

# Preparation and Characterization of Chain-Extended Bismaleimide Modified Polyurethane–Epoxy Matrices

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**ABSTRACT:** Intercrosslinked networks of bismaleimide (BMI) modified polyurethane–epoxy systems were prepared from chain-extended BMI and polyurethane modified epoxy and cured in the presence of 4,4'-diaminodiphenylmethane. Infrared spectral analysis was used to confirm the grafting of polyurethane onto the epoxy skeleton. The prepared matrices were characterized by mechanical, thermal, and morphological studies. The results, obtained from the mechanical and thermal studies, reveal that the incorporation of polyurethane into epoxy increases the mechanical

strength and decreases the glass-transition temperature and thermal stability. The incorporation of chain-extended BMI into polyurethane modified epoxy systems increases the thermal stability and both tensile and flexural properties, and decreases the impact strength and glass-transition temperature. Surface morphologies of polyurethane modified epoxy and chain-extended BMI modified polyurethane–epoxy systems were studied by scanning electron microscopy. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1562–1568, 2003

## INTRODUCTION

Recent research and development in polymer composites has led to materials with extremely high fracture toughness, better impact strength, good thermal stability, and improved mechanical properties and modulus-to-weight ratios. Epoxy resins are one of the most important classes of thermosetting matrices used for land, marine, and space transportation, automobile and electrical components, rehabilitation products, and pollution-control equipment. The characteristic properties of epoxy resins make them suitable for an increasing number of engineering applications, such as high strength and stiffness, good dielectric behavior, resistance to chemicals, corrosion and microbial organisms, low shrinkage during cure, and good thermal characteristics.<sup>1–7</sup>

Although epoxy composites exhibit a reasonably useful range of characteristic properties, they still need improvements in behavior, such as impact strength and thermal stability, to enable them to find a place in high performance engineering applications. A number of studies have reported on work to modify the toughness of epoxy resin by blending with different organic polymers, such as polyacrylates and functional nitrile rubbers, and also by use of modifiers and fillers.<sup>8,9</sup> Even though the modification of epoxy resin

with these polymeric materials enhances the impact behavior, they also reduce the stress–strain behavior and thermal stability and increase the moisture absorption character.

It is essential to improve the toughness and thermal stability of epoxy resin without sacrificing other mechanical properties. This can be achieved by the incorporation of flexible polymeric materials into the epoxy backbone. Among the elastomeric-toughening agents, polyurethane is considered to be one of the best elastomeric materials to improve the toughening of epoxy resin.<sup>10,11</sup> In addition, it has been reported that the introduction of bismaleimide (BMI) into epoxy resin improves the thermomechanical properties because of its superior chain rigidity, high glass-transition temperature ( $T_g$ ), excellent thermal and thermooxidative stability, and negligible tendency to absorb water.<sup>12–16</sup>

Hence in the present study, an attempt was made to synthesize chain-extended BMI and then introduce it into epoxy resin and polyurethane modified epoxy resin and to characterize thermomechanical behavior for possible use in the fabrication of advanced composites.

