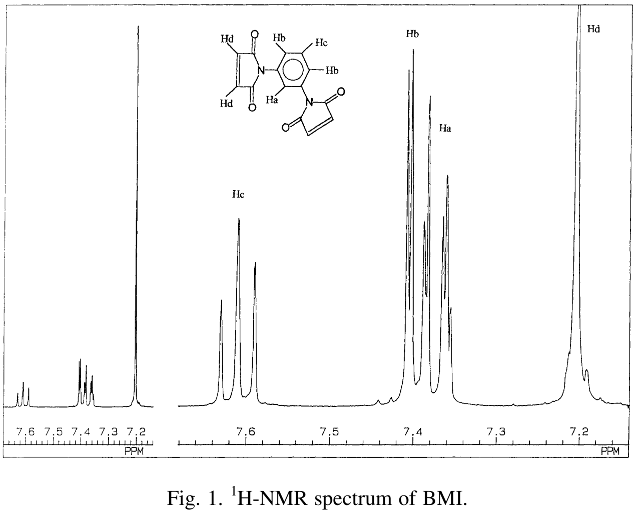


Fig. 1. ^{1}H-NMR spectrum of BMI.

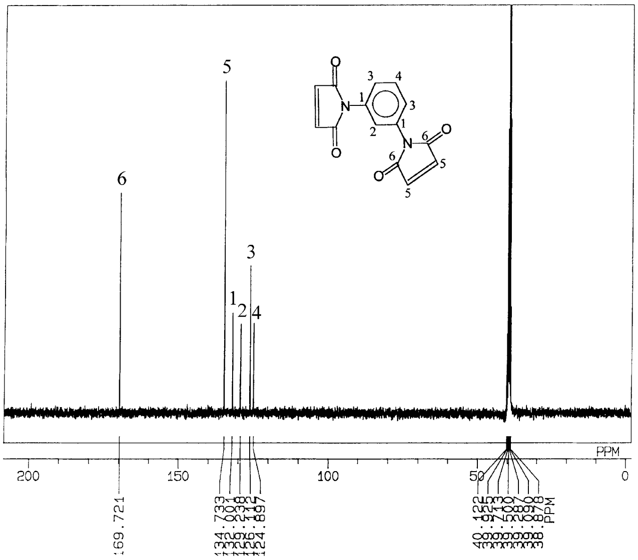


Fig. 2. ^{13}C-NMR spectrum of BMI.

3.2. Thermal properties

The unimodel reaction behavior for epoxy-DDM and γ-APS–epoxy-DDM systems has been ascertained by DSC by Ashok Kumar et al. [22].

DSC thermograms of the bismaleimide modified epoxy resin systems containing 5, 10 and 15% are presented in Fig. 3. From the figure, it can be seen that all the BMI incorporated epoxy systems show unimodel reaction exotherm due to its lower concentration. For all the BMI incorporated systems, the curing reaction commences at 120°C, and reaches the peak maximum temperature 172, 174 and 179°C for 5, 10 and 15%, respectively. Since, the concentration of BMI increment is small, a slight increase in peak maximum temperature is observed with increasing BMI content. The large exothermic peak for the BMI incorporated system is due to the following reactions: (i) oxirane ring opening reaction with active amine hydrogens of DDM, (ii) autocatalytic reaction of oxirane ring with pendent hydroxyl groups of epoxy resin and hydroxyl groups formed during the reaction (i), (iii) addition reaction of $-NH_2$ groups of DDM with double bonds of BMI (Michael addition) and (iv) BMI homopolymerization reaction. Earlier, it was reported that the reaction (iv) is least possible due to the requirement of higher activation energy to initiate homopolymerization of BMI and this reaction normally occurs at 203°C (Fig. 4). However, according to Musto et al., in the presence of epoxy resin, the same reaction (homopolymerization of BMI-1) starts at about 130–140°C, because of the formation of zwitter ion adduct between the oxirane ring and the double bond present in BMI. The slight increase in peak maximum temperature with increasing BMI concentration confirms the observation made by Musto et al. [26].

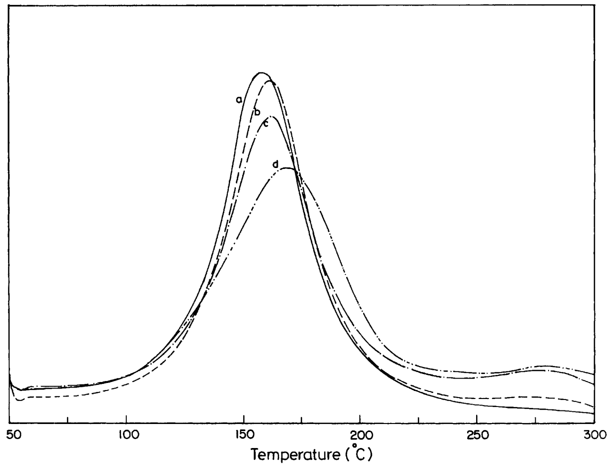


Fig. 3. DSC thermograms of epoxy-BMI systems during cure: (a) epoxy-DDM, (b) epoxy-DDM-5% BMI, (c) epoxy-DDM-10% BMI and (d) epoxy-DDM-15% BMI.

