Effect of polyethersulfone and *N,N'*-bismaleimido-4,4'-diphenyl methane on the mechanical and thermal properties of epoxy systems

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Received 12 February 2008; accepted in revised form 22 March 2008

Abstract. In order to improve thermo mechanical properties of cured epoxy resin, hydroxyl terminated polyethersulfone (PES) and *N,N'*-bismaleimido-4,4'-diphenyl methane (BMI) were incorporated to diglycidyl ether of bisphenol A (DGEBA) type epoxy resin and cured with diaminodiphenylmethane (DDM). The resulting hybrid matrices, in the form of castings, were characterized for their mechanical properties like tensile, flexural and impact strength. Differential scanning calorimetry, dynamic mechanical analysis and thermogravimetric analysis of the matrices were also performed to determine the glass transition temperature and thermal stability of the matrix systems. The results obtained from mechanical and thermal studies indicated that the incorporation of polyethersulfone into epoxy resin improved the toughness and thermal stability of the systems. This is attributed to the formation of interpenetration polymer networks (IPNs) composed of the epoxy network and the linear PES. The incorporation of BMI into polyethersulfone modified epoxy systems increased thermal stability, glass transition temperature, tensile and flexural properties and decreased the impact strength. Scanning electron microscopy studies of polyethersulfone modified epoxy and BMI incorporated polyethersulfone modified epoxy systems exhibit homogeneous morphology confirming efficient chemical interaction and formation of intercrosslinked network structure.

Keywords: polymer composites, thermal properties, mechanical properties, morphology, moisture absorption

1. Introduction

Epoxy resin systems are widely used for many important applications such as adhesives, encapsulating resins and as matrices in advanced structure composites in aerospace industry. Besides their adhesive properties, these highly cross linked networks possess excellent thermal and chemical stability as well as high modulus and strength [1–6]. However, the further use of epoxies is limited because of their inherent brittleness, poor crack resistance. In recent years, the feasibility of toughening highly crosslinked networks with high modulus and high T_g thermoplastics has been investi-

gated [7–12]. Addition of thermoplastics into thermosets leads to different phenomena. The initial mixture is generally homogeneous and phase separation could take place during curing of the thermoset. This technique is called reaction induced phase separation [13–15]. But, morphologies are controlled by many factors, such as the miscibility, modifier concentration, curing temperature and reaction rate [10, 16]. Several attempts have been made to dissolve the thermoplastics in the epoxy resin homogeneously [17–18]. The IPN or semi-IPN technique is one of the effective modifications of epoxy resin which makes it possible to attain

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homogeneous hybrid thermoplastic modified epoxy with low fractions of thermoplastics [18]. It is reported that the incorporation of high performance thermoplastics into a thermoset resin system leads to significant improvements in mechanical properties [9, 19–22].

In our laboratory, epoxy resin has been modified using different polymeric and chemical modifiers namely hydroxyl terminated polydimethylsiloxane [23], γ -aminopropyltriethoxysilane [24], unsaturated polyester [25], vinyl ester [26], bismaleimides, polyuretanes [27] and the results obtained have been published elsewhere.

The introduction of bismaleimide into epoxy resin improves the thermomechanical properties of epoxy resin [28–32]. Bismaleimides possess high crosslinking ability, high glass-transition temperature, high thermal ability, high char yield, excellent fire resistance, superior specific strength and specific modulus, and low water absorption. In contin-

uation of our earlier studies, an attempt has been made in the present investigation to improve both toughness and thermo-mechanical properties of epoxy resin by incorporating hydroxyl terminated polyethersulfone (PES) and *N,N'*-bismaleimido-4,4'-diphenyl methane (BMI).

2. Materials and methods

Epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] LY556 (epoxy equivalent 189 and viscosity 10 000 cP) and 4,4'-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy (India). *N,N'*-bismaleimido-4,4'-diphenyl methane was synthesized in our laboratory as per the reported procedure (Figure 1) [33]. Hydroxyl terminated polyethersulfone was supplied by Jilin University, China was used as received. The chemical structures of materials used are presented in Figure 2.

