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Thermal and Morphological Properties of Bisphenol Dicyanate–Epoxy–Bismaleimide Intercrosslinked Matrix Materials

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ABSTRACT

Intercrosslinked network of cyanate ester–bismaleimide modified epoxy matrix systems was developed. Epoxy systems modified with 4%, 8%, and 12% (by wt.) of cyanate ester were made by using epoxy resin and cyanate ester with diaminodiphenylmethane as curing agent. The reaction between cyanate ester and epoxy resin during the cure process of cyanate ester modified epoxy systems was studied using FTIR. The cyanate ester toughened epoxy systems were further modified with 4%, 8%, and 12% (by wt.) of bismaleimide (*N*,*N*′-bismaleimido-4,4′-diphenylmethane). BMI–CE–epoxy matrices were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and heat deflection temperature (HDT) analysis. The studies indicate that the thermal stability and resistant to water absorption behavior of epoxy resin has been enhanced by the introduction of cyanate ester. However, glass transition temperature and heat deflection temperature are found to decrease with increasing cyanate ester concentration, whereas, the incorporation of bismaleimide into epoxy resin enhanced the thermal properties according to its percentage content. However, the introduction of both cyanate ester and bismaleimide influences the thermal properties according to their percentage content. Differential scanning calorimetry thermogram of cyanate ester modified epoxy and BMI modified epoxy during cure show an unimodel reaction exotherms. The fractured surface of cyanate ester modified epoxy systems reveals the presence of homogeneous morphology, and a smooth fractured surface is observed with increasing bismaleimide content.

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Key Words: Epoxy resin; Cyanate ester; Matrix materials; Glass transition temperature; Thermal stability; Morphology.

INTRODUCTION

Epoxy based materials play a vital role in aerospace, automobile, land and marine transportation, chemical process industries, electrical and electronic industries due to its lightweight, high strength, extreme durability, stability under UV exposure, and chemical resistance. Moreover, many properties of epoxy resins can be easily improved or altered by preparing blends and composites.[1–4] As a result, FRP (fiber reinforced plastics) based on epoxy matrix has become established as a material of major importance in an ever-increasing number of applications. However, the use of epoxy resin as thermosetting matrix is often limited by their toughness properties, which affect the impact property, lifetime, and durability of the components. In order to improve its working performance further, to use in advanced engineering applications, chemical modification of epoxy resin is essential, mainly to improve impact and thermal resistance. Flexible polymeric materials such as amine-terminated acrylonitrile-butadiene (ATBN), carboxyl-terminated acrylonitrile-butadiene (CTBN), hydroxyl-terminated acrylonitrile-butadiene (HTBN), nitrile rubber, and polyacrylates, have mostly been used as impact modifiers for epoxy resins.[5–7] The resulting products have good impact behavior but inferior strength properties and are unsuitable for high performance engineering applications. The interpenetrating network structure having different polymer skeleton can be considered as an attractive method, since an interpenetrating network mechanism provide matrix materials with single T_g when compared with polymer blends. Interpenetrating polymer networks (IPNs) of thermoset–thermoset blends have been extensively studied due to their enhanced mechanical properties.[8–13]

Improvements in thermal properties and elastic modulus of epoxy resin have been investigated recently by modifying with a co-reactive component cyanate esters.[14,15] Cyanate esters encompass attractive physical, dielectric, thermal and mechanical characteristics and low water absorption, excellent heat resistance, low volume shrinkage, rendering them the material of choice in high-performance applications.[16,17] Improvement in thermo-mechanical properties was observed by the introduction of bismaleimide into epoxy resin,[18–21] siliconized epoxy,[22] and unsaturated polyester modified epoxy resin.[23] Since, bismaleimides possess high crosslinking ability, high glass transition temperature, high thermal stability, high char yield, excellent fire resistance, superior specific strength and specific modulus, and low water absorption. Hence, in the present investigation an attempt has been made to improve thermo-mechanical of epoxy resin by forming an intercrosslinked network with cyanate ester and bismaleimide.

EXPERIMENTAL

Materials

The commercially available epoxy resin (Diglycidyl ether of bisphenol A, DGEBA) GY 250 having epoxy equivalent of about 180–190, diamonodiphenylmethane were obtained from Ciba-Geigy Ltd., India. Cyanogen bromide and bisphenol-A (SRL, India) were used as received.

Cyanate ester was synthesized from cyanogen bromide and bispheol A using triethylamine catalyst according to the reported procedure.[24] The product was recrystallized from methonol : water (1 : 1). Yield 65%, mp 75°C. Bismaleimide was prepared according to the reported procedure.[25] The product was recrystallized from acetone/toluene. Yield 81% mp 158°C. The chemical structure of the materials used are presented in Fig. 1.

Preparation of Cyanate Ester Epoxy Blends

A fixed amount of epoxy resin, varying amounts of cyanate ester, stoichiometric amount of diaminodiphenylmethane (with respect to epoxy) were thoroughly blended at 100°C for 10 min with constant stirring. The content was then degassed to remove entrapped air and poured into a preheated mold and kept at 140°C for 3 h and post cured at 200°C for 2 h.

