

Mechanical properties of polyethersulfone modified epoxy/3,3'-bis(maleimidophenyl)phenylphosphine oxide (BMI) intercrosslinked matrices

R RAJASEKARAN[†] and M ALAGAR*

Department of Chemical Engineering, Anna University, Chennai 600 025, India

[†]Department of Chemistry, St. Joseph's College of Engineering, Chennai 600 119, India

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Abstract. Novel intercrosslinked networks of polyethersulfone modified epoxy-3,3'-bis(maleimidophenyl) phenylphosphine oxide matrix systems are developed. The polyethersulfone modification of epoxy resin is carried out by using tetramethyl ammonium hydroxide (TMAH) as a catalyst. The polyethersulfone modified epoxy systems are further modified with 4–12% 3,3'-bis(maleimidophenyl) phenylphosphine oxide and cured by using diaminodiphenylmethane. Tensile, flexural, impact properties and dynamic mechanical analysis (DMA) are carried out to assess the mechanical behaviour of the prepared neat resin castings. Mechanical studies indicate that the introduction of polyethersulfone into these epoxy resins improves the toughness without any reduction in the stress–strain values. But, the incorporation of bismaleimide (BMI) into the epoxy resin improves the stress–strain properties with a lowering of the toughness. The introduction of both polyethersulfone and bismaleimide into the epoxy resin influences the mechanical properties according to their content percentages.

Keywords. Epoxy resin; bismaleimide; hydroxyl-terminated polyethersulfone; dynamic mechanical analysis; impact strength; tensile strength; flexural strength.

1. Introduction

Epoxy resins have been noted for some unique properties including outstanding adhesion to various surfaces, lightweight, high strength, extreme durability, stability under UV exposure, and chemical resistance. They are used in aerospace, automobile, land and marine transportation, chemical process industries, electrical and electronic industries, because of their lightweight and good mechanical properties and excellent processability. However, epoxy resins are too brittle, which affect the impact property, life time and durability of the components, to be utilized alone. Therefore, numerous attempts have been made to reduce their brittleness. The introduction of flexible polymers and rubber, predominantly using amino-terminated acrylonitrile-butadiene (ATBN), carboxyl-terminated acrylonitrile-butadiene (CTBN) elastomers, is the general approach to increase the fracture toughness. However, the improvement of these modified materials is invariably accompanied by a significant drop in the modulus and the glass transition temperature (Bucknall and Yoshii 1978; Barlet *et al* 1985; Nir *et al* 1985; Yee and Pearson 1986). The preparation of an interpenetrating network structure

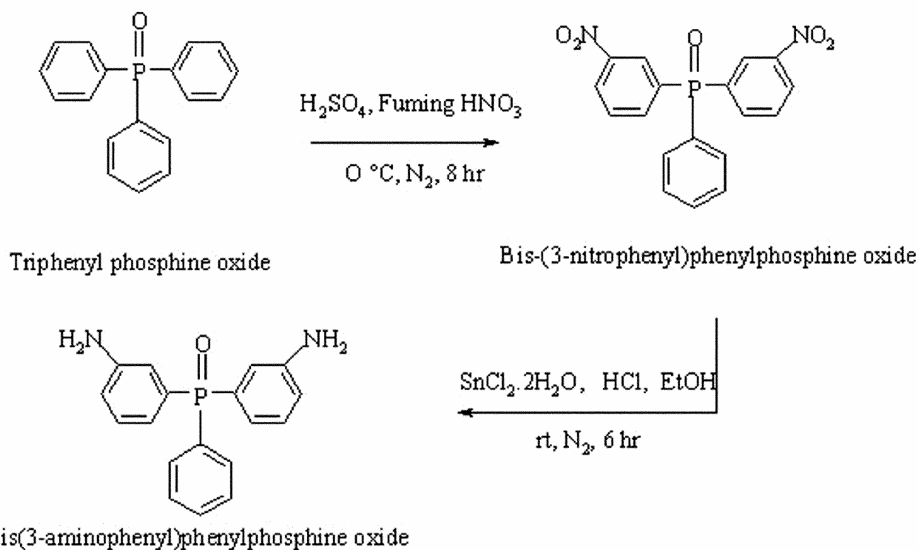
having different polymer skeletons can be considered as an attractive method, since an interpenetrating network mechanism provides matrix materials with single T_g when compared with polymer blends.