Figure 1. Synthesis of bismaleimide

Figure 2. Chemical structure of monomers and of oligomer epoxy resin

2.1. Preparation of epoxy

polyethersulfone/bismaleimide hybrid

The hybrid polyethersulfone epoxy matrices were prepared by dissolving varying percentages (4, 8, 12% by wt) of hydroxyl terminated polyethersulfone and tetramethyl ammonium hydroxide (TMAH) in known amount (100% by wt) of epoxy resin with continuous stirring at 150° C for two hours. The blend obtained was degassed under vacuum for half an hour and then cooled to 100°C. Then, calculated amount of bismaleimide was dissolved into polyethersulfone-epoxy blend at 100°C under vigorous stirring. The stoichiometric amount of 4,4'-diaminodiphenylmethane (with respect to epoxy) was added. The agitation was continued at 100° C until a homogeneous product was obtained. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120°C for 3 hours. The castings were then post cured at 180°C for 2 hours and finally removed from the mould and characterized.

2.2. Test methods

The IR spectra for unmodified epoxy, polyethersulfone modified epoxy and bismaleimide incorporated polyethersulfone modified epoxy matrices were recorded on a Perkin-Elmer (Model RX1) FT-IR spectrometer. Glass transition temperature (T_g) of the samples was determined using NETZSCH DSC 200PC analyzer (TA instruments USA) in the temperature range between 50 and 250°C at a heating rate of 10°C per minute in nitrogen atmosphere. Dynamic mechanical analysis of the samples was measured by using NETZSCH DMA 242 dynamic mechanical analyzer having dynamic strain of 0.3 and frequency of 1 Hz. Thermogravimetric analysis (TGA) was carried out using NETZSCH STA 409PC analyzer (TA instruments USA) at a heating rate of 10°C per minute in air. The heat deflection temperature (HDT) of the samples was tested as per ASTM D 648-72.

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/minute. The flexural properties were measured as per ASTM D 790, using an Instron testing machine (Model 6025 UK), at 10 mm/minute cross head speed. The Izod impact strength of the neat

resin castings was evaluated as per ASTM D-256. As many as five test pieces were used to generate the data points for the mechanical tests.

Scanning electron microscopy (SEM) JEOL JSM (Model 6360) was used to investigate the morphology of unmodified epoxy, polyethersulfone modified epoxy and bismaleimide incorporated polyethersulfone modified epoxy matrix systems. The water absorption property of the samples was determined as per ASTM D 570. The results obtained are presented in Tables 1, 2 and Figures 2–10.

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 oligomer and large molar excess of epoxy resin in the presence of tetramethyl ammonium hydroxide (Figure 3). The large excess of epoxy resin was used to endcap the polyethersulfone oligomers which essentially prevents the 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 4). The intensity of IR absorption peaks observed for oxirane ring of epoxy (Figure 4a) was very high at the initial stage of the reaction. The decrease in intensity of the peak for oxirane ring of epoxy confirms the reaction between epoxy and hydroxyl group of polyethersulfone (20%). The IR absorption peak of epoxy disappeared completely after the completion of the reaction between polyethersulfone modified epoxy and the curing agent, (DDM) (Figure 4d) which confirms the formation of interpenetrating polymer network structure (IPN).

3.2. Mechanical properties

The values of tensile properties observed for epoxy resin and epoxy systems modified with polyethersulfone and bismaleimide (BMI) are presented in Table 1. The introduction of 4, 8 and 12% polyethersulfone (by weight) into epoxy resin increased the tensile strength by marginal extent when compared with unmodified epoxy resin due to inherent rigid aromatic molecular structure of polyethersulfone which influences the enhancement of both tensile strength and modulus. The incorporation of 4, 8

Figure 3. Formation of polyethersulfone modified epoxy-DDM interpenetrating polymer network (IPN)

and 12% BMI (by weight) into the epoxy resin increased the tensile strength by 7.5, 20.9 and 38.1% respectively (Table 1). This may be explained by the formation of intercrosslinking network between epoxy and BMI, which in turn increased crosslinking density. Similarly, the introduction of both BMI and polyethersulfone into epoxy resin increased the value of tensile strength according to their percentage content. The tensile strength values of polyethersulfone-epoxy system increased with increasing BMI content. The values of tensile modulus obtained for the unmodified epoxy and

epoxy modified with polyethersulfone, bis-maleimide and combinations of both are presented in Table 1 and exhibited a similar trend to that of tensile strength.