Preparation of Cyanate Ester–Epoxy–Bismaleimide Blends

A typical blend (system E) was prepared as follows. 4 g of *N*,*N*′-bismaleimido-4,4′-diphenylmethane was dissolved in an epoxy resin and cyanate ester (100 : 4) mix at 120°C under vigorous stirring. After complete dissolution of bismaleimide, 27 g of 4,4′-diaminodiphenylmethane was added. The product was subject to vacuum to remove

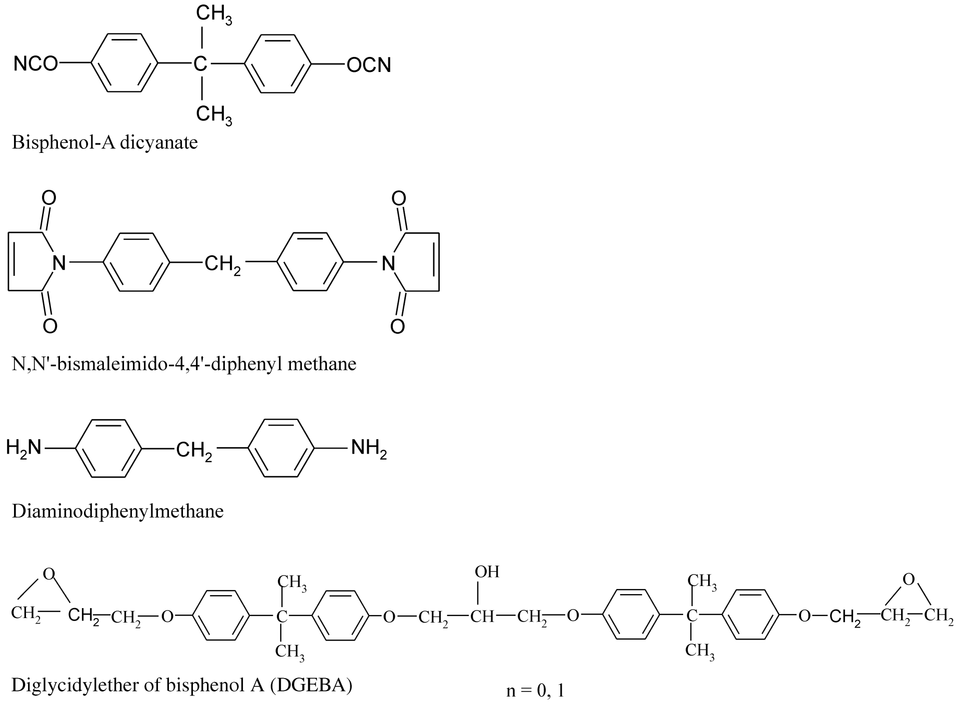


Figure 1. Chemical structure of materials.

trapped air and then cast and cured at 140°C for 3 h. The castings were then post cured at 200°C for 2 h and finally removed from the mold and characterized.

Test Methods

Glass transition temperature (T_g) of the samples was determined using a differential scanning calorimetry (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. Thermogravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA instruments, USA) at a heating rate of 10°C per min in air atmosphere. The heat deflection temperature (HDT) of the samples was tested as per ASTM D 648-72. The water absorption property of the samples was tested as per ASTM D 570.

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

RESULTS AND DISCUSSION

Thermal Properties

Differential scanning calorimetry thermograms of epoxy resin with 4%, 8%, and 12% of cyanate ester are presented in Fig. 2. It is observed from Fig. 2 that the cyanate esters

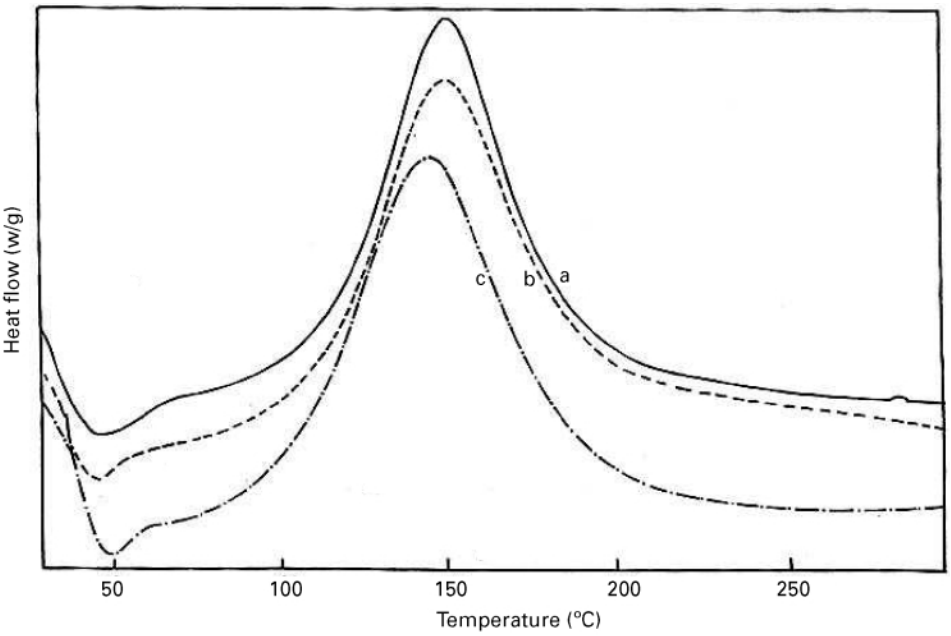


Figure 2. Differential scanning calorimetry thermograms of cyanate ester modified epoxy systems during cure: (a) 4%, (b) 8%, and (c) 12%.

modified epoxy systems show unimodel reaction exotherm due to the presence of lower concentrations of cyanate ester. The peak maximum temperatures obtained for 4%, 8%, and 12% of CE incorporated systems are 160°C, 151°C, and 148°C, respectively. The decrease in peak maximum temperature with increasing CE concentration confirms that the reaction between epoxy and cyanate ester which accelerates the reaction rate and reduces the curing temperature. The large exothermic peak obtained for CE–epoxy systems is due to the following reactions:[25,26] (1) polycyclotrimerization of cyanate monomers; (2) reaction of cyanate with amine; (3) cyanate with epoxide; and (4) epoxy with cyanurate (Fig. 3).

