

Preparation and Characterization of Bismaleimide-Modified Bisphenol Dicyanate Epoxy Matrices

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ABSTRACT: An intercrosslinked network of epoxy matrix systems modified by cyanate ester (CE) and bismaleimide (BMI) was developed. Epoxy systems modified with 4%, 8%, and 12% (by weight) cyanate ester were made by using epoxy resin and cyanate ester, with diaminodiphenylmethane as the curing agent. The reaction between the cyanate ester and the epoxy resin during the cure process of cyanate ester-modified epoxy systems was studied using Fourier transform infrared spectroscopy. The cyanate ester-toughened epoxy systems were further modified with 4%, 8%, and 12% (by weight) bismaleimide (*N,N'*-bismaleimido-4,4'-diphenylmethane). BMI-CE-Epoxy matrices were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis, and heat deflection temperature analysis. The matrices, in the form of castings, were characterized for their mechanical properties such as tensile strength, flexural strength, and unnotched Izod impact test as per ASTM methods. Mechanical studies indicated that the

introduction of cyanate ester into epoxy resin improved the toughness and flexural strength, with a reduction in tensile strength and glass-transition temperature, whereas the incorporation of bismaleimide into epoxy resin influenced the mechanical and thermal properties according to its percentage content. However, the introduction of both cyanate ester and bismaleimide influenced the mechanical properties according to their percentage content. DSC thermograms of cyanate ester-modified epoxy and BMI-modified epoxy showed unimodal reaction exotherms. The thermal degradation temperature and heat distortion temperature of the cured BMI-modified epoxy and CE-epoxy systems increased with increasing bismaleimide content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1596–1603, 2003

Key words: epoxy resin; cyanate ester; mechanical properties; glass-transition temperature; toughening; thermoset resin

INTRODUCTION

As a result of its light weight, high strength, extreme durability, stability under UV exposure, and chemical resistance, FRP (fiber-reinforced plastics) has become established as a material of major importance in an ever-increasing number of applications. FRP can be molded into an infinite number of forms and surface finishes and is capable of meeting stringent design standards while at the same time providing major cost benefits. Epoxy resins are used in the aerospace, automobile, land and marine transportation, chemical process, and electrical and electronic industries because of their light weight and good mechanical properties and excellent processability.^{1–2} However, the use of thermosetting materials is often limited by their toughness, which affects the impact property, lifetime, and durability of the components. Rubber toughening of epoxy, predominantly using amine terminated butadiene acrylonitrile rubber (ATBN) and carboxyl terminated butadiene acrylonitrile rubber (CTBN)

elastomers, increased fracture toughness. However, the improvement in these modified materials has invariably been accompanied by a significant drop in the modulus and glass-transition temperature.^{3–5} An interpenetrating network (IPN) structure having a different polymer skeleton can be considered as an attractive method because, unlike with polymer blends, an IPN mechanism provides matrix materials with a single glass-transition temperature (T_g). Interpenetrating polymer networks of thermoset–thermoset blends have been extensively studied because of their enhanced mechanical properties.^{6–10}

Improving thermal properties and elastic moduli of epoxy resins by modification with a coreactive component, cyanate esters, have been investigated recently.^{11–12} Cyanate esters have attractive physical, dielectric, thermal, and mechanical characteristics, low water absorption, excellent heat resistance, and low volume shrinkage, making them the material of choice in high-performance applications,^{13–14} including in the manufacture of spacecraft structures, automotive structures, insulation for fusion magnets, communications satellites, engine pistons, and high-performance coatings. Improvement in the thermomechanical properties was observed after the introduction of bismaleimide into epoxy resin,^{15–19} siliconized epoxy,²⁰ and unsaturated polyester-modified epoxy resin.²¹

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Bismaleimides have high crosslinking ability, high glass-transition temperature, high thermal stability, high char yield, excellent fire resistance, and superior specific strength and specific modulus, and they absorb little water. Hence, in the present investigation an attempt was made to improve both the toughness and thermal behavior of epoxy resin using bisphenol dicyanate and bismaleimide.

EXPERIMENTAL

Materials

A commercially available epoxy resin, diglycidyl ether of bisphenol A (DGEBA), GY 250, with an epoxy equivalent of about 180–190, and diaminodiphenylmethane was obtained from Ciba-Geigy, Ltd., Mumbai, India. Cyanogen bromide, cyclohexanone, and *o*-cresol (SRL, Mumbai, India) were used as received.