The data observed for the flexural behaviour of epoxy resin and epoxy systems modified with polyethersulfone and bismaleimide are presented in Table 1. The introduction of 4, 8 and 12% polyethersulfone into epoxy resin increased the flexural strength slightly when compared to unmodified epoxy resin which is attributed to the formation of interpenetrating polymer networks (IPN) composed

Figure 4. FTIR spectra of (a) unmodified epoxy resin, (b) polyethersulfone, (c) DDM-cured epoxy-polyethersulfone (100:20) cured at 140°C for 3 hours and postcured at 200°C for 2 hours

of the epoxy networks and linear PES. The high modulus in the rubbery region can be interpreted on the network interlock of the epoxy matrix and PES. The incorporation of 4, 8 and 12% BMI into the epoxy resin increased the flexural strength by 7.2, 19.9 and 27% respectively (Table 1). This may be explained by the occurrence of homopolymerization of bismaleimide and the formation of intercrosslinking network structure between epoxy and bismaleimides [32, 34–35]. Similarly, the values of flexural strength of polyethersulfone modified epoxy increased with increasing BMI content. The values of flexural modulus of polyethersulfone modified epoxy bismaleimide systems also follow the similar trend to that of flexural strength.

The values of unnotched Izod impact strength obtained for unmodified epoxy resin and epoxy modified with polyethersulfone, bismaleimide, and a combination of both are presented in Table 1. It can be concluded that the increase in the impact strength is attributed to the increase in the ductility of the modified resin by the formation of the IPN structure. Whereas the incorporation of bismaleimide into epoxy decreased the impact strength behavior as a result of an intercrosslinked network formation, which in turn enhanced the rigidity and crosslinking density. The incorporation of bismaleimide in both the cases of epoxy and polyethersulfone modified epoxy systems decreased the unnotched Izod impact strength according to their percentage content.

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

Sample code	Tensile strength [MPa]	Tensile modulus [MPa]	Flexural strength [MPa]	Flexural modulus [MPa]	Impact strength [J/m]
E ₁₀₀ PES ₀ BMI ₀	63.2 ± 5	2751.7 ± 28	110.0 ± 7	1812.9 ± 28	100.3 ± 5
E ₁₀₀ PES ₄ BMI ₀	63.5 ± 3	2773.1 ± 25	111.0 ± 6	1827.1 ± 25	130.3 ± 6
E ₁₀₀ PES ₈ BMI ₀	64.0 ± 4	2798.5 ± 26	112.6 ± 5	1855.8 ± 24	142.4 ± 5
E ₁₀₀ PES ₁₂ BMI ₀	64.9 ± 6	2815.9 ± 28	113.2 ± 6	1874.0 ± 28	168.1 ± 6
E ₁₀₀ PES ₄ BMI ₄	65.7 ± 5	2795.7 ± 20	113.2 ± 5	1863.2 ± 29	126.4 ± 5
E ₁₀₀ PES ₄ BMI ₈	67.1 ± 4	2861.0 ± 24	115.0 ± 4	1947.6 ± 31	120.3 ± 4
E ₁₀₀ PES ₄ BMI ₁₂	69.2 ± 3	2925.3 ± 29	117.9 ± 6	1974.5 ± 30	114.3 ± 6
E ₁₀₀ PES ₈ BMI ₄	65.5 ± 3	2816.5 ± 25	114.3 ± 5	1892.5 ± 29	134.3 ± 4
E ₁₀₀ PES ₈ BMI ₈	67.6 ± 4	2871.3 ± 26	116.8 ± 3	1922.2 ± 28	128.4 ± 6
E ₁₀₀ PES ₈ BMI ₁₂	69.8 ± 5	2926.3 ± 30	118.9 ± 5	1947.8 ± 25	120.4 ± 7
E ₁₀₀ PES ₁₂ BMI ₄	65.5 ± 4	2854.5 ± 21	115.5 ± 4	1909.3 ± 31	161.8 ± 5
E ₁₀₀ PES ₁₂ BMI ₈	68.8 ± 6	2918.2 ± 26	117.1 ± 6	1946.4 ± 32	153.8 ± 5
E ₁₀₀ PES ₁₂ BMI ₁₂	71.0 ± 5	2981.6 ± 28	119.4 ± 5	1998.2 ± 29	144.4 ± 6
E ₁₀₀ PES ₀ BMI ₄	65.8 ± 4	2820.4 ± 30	118.3 ± 5	2040.5 ± 26	93.1 ± 5
E ₁₀₀ PES ₀ BMI ₈	74.0 ± 2	2876.3 ± 29	127.3 ± 6	2275.9 ± 27	91.3 ± 4
E ₁₀₀ PES ₀ BMI ₁₂	84.5 ± 3	3053.9 ± 25	132.6 ± 7	2596.8 ± 30	87.9 ± 3