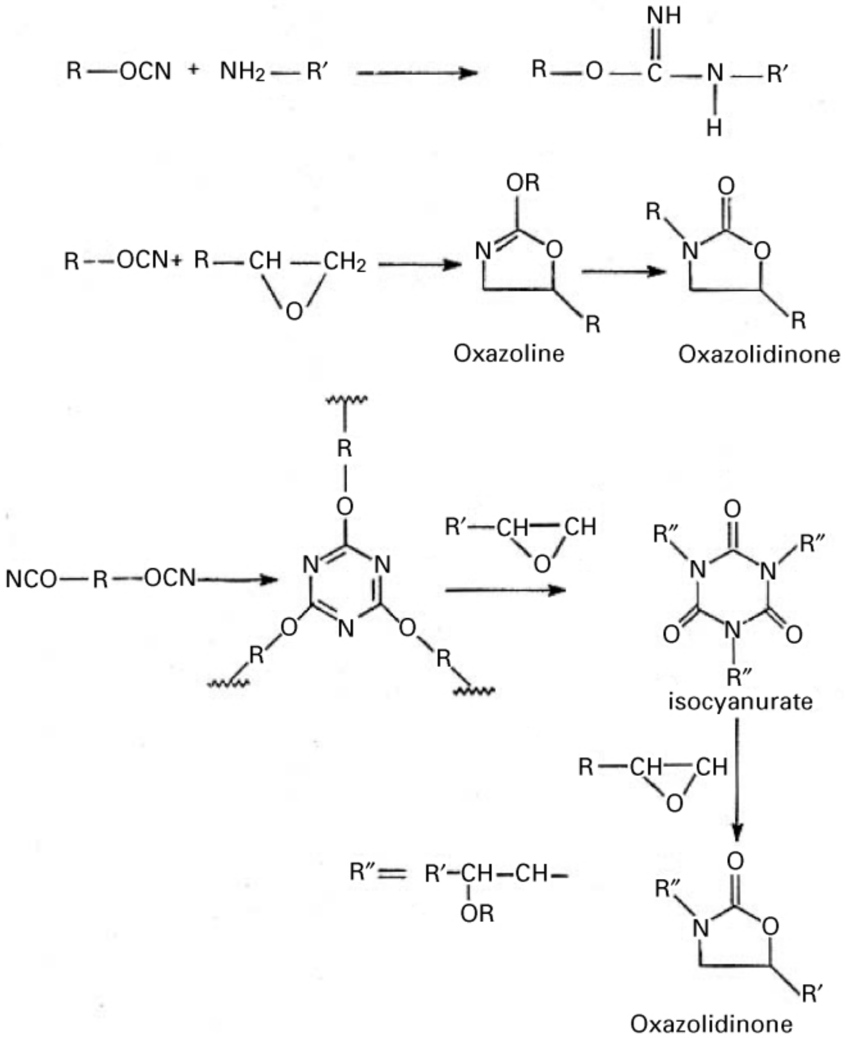


Figure 3. Reactions involved during the curing process of cyanate ester modified epoxy systems.

It is observed that all the bismaleimides modified epoxy systems show a unimodel reaction exotherm due to the presence of lower concentrations of bismaleimides. For all the bismaleimides incorporated systems, the reaction commences at 120°C. The peak maximum temperatures for 4%, 8%, and 12% of BMI incorporated systems are 168°C, 171°C, and 174°C, respectively (Fig. 4). The large exothermic peak obtained for the bismaleimides incorporated systems is due to 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) bismaleimides homopolymerization reaction. The slight increase in peak maximum temperature with increasing bismaleimide concentration confirms the occurrence of homopolymerization reaction.[21,28]

Glass Transition Temperature

The glass transition temperature obtained for epoxy-DDM system is 165°C. The incorporation of cyanate ester into epoxy resin has significant impact on T_g. T_g decreases with increase in concentration of cyanate ester as evidenced from Fig. 5. For example, the T_g values for 4%, 8%, and 12% of CE modified systems are 162°C,

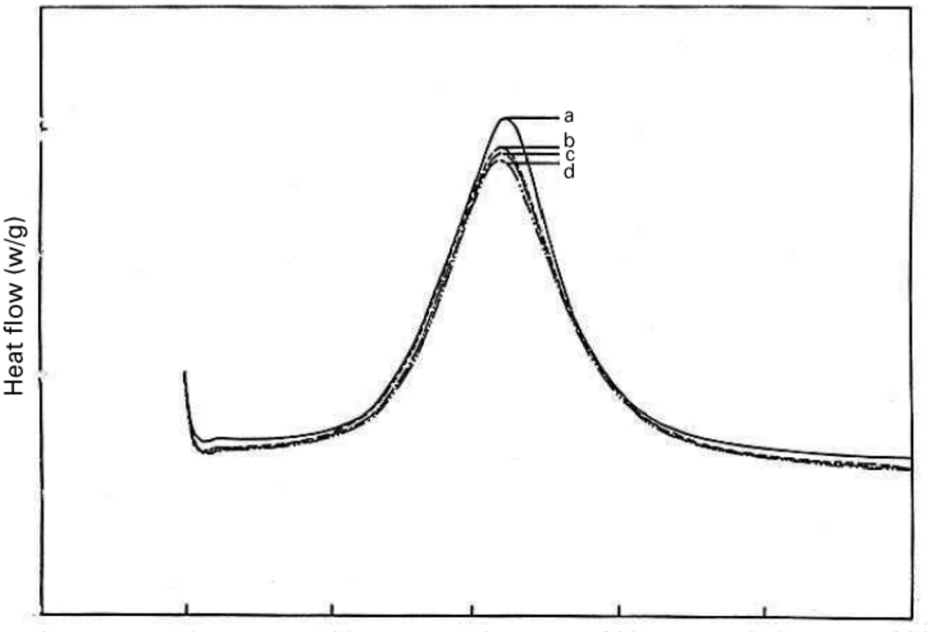


Figure 4. Differential scanning calorimetry thermograms of bismaleimide modified epoxy systems during cure: (a) unmodified epoxy, (b) 4% BMI, (c) 8% BMI, and (d) 12% BMI modified epoxy systems.