The cyanate ester was synthesized from cyanogen bromide and bisphenol A using a triethylamine catalyst according to the reported procedure.²² The product was recrystallized from methanol:water (1:1).

Yield 65%, mp 75°C. IR (KBr): ν (cm⁻¹) 2336, 2210 (OCN vibration); 2967, 1701, 1611, 1381. ¹H-NMR: δ = 1.63 (s, 6H), 6.69 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H). ¹³C-NMR (d₆-CDCl₃): δ = 154 (OCN), 141.5, 127.4, 120.0, 114.6 (C aromatic); 41.6, 31.0 (C aliphatic).

Bismaleimide was prepared according to the reported procedure.²³ The product was recrystallized from acetone–toluene.

Yield 81%, mp 158°C. IR (KBr): ν (cm⁻¹) 3097 (=C–H); 3467, 1700 (C=O); 1385, 1148 (C–N–C). ¹H-NMR (d₆-DMSO): 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, CH₂). ¹³C-NMR (d₆-DMSO): δ = 126.8, 129.1, 129.5, 134.6, 140.6, 169.9.

The chemical structures of the materials used are presented in Figure 1.

Preparation of cyanate ester–epoxy blends

A fixed amount of epoxy resin, varying amounts of cyanate ester, and stoichiometric amounts of diaminodiphenylmethane (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 and poured into a preheated mold and kept at 140°C for 3 h and postcured at 200°C for 2 h.

Preparation of cyanate ester–epoxy–bismaleimide blends

N,N'-bismaleimido-4,4'-diphenylmethane (4 g) was dissolved in a 100:4 mix of epoxy resin and cyanate ester at 120°C under vigorous stirring. After complete dissolution of bismaleimide, 27 g of 4,4'-diaminodi-

phenylmethane was added. The product was subjected to a vacuum to remove trapped air and then cast and cured at 140°C for 3 h. The castings were then postcured at 200°C for 2 h and finally removed from the mold and characterized.

Test methods

Tensile and flexural properties

The tensile properties were determined using dog-bone-shaped specimens according to ASTM Standard D 3039 using a universal testing machine (Model 6025; Instron, UK) at a crosshead speed of 2 mm/min. Flexural strength was measured as per ASTM Standard D 790.

Unnotched Izod impact test

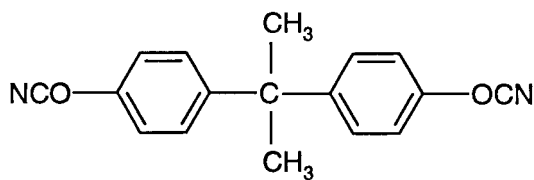
The unnotched Izod impact strength of each sample was tested as per ASTM Standard D 256-88. All samples were tested unnotched so that they would be more sensitive to the transition between ductility and brittleness. Specimens 3.2 mm thick, 10 mm in cross-section, and 64 mm long, were clamped in the base of the pendulum testing machine so that they cantilevered upward. The pendulum was released, and the force consumed in breaking the sample was calculated from the height the pendulum reached on the follow-through.

Thermal studies

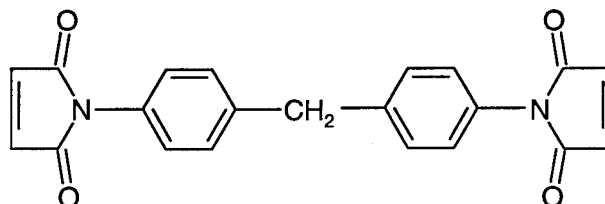
The glass-transition temperatures of the samples were determined using a DSC Netzsch (TA Instruments, USA) in a temperature range between 50°C and 250°C at a heating rate of 10°C/min in a nitrogen atmosphere whose flow rate was 1 mL/min. Differential scanning calorimetry (DSC) analysis was carried out in a closed aluminum pan. Thermogravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA instruments USA) at a heating rate of 10°C/min in a nitrogen atmosphere.