E – epoxy; PES – hydroxyl terminated polyethersulfone; BMI – bismaleimide

3.3. Thermal properties

DSC thermograms of unmodified epoxy, and epoxy systems modified with polyethersulfone and BMI are presented in Figures 5 and 6. The polyethersulfone modified epoxy hybrids exhibit transparent behaviour at ambient temperature and there was no evidence of phase separation noticed. Further the single value of T_g observed for polyethersulfone modified epoxy suggested that the hybrid is chemically bonded homogeneous products of amorphous nature. The value of the glass transition temperature of the epoxy system modified with polyether-

Figure 5. DSC traces of polyethersulfone modified epoxy systems (a) unmodified epoxy, (b) 4% PES modified epoxy, (c) 8% PES modified epoxy and (d) 12% PES modified epoxy

Figure 6. DSC traces of BMI modified polyethersulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI modified polyethersulfone (8%)-epoxy systems

sulfone was some what lower than that of unmodified epoxy resin. The incorporation of polyethersulfone raised the viscosity of the resulting hybrid epoxy system, which could result in an incomplete curing reaction due to the steric hindrance under the curing conditions [36]. The thickening effect and consequent chain lengthening of polyethersulfone skeleton lead to the reduction of the crosslinking density and hence molecular flexibility occurs at low temperature. The incorporation of BMI into both epoxy resin and polyethersulfone modified epoxy systems enhanced the T_g values (Table 2). An enhancement in the values of T_g is due to the occurrence of homopolymerisation of bis-maleimides rather than to Michael addition reaction and is confirmed from our earlier studies [24]. Since Michael addition reaction reduced the crosslink density due to chain extension.

The data resulted from dynamic mechanical analysis for unmodified epoxy and epoxy modified with polyethersulfone and BMI are given in Figure 7. A single $\tan\delta$ peak was observed for polyethersulfone modified epoxy hybrid. The glass transition temperature of polyethersulfone modified epoxy decreased when compared with that value of unmodified epoxy resin. However, the incorpora-

Table 2. Percentage water absorption, glass transition temperature percentage weight loss and heat distortion temperature of unmodified epoxy, polyethersulfone modified epoxy, BMI modified epoxy and BMI modified polyethersulfone-epoxy systems

Sample code	Water absorption [%]	Heat deflection temperature [°C]	Glass transition temperature [°C]
E ₁₀₀ PES ₀ BMI ₀	0.1201	153	165
E ₁₀₀ PES ₄ BMI ₀	0.1182	152	164
E ₁₀₀ PES ₈ BMI ₀	0.1123	151	162
E ₁₀₀ PES ₁₂ BMI ₀	0.1085	151	161
E ₁₀₀ PES ₄ BMI ₄	0.1131	153	166
E ₁₀₀ PES ₄ BMI ₈	0.1076	156	169
E ₁₀₀ PES ₄ BMI ₁₂	0.1024	158	171
E ₁₀₀ PES ₈ BMI ₄	0.1095	152	163
E ₁₀₀ PES ₈ BMI ₈	0.1031	154	167
E ₁₀₀ PES ₈ BMI ₁₂	0.0977	157	179
E ₁₀₀ PES ₁₂ BMI ₄	0.1019	152	162
E ₁₀₀ PES ₁₂ BMI ₈	0.0942	153	165
E ₁₀₀ PES ₁₂ BMI ₁₂	0.0893	156	168
E ₁₀₀ PES ₀ BMI ₄	0.0853	154	167
E ₁₀₀ PES ₀ BMI ₈	0.0781	156	172
E ₁₀₀ PES ₀ BMI ₁₂	0.0693	159	180