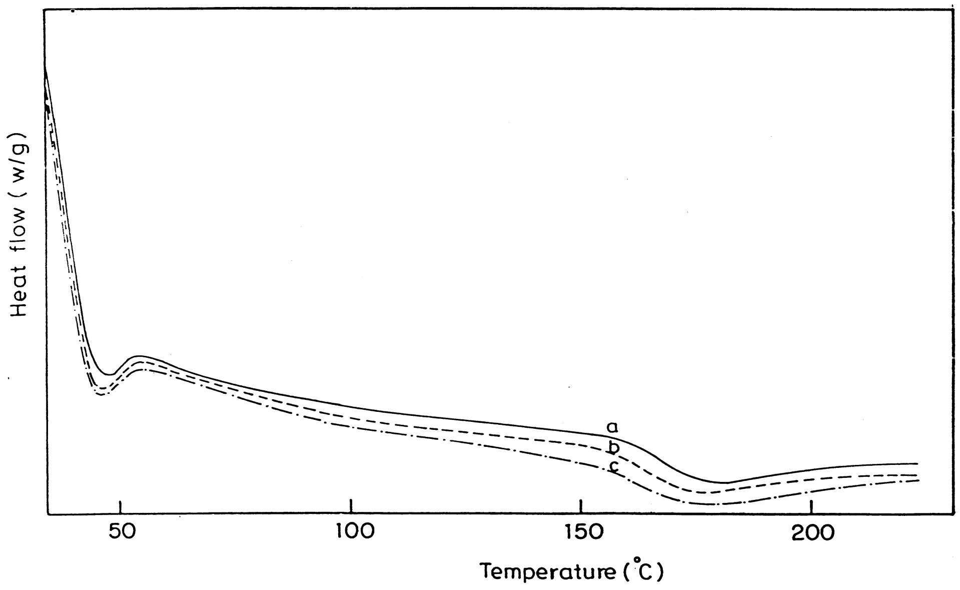


Figure 5. Differential scanning calorimetry traces of cyanate ester modified epoxy systems: (a) 4% CE, (b) 8% CE, and (c) 12% CE.

159°C, and 155°C, respectively and this may be due to the formation of oxazolidinone, reaction of epoxy with cyanurate, which decreases the glass transition due to its aliphatic nature and its formation decreases the effective crosslink density. The increase in T_g values of bismaleimide modified epoxy (Fig. 6) and bismalemide modified cyanate ester–epoxy systems (Fig. 7) are due to the homopolymerization of bismaleimides rather than Michael addition reaction.[28] Since Michael addition reaction leads to the formation of thermally weak amine linkages and ultimately reduces the crosslink density due to chain extension. The single T_g value obtained for both the bismaleimides modified epoxy and cyanate ester modified epoxy systems further confirm the formation of intercrosslinking network.

Thermogravimetric Analysis

The incorporation of cyanate ester into epoxy resin improves thermal stability and enhances the degradation temperature according to its percentage concentration. From Fig. 8, it is observed that the presence of cyanate ester networks in the epoxy system delays the degradation process, since high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. Thermally stable isocyanurate and oxazolidinone formed by the cyclotrimerization of cyanate esters and subsequent reaction with epoxide leads to the delay in degradation. This is in accordance with the results obtained earlier by Kim.[14]

The thermal degradation temperature of the bismaleimide modified epoxy systems are increased with increasing bismaleimide concentration (Fig. 9). This may be due to

