

Preparation and Characterization of Siliconized Epoxy/Bismaleimide (*N,N'*-Bismaleimido-4,4'-diphenyl methane) Intercrosslinked Matrices for Engineering Applications

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ABSTRACT: Novel hybrid intercrosslinked networks of hydroxyl-terminated polydimethylsiloxane-modified epoxy and bismaleimide matrix systems have been developed. Epoxy systems modified with 5, 10, and 15 wt % of hydroxyl-terminated polydimethylsiloxane (HTPDMS) were developed by using epoxy resin and hydroxyl-terminated polydimethylsiloxane with γ -aminopropyltriethoxysilane (γ -APS) as compatibilizer and dibutyltindilaurate as catalyst. The reaction between hydroxyl-terminated polydimethylsiloxane and epoxy resin was confirmed by IR spectral studies. The siliconized epoxy systems were further modified with 5, 10, and 15 wt % of bismaleimide (BMI). The matrices, in the form of castings, were characterized for their mechanical properties. Differential scanning calorimetry and thermogravimetric analysis of the matrix samples were also performed to determine the glass-transition temperature and thermal-degradation temperature of the systems. Data obtained from mechanical studies and thermal characterization indicate that the introduction of siloxane into epoxy improves the toughness and thermal stability of epoxy resin with reduction in strength and modulus values. Similarly the incorporation of bismaleimide into epoxy resin improved both tensile strength and thermal behavior of epoxy resin. However, the introduction of siloxane and bismaleimide into epoxy enhances both the mechanical and thermal properties according to their percentage content. Among the siliconized epoxy/bismaleimide intercrosslinked matrices, the epoxy matrix having 5% siloxane and 15% bismaleimide exhibited better mechanical and thermal properties than did matrices having other combinations. The resulting siliconized (5%) epoxy bismaleimide (15%) matrix can be used in the place of unmodified epoxy for the fabrication of aerospace and engineering composite components for better performance. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 38–46, 2001

Key words: epoxy resin; bismaleimide; polydimethylsiloxane; siliconized epoxy; glass-transition temperature; plain strain fracture toughness

INTRODUCTION

The need for the development of lightweight modified composite systems characterized by good

fracture toughness, high impact strength, high thermal stability, and improved mechanical properties has become increasingly evident, to utilize them in the place of conventional structural materials for high-performance engineering and aerospace applications.¹ Epoxy resin is a versatile and widely accepted matrix material for the fabrication of advanced composites, hardware components, electronic circuit board materials,

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Table I Composition of Curing Agent, Compatibilizer, and Catalyst

Epoxy (wt %)	Siloxane (wt %)	Amount of Curing Agent (g)	Compatibilizer (g)	Catalyst (g)
100	0	27	—	—
100	5	27	0.05	0.1
100	10	27	0.09	0.1
100	15	27	0.14	0.1

sealants, radomes, and missile equipment components because of its excellent bonding, physico-chemical, thermal, mechanical, dielectric, and aging characteristics.²⁻⁷

Toughening of epoxy resin is mainly carried out 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 toughening agents for epoxy resins.^{8,9} The resulting products have good impact behavior but inferior strength properties and are unsuitable for high-performance engineering applications. However, these materials can be used in application areas connected with structural adhesives, corrosion, and weather-resistant coatings.

A suitable polymeric toughening material is needed to retain the desirable properties of epoxy resin, like stiffness and glass-transition temperature, and at the same time to improve impact resistance and enhanced strain to fracture. To achieve this, development of an intercrosslinked polymer network with both flexible and rigid molecular segments can be considered as an attractive method. Hydroxyl-terminated polydimethylsiloxane and bismaleimide are selected to provide flexible and rigid segments, respectively, to the epoxy system.

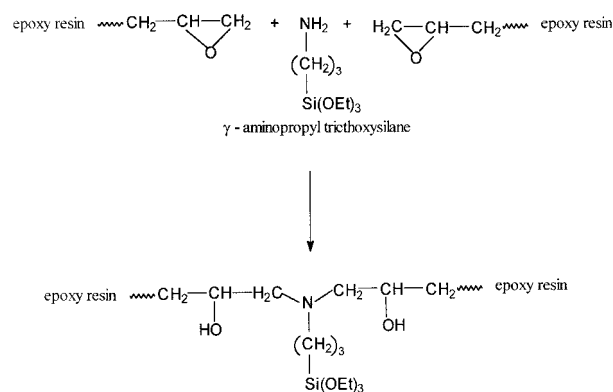
Among the different elastomeric materials used for toughening of epoxy resin, it is expected that the hydroxyl-terminated polydimethylsiloxane is the most suitable polymer because of its versatile behavior, for example, flexibility resulting from —Si—O—Si— linkage, high thermal and thermo-oxidative stability, high moisture resistance, good dielectric properties, and excellent UV and chemical resistance.¹⁰⁻¹⁸ In our earlier work, it was observed that siloxane incorporation into epoxy resin improves impact strength with insignificant change in glass-transition behavior but reduces stress-strain properties.¹⁹