E – epoxy; PES – hydroxyl terminated polyethersulfone; BMI – bismaleimide

Figure 7. Variation of $\tan\delta$ as a function of temperature (a) unmodified epoxy, (b) polyethersulfone modified epoxy and (c) BMI modified polyethersulfone-epoxy systems

Figure 8. TGA curves of epoxy and polyethersulfone-epoxy systems (a) unmodified epoxy, (b) 4%, (c) 8% and (d) 12% PES-epoxy systems

tion of BMI into both epoxy resin and polyethersulfone modified epoxy systems enhanced the T_g values according to the percentage content. The DMA results obtained are in good agreement with those obtained from DSC studies.

Heat distortion temperature values for epoxy, polyethersulfone modified epoxy, BMI modified epoxy and BMI modified polyethersulfone-epoxy systems are presented in Table 2. From Table 2 it is evident that the values of HDT were decreased with increasing polyethersulfone concentration whereas the reverse trend in HDT values are observed for BMI modified epoxy and BMI modified polyethersulfone-epoxy systems. The enhancement in the values of HDT for bismaleimide modified systems is due to the rigidity and improved crosslink density imparted by heterocyclic bismaleimide.

Polyethersulfone incorporation into epoxy resin improved thermal stability and enhanced the degradation temperature compared to the unmodified epoxy resin according to its percentage concentration (Figure 8). The presence of polyethersulfone skeleton in the epoxy system delays the degradation process and high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. The delay in degradation caused by the addition of polyethersulfone with a high T_g increased the viscosity of the system and in turn induced the formation of inter-

penetrating polymer network (IPN) within the system. The thermal degradation temperature of the BMI modified epoxy systems and BMI modified polyethersulfone epoxy systems were found to be increased with increasing bismaleimide concentration. It is evident from Figure 9 that the degradation temperature was increased with increasing BMI concentrations as observed in the case of polyethersulfone modified systems and this may be due to the rigidity and enhanced crosslink density imparted by bismaleimide.

Figure 9. TGA curves of BMI modified polyethersulfone-epoxy systems (a) 4%, (b) 8% and (c) 12% BMI modified PES (8%)-epoxy systems

3.4. Morphology

The scanning electron micrographs of fractured surfaces of the unmodified epoxy, polyethersulfone modified epoxy and polyethersulfone modified bismaleimide incorporated epoxy systems revealed smooth and homogeneous microstructures (Figures 10a–d). This confirmed that the hybrid product is having single chemical entity. Further this observation supports the results obtained from DMA and DSC analysis. The efficient interaction between polyethersulfone and epoxy resin and consequent IPN formation may be the cause for the development of homogeneous morphology.

3.5. Water absorption behavior

The polyethersulfone incorporation into epoxy system and the incorporation of BMI into both epoxy resin and polyethersulfone modified epoxy systems decreased the water absorption behavior, due to the

hydrophobic behaviour imparted by polyethersulfone and enhanced cross linking density coupled with water repellency induced by bismaleimide (Table 2).

4. Conclusions

The polyethersulfone modified epoxy, BMI modified epoxy and BMI modified polyethersulfone-epoxy intercrosslinked network having varied concentrations of BMI and polyethersulfone were prepared. The decreased thermal properties such as T_g , HDT were observed for polyethersulfone modified epoxy systems due to chain lengthening and consequent reduction in crosslink density induced by polyethersulfone skeleton. The values of mechanical properties indicated that the incorporation of polyethersulfone into epoxy resin improved tensile strength, flexural strength and fracture toughness and the incorporation of bismaleimide also increased

a)

b)

c)

d)

Figure 10. SEM micrographs of (a) unmodified epoxy, (b) 12% PES modified epoxy, (c) 12% BMI modified epoxy and (d) 12% PES and 12% BMI modified epoxy systems

the stress and strain properties with a marginal reduction in toughness and impact strength. It was also observed that the moisture absorption behavior decreased with the increasing polyethersulfone and BMI content in the epoxy systems. The incorporation of BMI plays an important role in reducing moisture absorption of epoxy resin. Data on mechanical properties indicated that by altering the percentage incorporation of polyethersulfone and BMI into epoxy resin, it is possible for the development of modified epoxy hybrid matrix materials with desired mechanical and thermal properties which can be used for high performance aerospace engineering applications.