Heat deflection temperature analysis

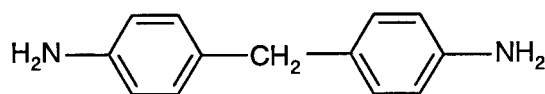
The heat deflection temperature of the samples was tested as per ASTM Standard D 648-72. The heat deflection temperature measures the temperature at which deformation occurs when composite specimens 127 mm long, 3 mm wide, and 13 mm thick are placed in an oil bath under a load of 1.82 MPa with the temperature increasing at a rate of 2°C/min. The temperature at which a specimen deflected by 0.25 mm was noted. Deflection was monitored using a linear variable displacement transducer.



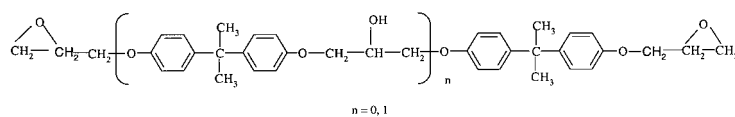
Bisphenol-A dicyanate



N,N'-bismaleimido-4,4'-diphenyl methane



Diaminodiphenylmethane



Diglycidyl ether of bisphenol A (DGEBA)

Figure 1 Chemical structure of materials.

Water absorption

The water absorption property of the samples was tested as per ASTM Standard D 570. The cured specimens, which were 60 mm in length and width and 3 mm thick, were immersed in distilled water for 24 h. Specimens were drawn, and the surface water was removed using a tissue paper and weighed to an accuracy of 0.001 g.

RESULTS AND DISCUSSION

FTIR spectral analysis

The reaction between epoxy and cyanate during the cure process of cyanate ester-modified epoxy systems was confirmed by Fourier transform infrared (FTIR)

spectroscopy. The proposed reaction consisted of several steps, shown in Figure 2. As reported by several authors,^{24–30} the cyclotrimerization of cyanate groups, followed by the reaction with epoxy groups, resulted in the formation of several intermediates including isocyanurate, oxazoline, and oxazolidinone.

The appearance of new absorption bands at 1750 cm^{-1} [Fig. 3(b)], because of the formation of oxazolidinone, and other absorptions at 1650, 1690, and 1750 cm^{-1} , were a result of the formation of the products oxazoline, isocyanurate, and cyanurate, respectively.^{26–27} Further, it was also evidenced that the reaction of epoxy and isocyanurate caused a considerable decrease in the intensity of the epoxy band at 914 cm^{-1} .

FTIR spectra of DDM-cured cyanate ester (CE)-epoxy [Fig. 3(c)] system show the absorption at 1750 and

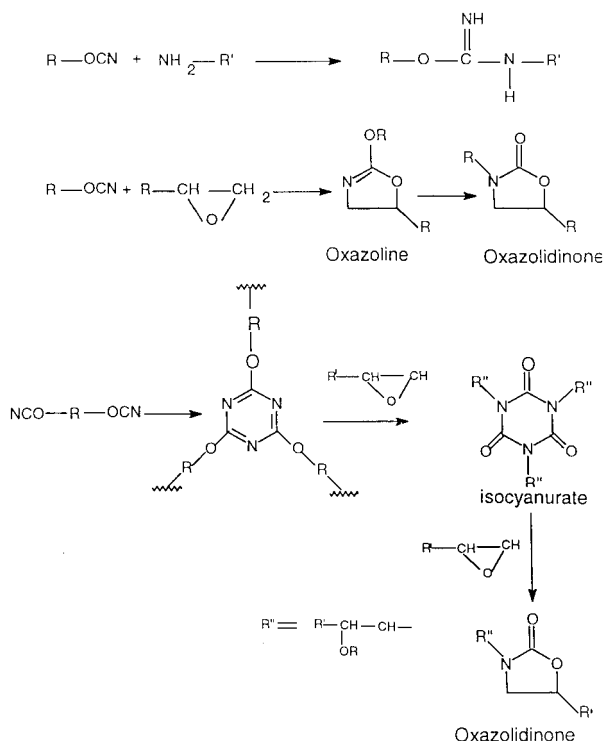


Figure 2 Reactions involved during curing process of cyanate ester-modified epoxy systems.

1690 cm^{-1} , confirming the formation of oxazolidinone and isocyanurate,^{28–30} which was absent in the DDM-cured epoxy matrix [Fig. 3(d)]. There was no absorption for triazine vibration at 1565 cm^{-1} , further confirming the conversion of cyanurate into oxazolidinone and isocyanurate by the reaction with epoxy.

