

Preparation and Characterization of Bismaleimide (*N,N'*-bismaleimido-4,4'-diphenyl methane)–Unsaturated Polyester Modified Epoxy Intercrosslinked Matrices

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ABSTRACT: An intercrosslinked network of unsaturated polyester–bismaleimide modified epoxy matrix systems was developed. Epoxy systems modified with 10, 20, and 30% (by weight) of unsaturated polyester were made by using epoxy resin and unsaturated polyester with benzoyl peroxide and diaminodiphenylmethane as curing agents. The reaction between unsaturated polyester and epoxy resin was confirmed by IR spectral studies. The unsaturated polyester toughened epoxy systems were further modified with 5, 10, and 15% (by weight) of bismaleimide (BMI). The matrices, in the form of castings, were characterized for their mechanical properties. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the matrix samples were performed to determine the glass transition temperature (T_g) and thermal degradation temperature of the systems, respectively. Mechanical properties, viz: tensile strength, flexural strength, and plain strain fracture toughness of intercrosslinked epoxy systems, were studied by ASTM methods. Data obtained from mechanical and thermal studies indicated that the introduction of unsaturated polyester into epoxy resin improves toughness but with a reduction in glass transition, whereas the incorporation of bismaleimide into epoxy resin improved both mechanical strength and thermal behavior of epoxy resin. The introduction of bismaleimide into unsaturated polyester-modified epoxy resin altered thermomechanical properties according to their percentage concentration. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2853–2861, 2002

Key words: polyesters; crosslinking; matrix; resins

INTRODUCTION

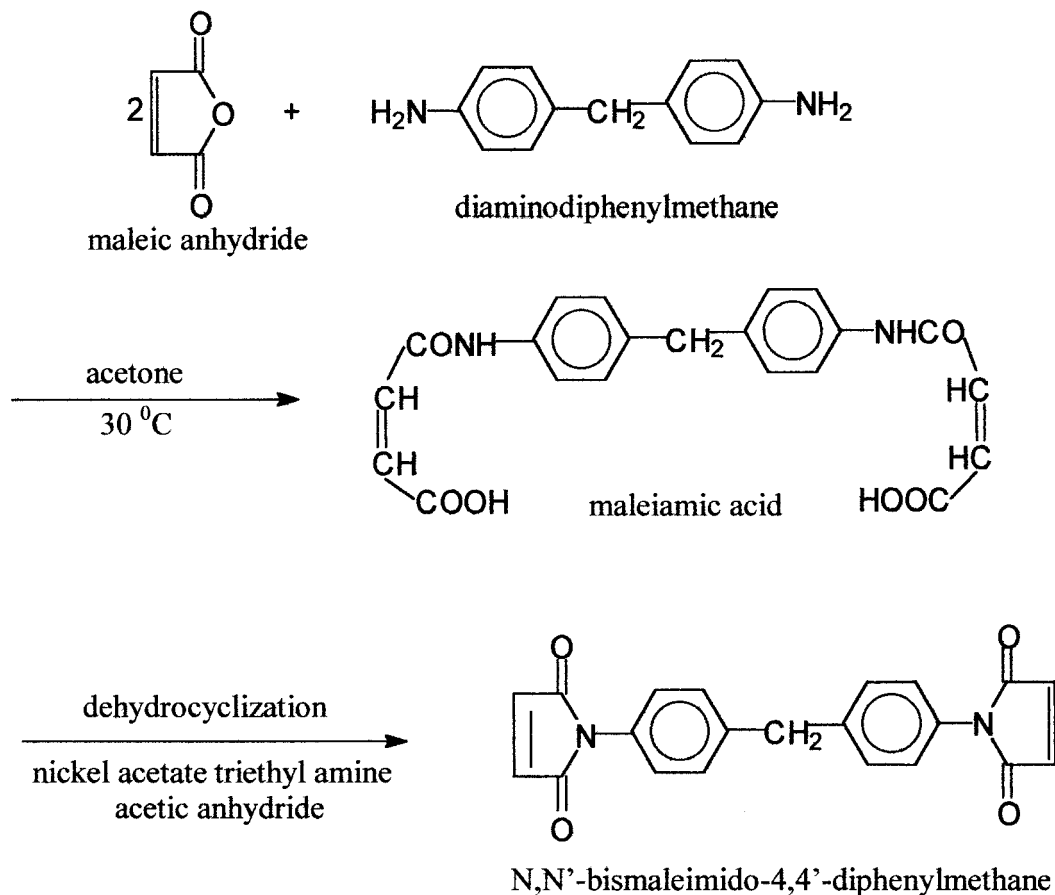
Epoxy resin is a versatile and widely accepted matrix material for the fabrication of advanced composites, hardware components, electronic circuit board materials, sealants, radomes, and missile equipment components because of its excellent bonding, physico-chemical, thermal, mechan-