References

- [1] Akutsu U., Inoki M., Daicho N., Kasashima Y., Srirish N., Marushima I.: Curing behavior and properties of epoxy resins cured with the diamine having the quinoxaline or triazine structure. *Journal of Applied Polymer Science*, **69**, 1737–1741 (1998).
- [2] Vabrik Y., Czajlik I., Túry G., Rusznák I., Ille A., Víg A.: A study of epoxy resin-acrylated polyurethane semi-interpenetrating polymer networks. *Journal of Applied Polymer Science*, **68**, 111–119 (1998).
- [3] Lin M. S., Liu C. C., Lee C. T.: Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy. *Journal of Applied Polymer Science*, **72**, 585–592 (1999).
- [4] Li Y., Shen S., Liu Y., Gao J.: Kinetics of 4,4'-diaminodiphenylmethane curing of bisphenol-S epoxy resin. *Journal of Applied Polymer Science*, **73**, 1799–1803 (1999).
- [5] Deng B-L., Hu Y-S., Chen L-A., Chiu W-Y., Wu T-R.: The curing reaction and physical properties of DGEBA/DETA epoxy resin blended with propyl ester phosphazene. *Journal of Applied Polymer Science*, **74**, 229–237 (1999).
- [6] Kaji M., Nakahara K., Endo T.: Synthesis of a bifunctional epoxy monomer containing biphenyl moiety and properties of its cured polymer with phenol novolac. *Journal of Applied Polymer Science*, **74**, 690–698 (1999).
- [7] Hedrick J. L., Yilgor I., Jurek M., Hedrick J. C., Wilkes G. I., McGrath J. E.: Chemical modification of matrix resin networks with engineering thermoplastics: 1. Synthesis, morphology, physical behaviour and toughening mechanisms of poly(arylene ether sulfone) modified epoxy networks. *Polymer*, **32**, 2020–2032 (1991).
- [8] Mackinnon A. J., Jenkins S. D., McGrail P. T., Pethrick R. A.: Dielectric, mechanical and rheological studies of phase separation and cure of a thermoplastic modified epoxy resin: Incorporation of reactively terminated polysulfones. *Polymer*, **34**, 3252–3263 (1993).
- [9] Huang P., Zheng S., Huang J., Geo Q., Zhu W.: Miscibility and mechanical properties of epoxy resin/poly-sulfone blends. *Polymer*, **38**, 5565–5571 (1997).
- [10] Mimura K., Ito H., Fujioka H.: Improvement of thermal and mechanical properties by control of morphologies in PES-modified epoxy resins. *Polymer*, **41**, 4451–4459 (2000).
- [11] Jiang X. L., Sunl K., Zhang Y. X.: Effects of dynamical cure and compatibilization on the morphology and properties of the PP/epoxy blends. *Express Polymer Letters*, **1**, 283–291 (2007).
- [12] Cho J. B., Hwang J. W., Cho K., An J. H., Park C. E.: Effects of morphology on toughening of tetrafunctional epoxy resins with poly(ether imide). *Polymer*, **34**, 4832–4836 (1993).
- [13] Oyanguren P. A., Riccardi C. C., Williams R. J. J., Mondragon I.: Phase separation induced by a chain polymerization: Polysulfone-modified epoxy/anhydride systems. *Journal of Polymer Science, Part B: Polymer Physics*, **36**, 1349–1359 (1998).
- [14] Giannotti M. I., Mondragon I., Galante M. J., Oyanguren P. A.: Reaction-induced phase separation in epoxy/polysulfone/poly(ether imide) systems. II. Generated morphologies. *Journal of Polymer Science, Part B: Polymer Physics*, **42**, 3964–3975 (2004).
- [15] Siddhamalli S. K., Kyu T.: Toughening of thermoset/thermoplastic composites via reaction-induced phase separation: Epoxy/phenoxy blends. *Journal of Applied Polymer Science*, **77**, 1257–1268 (2000).
- [16] Giannotti M. I., Solsona M. S., Galante M. J., Oyanguren P. A.: Morphology control in polysulfone-modified epoxy resins by demixing behavior. *Journal of Applied Polymer Science*, **89**, 405–412 (2003).
- [17] Teng K-C., Chang F-C.: Single-phase and multiple-phase thermoplastic/thermoset polyblends: 2. Morphologies and mechanical properties of phenoxy/ epoxy blends. *Polymer*, **37**, 2385–2394 (1996).
- [18] Tanaka N., Iijima T., Fukuda W., Tomoi M.: Synthesis and properties of interpenetrating polymer networks composed of epoxy resins and polysulphones with cross-linkable pendant vinylbenzyl groups. *Polymer International*, **42**, 95–106 (1997).
- [19] Hedrick J. L., Yilgor I., Wilkes G. L., McGrath J. E.: Chemical modification of matrix resin networks with engineering thermoplastics. *Polymer Bulletin*, **13**, 201–208 (1985).
- [20] Hedrick J. L., Yilgor I., Jurek M., Hedrick J. C., Wilkes G. L., McGrath J. E.: Chemical modification of matrix resin networks with engineering thermoplastics: 1. Synthesis, morphology, physical behaviour and toughening mechanisms of poly(arylene ether sulfone) modified epoxy networks. *Polymer*, **32**, 2020–2032 (1991).
- [21] Rajasekaran R., Alagar M.: Mechanical properties of bismaleimides modified polysulfone epoxy matrices for engineering applications. *International Journal of Polymer Materials*, **56**, 911–927 (2007).