Mechanical properties

The observed values for tensile properties of the epoxy system and the epoxy system modified with CE and bismaleimide (BMI) are presented in Figure 4. The introduction of 4%, 8%, and 12% (by weight) of CE into epoxy resin decreased tensile strength by 1.7%, 4.5%, and 7.5%, respectively, when compared with the unmodified epoxy system. This may be explained by the formation of oxazolidinone from the reaction between epoxy and isocyanurate. The oxazolidinone-rich composition exhibited a more thermoplastic character and reduced the tensile strength. The incorporation of 4%, 8%, and 12% (by weight) BMI into the epoxy resin increased tensile strength by 7.2%, 15.0%, and 36.8%, respectively. This may be explained by the incorporation of bismaleimide increasing the crosslink density and the effective compatibility between the epoxy and bismaleimide networks. The introduction of both cyanate esters and bismaleimides into epoxy resin altered the tensile strength according to their percentage content. The tensile strength of cyanate

ester-epoxy systems increased with increasing bismaleimide content. The tensile modulus values obtained for the unmodified epoxy and epoxy modified with CE and BMI showed a trend similar to that observed for tensile strength.

The flexural behavior of unmodified epoxy and epoxy modified with cyanate ester and bismaleimide is presented in Figure 5. Introduction of 4%, 8%, and 12% cyanate ester into the epoxy resin increased the flexural strength by 5.7%, 12.9%, and 19.5%, respectively, above that of the unmodified epoxy system. This may be attributed to the formation of a network structure between cyanate ester and the epoxy matrix. The formation of aliphatic oxazolidinone conferred a more thermoplastic character that imparted resistance to bending stress and improved toughness. An enhancement in flexural strength from the incorporation of bismaleimide according to its percentage concentra-

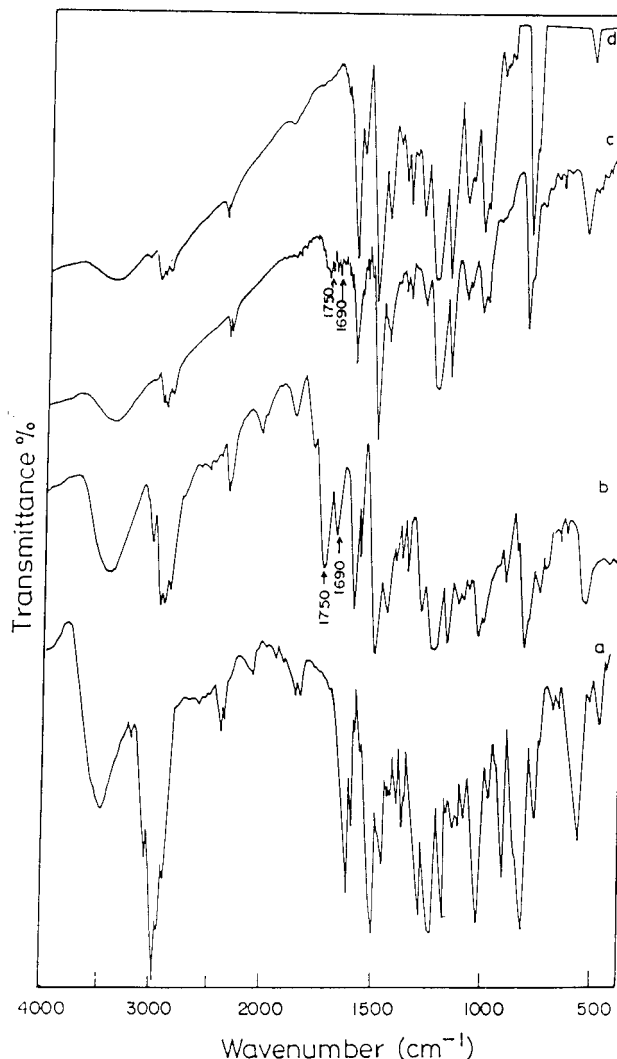


Figure 3 FTIR spectra of (a) uncured unmodified epoxy, (b) epoxy-CE (100:20) taken after heating at 140°C for 3 h, (c) epoxy-CE (100:20) cured with DDM at 140°C for 3 h and postcured at 200°C , and (d) DDM-cured epoxy system.