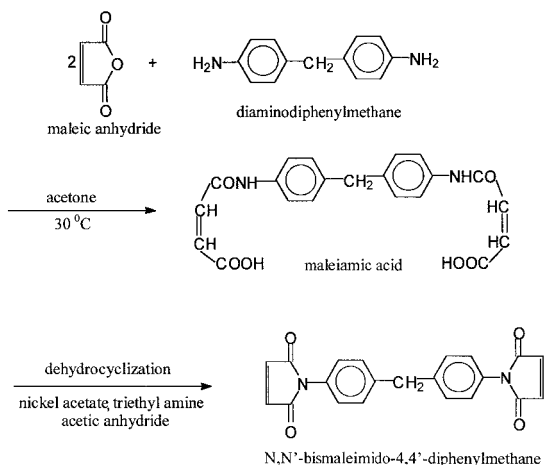
Improvement in thermomechanical properties of epoxy resin was observed by the introduction of bismaleimide.²⁰⁻²⁴ Bismaleimides possess high crosslinking ability, high glass-transition temperature, high thermal stability, high char yield, excellent fire resistance, superior specific strength and specific modulus, and low water absorption. Hence, in the present study, an attempt was made to improve both toughness and thermomechanical behavior of epoxy resin by forming an intercrosslinked network with hydroxyl-terminated polydimethylsiloxane and bismaleimide.

EXPERIMENTAL

Materials

Epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] LY556 (epoxy equivalent about 180–190, viscosity about 10,000 cP) and 4,4-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy (India). *N,N'*-Bismaleimido-4,4'-diphenyl methane and hydroxyl-terminated polydimethylsiloxane (molecular weight 17,000–18,000, viscosity 800–900 cP) were prepared by previously reported procedures.²⁵ The hydroxyl-terminated polydimethylsiloxane (HTPDMS) used in the

**Scheme 1** Preparation of siliconized epoxy resin.



Scheme 2 Synthesis of *N,N'*-bismaleimido-4,4'-diphenyl methane.

present study was synthesized from octamethylcyclotetrasiloxane by the ring-opening polymerization technique. The compatibilizer γ -aminopropyltriethoxysilane (γ -APS) and dibutyltindilaurate catalyst were obtained from Union Carbide (New York, NY) and Merck (Darmstadt, Germany), respectively.

Preparation of Siliconized Epoxy Prepolymer

A fixed amount of epoxy resin, varying amounts of HTPDMS, and stoichiometric amounts of γ -APS (with respect to hydroxyl groups of HTPDMS) and dibutyltindilaurate catalyst (Table I) were thoroughly mixed at 90°C for 10 min with constant stirring (see Scheme 1). The product was then degassed to remove ethanol formed during the condensation reaction between γ -APS and HTPDMS.

Preparation of *N,N'*-Bismaleimido-4,4'-diphenyl methane

Bismaleimide was prepared according to previously reported procedures.²⁶ The reaction scheme for the preparation of bismaleimide is given in Scheme 2.

Preparation of Siliconized Epoxy/Bismaleimide Blend

The stoichiometric amount of 4,4'-diaminodiphenylmethane was dissolved into siliconized epoxy at 90°C under vigorous stirring. After complete dissolution, the calculated amount of *N,N'*-bismaleimido-4,4'-diphenyl methane was added. The agitation was continued at 100°C until a homoge-

neous product 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 postcured at 180°C for 2 h and finally removed from the mold and characterized.

Test Methods

The IR spectra were recorded on a Perkin-Elmer 781 infrared spectrometer (Perkin-Elmer, Palo Alto, CA) and are presented in Figure 1.

The tensile (stress-strain) properties were determined using dog bone-shaped specimens according to ASTM-D3039, using an Instron testing machine (Model 6025; Instron, UK), at a cross-head speed of 2 mm/min. The flexural strength was measured as per ASTM-D790. 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. The results are presented in Table II and Figures 2–11.

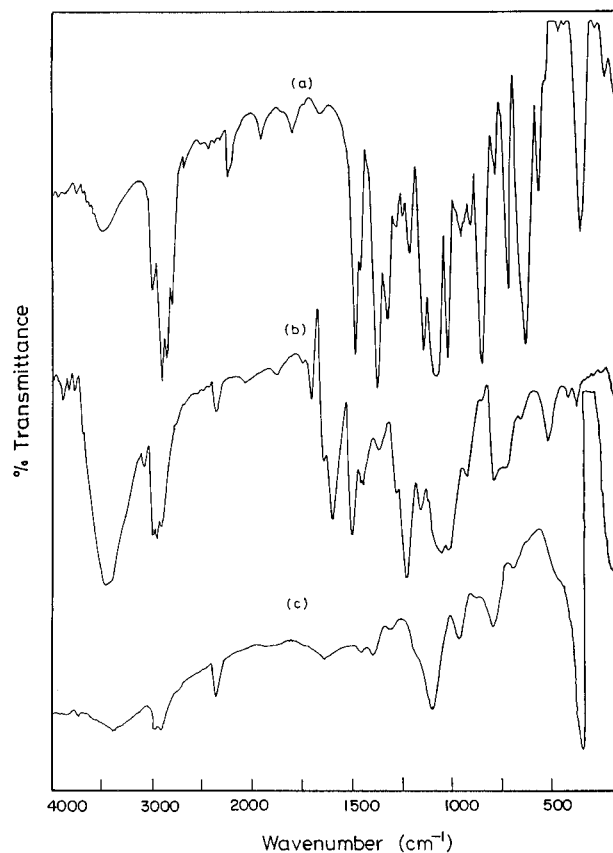


Figure 1 IR spectra of (a) unmodified epoxy, (b) γ -APS-cured epoxy, and (c) γ -APS.