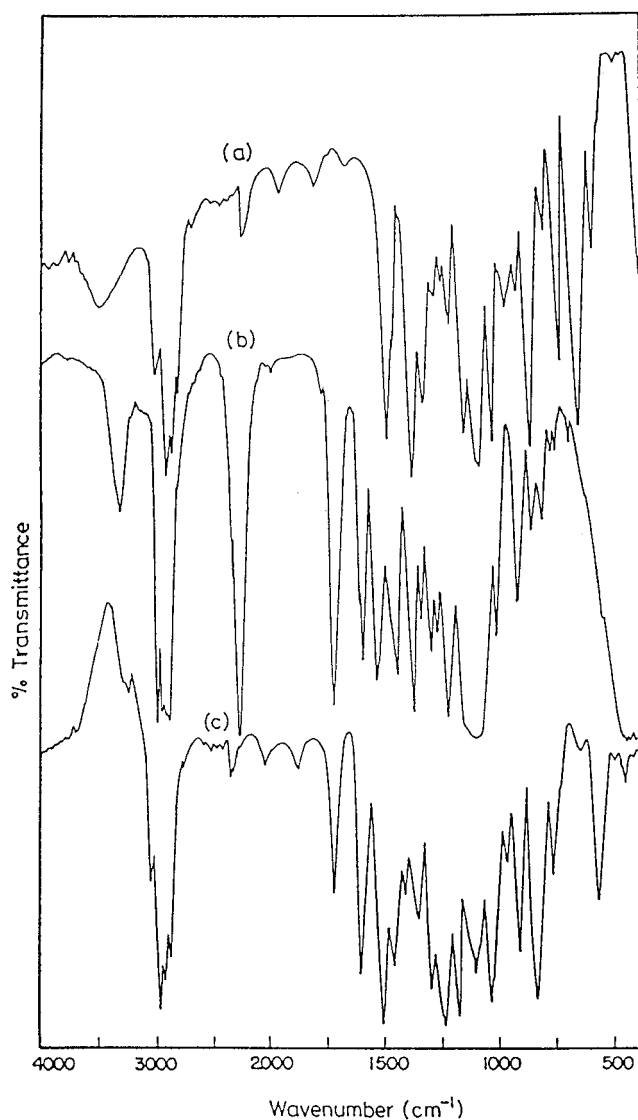
## EXPERIMENTAL

### Materials

Commercially available diglycidylether of bisphenol-A (DGEBA)–based epoxy resin LY-556 (Ciba-Geigy, Summit, NJ), having an epoxy equivalent of about 180–190, and 4,4'-diaminodiphenylmethane (Ciba-Geigy) were used as curing agents. Polyurethane prepolymer was prepared from 2,4-toluene diisocyanate

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

and polypropylene glycol (MW 1000), and dibutyltin-dilaurate (Merck, West Point, PA) was used as catalyst.

#### Preparation of polyurethane-epoxy prepolymer

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

#### Preparation of chain-extended bmis

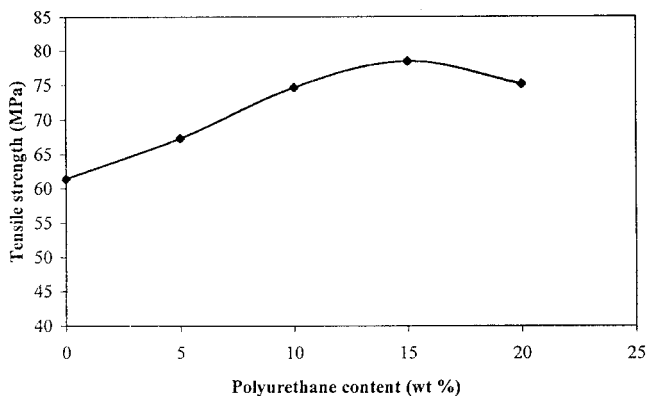
Maleimido benzoic acid chloride was prepared according to reported procedures.<sup>17</sup> Chain-extended BMI having ester linkage was prepared as follows. Maleimido benzoic acid chloride (4.7 g; 0.02 mol) was dissolved in 15 mL dimethylformamide and cooled in an ice bath. Resorcinol-A (1.1 g; 0.01 mol) was added to this cooled solution and pyridine (0.02 mol) in 5 mL dimethyl formamide was added dropwise with continuous stirring for 30 min. The mixture was filtered and poured into distilled water. The precipitate was treated with sodium bicarbonate solution and thoroughly washed with water. The filtered precipitate was dried in an oven.