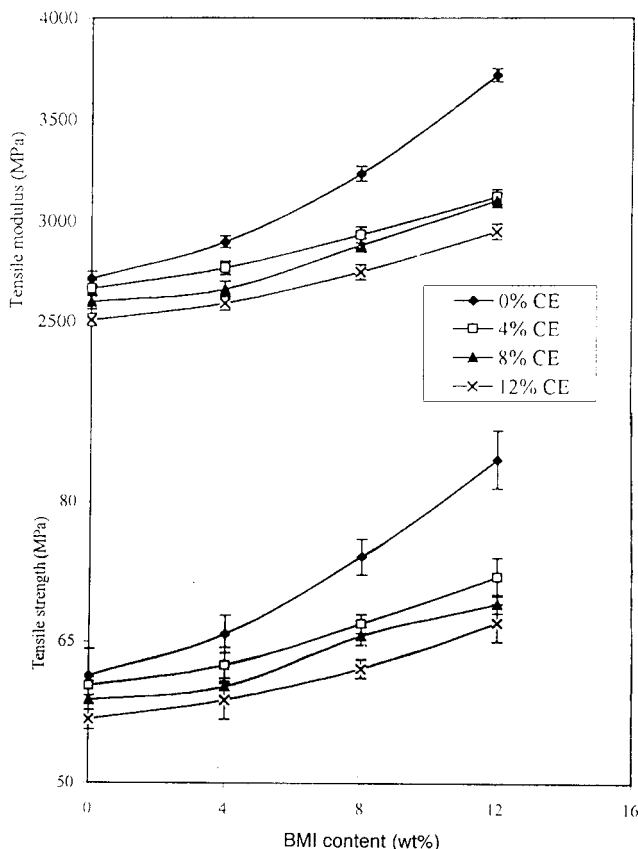


Figure 4 Effect of bismaleimide content on tensile properties of epoxy and cyanate ester-modified epoxy systems.

tion was observed for tensile strength. The increase in flexural strength was influenced by the homopolymerization of bismaleimide.

Cyanate ester incorporation into epoxy resin, which improved the toughness according to the percentage content of cyanate ester, was a result of the reduced crosslink density and a high percentage of flexible ether linkages in the network. The impact behavior of the unmodified epoxy and cyanate ester-modified epoxy systems was lowered when bismaleimide was incorporated (Fig. 6). The reduction in untouched Izod impact strength may be explained by the increased crosslink density and rigidity imparted by bismaleimide.

Thermal properties

DSC thermograms of epoxy resin with 4%, 8%, and 12% of cyanate ester are presented in Figure 7. It can be observed from Figure 7 that the cyanate ester-modified epoxy systems showed a unimodal reaction exotherm because of the presence of lower concentrations of cyanate ester. The peak maximum temperatures obtained for 4%, 8%, and 12% of CE-incorporated systems were 160°C, 151°C, and 148°C, respectively. The decrease in peak maximum temperature

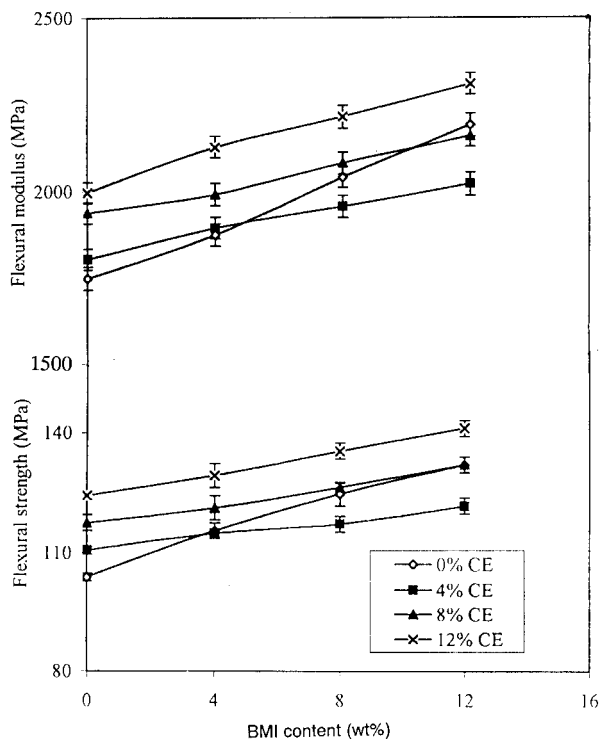


Figure 5 Effect of bismaleimide content on flexural properties of epoxy and cyanate ester-modified epoxy systems.