Table II Mechanical Properties of Epoxy, Siliconized Epoxy, BMI-Modified Epoxy, and BMI-Modified Siliconized Epoxy Systems

Matrix System	Epoxy/HTPDMS/BMI ^a Composition	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Plain Strain Fracture Toughness (MPa m ^{1/2})
A	100/00/00	63.2 ± 9	2751.7 ± 39	110.0 ± 10	1812.9 ± 42	1.14 ± 0.10
B	100/05/00	40.1 ± 3	2272.9 ± 30	70.6 ± 6	1735.4 ± 39	2.31 ± 0.05
C	100/10/00	33.6 ± 4	2119.9 ± 29	52.3 ± 4	1710.9 ± 28	2.61 ± 0.04
D	100/15/00	26.6 ± 5	1852.1 ± 40	49.1 ± 2	1373.4 ± 31	2.93 ± 0.15
E	100/05/05	44.4 ± 3	2405.4 ± 25	83.8 ± 3	1854.1 ± 40	1.91 ± 0.10
F	100/05/10	57.2 ± 4	2509.4 ± 32	88.8 ± 4	2050.3 ± 25	1.47 ± 0.06
G	100/05/15	61.8 ± 2	2638.9 ± 39	101.0 ± 7	2099.3 ± 27	1.31 ± 0.07
H	100/10/05	39.0 ± 2	2206.3 ± 42	64.9 ± 3	1795.2 ± 32	2.06 ± 0.09
I	100/10/10	46.6 ± 5	2470.2 ± 31	74.0 ± 3	1814.9 ± 29	1.80 ± 0.08
J	100/10/15	50.9 ± 3	2550.6 ± 29	78.0 ± 5	1863.9 ± 41	1.54 ± 0.05
K	100/15/05	31.6 ± 3	1903.1 ± 27	60.2 ± 4	1434.2 ± 37	2.17 ± 0.06
L	100/15/10	39.0 ± 2	2079.7 ± 49	70.7 ± 3	1652.9 ± 27	1.96 ± 0.03
M	100/15/15	43.0 ± 5	2177.8 ± 36	75.0 ± 5	1672.6 ± 31	1.69 ± 0.07
N	100/00/05	66.2 ± 9	2820.4 ± 40	111.3 ± 9	2040.5 ± 41	1.13 ± 0.05
O	100/00/10	71.0 ± 4	2876.3 ± 31	127.3 ± 7	2275.9 ± 32	1.04 ± 0.09
P	100/00/15	85.4 ± 5	3053.9 ± 37	132.6 ± 5	2596.8 ± 35	0.98 ± 0.08

^a HTPDMS, hydroxyl-terminated polydimethyl siloxane; BMI, *N,N'*-bismaleimido-4,4'-diphenyl methane.

Glass-transition temperatures (T_g) of the samples were determined using a DSC 2910 (TA Instruments) 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 a Thermal Analyst 2000 (TA Instruments) at a heating rate of 10°C min⁻¹. The results are presented in Figures 12–14.

The viscosities of the unmodified epoxy and siliconized epoxy prepolymer were measured at 30°C on a cone-and-plate setup with a 2.4-cm cone diameter at a 3° angle.

RESULTS AND DISCUSSION

Spectral Analysis

The formation of a siliconized epoxy network structure proceeds in two steps and is evaluated by IR (Fig. 1). The first step involves the reaction between the epoxide ring of the epoxy resin and the amino group of γ -APS, and is confirmed by the disappearance of the epoxy band at 913 cm⁻¹ and the appearance of a hydroxyl band at 3420 cm⁻¹. Absorption peaks appeared at 2980, 2850, and 1370 cm⁻¹, which confirm the presence of —Si—O—CH₂CH₃ and —Si—(CH₂)₃—, respectively. In the second step the alkoxy groups present in the γ -APS react with the hydroxyl groups of HTPDMS. From Table III, it is observed that the viscosity of epoxy resin increases with increasing siloxane content, which implies that the siliconization of epoxy resin is effective.

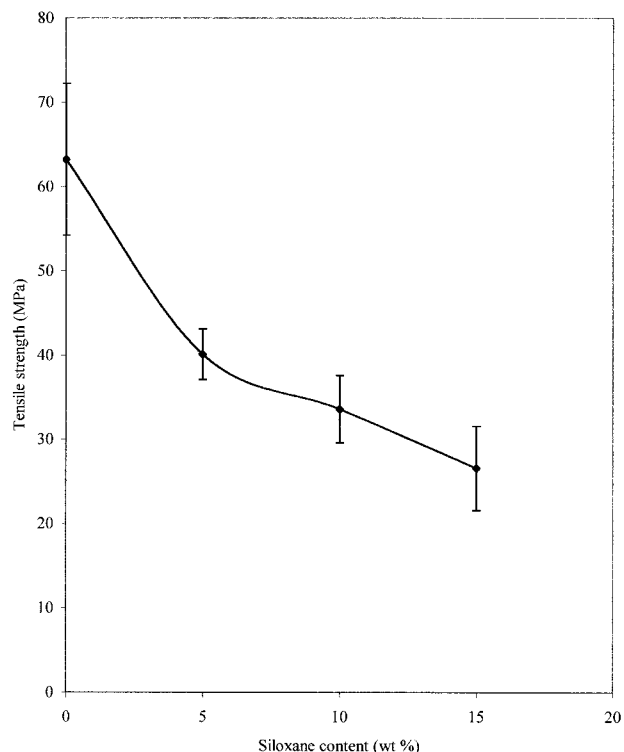


Figure 2 Effect of siloxane content on tensile strength of epoxy system.