ical, dielectric, and aging characteristics.^{1–6} To improve its working performance further, to use in advanced engineering applications, chemical modification of epoxy resin is essential, mainly to improve impact 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.^{7,8} The resulting products have good impact behavior but inferior strength properties, and are unsuitable for high-performance engineering applications.

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Scheme 1 Synthesis of *N,N'*-bismaleimido-4,4'-diphenylmethane.

However, epoxy resin modified with these materials can be used in application areas connected with structural adhesives, corrosion, and weather resistant coatings. In our earlier work, it was observed that the incorporation of siloxane into epoxy resin improves impact strength at the expense of stress-strain properties with insignificant change in glass transition behavior.^{9,10} Interpenetrating polymer networks (IPNs) of thermoset thermoset blends have been extensively studied due to their enhanced mechanical properties.¹¹⁻¹⁹

Improvement in thermo-mechanical properties has been obtained by the introduction of bismaleimide into epoxy resin,²⁰⁻²⁴ siliconized epoxy,²⁵ and unsaturated polyester resin.²⁶ 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 work, the effect of bismaleimide on unsaturated polyester-modi-

fied epoxy has been studied by forming intercrosslinked networks of epoxy, with unsaturated polyester and bismaleimide of varying concentrations, which were then characterized for their thermo-mechanical properties.

EXPERIMENTAL

Materials

Epoxy resin (Diglycidyl ether of bisphenol A, DGEBA) LY556 having epoxy equivalent of about 180-190, with viscosity of about 10,000 cP and 4,4-diaminodiphenylmethane (DDM), epoxy curing agent, were obtained from Ciba-Geigy Ltd., India. *N,N'*-bismaleimido-4,4'-diphenyl methane was prepared in the laboratory. The commercially available unsaturated polyester resin used was manufactured using isophthalic acid, maleic anhydride, and propylene glycol with 25% styrene