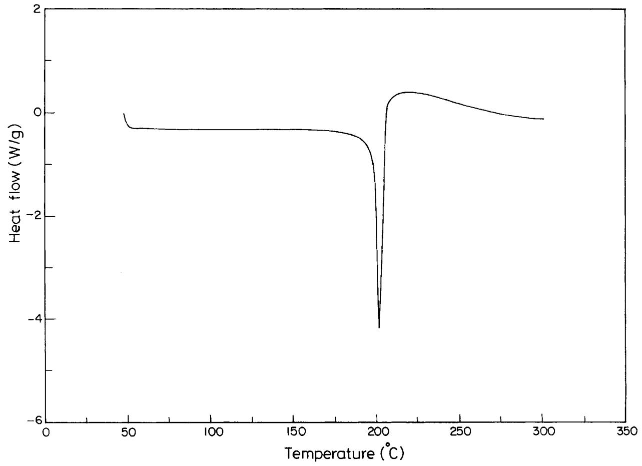


Fig. 4. DSC thermograms of BMI during cure.

The glass transition temperature of matrix systems is presented in Table 1 and Figs. 5 and 6. The glass transition

Table 1
Heat distortion temperatures and glass transition temperatures of epoxy, siliconized epoxy, BMI modified epoxy and BMI modified siliconized epoxy systems (HTPDMS: Hydroxyl-terminated polydimethyl siloxane; BMI: 1,3-bis(maleimido)benzene)

Matrix system	Epoxy/ HTPDMS/ BMI composition	Heat distortion temperature (°C)	Glass transition temperature (°C)
A	100/00/00	153	164
B	100/05/00	150	163
C	100/10/00	145	162
D	100/15/00	139	160
E	100/10/05	161	172
F	100/10/10	170	184
G	100/10/15	175	189
H	100/00/05	168	178
I	100/00/10	176	188
J	100/00/15	182	191

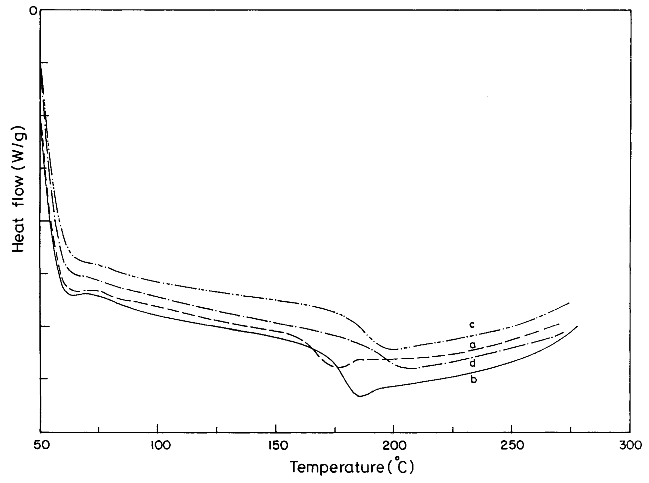


Fig. 5. DSC traces of BMI modified epoxy system: (a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% BMI modified epoxy systems.

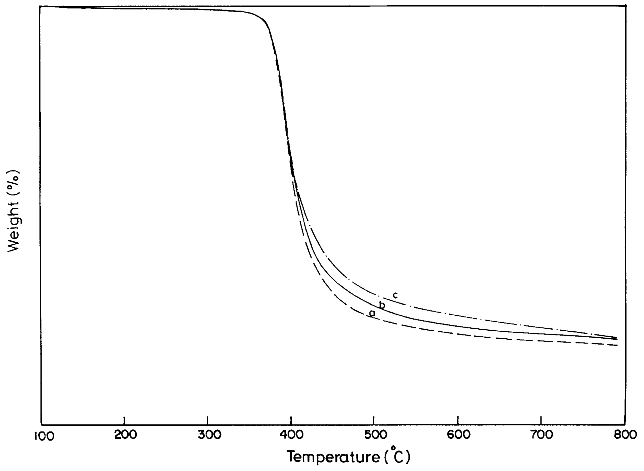


Fig. 7. TGA curves BMI modified epoxy systems: (a) 5%, (b) 10% and (c) 15% BMI modified epoxy systems.