Among the different materials used for the modification of epoxy resins, thermoplastics are expected to be the best materials to improve thermomechanical properties (Bucknall and Gilbert 1989; Husang *et al* 1997; Mimura *et al* 2000; Rajasekaran and Alagar 2007), due to their attractive physical, dielectric, thermal, and mechanical characteristics and low water absorption and low volume shrinkage, rendering them the material of choice in high-performance applications. The improvement in thermomechanical properties was observed by the introduction of bismaleimide (BMI) into epoxy resin (Kim *et al* 1995; Han and Li 1998; Han *et al* 1998; Musto *et al* 1998). Recently, we studied the modification of epoxy resin by using polydimethylsiloxane (Ashok Kumar *et al* 2001), unsaturated polyester (Dinakaran and Alagar 2002), polyurethane (Mahesh and Alagar 2003) etc and the results have been published elsewhere.

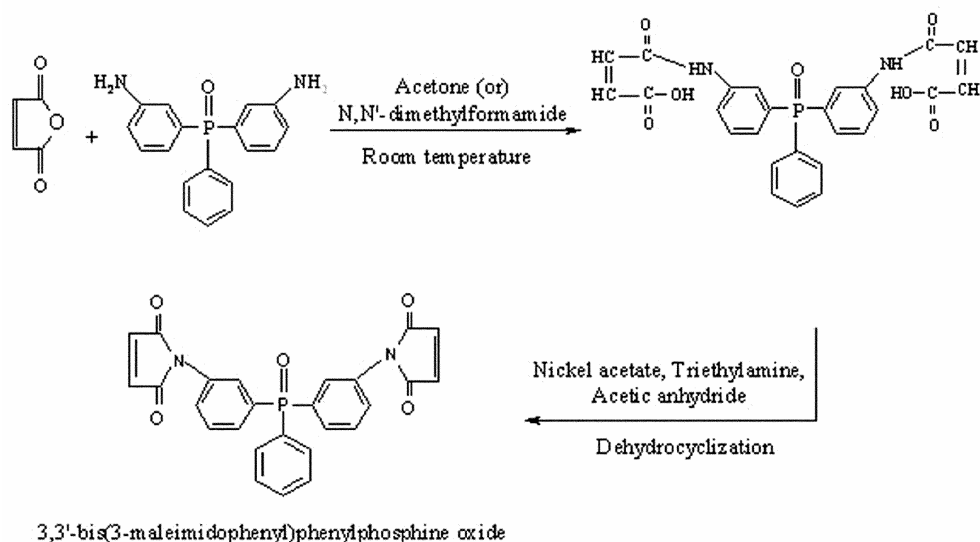
An attempt has been made in the present investigation by incorporating varying percentages of hydroxyl terminated polyethersulfone and bismaleimide as thermoplastic and chemical modifiers, respectively for epoxy resin to obtain hybrid epoxy matrices with improved characteristic

*Author for correspondence (mkalagar@yahoo.com)

STAGE I



STAGE II



Scheme 1. Synthesis of 3,3'-bis(maleimidophenyl)phenylphosphine oxide (BMI).

properties, mainly toughness and thermomechanical properties to utilize them for different industrial and engineering applications for better performance and longevity.

2. Experimental

2.1 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). Hydroxyl terminated polyethersulfone ($\text{Mw} = 1.38 \text{ KDa}$, $T_g = 225^\circ\text{C}$)

received from Jilin University, China was used as received. Bismaleimide (3,3'-bis(maleimidophenyl) phenylphosphine oxide) was prepared according to the reported procedure (Liu *et al* 2001). The synthesis route of bismaleimide is presented in scheme 1. The chemical structures of materials used are presented in figure 1.

2.2 Preparation of bismaleimide modified polyethersulfone epoxy matrices

The hybrid, polyethersulfone modified epoxy matrices, were prepared by dissolving varying percentages (4, 8, 12% by wt) of hydroxyl terminated polyethersulfone in