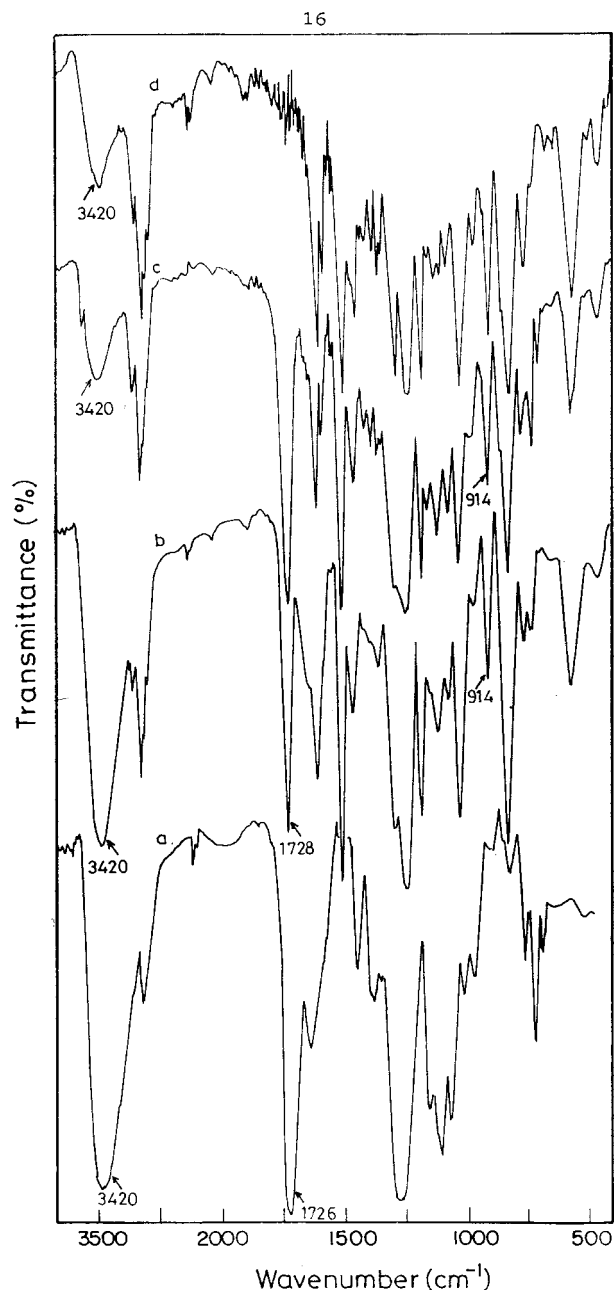


Figure 1 FTIR spectra of (a) unsaturated polyester resin, (b) uncured epoxy-unsaturated polyester blend with the composition of 100 : 30, (c) uncured epoxy-unsaturated polyester blend with the composition of 100 : 30 taken after heating at 80°C for 3 h, (d) unmodified epoxy resin.

having a viscosity of 600 cP. Benzoyl peroxide was used as the radical initiator.

Preparation of Unsaturated Polyester Epoxy Blends

A fixed amount of epoxy resin (100 g), varying amounts of unsaturated polyester resin (10, 20,

and 30 g), a stoichiometric amount of diaminodiphenylmethane (27.2 g), with respect to epoxy resin, and benzoyl peroxide (2 wt %) were mixed at 50°C for 10 min with constant stirring. The product was then degassed to remove entrapped air, and was then transferred into a preheated mold kept at 80°C for 3 h and postcured at 150°C for 2 h.

Preparation of *N,N'*-bismaleimido-4,4'-diphenylmethane

Bismaleimide was prepared according to the reported procedure.²⁷ The product was recrystallized from acetone/toluene 81% yield. The reaction scheme for the preparation of bismaleimide is given below (Scheme 1)

Preparation of Unsaturated Polyester Epoxy Bismaleimide Blend

A typical blend (System E) was prepared as follows: 5 g of *N,N'*-bismaleimido-4,4'-diphenylmethane was dissolved in an epoxy resin (100 g) and unsaturated polyester (10 g) mix at 100°C under vigorous stirring. After complete dissolution of bismaleimide, the temperature was reduced to 50°C and 27 g of 4,4'-diaminodiphenylmethane and benzoyl peroxide were added. The product was subjected to vacuum to remove trapped air and then cast and cured at 80°C for 3 h. The castings were then postcured at 150°C for 2 h and finally removed from the mold and characterized.

Test Methods

The IR spectra for resinous materials were recorded on a Perkin-Elmer 781 infrared spectrometer. The spectra were collected on thin films of the uncured resinous mixture between two KBr windows. The tensile (stress-strain) properties were determined using dog bone shaped specimens according to ASTM-D3039 method using on Instron testing machine (Model 6025 UK), at a crosshead speed of 2 mm per minute. 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-E399-74.²⁸ Five test pieces were used to generate the data points for the mechanical tests.

Glass transition temperatures (T_g) of samples were determined using a DSC 2910 (TA Instruments USA) in the temperature range between 50

Table I Mechanical Properties of Epoxy, Unsaturated Polyester-Modified Epoxy, BMI-Modified Epoxy and BMI-Modified Unsaturated Polyester-Epoxy System