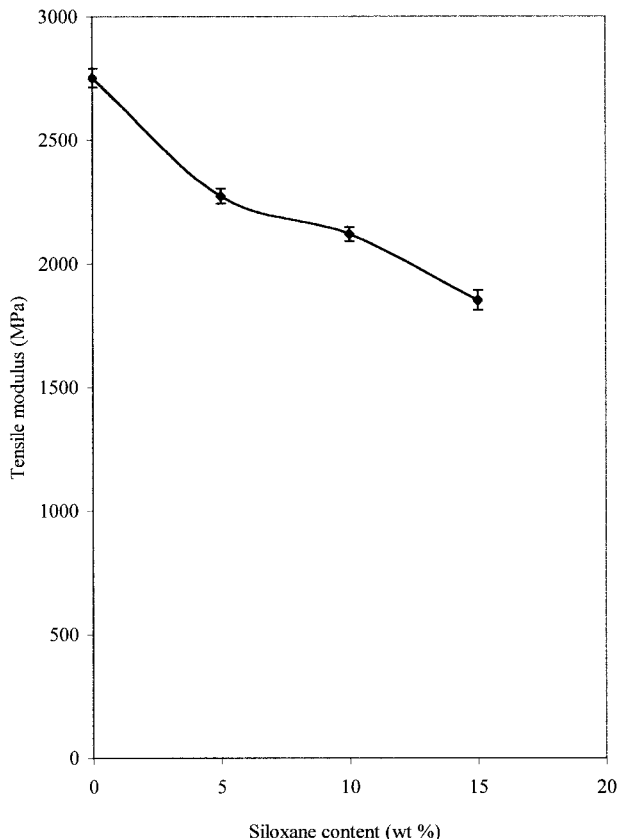


Figure 3 Effect of siloxane content on tensile modulus of epoxy system.

Tensile Properties

Tensile strength values of epoxy and siliconized epoxy modified with bismaleimide (matrix systems A to P) are presented in Table II. Introduction of 5, 10, and 15 wt % siloxane into epoxy resin (systems B, C, and D) decreases the tensile strength (Fig. 2) by 36.6, 46.8, and 57.9%, respectively, compared with that of unmodified epoxy (system A), a result that may be explained by the flexible Si—O—Si skeleton. In contrast to the introduction of siloxane, the 5, 10, and 15% bismaleimide incorporation into epoxy resin (systems N, O, and P) enhances the tensile strength (Fig. 4) by 4.7, 12.3, and 35.1%, respectively, resulting from the intercrosslinking of bismaleimide with epoxy resin and increase in density of crosslinking. However, the introduction of a combination of both siloxane and bismaleimide into epoxy resins (systems E to M) alters the tensile strength according to their percentage content (Fig. 4). Tensile strength values increase with increasing bismaleimide content, which is the result of the formation of an intercrosslinking network between

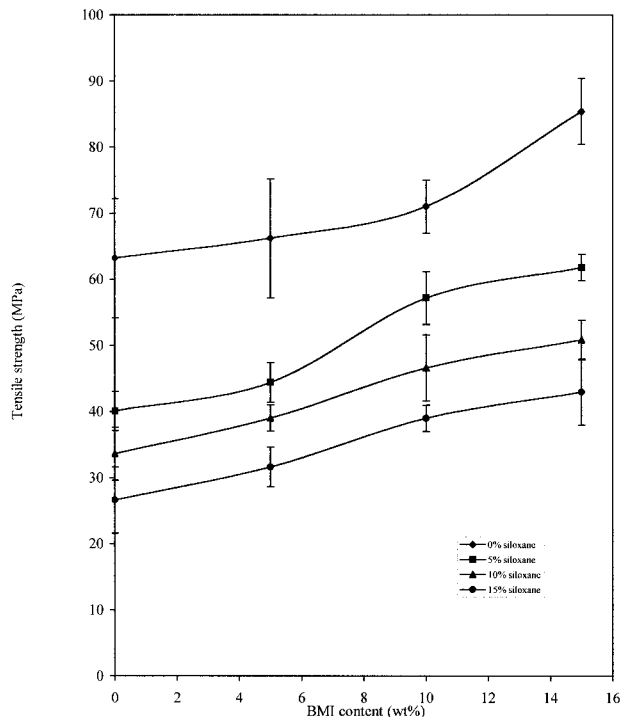


Figure 4 Effect of BMI content on tensile strength of epoxy and siliconized epoxy systems.