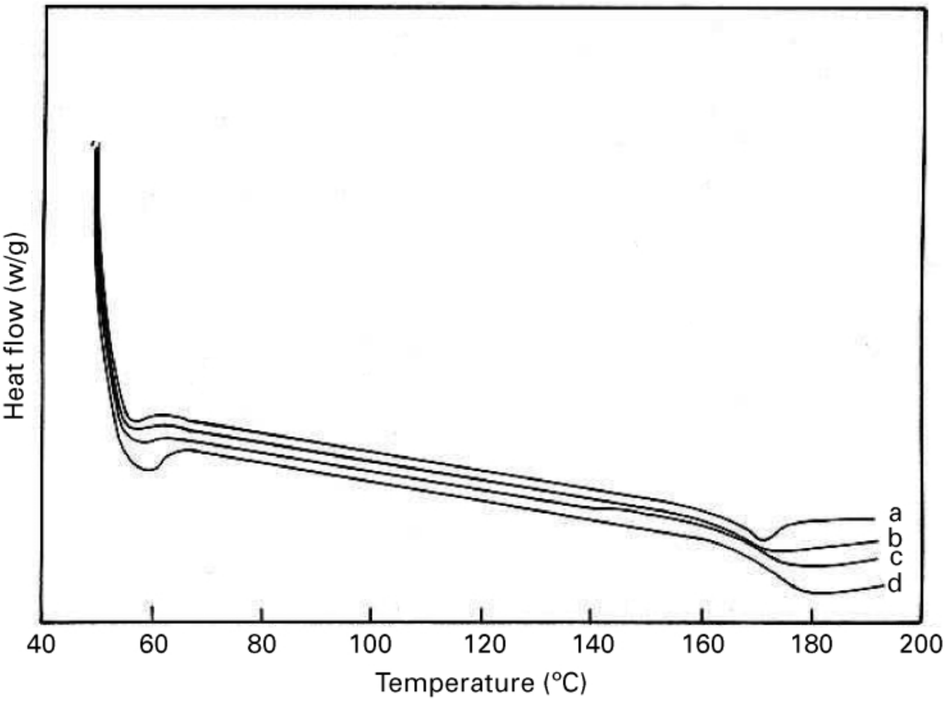


Figure 6. Differential scanning calorimetry traces of bismaleimide modified epoxy systems: (a) unmodified epoxy, (b) 4% BMI, (c) 8% BMI, and (d) 12% BMI.

the formation of intercrosslinking network between epoxy and bismaleimides and the presence of rigid heterocyclic ring structure. A similar trend is observed in the case of bismaleimides and cyanate ester modified epoxy systems. However, the thermal stability of bismaleimide and cyanate esters modified epoxy systems (Fig. 10) are slightly higher than that of bismaleimides modified epoxy systems.

Heat Distortion Temperature

Heat distortion temperature is carried out to determine the thermo-mechanical behavior of matrix systems. Heat deflection temperature values for epoxy, cyanate ester modified epoxy, and bismaleimide modified epoxy and cyanate ester–epoxy systems are presented in Table 1. The HDT values are decreased with increasing CE concentration. This may be explained due to the formation of oxazolidinone, which in turn reduces the crosslink density. The incorporation of bismaleimide into epoxy and cyanate ester modified epoxy systems, the values of HDT are increased with increase in BMI concentration. The enhancement in the values of HDT for bismaleimides modified systems are due to high crosslink density and rigidity imparted by heterocyclic bismaleimides.

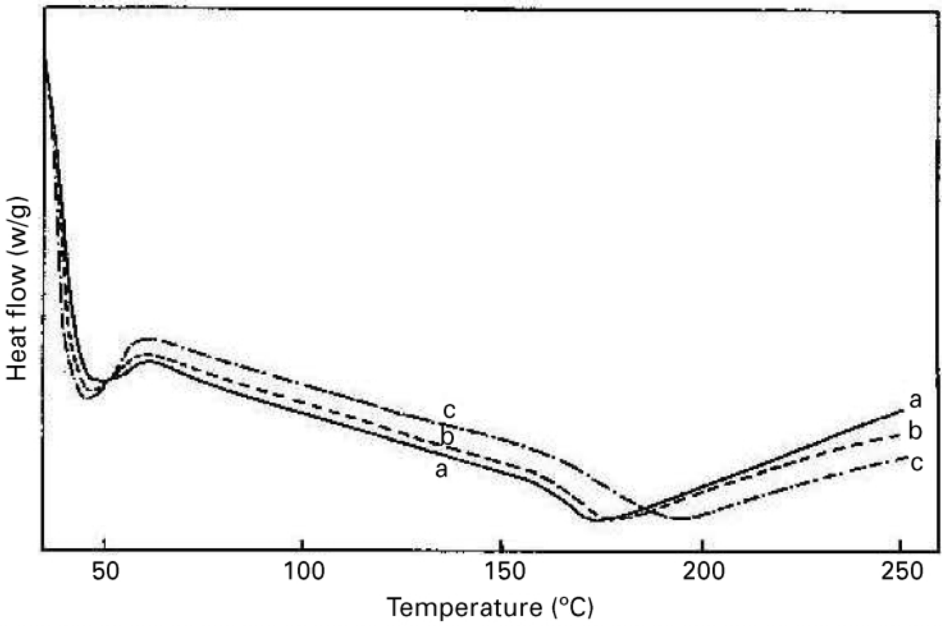


Figure 7. Differential scanning calorimetry traces of bismaleimide modified CE(8%)–epoxy systems: (a) 4% BMI, (b) 8% BMI, and (c) 12% BMI.

Dynamic Mechanical Analysis

The ability of a polymeric material to withstand loads at elevated temperatures is one of the key aspects of engineering performance 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 crosslink density of polymeric materials.

Figures 11 and 12 shows the DMA curves of unmodified epoxy, cyanate ester modified epoxy, and bismaleimide modified CE–epoxy systems at a heating rate of 10°C per min from 30 to 300°C. At temperatures above T_g damping decreases with increasing crosslinking. All the systems show similar dynamic mechanical behavior ($\tan\delta$ and E'). However, the cyanate ester modified epoxy system exhibits lower modulus than unmodified epoxy, this is due to the more flexibility or less stiffness compared to unmodified epoxy. The $\tan\delta$ max value also decreases with increasing cyanate ester content, this indicates that the CE–epoxy system has less crosslink density than unmodified epoxy system. The incorporation of bismaleimide increased the $\tan\delta$ max value, due to increased crosslink density. This further supports the data resulted from thermal studies (T_g).