Matrix System	Epoxy/UP/BMI composition (g)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Plain Strain Fracture Toughness (MPa m ^{1/2})
A	100/00/00	61.6 ± 7	2721.7 ± 36	110.0 ± 9	1812.9 ± 37	1.14 ± 0.10
B	100/10/00	62.4 ± 4	2772.9 ± 32	112.6 ± 2	1935.4 ± 29	2.51 ± 0.15
C	100/20/00	68.9 ± 3	2819.9 ± 27	135.5 ± 4	2610.9 ± 38	3.61 ± 0.04
D	100/30/00	79.5 ± 2	2952.1 ± 38	145.2 ± 5	3373.4 ± 32	4.33 ± 0.15
E	100/10/05	61.8 ± 3	2638.9 ± 35	114.0 ± 6	1899.3 ± 27	2.71 ± 0.12
F	100/10/10	59.4 ± 2	2405.4 ± 24	92.6 ± 4	1814.9 ± 23	2.47 ± 0.16
G	100/10/15	57.2 ± 5	2369.4 ± 32	88.8 ± 3	1654.1 ± 40	2.31 ± 0.10
H	100/20/05	64.3 ± 3	2550.2 ± 41	116.9 ± 3	2195.2 ± 23	3.06 ± 0.09
I	100/20/10	58.9 ± 5	2450.6 ± 28	105.0 ± 3	2050.3 ± 28	2.84 ± 0.05
J	100/20/15	54.7 ± 3	2106.3 ± 31	102.0 ± 4	1803.9 ± 37	2.64 ± 0.09
K	100/30/05	60.5 ± 3	2379.7 ± 36	100.2 ± 4	1834.2 ± 39	4.07 ± 0.09
L	100/30/10	64.0 ± 2	2603.1 ± 29	106.7 ± 5	1952.9 ± 24	3.36 ± 0.07
M	100/30/15	68.0 ± 4	2877.8 ± 32	127.0 ± 3	2242.6 ± 32	3.29 ± 0.04
N	00/00/05	66.2 ± 8	2820.4 ± 32	111.3 ± 7	2040.5 ± 21	1.13 ± 0.05
O	100/00/10	71.0 ± 5	2876.3 ± 37	127.3 ± 7	2275.9 ± 32	1.04 ± 0.09
P	100/00/15	85.4 ± 4	3053.9 ± 31	132.6 ± 5	2596.8 ± 35	0.98 ± 0.08

UP: Unsaturated polyester.

BMI: *N,N'*-bismaleimido-4,4'-diphenylmethane.

and 250°C at a heating rate of 10°C per minute. Thermogravimetric analysis (TGA) was carried out using a Thermal Analyser 2000 (TA Instruments USA) at a heating rate of 10°C per minute.

RESULTS AND DISCUSSION

Spectral Analysis

Figure 1(a) and (d) represents the FTIR spectra of uncured unsaturated polyester resin and uncured epoxy resin, respectively. Figure 1(b) represents the FTIR spectra of blend of uncured epoxy and

unsaturated polyester with a composition of 100 : 30. The IR spectrum of uncured epoxy and unsaturated polyester with a composition of 100 : 30, taken after heating at 80°C for 3 h, is given in Figure 1(c). The formation of a network structure of unsaturated polyester–epoxy involves reaction between the epoxide ring of epoxy resin and the hydroxyl group of an unsaturated polyester, and is confirmed by the decrease in the intensity of the epoxy band at 913 cm⁻¹ and the hydroxyl band at 3420 cm⁻¹ [Fig. 1(b) and (c)]. The epoxy resin and

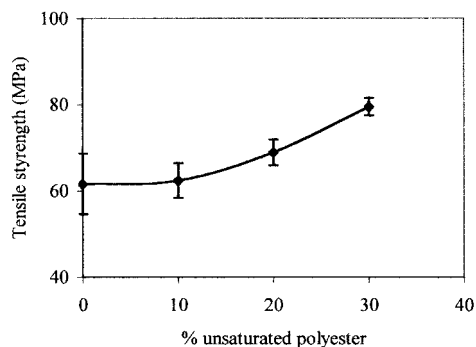


Figure 2 Effect of unsaturated polyester content on tensile strength.

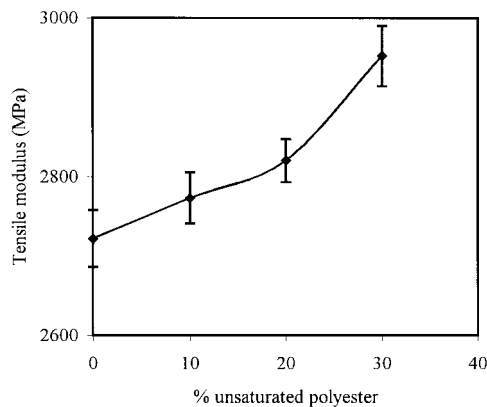


Figure 3 Effect of unsaturated polyester on tensile modulus.