#### Preparation of chain-extended bmi modified polyurethane-epoxy blend

The calculated amount of chain-extended BMI was dissolved in polyurethane-epoxy prepolymer at

**TABLE I**  
Mechanical Properties of Unmodified Epoxy, Polyurethane Modified epoxy, Bismaleimide Modified Epoxy, and Bismaleimide Modified 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	2714.7	103.7	1805.4	95.7
100/05/00	67.3	2843.2	110.4	1825.3	102.4
100/10/00	74.7	2913.5	118.5	1916.4	108.3
100/15/00	78.4	2985.3	124.9	1987.7	114.9
100/20/00	75.2	2944.4	121.7	1956.2	119.2
100/00/04	65.4	2812.3	109.7	1828.0	91.8
100/00/08	71.7	2869.1	116.5	1914.7	89.3
100/00/12	79.3	2994.5	120.4	1998.3	86.4
100/10/04	78.4	2976.9	124.2	2073.6	104.2
100/10/08	83.3	3014.2	131.5	2135.44	100.9
100/10/12	87.7	3081.5	136.1	2197.7	96.7

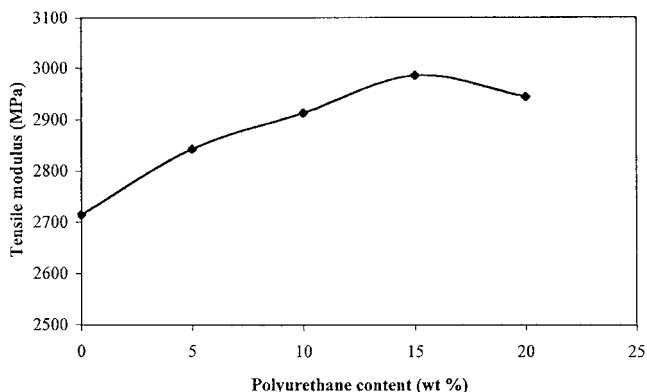


**Figure 2** Effect of polyurethane content on tensile strength of epoxy system.

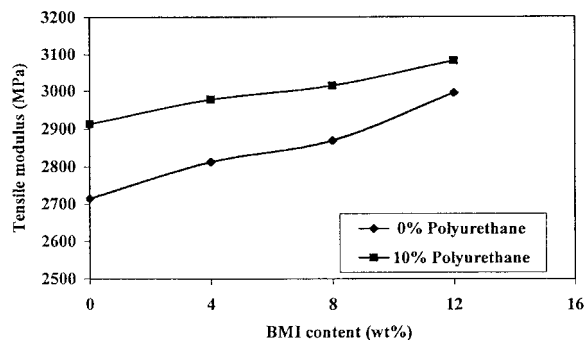
120°C with continuous stirring. After completion of dissolution, the temperature was brought down to 90°C after which a stoichiometric amount of 4,4'-diaminodiphenylmethane was added to the epoxy-polyurethane-bismaleimide prepolymer and vacuum was applied to remove the entrapped air. The product was cast in the mold and cured at 120°C for 1 h and then postcured at 180°C for 2 h.

### Test methods

Infrared spectral analyses were recorded on a Perkin-Elmer 781 infrared spectrometer (Perkin-Elmer, Palo Alto, CA). Tensile properties were studied according to ASTM D 3039 using an Instron testing machine (Model 6025 UK). Flexural properties were carried out according to ASTM D 790 and Izod impact strength was studied according to ASTM D 256. Glass-transition temperature of the matrix samples was performed in the temperature range between 50 and 300°C on a DSC 2916 (TA Instruments, New Castle, DE) at a heating rate of 10°C min<sup>-1</sup>. Surface morphology of the fractured surface of the samples was performed by use of a scanning electron microscope (Ste-



**Figure 3** Effect of polyurethane content on tensile modulus of epoxy systems.



**Figure 4** Effect of BMI content on tensile strength of epoxy and polyurethane-epoxy systems.

reoscan Model 440; Leica Imaging Systems, Cambridge, UK).