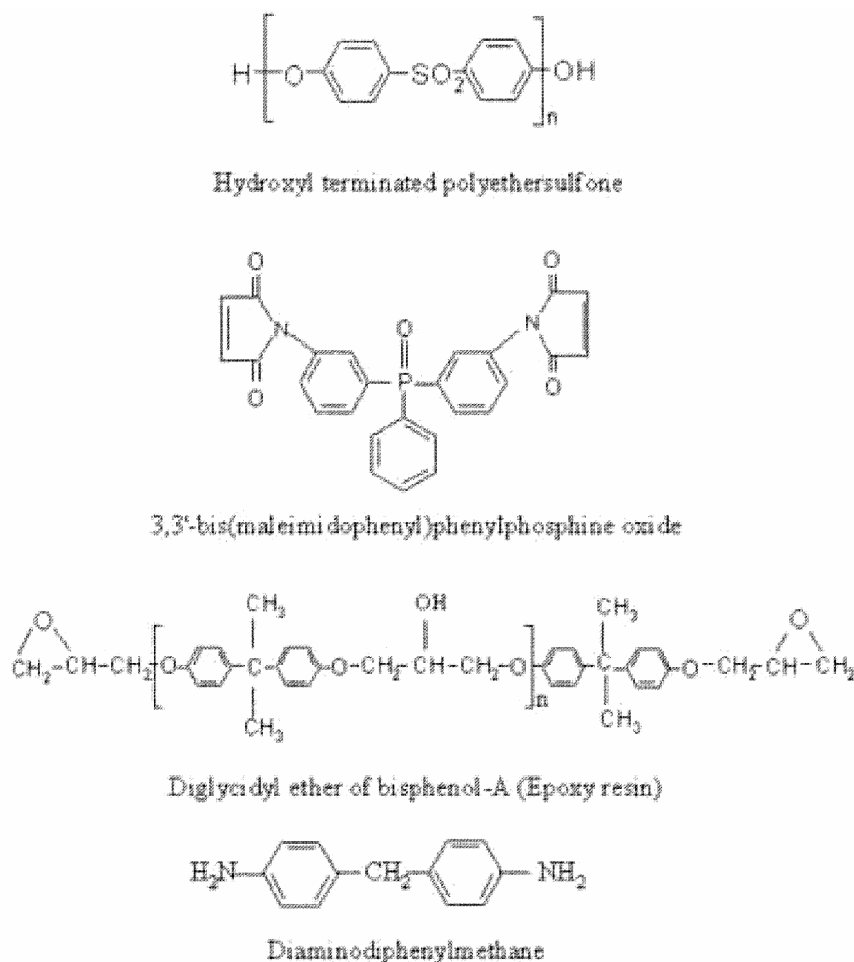


Figure 1. Chemical structures of monomer and oligomer epoxy resins.

epoxy resin using tetra methyl ammonium hydroxide (TMAH) as catalyst with continuous stirring at 150°C for 2 h. The hybrid, polyethersulfone modified epoxy matrix, obtained was degassed under vacuum for 30 min and then cooled to 90°C. Further, the calculated amount of bismaleimide was dissolved into hybrid polyethersulfone-epoxy resin under vigorous stirring followed by the addition of stoichiometric amount of 4,4'-diaminodiphenylmethane curative (with respect to epoxy). The agitation was continued at 100°C until a homogeneous product was obtained. The product (scheme 2) was subjected to vacuum to remove the trapped air and then cast and cured at 120°C for 3 h. The castings were then post cured at 180°C for 2 h and finally removed from the mould and characterized.

2.3 Test methods

The IR spectra for unmodified epoxy, polyethersulfone modified epoxy and bismaleimides incorporated polyethersulfone modified epoxy matrices were recorded on a Perkin-Elmer (Model RX1) FT-IR Spectrometer.

The tensile strength was determined using dog bone-shaped specimens according to ASTM-D3039, using an

Instron testing machine (Model 6025; Instron, UK), at a crosshead speed of 10 mm/min. The flexural properties were measured as per ASTM-D790, using an Instron testing machine (Model 6025 UK), at 10 mm/min cross-head speed. The Izod impact strength was evaluated as per ASTM D-256. Hardness of the specimens was measured using Durometer-type D as per ASTM D2240. As many as five test pieces were used to generate the data points for the mechanical tests.

Dynamic mechanical analyses of the samples were measured by using NETZSCH DMA 242 dynamic mechanical analyser. The experiments were conducted at dynamic strain of 0.3 and frequency of 1 Hz. The results are presented in table 1 and figures 1–3.