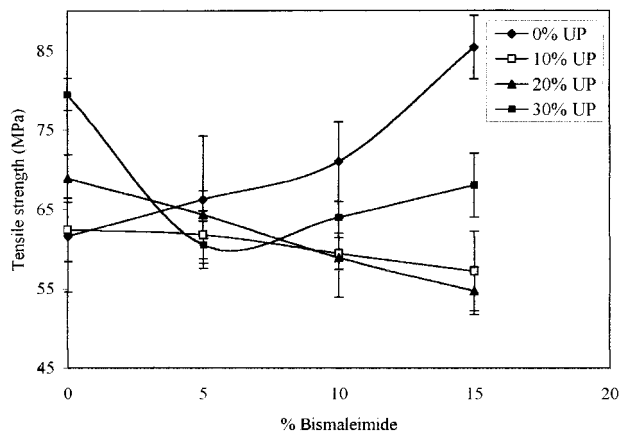


Figure 4 Effect of BMI content on tensile strength.

unsaturated polyester also interact through intermolecular hydrogen bonding¹⁹ between the carbonyl group on the polyester and the epoxide ring. In the presence of an epoxide ring the carbonyl absorption of the polyester is shifted from 1726 to 1728 cm^{-1} [Fig. 1(a) and (b)].

Tensile Properties

The values of tensile strength of unmodified epoxy resin (system A) and epoxy system modified with varying percentage of unsaturated polyester and bismaleimide (matrix systems B to P) are presented in Table I and Figures 2–5. From the data, it is observed that the incorporation of unsaturated polyester and bismaleimide has a specific influence on the value of tensile strength. Incorporation of 10, 20, and 30% unsaturated polyester (by weight) into epoxy resin (systems B, C, and D) increases the tensile strength (Fig. 2) by 2.1, 11.8, and 29%, respectively, when compared with unmodified epoxy (A) system. This may be explained as being due to the formation of net-

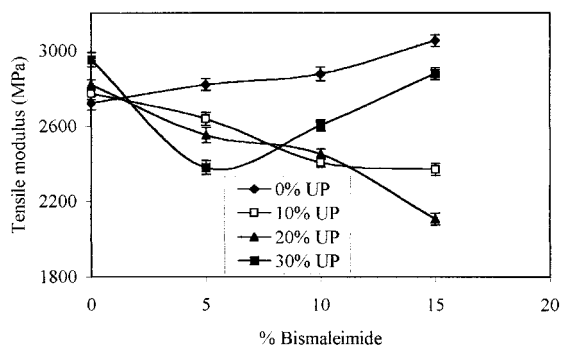


Figure 5 Effect of BMI on tensile modulus.

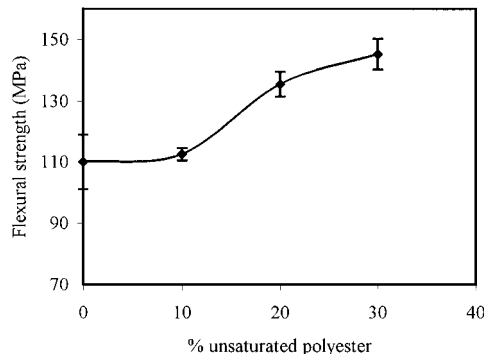


Figure 6 Effect unsaturated polyester content on flexural strength.

work chain entanglements between the unsaturated polyester chains and epoxy resin. Similarly, the incorporation of 5, 10, and 15% (by weight) bismaleimide into epoxy resin (Systems N, O, and P) increases the tensile strength by 7.4, 15.2, and 37.9%, respectively, when compared with the system A, due to higher crosslinking density and rigidity imparted by bismaleimide molecules. Incorporation of bismaleimide into 10% and 20% unsaturated polyester modified epoxy systems (Systems E to K) lowers the tensile strength. This is explained as being due to the addition of bismaleimide into the unsaturated polyester-modified epoxy system disrupting the entanglement of molecular chains between unsaturated polyester and epoxy, and in turn, restricting the formation of IPN.¹⁸ Hence, lowered values of tensile strength are observed (Fig. 4). However, increased concentration of unsaturated polyester (30%) in the epoxy system enhances the values (Systems L and M) of the tensile strength. This may be explained as being due to the formation of

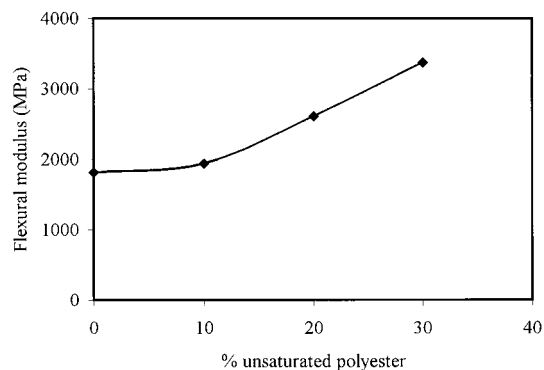


Figure 7 Effect of unsaturated polyester content on flexural modulus.