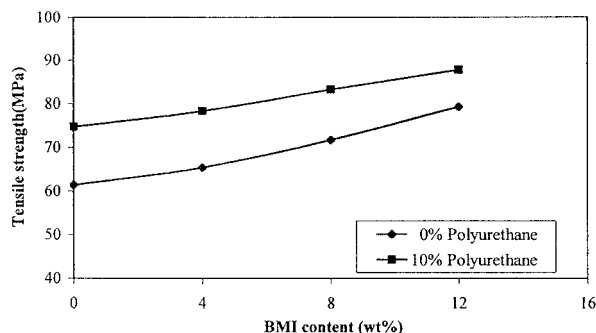
## RESULTS AND DISCUSSION

### Spectral analysis

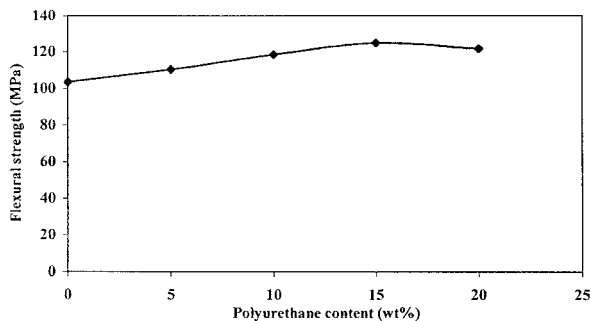
The formation of graft IPN of epoxy and polyurethane proceeded through the reaction between isocyanate groups of polyurethane prepolymer and pendant hydroxyl groups of the epoxy resin. The disappearance of IR absorption for isocyanate groups (2270 cm<sup>-1</sup>) was used to ascertain the completion of the reaction. The intensity of the IR absorption peaks observed for the isocyanate group was very high at the beginning stage of the reaction (Fig. 1). As the reaction proceeded, the intensity of the peak for isocyanate groups decreased and then disappeared after completion of the reaction. This confirms the formation of the graft IPN structure.

### Tensile properties

The values of tensile strength of polyurethane modified epoxy system are presented in Table I. The incorporation of polyurethane into the epoxy system enhanced the tensile properties up to 15 wt %, above which both the tensile and the flexural properties de-



**Figure 5** Effect of BMI content on tensile modulus of epoxy and polyurethane-epoxy systems.

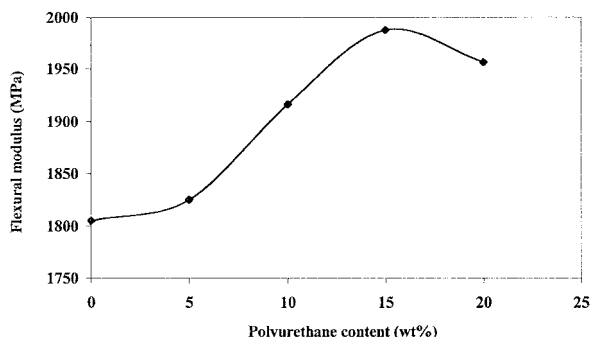


**Figure 6** Effect of polyurethane content on flexural strength of epoxy system.

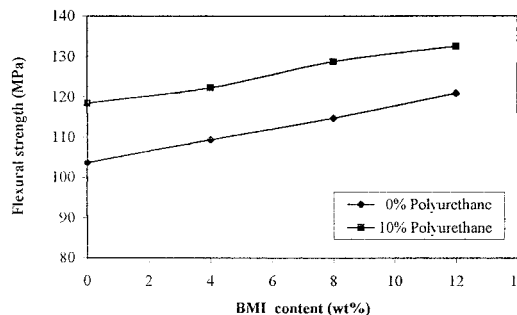
creased (Figs. 2 and 3). The improvement in tensile properties may be explained by the formation of an increased degree of the interpenetrating network between the molecular chains of epoxy and polyurethanes. Beyond 15 wt %, polyurethane incorporation decreased the tensile and flexural behavior attributed to improved flexibility and decreased crosslink density of the resulting matrix system. Incorporation of BMI into the epoxy and polyurethane (10%) modified epoxy systems increased the tensile properties according to BMI concentration (Figs. 4 and 5), probably as a result of the formation of the intercrosslinking network between BMI and the epoxy system.