with increasing CE concentration confirmed that the reaction between epoxy and cyanate, which accelerated the reaction rate, also reduced the curing temperature. The large exothermic peak obtained for the CE-epoxy systems resulted from the following reactions: (1) polycyclotrimerization of cyanate monomers, (2) reaction of cyanate with amine, (3) reaction of cyanate with epoxide, and (4) reaction of epoxy with cyanurate.

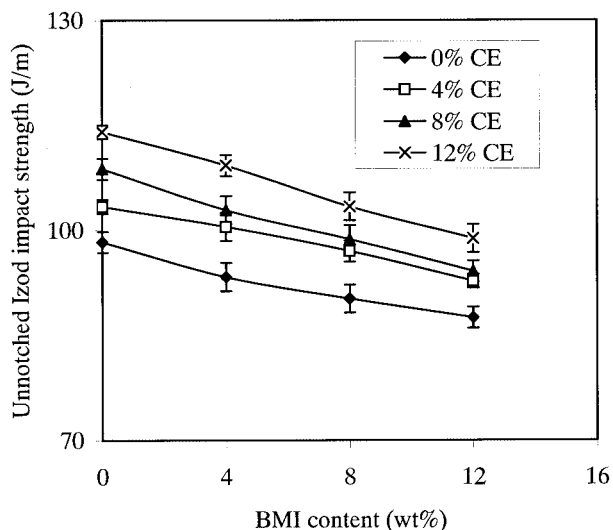


Figure 6 Effect of bismaleimide content on impact strength of epoxy and cyanate ester-modified epoxy systems.

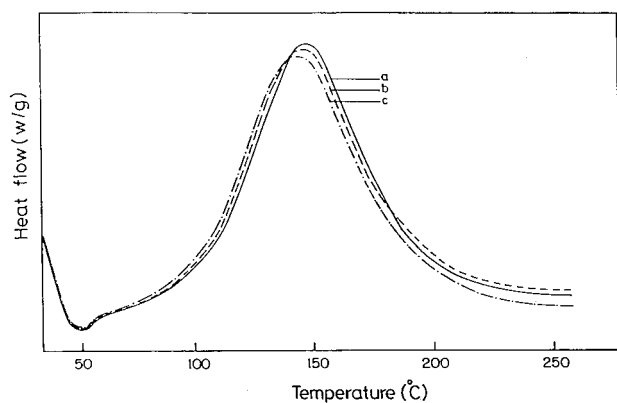


Figure 7 DSC thermograms of cyanate ester-modified epoxy systems during cure: (a) 4% CE, (b) 8% CE, and (c) 12% CE.

It was observed, as shown in Figure 8, that all the bismaleimide-modified epoxy systems showed a uni-model reaction exotherm because of the presence of a lower concentration of bismaleimides. For all the bismaleimide-incorporated systems, the reaction commenced at 120°C. The peak maximum temperatures for 4%, 8%, and 12% of BMI-incorporated systems were 168°C, 171°C, and 174°C, respectively (Fig. 8). The large exothermic peak obtained for the bismaleimide-incorporated systems resulted from the following reactions: (1) oxirane ring opening reaction with active amine hydrogen of DDM, (2) autocatalytic reaction of oxirane ring with pendent hydroxyl groups of epoxy resin and hydroxyl groups formed during the reaction, (3) addition reaction of —NH_2 groups of DDM with double bonds of bismaleimides (Michael addition), and (4) bismaleimide homopolymerization reaction. The slight increase in peak maximum temperature with increasing bismaleimide concentration