temperature obtained for epoxy-DDM system is 165°C. Incorporation of HTPDMS into epoxy resin has no significant effect on T_g (Table 1). However, a slight decreasing trend in T_g was observed with increasing HTPDMS concentration [22]. The incorporation of BMI into both epoxy and siliconized epoxy systems enhances T_g values (Figs. 5 and 6). The values of T_g for 5, 10 and 15% BMI modified epoxy systems are 178, 188 and 191°C, respectively. The increase in values of T_g for both BMI modified epoxy and BMI modified siliconized epoxy systems is also due to homopolymerization of BMI rather than Michael addition. Since Michael addition leads to the formation of thermally weak amine linkage and ultimately reduces the crosslinking density due to chain extension [31], whereas BMI homopolymerization leads to thermally stable C–C linkage. Moreover, only stoichiometric amount of amine (with respect to oxirane ring of epoxy resin) was added to all the BMI modified epoxy systems. If Michael addition reaction predominates, it reduces the number of available hydrogen to cure epoxy resin and also reduces the crosslink density due to chain extension, which in turn reduces the T_g. Hence, observed rise in T_g confirms the predominating behavior of BMI homopolymerization reaction rather than that of Michael addition reaction. Further, it lends support that the earlier observation made by Musto et al. that in the presence of epoxy resin BMI homopolymerization reaction starts even at 130–140°C [26]. Hence, epoxy resin assists the BMI homopolymerization reaction. The single T_g value obtained for the BMI modified systems further confirms the presence of intercrosslinked network structure.

Incorporation of siloxane into epoxy resin improves thermal stability and enhances degradation temperature proportionate to its percentage concentration [22]. From Figs. 7 and 8, it is observed that the thermal degradation temperature of both BMI modified epoxy (Fig. 7) and BMI modified siliconized epoxy systems (Fig. 8) are increased with increasing BMI contents. The delay in degradation is mainly due to thermally stable aromatic-heterocyclic

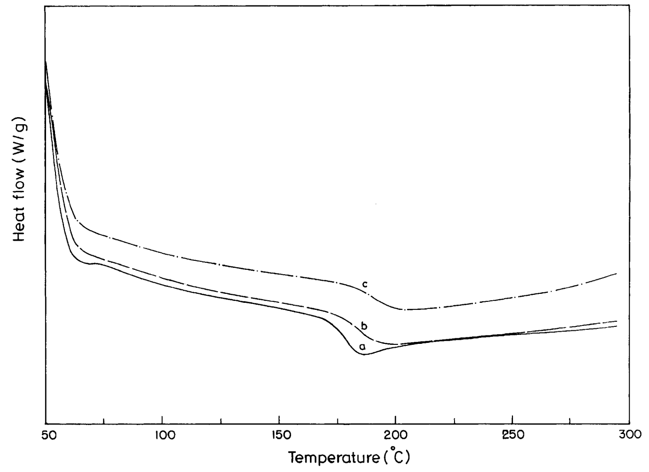


Fig. 6. DSC traces of 10% siliconized epoxy BMI modified systems: (a) 5%, (b)10% and (c) 15% BMI modified 10% siliconized epoxy systems.

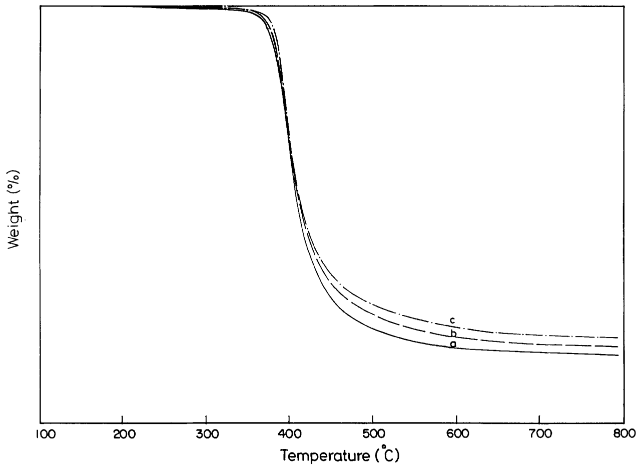


Fig. 8. TGA curves 10% siliconized epoxy BMI modified epoxy systems: (a) 5%, (b) 10% and (c) 15% BMI modified 10% siliconized epoxy systems.

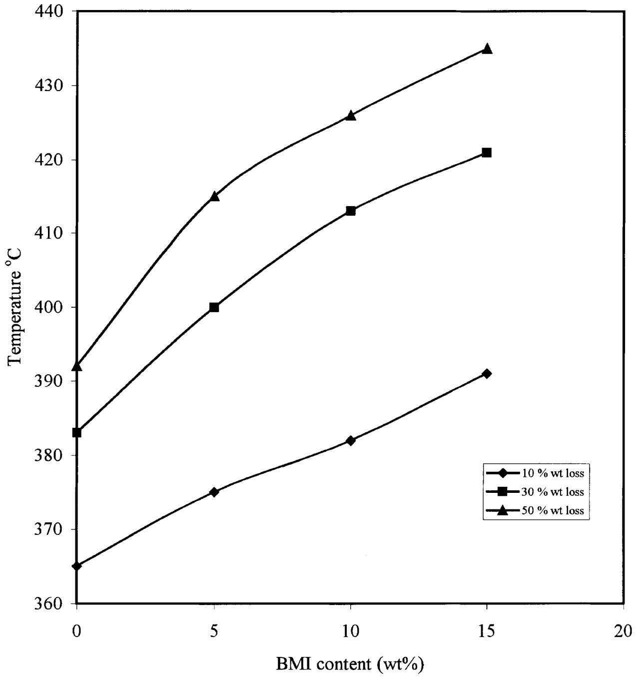


Fig. 9. Effect of BMI content on percentage weight loss of epoxy system.