**Flexural properties**

The values of flexural strength of epoxy and polyurethane modified epoxy systems are presented in Table I. The value of flexural strength of an epoxy system is increased when polyurethane is incorporated into the epoxy system (Figs. 6 and 7). For example, the flexural strength value of epoxy systems is increased by 6.7, 12.8, 16.9, and 14.8% with increasing concentration of polyurethane by 5, 10, 15, and 20% (wt %), respectively, because of the increased degree of interpenetrating network formed between the epoxy and polyurethane molecules and also the presence of equimolar quantities of isocyanate groups of the polyurethane



**Figure 7** Effect of polyurethane content on flexural modulus of epoxy systems.

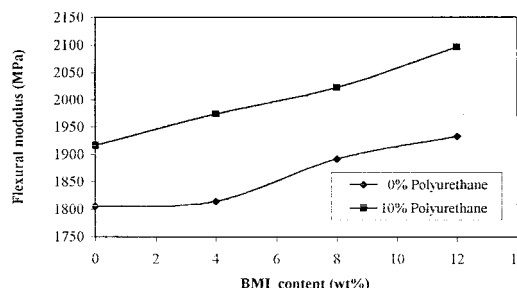


**Figure 8** Effect of BMI content on flexural strength of epoxy and epoxy-polyurethane systems.

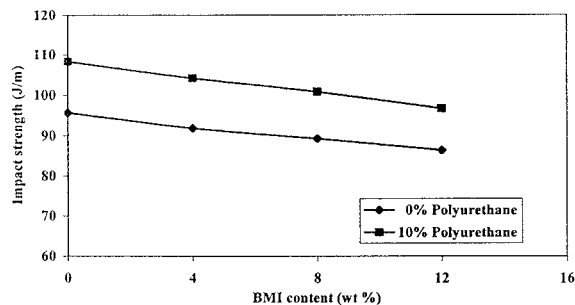
prepolymer and hydroxyl groups of epoxy resin. Similarly, incorporation of BMI into epoxy and polyurethane (10%) modified epoxy systems increased the flexural strength (Figs. 8 and 9), because of the formation of intercrosslinked network structure induced by BMI’s skeleton, and also increased the crosslink density and rigidity.

**Impact strength**

The values of impact strength of unmodified epoxy and polyurethane modified epoxy systems are presented in Table I. Incorporation of polyurethane into this epoxy system improved the impact strength compared to that of unmodified epoxy system (Fig. 10). The incorporation of 5, 10, 15, and 20% polyurethane into the epoxy system enhanced the values of impact strength by 6.5, 11.6, 16.6, and 19.7%, respectively, probably because of the long flexible and resilient nature of the polyurethane chain (Fig. 11). Incorporation of BMI into epoxy and polyurethane (10%) modified epoxy systems decreased the values of impact strength when compared to that of unmodified epoxy system. The decrease in values of impact strength is based on the concentration of BMI. The restricted chain mobility resulting from the formation of network structure and reduced free volume may be the cause of the reduced impact strength.