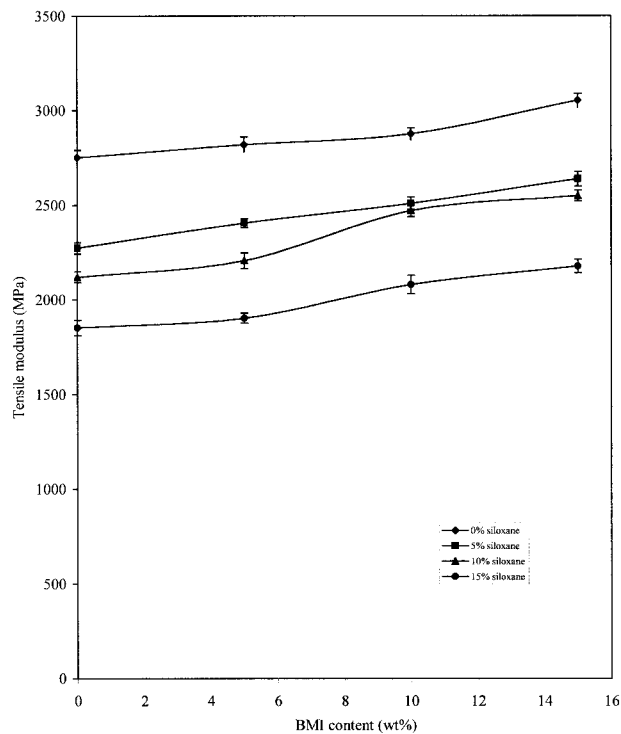


Figure 5 Effect of BMI content on tensile modulus of epoxy and siliconized epoxy systems.

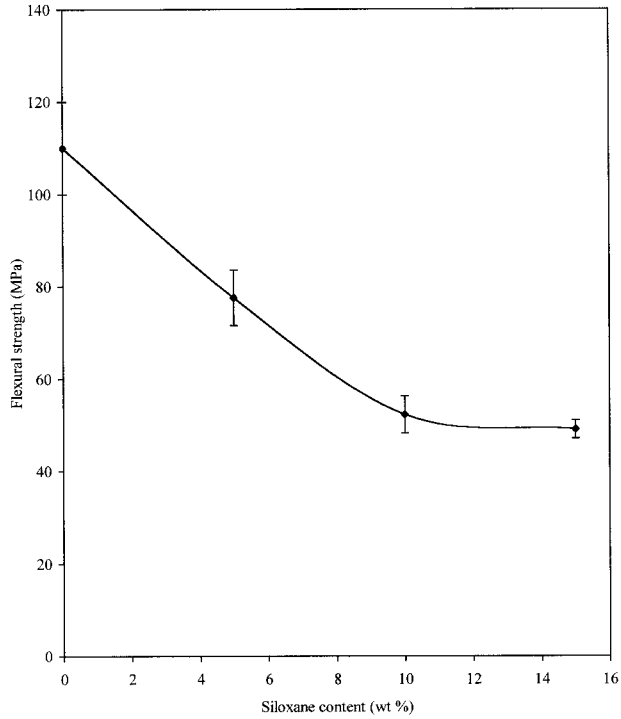


Figure 6 Effect of siloxane content on flexural strength of epoxy system.

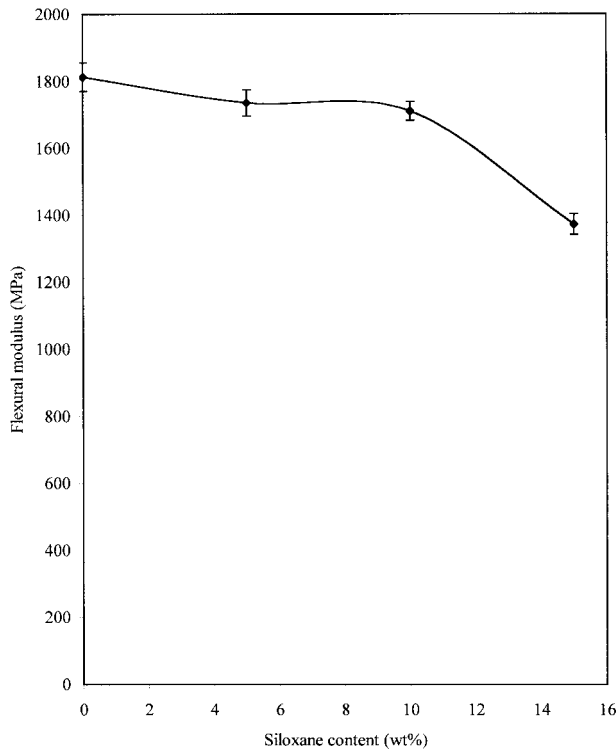


Figure 7 Effect of siloxane content on flexural modulus of epoxy system.