3. Results and discussion

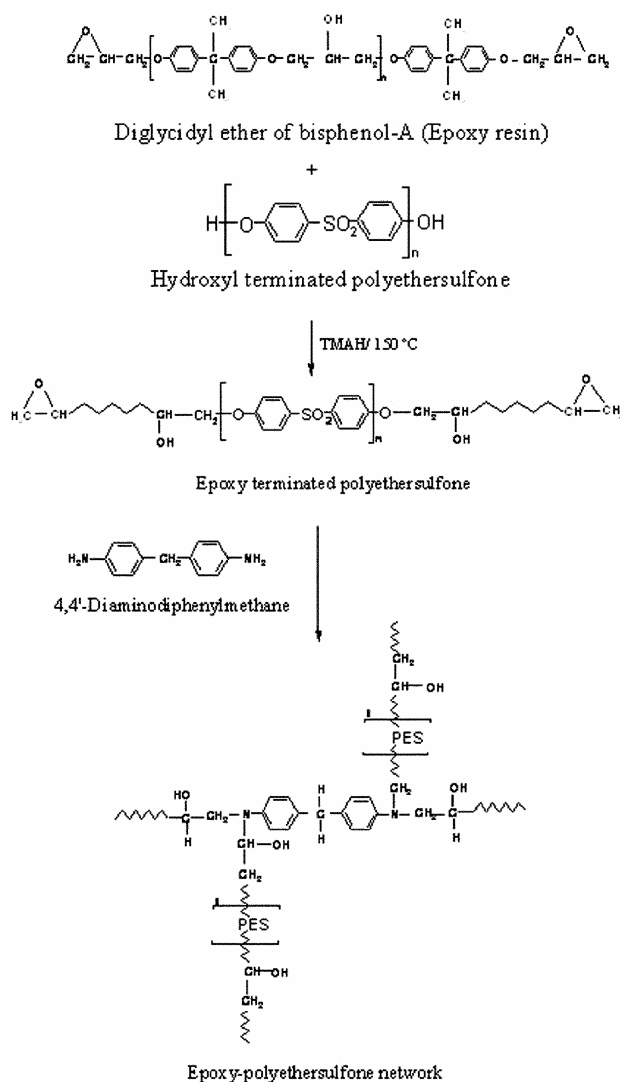
3.1 IR spectroscopy

The formation of interpenetrating network of epoxy and polyethersulfone proceeds through the reaction between hydroxyl terminated polyethersulfone (PSF) oligomer and large molar excess of epoxy resin in the presence of tetramethyl ammonium hydroxide (TMAH). The large excess

of epoxy resin was used to endcap the polyethersulfone oligomers which essentially prevents further polymerization. The disappearance of IR absorption for oxirane ring of epoxy at 914 cm^{-1} was used to ascertain the completion of the reaction (figure 2). The intensity of IR absorption peaks observed for oxirane ring of epoxy (figure 2a) was very high at the initial stage of the reaction. The intensity of the peak for oxirane ring of epoxy disappeared (figure 2c) after the completion of the reaction. This confirms the reaction between epoxy and polyethersulfone and the formation of interpenetrating polymer network structure (IPN).

3.2 Tensile properties

3.2a Polyethersulfone modified epoxy systems: The values of tensile strength of polyethersulfone modified



Scheme 2. Formation of polyethersulfone modified-epoxy-DDM interpenetrating polymer network (IPN).

epoxy matrices cured with DDM are presented in table 1. It is noticed that the introduction of 4%, 8% and 12% polyethersulfone (by wt%) into epoxy resin marginally enhances the values of tensile strength. The little improvement in the values of tensile strength is explained due to the inherent rigid aromatic molecular structure of polyethersulfone and the formation of graft network between epoxy and polyethersulfone. The values of tensile modulus obtained for the unmodified epoxy and polyethersulfone modified epoxy systems are also presented in table 1 and they exhibit similar trends as observed in the case of values of tensile strength.

3.2b Bismaleimide modified polyethersulfone-epoxy systems: The introduction of combination of both polyethersulfone and varying concentrations of bismaleimide into epoxy resin alters the values of tensile strength according to their percentage concentration. The values of tensile strength of bismaleimide modified polyethersulfone-epoxy systems are increased with increasing percentage concentration of bismaleimide due to the formation of inter cross-linking network between the