structure of BMI and the formation of intercrosslinking network and also due to the presence of BMI homopolymerized product. The plots of degradation temperature of BMI modified epoxy system and BMI modified siliconized epoxy systems against BMI concentration are presented in Figs. 9 and 10, respectively. The temperatures required for 10, 30 and 50% weight losses of unmodified epoxy-DDM system are 365, 383 and 392°C where as the temperatures required to attain the same weight losses for 15% BMI modified system are found to be increased to 391, 421 and 435°C, respectively. A similar trend is observed for 5 and 10% BMI modified epoxy systems and BMI modified siliconized epoxy systems. The thermal stability of BMI modified siliconized epoxy system is slightly higher than that of BMI modified epoxy and HTPDMS modified epoxy systems. For example, the temperature required for 50% weight loss of epoxy modified with 10% HTPDMS and epoxy modified with 15% BMI systems are 403 and 435°C, respectively, whereas to attain the same weight loss (50%) for the epoxy system modified with 15% BMI and 10% HTPDMS enhanced to 440°C. This enhancement is mainly due to synergistic effect of BMI and HTPDMS [27].

HDT values for epoxy, HTPDMS modified epoxy, BMI modified epoxy and BMI modified siliconized epoxy systems are presented in Table 1. From the table, it is evident that HDT decreases with increasing HTPDMS concentration, which may be explained due to the presence of flexible –Si–O–Si– linkage. However, increasing trend in HDT values are observed for BMI modified epoxy and BMI modified siliconized epoxy systems. The enhancement in the values of HDT for BMI modified systems is due to the high crosslinking and rigid heterocyclic-aromatic structure imparted by BMI.

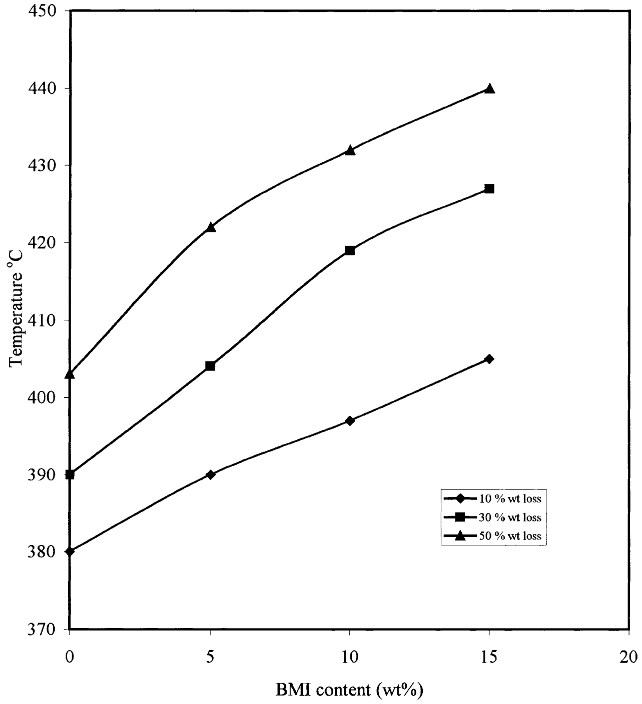


Fig. 10. Effect of BMI content on percentage weight loss of 10% siliconized epoxy systems.

3.3. *Homopolymerization of BMI in the presence of epoxy resin*

It is inferred that from the data obtained from thermal studies, that the homopolymerization reaction of BMI is predominant than that of Michael addition reaction during network formation. To ascertain the role of influence of the epoxy resin for the homopolymerization reaction of BMI, IR and NMR spectra were taken for epoxy and BMI mixture without amine curative (addition of amine curative is avoided to prevent the Michael addition reaction) before and after heat treatment.

Fig. 11 represents IR spectra that reveal the evidence for the BMI homopolymerization at lower temperatures (140–150°C) in the presence of epoxy resin.

Fig. 11a and b represents IR spectrum of pure BMI and unmodified epoxy resin, respectively. Fig. 11c and d represents IR spectrum of the mixture of epoxy resin and bismaleimide, BMI with a composition of 100:10 and 100:50, respectively. The IR spectrum of the mixture of epoxy resin and bismaleimide (BMI) with a composition of 100:50 taken after heating at 150°C for 4–5 h is given in Fig. 11e.