Water Absorption Behavior

The cyanate ester incorporation into epoxy system decreases the water absorption behavior with increasing its concentration. The decrease in percentage water uptake for

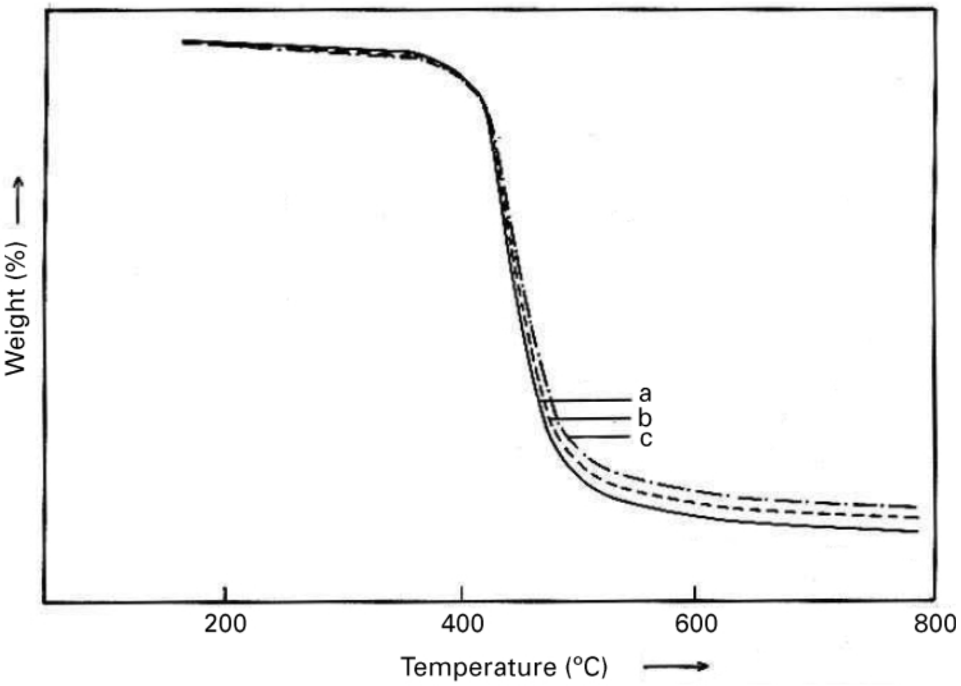


Figure 8. Thermogravimetric analysis curves of cyanate ester modified epoxy systems: (a) 4% CE, (b) 8% CE, and (c) 12% CE.

cyanate ester incorporated system is due to the inherent hydrophobic nature of cyanate ester networks. All BMI modified systems showed a good resistance to moisture absorption because of the rigid aromatic hydrophobic structure. The moisture resistance property increases with increasing BMI content (Table 1) and it is observed that the BMI incorporation plays an important role in improving resistance to moisture absorption of epoxy matrix systems.

Microscopic Investigation

Scanning electron microscope is used to investigate the morphology of matrix systems. The SEM photographs of the matrices are presented in Fig. 13. The SEM photograph of fractured surfaces of the unmodified epoxy, cyanate ester modified epoxy resin systems reveals smooth, glassy, and homogeneous microstructure without any plastic deformation. The fractured surfaces of the system reveals the presence of homogeneous morphology due to the efficient interaction between the cyanate ester and epoxy resin.

The SEM photograph of the fractured surface of bismaleimides modified epoxy system is almost similar to that of unmodified epoxy system. This indicates that there are no separate phase domains of the two components and it also suggests that the formation of homogeneous intercrosslinked network. Further, smooth fractured surface is

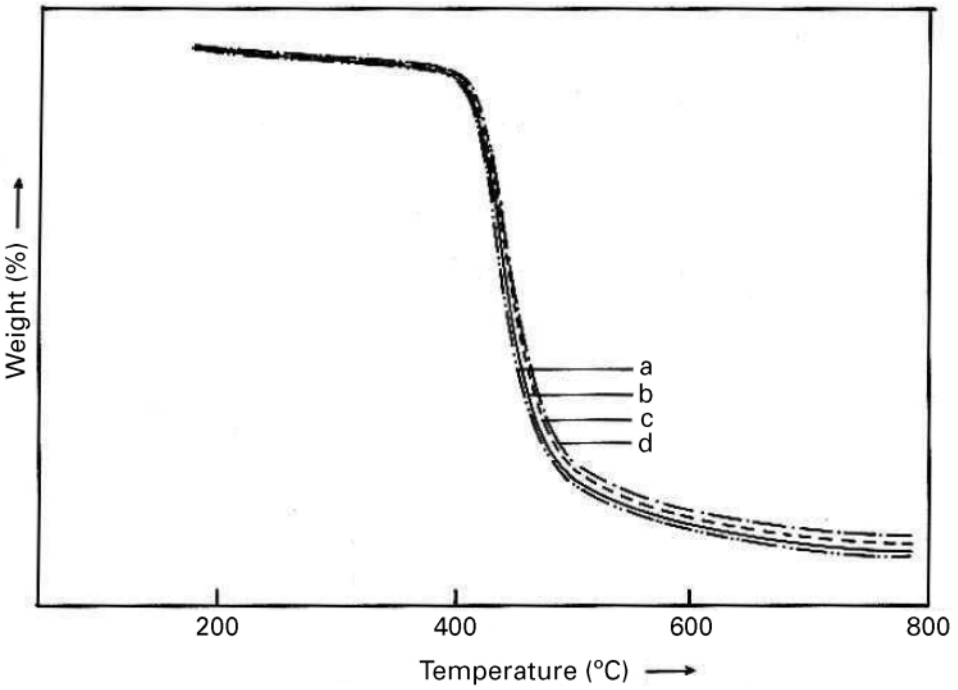


Figure 9. Thermogravimetric analysis curves of bismaleimide modified epoxy systems: (a) unmodified epoxy, (b) 4% BMI, (c) 8% BMI, and (d) 12% BMI.

observed with increasing bismaleimide content due to the brittle behavior imparted by bismaleimides.