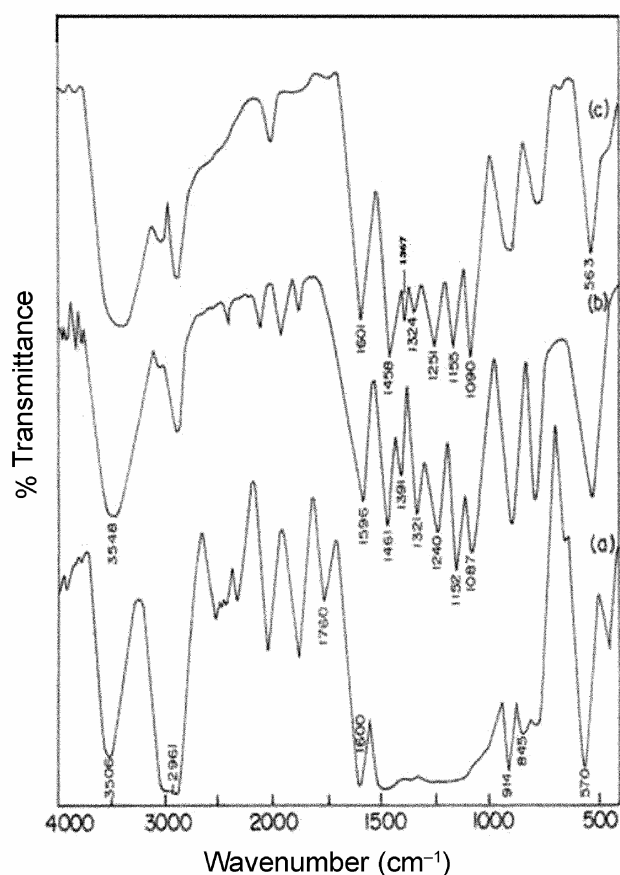


Figure 2. FTIR spectra of (a) unmodified epoxy resin, (b) polyethersulfone, (c) DDM-cured epoxy-polyethersulfone (100 : 20) cured at 140°C for 3 h and postcured at 200°C for 2 h.

Table 1. Mechanical properties of BMI modified epoxy and BMI modified polyethersulfone-epoxy systems.

Composition (wt%)			Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
Epoxy	PES*	BMI*					
100	0	0	61.2	2713.7	104	1753.9	98.3
100	4	0	61.5	2720.5	104.8	1768.5	130.3
100	8	0	62.1	2731.2	105.6	1786.9	142.4
100	12	0	62.9	2748.6	106.9	1815.8	168.1
100	4	4	62.1	2796.8	105.9	1804.3	120.9
100	4	8	62.9	2910.1	108.9	1891.6	118.2
100	4	12	65.8	3010.6	113.8	2020.9	114.2
100	8	4	63.8	2862.6	108.6	1862.5	128.6
100	8	8	65.2	3020.1	110.1	1915.6	123.5
100	8	12	67.9	3185.2	114.6	2050.1	120.6
100	12	4	64.1	2869.2	111.8	1891.5	140.5
100	12	8	65.2	2938.4	114.3	2046.2	134.6
100	12	12	70.6	3175.8	117.1	2168.9	131.2
100	0	4	67.3	2786.4	113.7	1874.6	96.8
100	0	8	70.2	2894.6	118.4	2038.4	94.4
100	0	12	76.9	3075.1	123.4	2190.4	92.7

PES, Hydroxyl terminated polyethersulfone; BMI, 3,3'-bis(maleimidophenyl)phenylphosphine oxide.

bismaleimide and epoxy systems. The values of tensile modulus obtained for bismaleimide modified polyethersulfone epoxy systems are also presented in table 1 and they exhibit similar trend as observed in the case of values of tensile strength.

3.3 Flexural properties

3.3a Polyethersulfone modified epoxy systems: The values of flexural strength and flexural modulus of unmodified epoxy and polyethersulfone modified epoxy are presented in table 1. The introduction of 4%, 8% and 12% polyethersulfone (by wt%) into epoxy resin enhances the values of flexural strength only to an insignificant extent when compared with that of unmodified epoxy system. The enhancement in the values of flexural strength is explained due to the resilient behaviour imparted by molecular structure of polyethersulfone. Further the formation of network structure between epoxy and polyethersulfone also influences the flexural behaviour.

3.3b Bismaleimide modified polyethersulfone-epoxy systems: The values of flexural strength of bismaleimide modified polyethersulfone epoxy systems are presented in table 1. The improvement in the values of flexural strength is observed, when bismaleimide is incorporated into polyethersulfone-epoxy systems. The enhancement in the value of flexural strength is influenced by the occurrence of homopolymerization of bismaleimide and the formation of intercross linking network structure between the epoxy and bismaleimide. The values of flexural modulus of modified epoxy systems follow the similar trend (table 1).