**Figure 9** Effect of BMI content on flexural modulus of epoxy and epoxy-polyurethane systems.

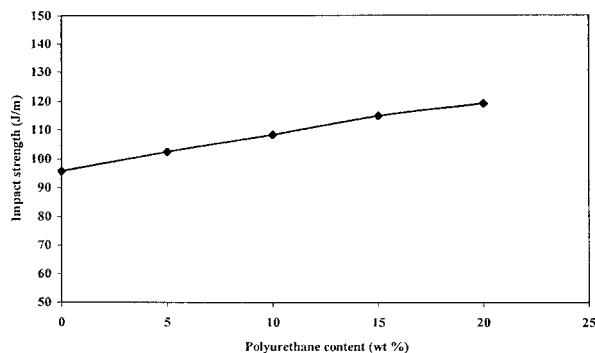


**Figure 10** Effect of BMI content on impact strength of epoxy and polyurethane-epoxy systems.

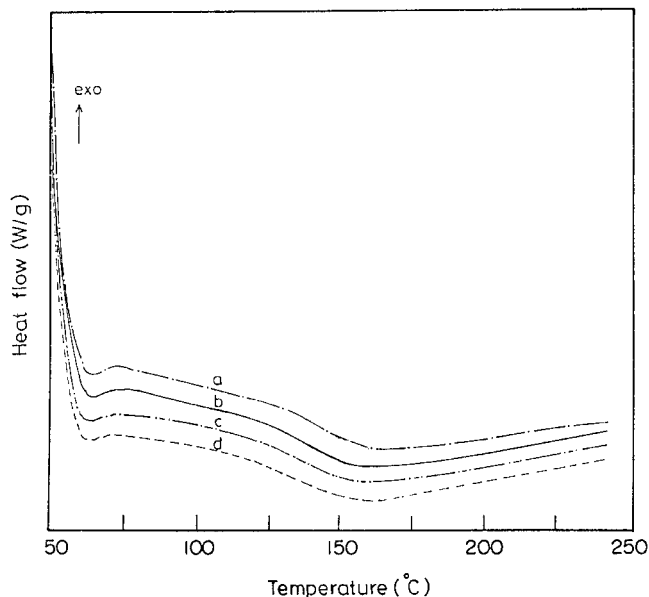
### Glass-transition temperature

The value of glass-transition temperature ( $T_g$ ) of the epoxy system is decreased when polyurethane is incorporated (Fig. 12). For example, the  $T_g$  values obtained for 5, 10, and 15% polyurethane modified epoxy systems are 146, 138, and 131°C, respectively, when compared with the  $T_g$  value of 154°C obtained for the unmodified epoxy system because of the incorporation of the polyurethane skeleton, which enhances the chain length and, in turn, reduces the crosslink density. It also plasticizes the epoxy matrix system internally, which creates more available free volume for molecular relaxation and hence lowers the value of  $T_g$ .

The BMI modified epoxy and BMI modified polyurethane-epoxy systems have  $T_g$  values that are decreased when compared to that of the unmodified epoxy system (Fig. 13). For example, the  $T_g$  values obtained for 4, 8, and 12% BMI modified epoxy systems are 151, 146, and 141°C, respectively; in the cases of BMI modified polyurethane (10%)-epoxy systems the  $T_g$  values are 142, 136, and 131°C, respectively (Fig. 14). The decrease in  $T_g$  values of BMI modified epoxy and the BMI modified polyurethane (10%)-epoxy system may be attributed to the Michael addition reaction, which is more favorable than that of homopolymerization reaction, given the higher temperature required for homopolymerization of BMI. Further, the



**Figure 11** Effect of polyurethane content on impact strength of epoxy system.

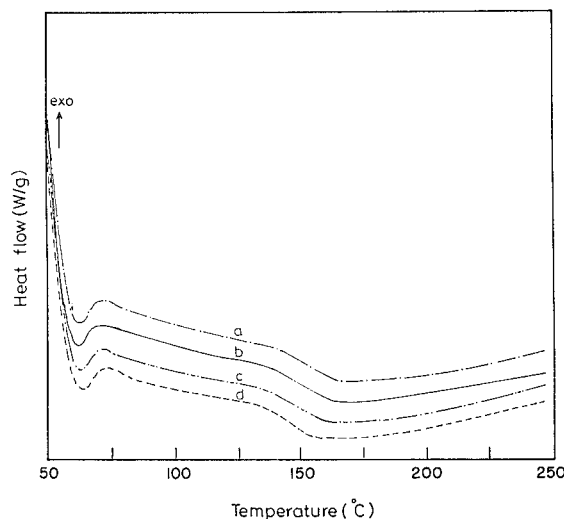


**Figure 12** DSC traces of epoxy and polyurethane modified epoxy systems. (a) Unmodified epoxy; polyurethane modified epoxy systems: (b) 5%; (c) 10%; (d) 15%.

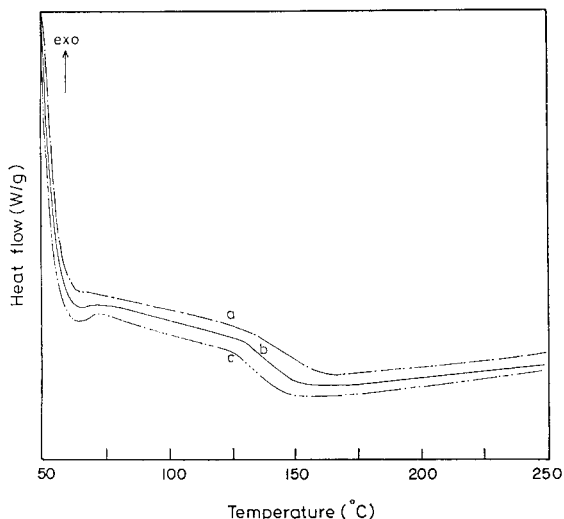
presence of the high electron withdrawing nature of ester groups present in chain-extended BMI enhanced the cure temperature and reduced the cure rate.