The peak appeared at 3105 cm^{-1} in Fig. 10a is due to H–C= vibration of bismaleimide (BMI) and is widely accepted as reference to follow the conversion of BMI double bonds.

The peak observed at 3105 cm^{-1} in Fig. 11d confirms the presence of BMI in the epoxy mixture. The corresponding peak is poorly resolved in Fig. 11c due to lower concentration of bismaleimide.

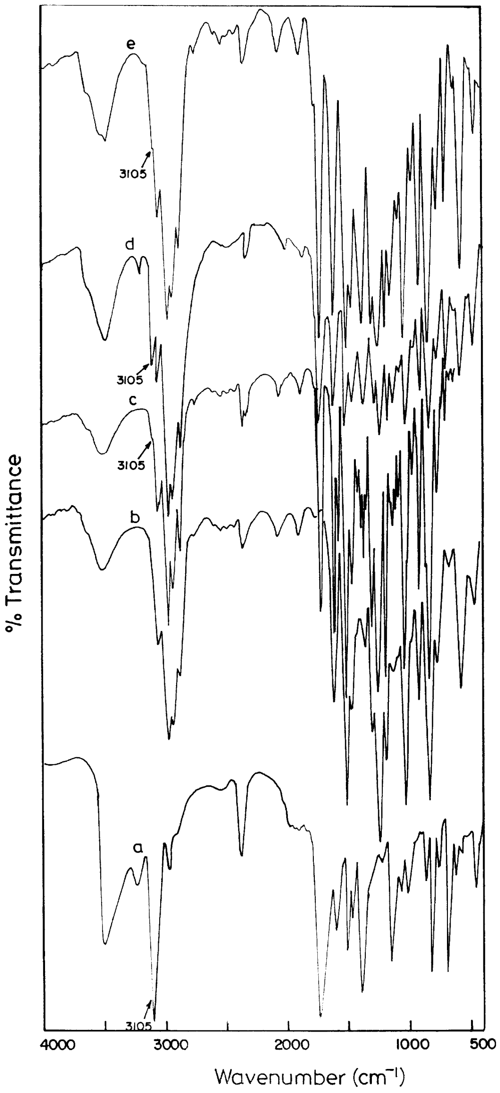


Fig. 11. FTIR spectra of (a) pure BMI, (b) unmodified epoxy, (c) epoxy/BMI: 100/10 (d) epoxy/BMI: 100/50 and (e) epoxy/BMI: 100/50 after heating at 150°C for 4 h.

There is a considerable decrease in the intensity of peak at 3105 cm^{-1} in the IR spectra of the mixture of epoxy resin and bismaleimide BMI with a composition of 100:50 taken after heating at 150°C for 4–5 h (Fig. 11e). This confirms the occurrence of bismaleimide homopolymerization reaction at lower temperatures (140–150°C) in the presence of epoxy resin. This may be due to the formation of zwitter ion adduct between the oxirane ring of epoxy resin and double bond of bismaleimide, which anionically induce homopolymerization reaction at lower temperatures [26], whereas the homopolymerization reaction of pure bismaleimide BMI normally takes place at 203°C. Hence epoxy resin effectively aids the homopolymerization reaction of bismaleimide at lower temperatures. This observation is well in agreement with the investigation by Musto et al. [26] and Ashok Kumar et al. [22].

To further confirm this observation, ^{1}H-NMR spectra were recorded for epoxy/BMI mixture before and after heat treatment in the absence of amine curing agent. In ^{1}H-NMR spectra also, decrease in the intensity of the olefinic proton peak was observed at 7.2 ppm, whereas no peak was observed with respect to BMI homopolymerized product, and is due to the poor solubility of the homopolymerized product of BMI. Hence, epoxy/BMI mixture was repeatedly washed with DMF to separate the insoluble BMI homopolymer. Then it (homopolymer) was washed with dry acetone, filtered and dried. The pure dried BMI homopolymer product thus obtained was analyzed by IR and compared with the IR spectrum of pure BMI monomer (Fig. 12). From Fig. 12b, it is observed that there is a drastic reduction in the intensity of peak at 3105 cm^{-1}, which confirms the presence of BMI homopolymer.

Based on the spectroscopic data presented in Figs. 11 and 12, it is inferred that the epoxy resin assists the BMI homopolymerization reaction by the formation of zwitter ion adduct. The probable mechanism for the formation of zwitter ion adduct is presented in Scheme 3 (Probable mechanism for the formation zwitter ion adduct).