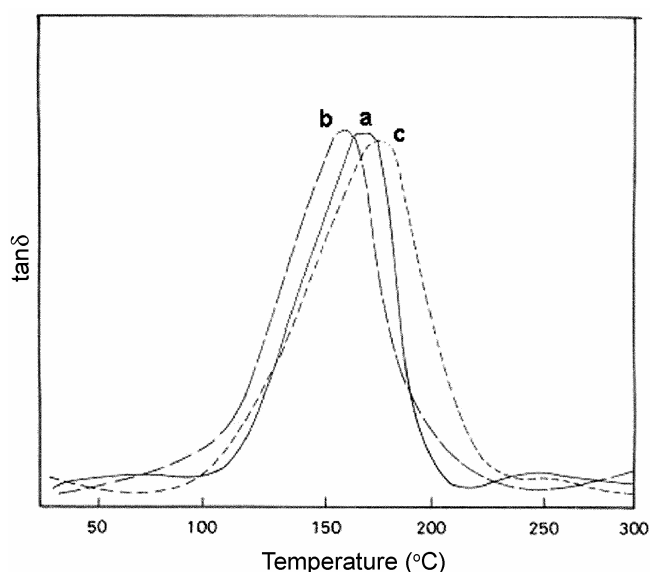


Figure 3. Variation of $\tan \delta$ as a function of temperature a. unmodified epoxy, b. polyethersulfone-epoxy and c. BMI modified polyethersulfone-epoxy systems.

3.4 Izod impact strength

3.4a Polyethersulfone modified epoxy systems: Polyethersulfone incorporation into epoxy resin improves the values of impact strength when compared with that of unmodified epoxy system. The incorporation of 4%, 8% and 12% polyethersulfone into epoxy system enhances the values of impact strength by 32.5%, 44.8% and 71.0%, respectively (table 1). The improvement is explained due to the chain lengthening by the introduction of polyether-

sulfone and formation of flexible network structure within the system. Further, the presence of ether linkage in the polyethersulfone skeleton is also responsible for the enhancement in the values of impact strength due to its free molecular rotation.

3.4b Bismaleimide modified polyethersulfone-epoxy systems: The values of impact strength of bismaleimide modified polyethersulfone-epoxy systems are lowered when bismaleimide are incorporated. The decrease in the values of impact strength is based on the nature and concentration of bismaleimide. The restricted chain mobility due to the formation of network structure is the cause for lowering of impact strength. However, the values of impact strength of bismaleimide modified polyethersulfone epoxy systems are greater than that of unmodified epoxy system.

4. Hardness

It is noticed that the introduction of polyethersulfone into epoxy resin marginally enhances the values of hardness. For example, the hardness value of unmodified epoxy system is 84, whereas the values of 4%, 8% and 12% polyethersulfone modified epoxy systems are 86, 87 and 89. This may be explained due to the inherent rigid aromatic molecular structure of polyethersulfone and the formation of flexible network structure between polyethersulfone and epoxy system. The incorporation of 4%, 8% and 12% (by weight) bismaleimide into epoxy and polyethersulfone modified epoxy systems increases the values of hardness between 88 and 91. This may be explained due to the occurrence of homopolymerization of bismaleimide and the formation of intercross linking network structure between the epoxy and bismaleimide.

5. Dynamic mechanical analysis

The dynamic mechanical analysis spectrum of unmodified epoxy and epoxy modified with polyethersulfone and bismaleimides are presented in figure 3. A single $\tan\delta$ peak was observed for polyethersulfone modified epoxy systems. All the modified epoxy systems show similar dynamic mechanical behaviour ($\tan\delta$). However, the polyethersulfone modified epoxy systems exhibit higher values of $\tan\delta$ than that of unmodified epoxy, indicating

the presence of lower crosslink density. The incorporation of bismaleimide into polyethersulfone modified epoxy systems decreased the value of $\tan\delta$ due to increased crosslink density.

6. Conclusions

Data resulted from mechanical studies indicate that the incorporation of polyethersulfone into epoxy resin improved tensile strength, flexural strength and impact strength. Similarly, the incorporation of bismaleimide also increased the stress and strain properties with a marginal reduction in impact strength. Dynamic mechanical analysis was used to ascertain the formation of network structure between epoxy and polymeric modifiers (polyethersulfone and BMI). Data resulted from mechanical studies suggest that these bismaleimide modified polyethersulfone-epoxy hybrid systems can be used in the form of coatings, adhesives and matrices for the fabrication of advanced composites for different industrial and engineering applications for better performance and longevity than unmodified epoxy systems.

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