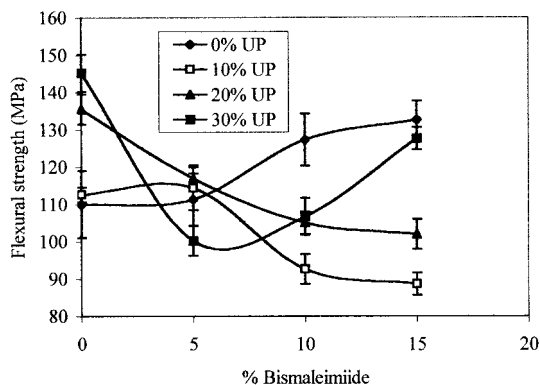


Figure 8 Effect of BMI on flexural strength.

a highly crosslinked network structure imparted by more double bonds present in the 30% unsaturated polyester modified system when compared to the 10 and 20% unsaturated polyester-modified epoxy systems. Further, in 10 and 20% unsaturated polyester-modified systems, most of the bismaleimide will undergo the Michael addition reaction with amine²⁹ and hydroxyl groups³⁰ due to a lesser number of double bonds available for crosslinking, which also plasticize the matrix, and in turn, reduce the tensile strength. Iisaka has also observed higher values of tensile strength for a 50/50 composition of epoxy and bismaleimide-allyl ester comonomer IPN.^{31,32}

The highest tensile value of 68 MPa, higher than the original value 61.6 MPa of unmodified epoxy, is obtained from the modified epoxy system with a combination of 30% unsaturated polyester and 15% bismaleimide (System K). The lowest tensile value of 54.7 MPa is obtained for the (System J) epoxy system modified with 20% unsaturated polyester and 15% bismaleimide. The other

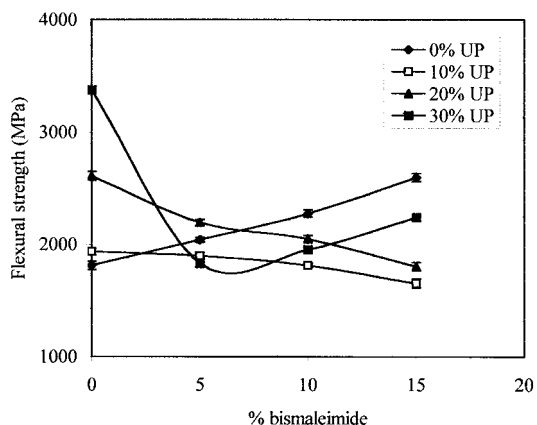


Figure 9 Effect of BMI on flexural modulus.

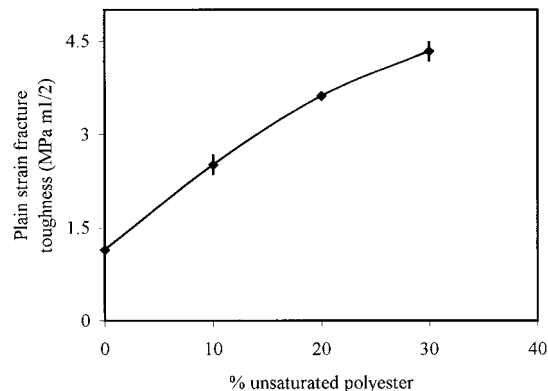


Figure 10 Effect of unsaturated polyester on fracture toughness.

systems (E to M) exhibit tensile behavior between the above two extremes (66.5 MPa and 54.7 MPa).