3.4. Mechanical properties

Introduction of HTPDMS into epoxy resin decreases the tensile and flexural strengths and this may be explained due to the presence of flexible siloxane linkage due to the free rotation of –Si–O–Si– bond, weak interfacial attraction force of pendent methyl groups present in the HTPDMS and weak interface boundary between siloxane and epoxy

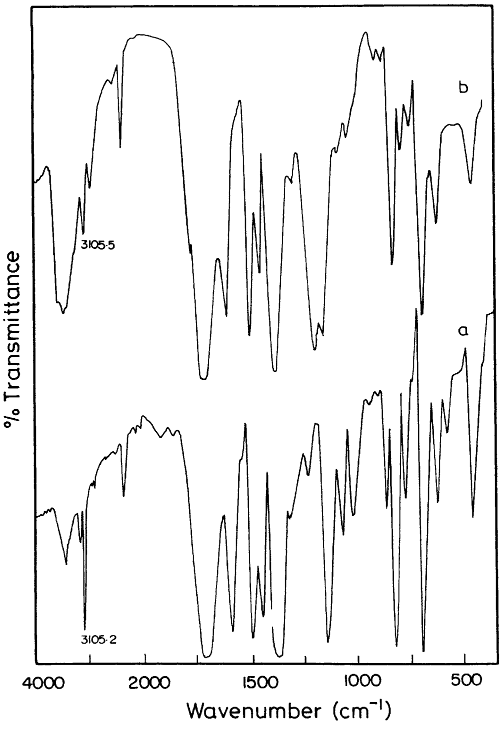
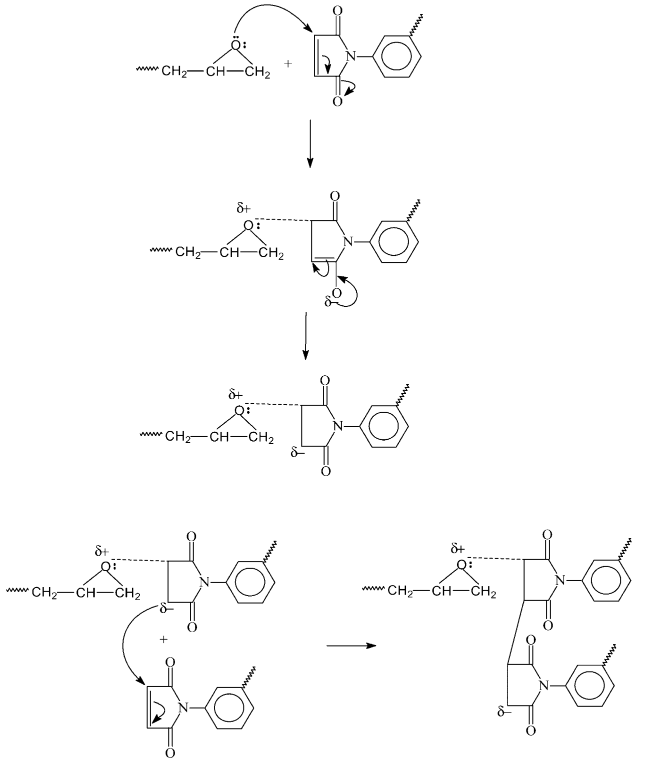


Fig. 12. FTIR spectra of (a) pure BMI monomer and (b) homopolymerized product of BMI.



Scheme 3.

matrix [21,22]. BMI incorporation into epoxy system increases the tensile and flexural strength (Figs. 13 and 14), this may be explained as the incorporation of bismaleimide increases the crosslink density due to the formation of intercrosslinking network [22].

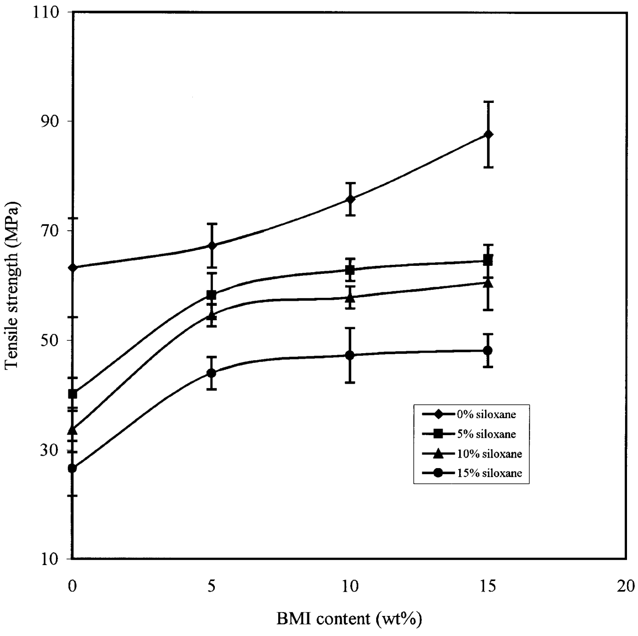


Fig. 13. Effect of BMI content on tensile strength of epoxy and siliconized epoxy systems.