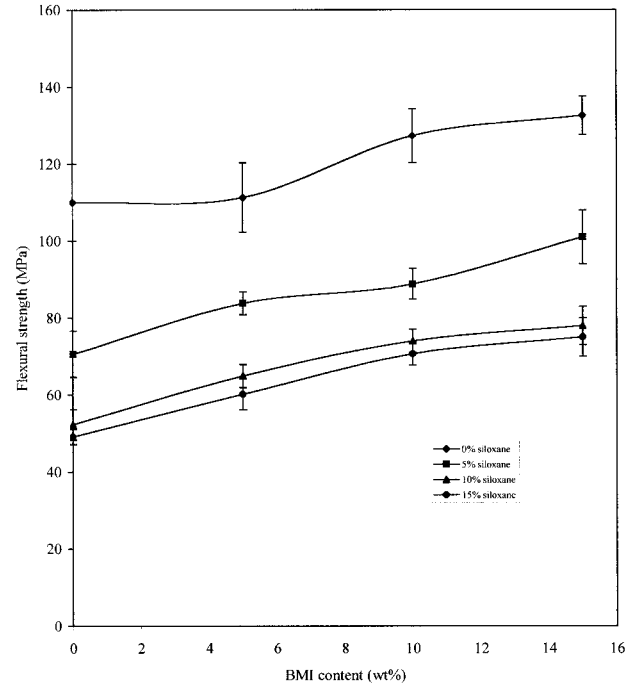


Figure 8 Effect of BMI content on flexural strength of epoxy and siliconized epoxy systems.

bismaleimide and the siliconized epoxy system. The highest tensile value, 61.8 MPa, close to that of the original value 63.2 MPa of unmodified epoxy, is obtained from the modified epoxy system with a combination of 5% siloxane and 15% bismaleimide (system G), resulting from the presence of a higher percentage of bismaleimide, which in turn increases the crosslinking density. Similarly, the lowest tensile value, 31.6 MPa, is obtained for the system K epoxy system modified with 15% siloxane and 5% bismaleimide. The other systems (E, F, H, I, J, L, and M) exhibit tensile behavior between the above-noted two extremes (61.8 and 31.6 MPa). The values of tensile modulus obtained for the unmodified epoxy and epoxy modified with siloxane, bismaleimide, and combinations of both are presented in Table II and exhibit a similar trend to that of tensile strength (Figs. 3 and 5).

Flexural Properties

Flexural behaviors of unmodified epoxy and epoxy modified with siloxane, bismaleimide, and combinations of both are presented in Table II and Figures 6–9. Introduction of 5, 10, and 15 wt % siloxane into epoxy resin (systems B, C, and D) decreases the flexural strength (Fig. 6) by 35.8,

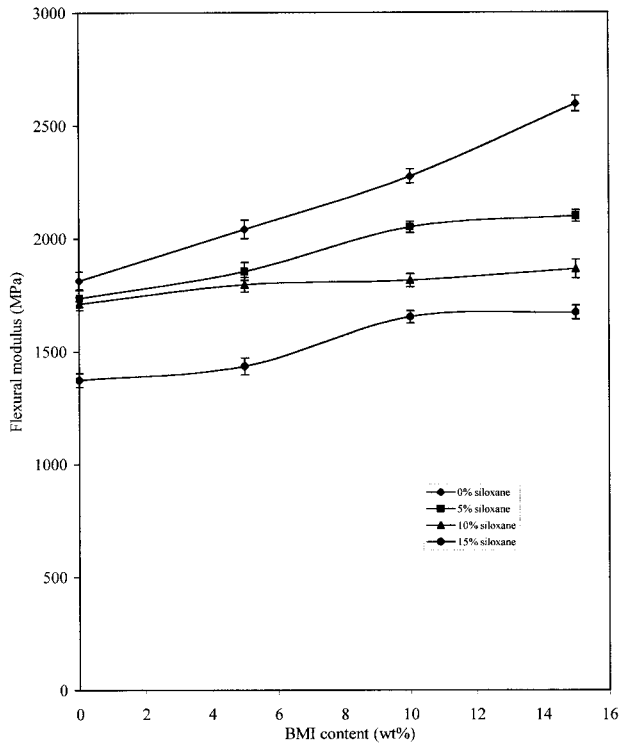


Figure 9 Effect of BMI content on flexural modulus of epoxy and siliconized epoxy systems.

52.5, and 55.4%, respectively, compared with that of the unmodified epoxy system (system A). This may be attributed to the weak interface boundary between siloxane and epoxy matrix, whereas bismaleimide incorporation into the epoxy system enhances the flexural strength by 1.2, 15.7, and 20.5% for 5, 10, and 15 wt %, respectively, resulting from the formation of an intercrosslinking network between bismaleimide and epoxy resin (Fig. 8). In the cases of combination of both siloxane and bismaleimide introduction into epoxy, the flexural property varies according to their percentage concentrations, similar to the effect observed in the case of tensile properties (Fig. 8). An approximately 45% loss of flexural value is noticed with incorporation of 15% siloxane and 5% bismaleimide (system K), whereas an 8.2% loss is observed for the system containing 5% siloxane and 15% bismaleimide (system G). For other systems (E, F, G, H, I, J, L, and M) the percentage loss of flexural value lies between 19.3 and 41%. The flexural modulus follows a similar trend to that of flexural strength (Figs. 7 and 9).