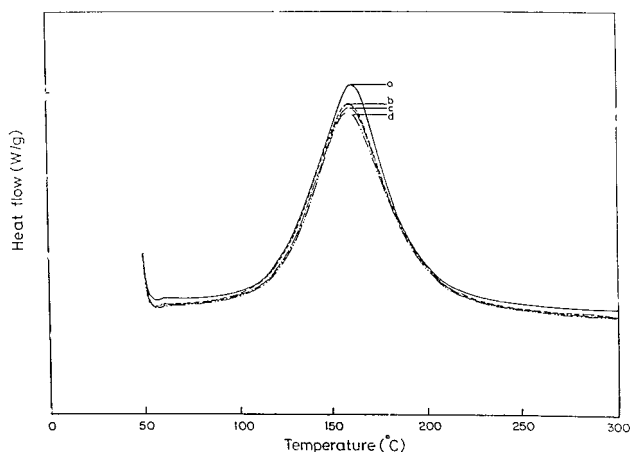


Figure 8 DSC thermograms of bismaleimide modified epoxy systems during cure: (a) unmodified epoxy, (b) 4% BMI, (c) 8% BMI, and (d) 12% BMI.

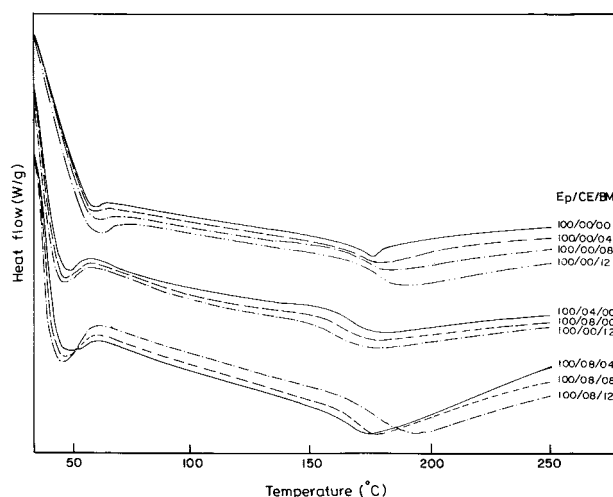


Figure 9 DSC traces of BMI-CE-epoxy matrix epoxy systems.

confirmed the occurrence of the homopolymerization reaction.

The incorporation of cyanate ester into epoxy resin had a significant impact on the glass-transition temperature (T_g), which decreased with an increase in the concentration of cyanate ester (Fig. 9). For example, the T_g values for 4%, 8%, and 12% of CE-modified systems were 162°C, 159°C, and 155°C, respectively. This may be a result of the formation of oxazolidinone, which decreases the glass-transition temperature because of its aliphatic nature, and its formation decreased the effective crosslink density. The increase in T_g values of bismaleimide-modified epoxy and bismaleimide-modified cyanate ester-epoxy systems was a result of the homopolymerization of bismaleimides rather than the Michael addition reaction,³¹ as the latter decreased the crosslink density because of the chain extension.

The incorporation of cyanate ester into epoxy resin improved the thermal stability and enhanced the degradation temperature according to its percentage concentration (Fig. 10). The formation of thermally stable isocyanurate and oxazolidinone, formed by the cyclotrimerization of cyanate esters and the subsequent reaction with epoxide, led to a delay in degradation. This is in accord with the results obtained by Kim.¹¹ The thermal degradation temperature of the bismaleimide-modified epoxy systems was increased with an increasing bismaleimide concentration (Fig. 11). A similar trend was observed for bismaleimide- and cyanate ester-modified epoxy systems; however, the thermal stability of these systems was slightly higher than that of bismaleimide-modified epoxy systems.

Analysis of the heat distortion temperature was done to determine the thermomechanical behavior of the matrix systems. Heat deflection temperature (HDT) values for epoxy, cyanate ester-modified ep-

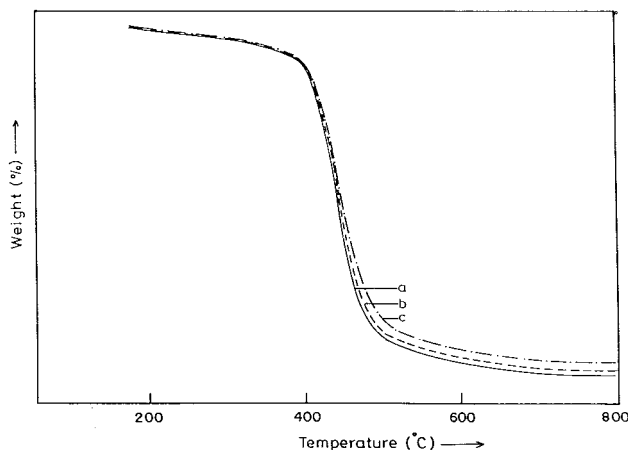


Figure 10 TGA curves of cyanate ester-modified epoxy systems: (a) 4% CE, (b) 8% CE and (c) 12% CE.