CONCLUSION

The cyanate ester modified epoxy, BMI modified epoxy, and BMI modified CE–epoxy intercrosslinked network having varied concentrations of BMI and CE were developed. The thermal properties viz: glass transition temperature, heat distortion temperature and thermal stability of BMI modified epoxy and CE–epoxy systems have been compared with those of unmodified epoxy systems and showed that an increasing trend with bismaleimide concentration. The reduction in the values of T_g of CE modified epoxy confirms the reaction between epoxy and cyanate ester which reduces the effective crosslink density by the formation of oxazolidinone and isocyanurate which has been further proven by the dynamic mechanical analysis. The single glass transition temperature obtained for both BMI modified epoxy and CE modified epoxy and BMI modified CE–epoxy reveals the presence of intercrosslinked network. The incorporation of cyanate ester and bismaleimide into epoxy resin improves thermal stability and enhances the degradation temperature according to their percentage concentration. It was also observed that the resistance to water absorption increases with increasing cyanate ester and BMI

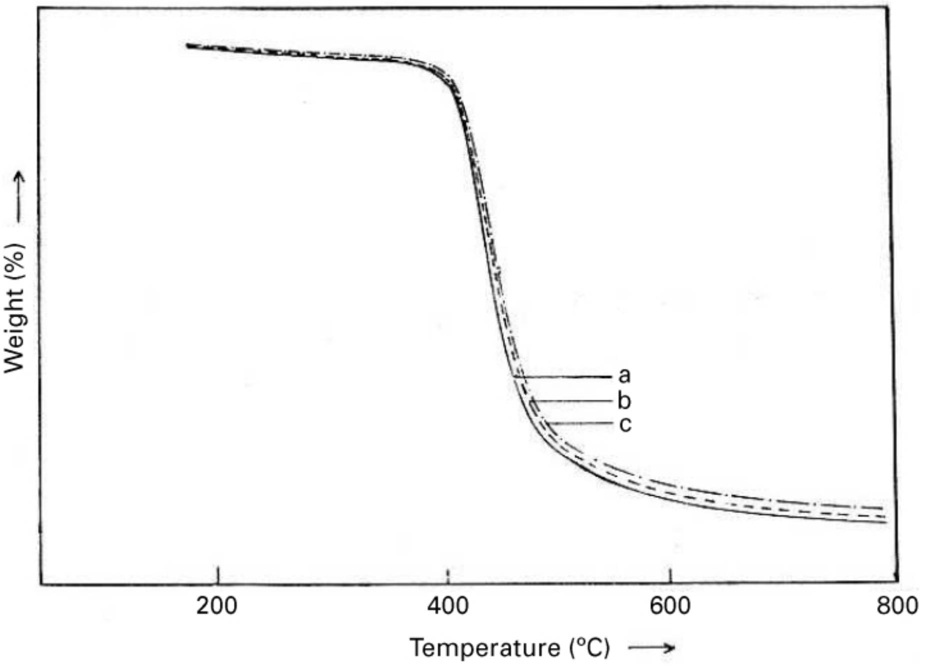


Figure 10. Thermogravimetric analysis curves of bismaleimide modified CE(8%)–epoxy systems: (a) 4% BMI, (b) 8% BMI, and (c) 12% BMI

Table 1. Heat deflection temperature and water absorption properties of BMI–CE–Epoxy matrices.

Sample code	Epoxy/CE/BMI composition	Water absorption (%)	Heat deflection temperature (°C)
A	100/00/00	0.1201	
B	100/04/00	0.1152	
C	100/08/00	0.1105	
D	100/12/00	0.1032	
E	100/04/04	0.1045	
F	100/04/08	0.0965	
G	100/04/12	0.0835	
H	100/08/04	0.0711	
I	100/08/08	0.0646	
J	100/08/12	0.0566	
K	100/12/04	0.0895	
L	100/12/08	0.0712	
M	100/12/12	0.0623	
N	100/00/04	0.0816	
O	100/00/08	0.0786	
P	100/00/12	0.0697	

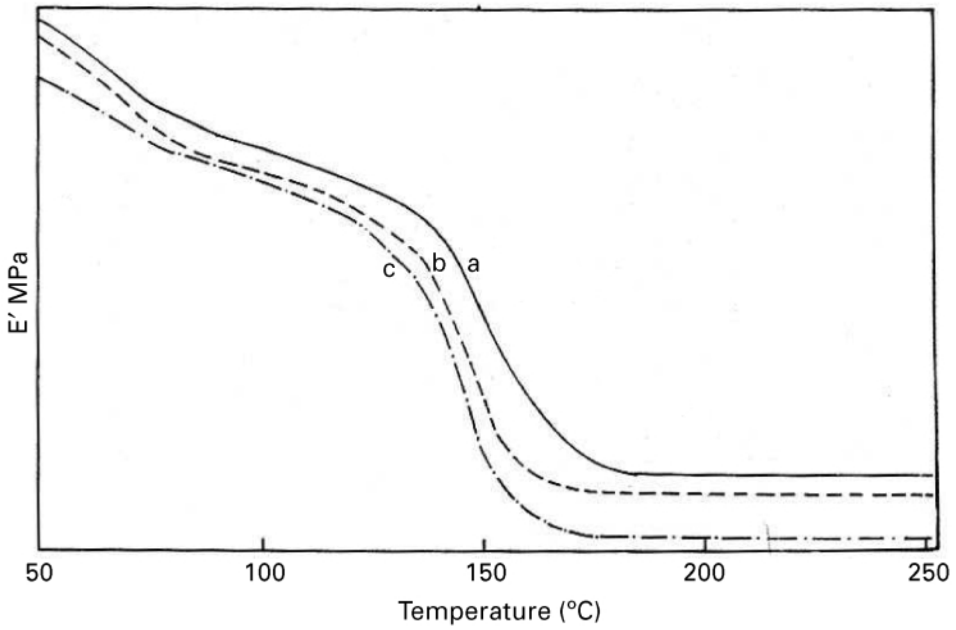


Figure 11. Variation of storage modulus (E') as a function of temperature: (a) unmodified epoxy, (b) CE modified epoxy, and (c) BMI modified CE–epoxy systems.