### Thermogravimetric analysis

Incorporation of polyurethane into the unmodified epoxy resin decreased the thermal stability and degradation temperature because of the presence of thermally weak urethane linkages in the epoxy backbone (Fig. 15). Bismaleimide modified epoxy and BMI modified polyurethane-epoxy systems improve the ther-



**Figure 13** DSC traces of BMI modified epoxy systems. (a) Unmodified epoxy; BMI modified epoxy systems: (b) 4%; (c) 8%; (d) 12%.

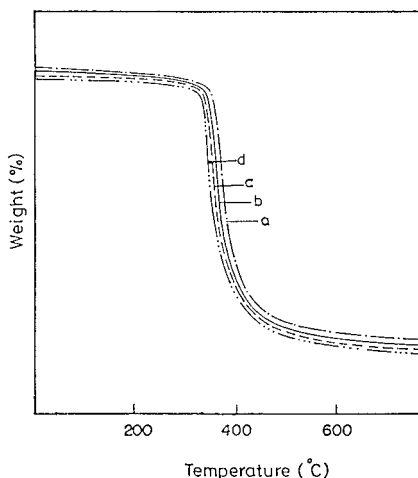


**Figure 14** DSC traces of BMI modified polyurethane-epoxy systems: (a) 4%, (b) 8%; and (c) 12% BMI modified polyurethane (10%)-epoxy systems.

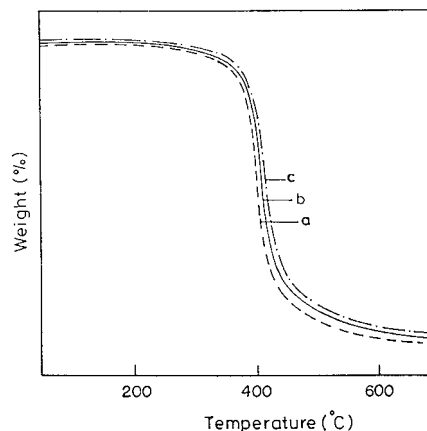
mal stability and degradation temperature according to the concentration (Figs. 16 and 17), probably because of the presence of the rigid phenyl group with the heterocyclic ring structure of BMI.

**Microscopy results**

The surface morphology of the unmodified epoxy system was characterized by scanning electron microscopy and showed a smooth, glassy surface and homogeneous microstructure, whereas the fractured surface of the polyurethane modified epoxy system exhibited heterogeneous morphology (Fig. 18). The micrographs of fractured surfaces of BMI modified epoxy systems showed close similarity to that obtained for the unmodified epoxy system. These results showed that



**Figure 15** TGA curves of polyurethane modified epoxy system. (a) Unmodified epoxy; polyurethane modified epoxy systems: (b) 5%; (c) 10%; (d) 15%.