Fracture Toughness

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

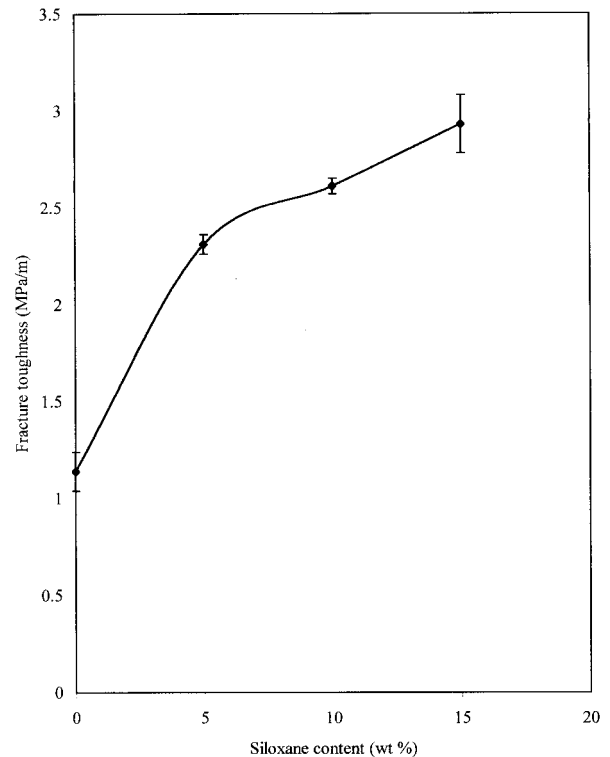


Figure 10 Effect of siloxane content on plain strain fracture toughness of epoxy system.

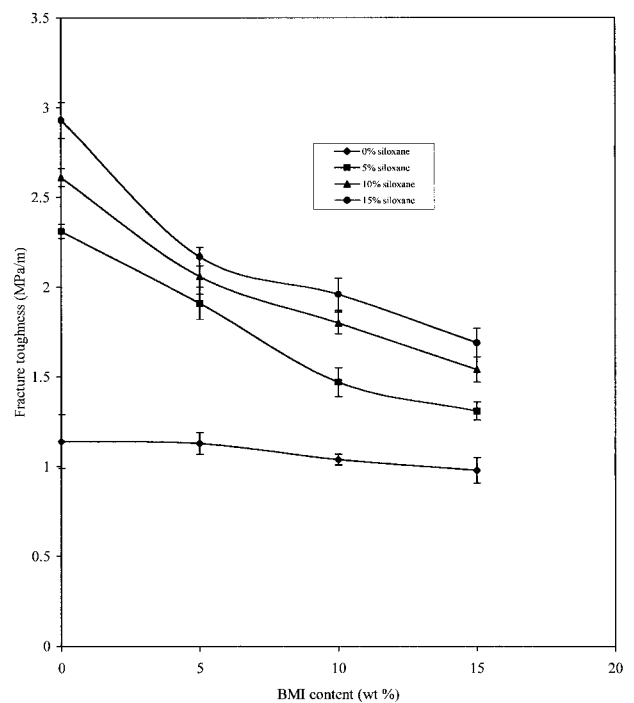


Figure 11 Effect of BMI content on plain strain fracture toughness of epoxy and siliconized epoxy systems.

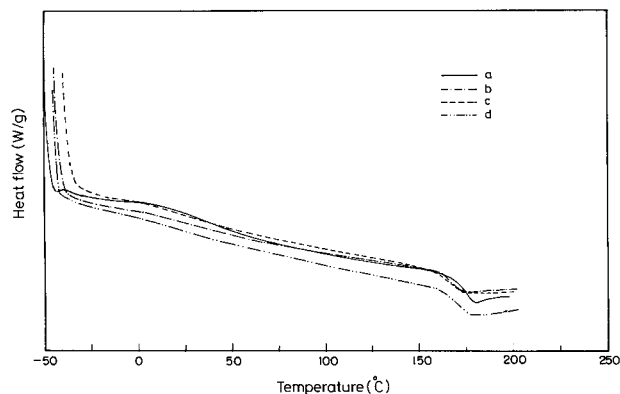


Figure 12 DSC traces of epoxy and siliconized epoxy systems: (a) system A; (b) system B; (c) system C; (d) system D.

with siloxane, bismaleimide, and a combination of both are presented in Table II and Figures 10 and 11. Siloxane incorporation into epoxy resin enhances the toughness according to the percentage content of siloxane that results from high-energy absorption and the resilient behavior of the flexible siloxane molecule. The influence of toughness by siloxane varies as 102, 129.5, and 157.5% for the siloxane concentrations of 5, 10, and 15%, respectively. A noticeable (steep) increase (Fig. 10) is observed for 5% siloxane introduction when compared with the gradual increase observed for higher concentrations (10 and 15% siloxane). Incorporation of 5, 10, and 15 wt % bismaleimide into epoxy (systems N, O, and P) decreases the toughness behavior by 2.8, 8.3, and 13.9%, respectively, as a result of an intercrosslinked network formation, which in turn enhances crosslinking

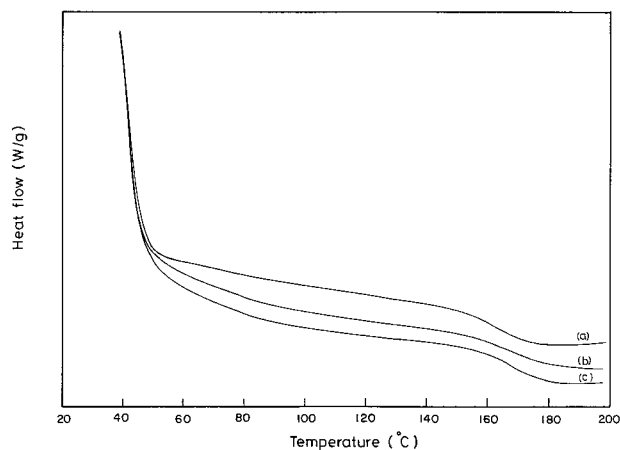


Figure 13 DSC traces of 10% siliconized epoxy/BMI systems: (a) system H; (b) system I; (c) system J.