Flexural Properties

Flexural behaviors of unmodified epoxy resin, epoxy modified with unsaturated polyester, bismaleimide, and combinations of both are presented in Table I and Figures 6–9. Introduction of 10, 20, and 30% unsaturated polyester (by weight) into epoxy resin (systems B, C, and D) enhances the flexural strength (Fig. 6) by 5.1, 21.7, and 30.9%, respectively, when compared with the unmodified epoxy system (A). This may be attributed to physical entanglement between unsaturated polyester and the epoxy matrix, which in turn, enhances the mechanical properties. Similarly, the incorporation of 5, 10, and 15% bismaleimide incorporation into the unmodified epoxy system enhances the value of flexural strength by 1.1, 15.7, and

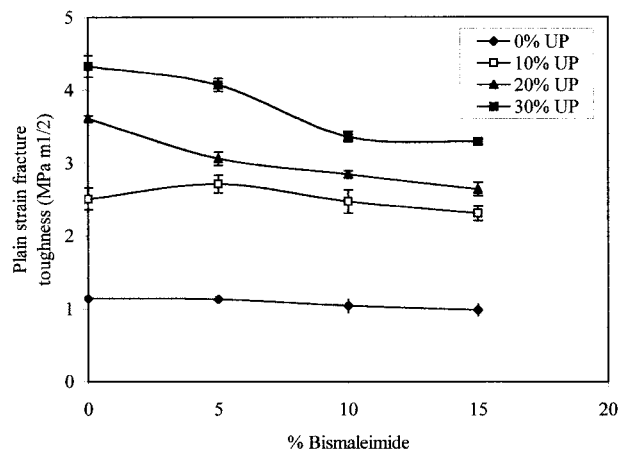


Figure 11 Effect of BMI on fracture toughness.

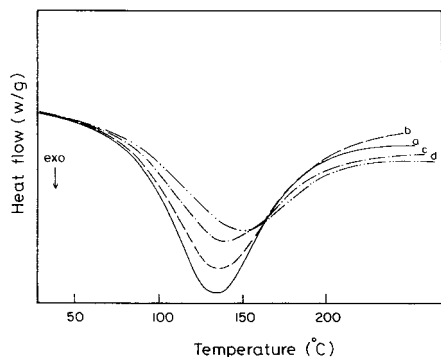


Figure 12 DSC cure exothermic curves of epoxy-unsaturated polyester (30% by weight) modified with (a) 0% bismaleimide, (b) 5% bismaleimide, (c) 10% bismaleimide, (d) 15% bismaleimide.

20.5%, respectively, due to the rigidity imparted by the bismaleimide network. However, the bismaleimide incorporated unsaturated polyester-modified epoxy resin systems (E to L) have decreased values of flexural strength, as observed in the case of tensile strength, due to branching with more free volume, which affects close packing of molecules in addition to plasticization effect. The highest value of 127 Mpa is observed for the system M with 30% (by weight) unsaturated polyester and 15% (by weight) bismaleimide, and the lowest value of 88 Mpa is observed in the case of system G with 10% (by weight) unsaturated polyester and 15% (by weight) bismaleimide.

Fracture Toughness

The values of plain strain fracture toughness obtained for unmodified epoxy, epoxy modified with

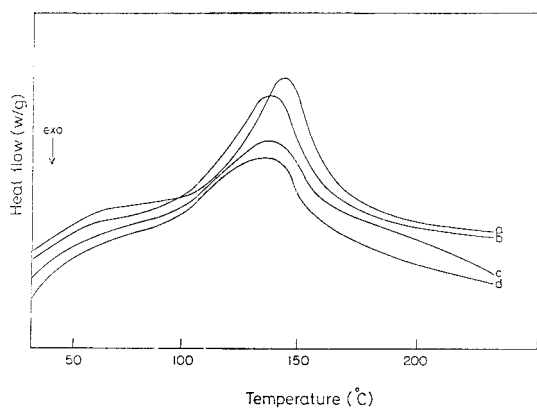


Figure 13 Glass transition temperatures of epoxy modified with (a) 0% polyester, (b) 10% polyester, (c) 20% polyester, (d) 30% polyester.