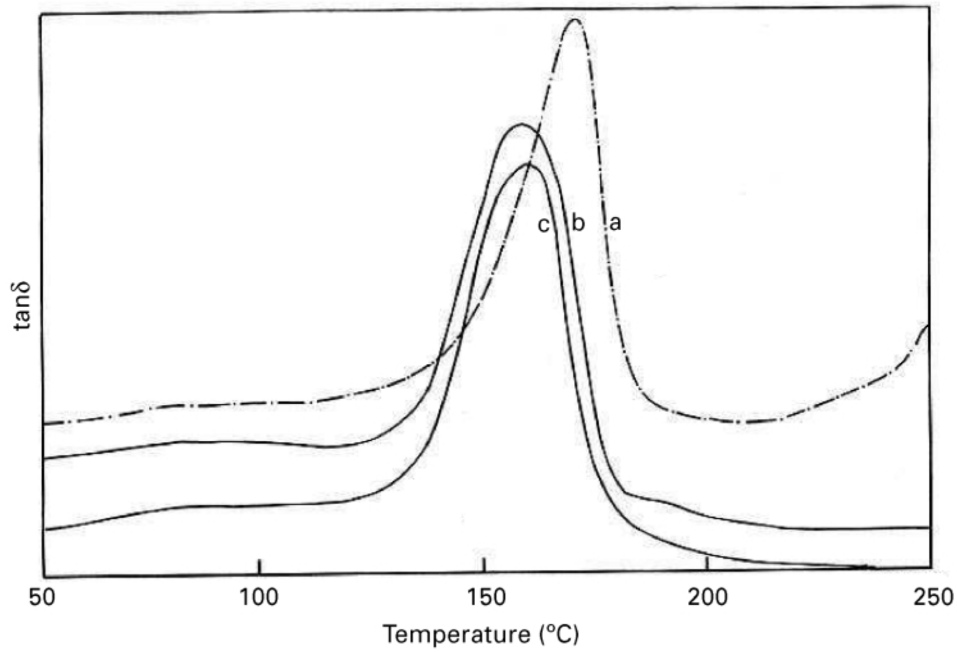
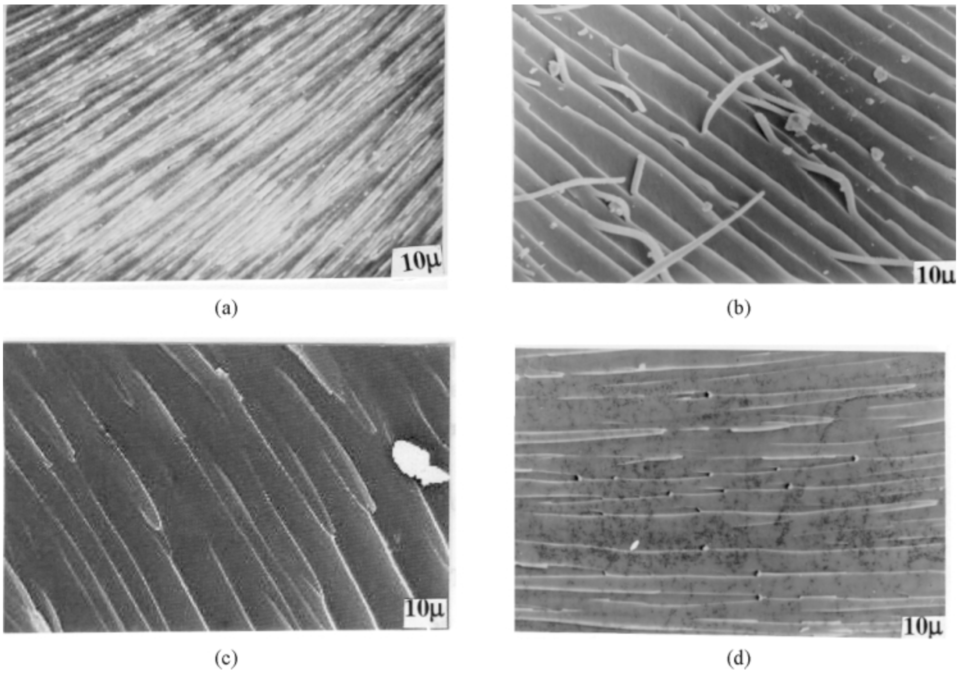


Figure 12. Variation of tan δ as a function of temperature: (a) unmodified epoxy, (b) CE modified epoxy, and (c) BMI modified CE–epoxy systems.



(a) (b)

(c) (d)

Figure 13. SEM micrographs of BMI modified epoxy and BMI modified CE–epoxy systems: (a) unmodified epoxy, (b) cyanate ester–epoxy, (c) BMI modified epoxy, and (d) BMI modified CE–epoxy system.

content. BMI incorporation plays an important role in reducing moisture absorption of epoxy resin. The fractured surfaces of the cyanate ester modified epoxy system reveals the presence of homogeneous morphology and BMI modified epoxy systems also showed homogenous microstructure without any plastic deformation.

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