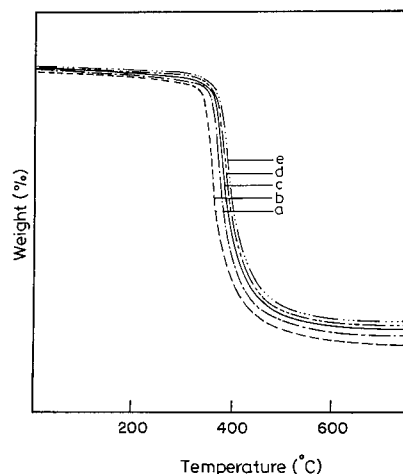


**Figure 16** TGA curves of BMI modified epoxy system: (a) 4%, (b) 8%; and (c) 12% BMI modified epoxy systems.

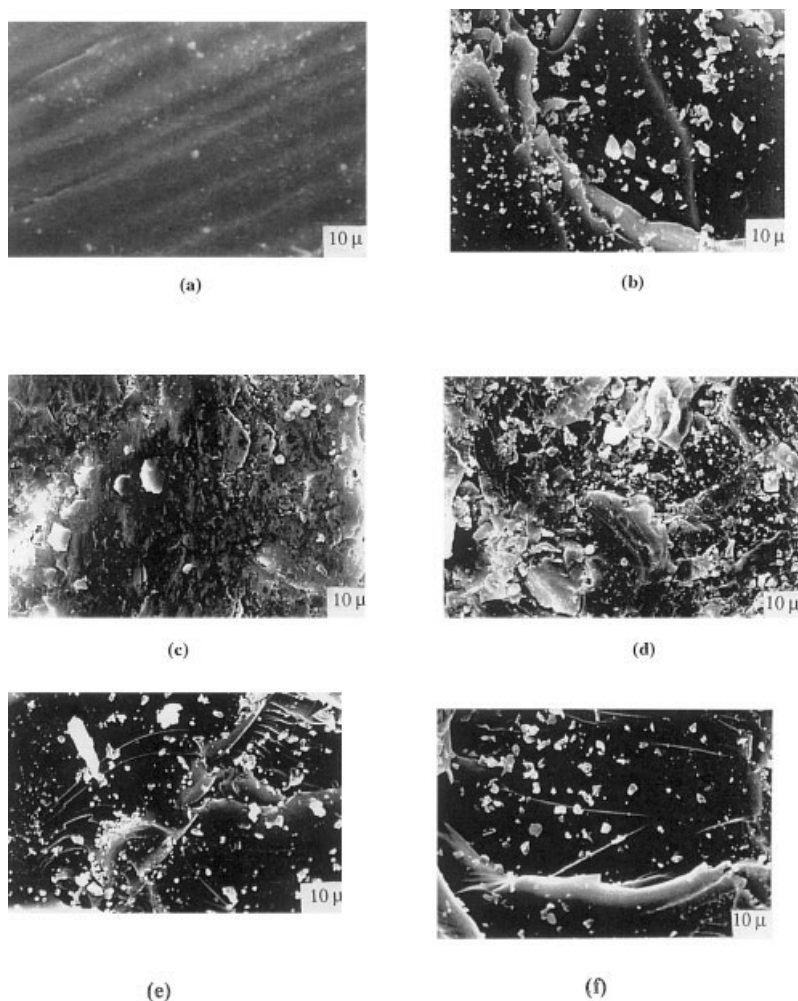
there are no separate phase domains in the BMI modified epoxy systems and confirmed the formation of a homogeneous intercrosslinked network structure. The fractured surfaces of the BMI modified polyurethane-epoxy systems showed heterogeneous morphology.

**CONCLUSIONS**

From the data it is concluded that significant improvements in toughness and stress-strain properties of the epoxy matrix were made by forming an intercrosslinking network with polyurethane. Further, it was noticed that the incorporation of polyurethane into the epoxy matrix lowered both thermal stability and glass-transition temperature. The incorporation of BMI into polyurethane-toughened epoxy increased the stress-strain properties and thermal stability and decreased the glass-transition temperature and impact strength. The SEM micrographs of fractured surfaces



**Figure 17** TGA curves of BMI modified polyurethane (10%)-epoxy systems: (a) unmodified epoxy; (b) polyurethane (10%) modified epoxy; (c) 4% BMI; (d) 8% BMI; (e) 12% BMI modified polyurethane (10%)-epoxy systems.



**Figure 18** SEM micrographs of (a) unmodified epoxy, (b) 5% (c) 10% and (d) 15% polyurethane modified epoxy, (e) BMI (8%) modified epoxy and (f) BMI (8%) modified polyurethane (10%)—epoxy systems.

of unmodified epoxy and BMI modified epoxy systems showed a smooth, glassy surface and homogeneous microstructure, whereas the fractured surfaces of polyurethane modified epoxy and chain-extended BMI modified polyurethane–epoxy systems exhibited heterogeneous morphology.

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