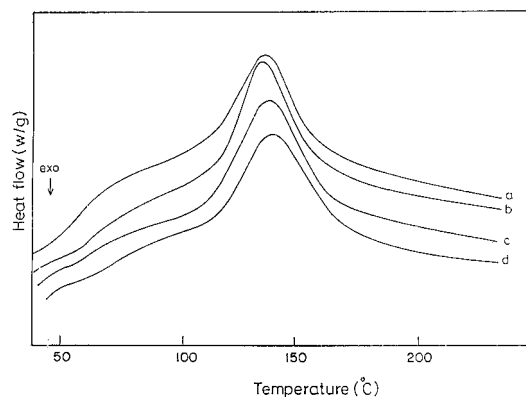


Figure 14 Glass transition temperature of epoxy/unsaturated polyester (30% by weight)/bismaleimide blends on various bismaleimide concentrations: (a) 0% bismaleimide, (b) 5% bismaleimide, (c) 10% bismaleimide, and (d) 15% bismaleimide.

unsaturated polyester, bismaleimide, and combinations of both are presented in Figures 10 and 11. From Figure 10 it is observed that the incorporation of unsaturated polyester into epoxy resin enhances the toughness according to the percentage content of unsaturated polyester due to the excess free volume with high-energy absorption. The influence on toughness by unsaturated polyester shows increases of 120, 216, and 279% for the unsaturated polyester concentrations of 10, 20, and 30% (by weight), respectively. A noticeable (steep) increase (Fig. 10) in the values is observed. From Figure 11 it is observed that the incorporation of 5, 10, and 15% bismaleimide into

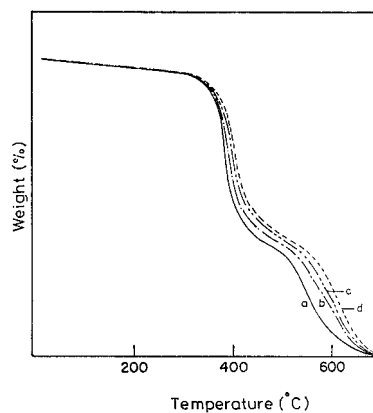


Figure 15 Thermograms of (a) unmodified epoxy, (b) epoxy-unsaturated polyester (30% by weight) blend, and epoxy-unsaturated polyester with (c) 5% bismaleimide, (d) 10% bismaleimide, and (e) 15% bismaleimide.

unsaturated polyester-modified epoxy systems decreases the toughness behavior due to formation of an intercrosslinked network and rigid molecular structure. The increase in toughness behavior is most evident in the case of the 30 wt % unsaturated polyester-modified system. This also can be explained as being due to the higher crosslinking imparted by more double bonds present at the higher concentration of unsaturated polyester (30% by weight).

Thermal Characteristics

The curing exotherms of unsaturated polyester-modified epoxy resin and bismaleimide incorporated unsaturated polyester-epoxy resins are presented in Figure 12. All the modified systems show exothermic peaks at higher and broader temperatures than the unmodified epoxy systems. The peak maximum temperature and peak area increase due to the restricted chain mobility of the network with increasing concentration of bismaleimide.

The glass transition temperatures of unsaturated polyester-modified epoxy resin are presented in Figure 13. The value of T_g is lowered with increasing unsaturated polyester concentration due to the reduced crosslink density caused by the unsaturated polyester chains. T_g values of both unmodified epoxy, and bismaleimide-incorporated unsaturated polyester (30% by weight)-modified epoxy resin are increased with an increase in bismaleimide content (Fig. 14).

Thermograms (TGA) of bismaleimide-incorporated unsaturated polyester-modified epoxy systems are presented in Figure 15. The bismaleimide-modified epoxy-unsaturated polyester shows two thermal degradation temperatures, one at 600°C and the other at 350°C. The degradation temperature increases with increasing bismaleimide concentration. The delay in degradation is due to the thermally stable aromatic heterocyclic nature of bismaleimide.

CONCLUSION

The mechanical properties of these epoxy systems increase with increasing unsaturated polyester content in the epoxy matrix due to the chain entanglement and network formation at the expense of thermal properties. The introduction of bismaleimide into the unsaturated polyester-modified epoxy matrix system is found to increase

the stress-strain properties, glass transition temperature, and thermal degradation temperature at higher concentration of unsaturated polyester, whereas the plain strain fracture toughness decreases with increasing bismaleimide concentration. Among the different combinations of matrix systems studied, the matrix system M is the best combination, because it exhibits higher strength properties associated with improvement in toughness and thermal behavior than all the other systems. This matrix system can be used to fabricate advanced composite components of improved toughness with better thermo-mechanical behavior for engineering applications.

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