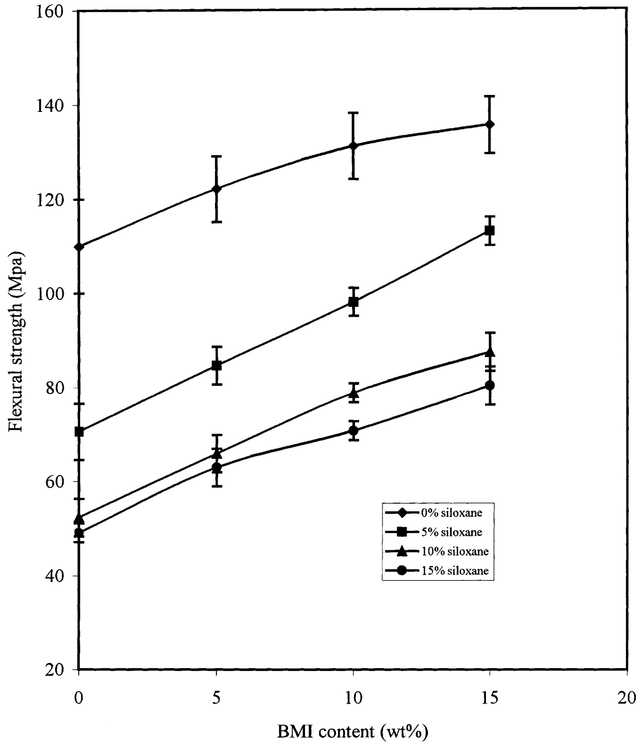


Fig. 14. Effect of BMI content on flexural strength of epoxy and siliconized epoxy systems.

The introduction of combination of both siloxane and bismaleimide 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 siliconized epoxy system steadily increase with increasing bismaleimide content (Figs. 13 and 14). Like tensile and flexural strength, the values of tensile and flexural modulus also follows the similar trend (Figs. 15 and 16).

Siloxane incorporation into epoxy resin enhances the toughness according to the percentage content of siloxane due to high-energy absorption and resilient behavior of flexible siloxane molecule [22]. The incorporation of bismaleimide in both epoxy and siliconized epoxy decreases the toughness and this is due to increase in crosslinking density and the rigidity imparted by bismaleimide (Fig. 17).

3.5. Microscopy investigation

SEM micrograph of fractured surface of the unmodified epoxy system (Fig. 18a) reveals a smooth, glassy and homogeneous microstructure without any plastic deformation. The micrograph of the fractured surface of BMI modified epoxy system (Fig. 18b) is also similar to that of unmodified epoxy system. This indicates that there are no separate phase domains of the two components involved and it also suggests the formation of homogeneous intercrosslinked network. The fractured surface of the BMI modified siliconized system reveals the presence of heterogeneous morphology (Fig. 18c–e) due to partial incompatibility of HTPDMS.

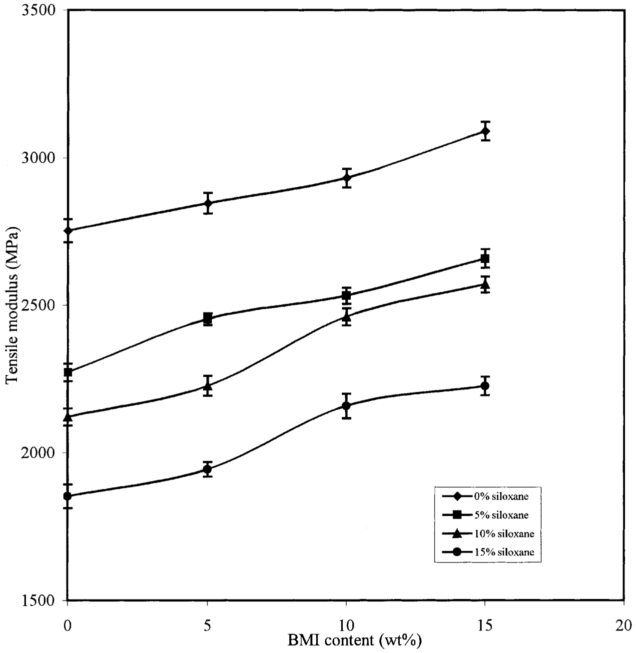


Fig. 15. Effect of BMI content on tensile modulus of epoxy and siliconized epoxy systems.

4. Conclusion

BMI modified epoxy and siliconized epoxy intercrosslinked network having varied concentrations of BMI and siloxane units were developed. Thermal properties, viz. glass transition temperature, heat distortion temperature and thermal stability of BMI modified epoxy and siliconized epoxy matrices have been compared with those of unmodified epoxy systems and showed an increasing trend with increasing bismaleimide concentration. Based on thermal and spectral analysis, it is evident that the BMI homopolymerization