oxy, bismaleimide-modified epoxy, and cyanate ester-epoxy systems are presented in Table I. HDT values decreased with increasing CE concentration. This may be explained by the formation of oxazolidinone, which in turn reduced crosslink density. With the incorporation of bismaleimide into epoxy and cyanate ester-modified epoxy systems, the values of HDT increased with increasing BMI concentration. The enhanced HDT of bismaleimide-modified systems was a result of the high crosslink density and rigidity imparted by heterocyclic bismaleimides.

Water absorption behavior

The incorporation of cyanate ester into the epoxy system decreased water absorption with increasing CE concentration. The decrease in the percentage of water uptake for the cyanate ester-incorporated system resulted from the inherent hydrophobic nature of cy-

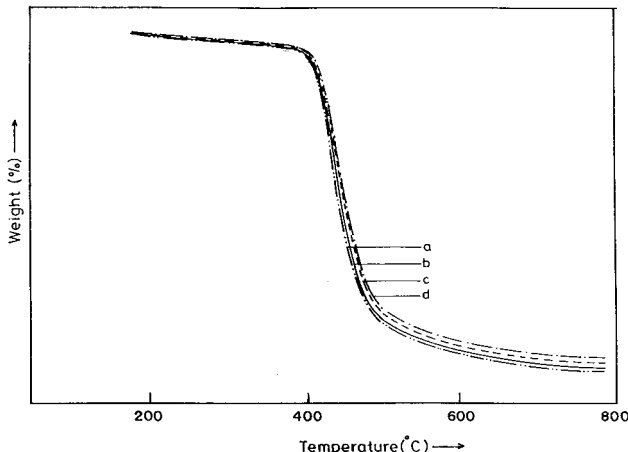


Figure 11 TGA curves of bismaleimide modified epoxy systems: (a) unmodified epoxy, (b) 4% BMI, (c) 8% BMI, and (d) 12% BMI.

TABLE I
Heat Deflection Temperature and Water Absorption properties of BMI-CE-Epoxy Matrices

Epoxy:CE: BMI composition	Water absorption (%)	Heat deflection temperature (°C)
100:00:00	0.1201	153
100:04:00	0.1152	150
100:08:00	0.1105	148
100:12:00	0.1032	143
100:04:04	0.1045	153
100:04:08	0.0965	155
100:04:12	0.0835	158
100:08:04	0.0711	150
100:08:08	0.0646	152
100:08:12	0.0566	154
100:12:04	0.0895	151
100:12:08	0.0712	153
100:12:12	0.0623	155
100:00:04	0.0816	154
100:00:08	0.0786	156
100:00:12	0.0697	159

anate ester networks. All BMI-modified systems showed good resistance to moisture absorption because of the rigid aromatic hydrophobic structure. Moisture resistance increased with increasing BMI content (Table I), and it was observed that BMI incorporation played an important role in improving resistance to moisture absorption of the epoxy matrix systems.

CONCLUSIONS

Cyanate ester-modified epoxy, BMI-modified epoxy, and BMI-modified CE-epoxy intercrosslinked networks having varied concentrations of BMI and CE were developed. Thermal properties, such as glass-transition temperature, heat distortion temperature, and thermal stability, of BMI-modified epoxy and CE-epoxy systems were compared with those of unmodified epoxy systems, showing an increasing trend with bismaleimide concentration. The reduction in the T_g values of CE-modified epoxy confirmed the reaction between epoxy and cyanate ester, which reduced the effective crosslink density by the formation of oxazolidinone and isocyanurate, which was further evidenced by dynamic mechanical analysis. The mechanical studies revealed that the incorporation of cyanate ester into epoxy improved the flexural and impact strength with a marginal reduction in tensile strength, whereas the incorporation of bismaleimide increased the stress-strain properties according to its percentage content, with a reduction in impact strength. It was observed that moisture resistance increased with increasing cyanate ester and BMI content. BMI incorporation played an important role in reducing moisture absorption of this epoxy resin.

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