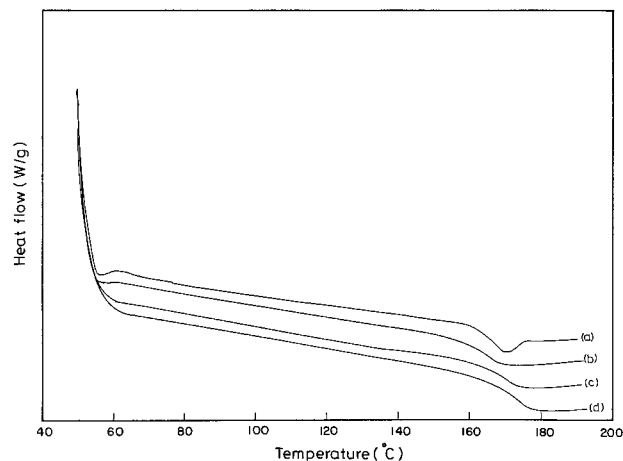


Figure 14 DSC traces of bismaleimide-modified epoxy systems: (a) system A; (b) system N; (c) system O; (d) system P.

density. The highest improvement (90.7%) of plain strain fracture toughness is observed in the case of system K and the lowest improvement (14.7%) is observed in the case of system G.

Thermal Characteristics

DSC thermograms of epoxy and siliconized epoxy modified with different percentages of bismaleimide are presented in Figures 12–14. All the modified epoxy systems exhibit a single T_g , which implies the presence of an intercrosslinked network. A slight decreasing trend in T_g of the epoxy system is observed with increasing HTPDMS concentration (Fig. 12). T_g values of both epoxy and siliconized epoxy systems modified with bismaleimide are increased with an increase in bismaleimide content (Figs. 13 and 14).

Thermogravimetric analysis of siliconized epoxy bismaleimide systems is presented in Figure 15. The thermal-degradation temperature of the siliconized epoxy/bismaleimide system increases

Table III Viscosity of Siliconized Epoxy Prepolymer

Sample No.	Epoxy/HTPDMS ^a Composition	Viscosity (cP) at 30°C
1	100/00	9200–10,004
2	100/05	14,600–15,700
3	100/10	23,400–24,200
4	100/15	31,300–32,700

^a HTPDMS, Hydroxyl-terminated polydimethyl siloxane.

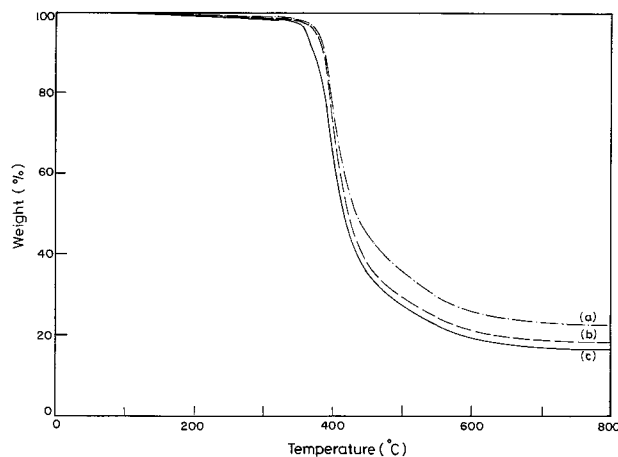


Figure 15 TGA curves of 10% siliconized epoxy/BMI systems: (a) system H; (b) system I; (c) system J.

with increasing bismaleimide concentration, which in turn enhances service temperature. Improvement in thermal stability and glass-transition temperature can be explained as a result of the presence of thermally stable inorganic silicon–oxygen bonds and the heterocyclic aromatic nature of bismaleimide.

CONCLUSIONS

The stress–strain properties of the epoxy system decrease with increasing siloxane content, whereas the plain strain fracture toughness increases with increasing siloxane content.

The stress–strain properties, glass-transition temperature, and thermal-degradation temperature of the siliconized epoxy system increase with increasing bismaleimide concentration, whereas the plain strain fracture toughness decreases with increasing bismaleimide concentration. The single glass transition observed from the DSC studies confirms the presence of a siliconized epoxy/bismaleimide intercrosslinked network.

Among the different matrix systems studied, matrix system G is the best combination, because it exhibits higher strength properties associated with improvement in toughness and thermal behavior than those of all other systems. This matrix system can be used to fabricate advanced composite components of improved toughness and thermomechanical behavior for aerospace and engineering applications.

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