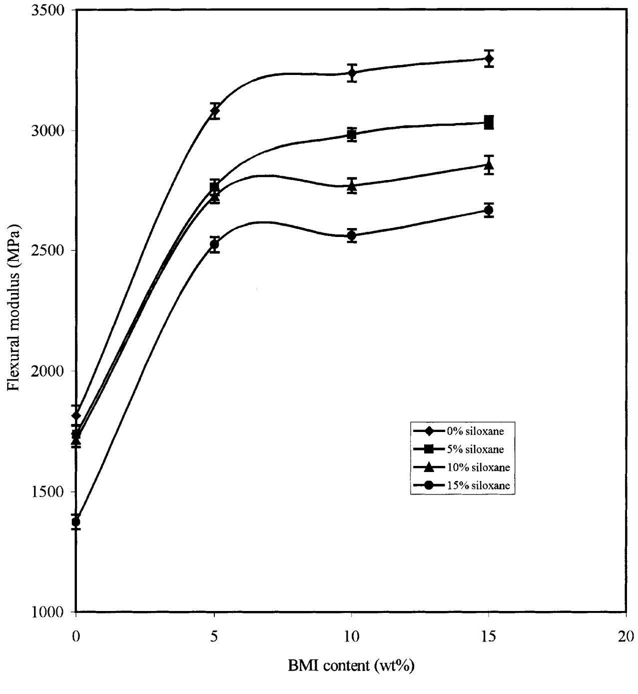


Fig. 16. Effect of BMI content on flexural modulus of epoxy and siliconized epoxy systems.

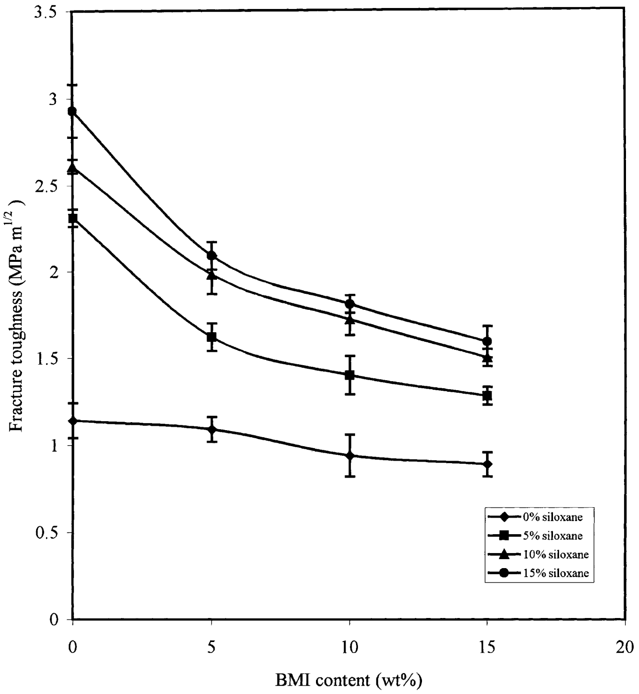


Fig. 17. Effect of BMI content on plain strain fracture toughness of epoxy and siliconized epoxy systems.

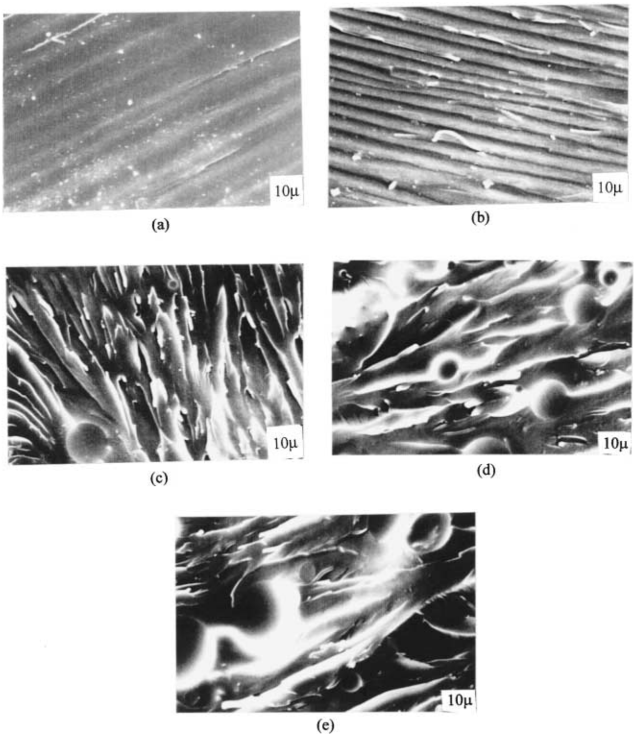


Fig. 18. SEM micrographs of (a) unmodified epoxy, (b) 10% BMI modified epoxy and (c) 5%, (d) 10%, (e) 15% BMI modified 10% siliconized epoxy systems.

reaction is predominant over Michael addition reaction. The single glass transition values obtained for the both BMI modified epoxy and BMI modified siliconized epoxy systems reveal the presence intercrosslinking network.

The stress–strain properties of epoxy and siliconized epoxy systems increase with increasing bismaleimide concentration, whereas, the plain strain fracture toughness decreases with increasing bismaleimide concentration. The morphology study revealed that BMI modified epoxy systems showed homogeneous morphology, whereas siliconized epoxy-BMI systems showed heterogeneous morphology.

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