- [22] Rajasekaran R., Karikal Chozhan C., Alagar M.: Preparation and characterization of 3,3'-bis(maleimido)phenylphosphine oxide BMI/polysulfone modified epoxy intercrosslinked matrices. *Polymer Composites*, in press (2008).
- [23] Ashok Kumar A., Dinakaran K., Alagar M.: Preparation and characterization of siliconized epoxy-1,2-bis(maleimido) ethane intercrosslinked matrix materials. *Journal of Applied Polymer Science*, **89**, 3808–3817 (2003).
- [24] Ashok Kumar A., Alagar M., Rao R. M. V. G. K.: Synthesis and characterization of siliconized epoxy-1,3-bis(maleimido)benzene intercrosslinked matrix materials. *Polymer*, **43**, 693–702 (2002).
- [25] Dinakaran K., Alagar M.: Preparation and characterization of bismaleimide (*N,N'*-bismaleimido-4,4'-diphenyl methane)-unsaturated polyester modified epoxy intercrosslinked matrices. *Journal of Applied Polymer Science*, **85**, 2853–2861 (2002).
- [26] Dinakaran K., Alagar M.: Preparation and characterization of bismaleimide (*N,N'*-bismaleimido-4,4'-diphenyl methane)-vinyl ester oligomer-modified unsaturated polyester interpenetrating matrices for advanced composites. *Journal of Applied Polymer Science*, **86**, 2502–2508 (2002).
- [27] Mahesh K. P. O., Alagar M.: Preparation and characterization of chain-extended bismaleimide modified polyurethane-epoxy matrices. *Journal of Applied Polymer Science*, **87**, 1562–1568 (2003).
- [28] Ashok Kumar A., Alagar M., Rao R. M. V. G. K.: Preparation and characterization of siliconized epoxy/bismaleimide (*N,N'*-bismaleimido-4,4'-diphenyl methane) intercrosslinked matrices for engineering applications. *Journal of Applied Polymer Science*, **81**, 38–46 (2001).
- [29] Ashok Kumar A., Alagar M., Rao R. M. V. G. K.: Studies on thermal and morphological behavior of siliconized epoxy bismaleimide matrices. *Journal of Applied Polymer Science*, **81**, 2330–2346 (2001).
- [30] Kim D. S., Han M. J., Lee J. R.: Cure behavior and properties of an epoxy resin modified with a bismaleimide resin. *Polymer Engineering and Science*, **35**, 1353–1358 (1995).
- [31] Lin K-F., Lin J-S., Cheng C-H.: High temperature resins based on allylamine/bismaleimides. *Polymer*, **37**, 4729–4737 (1996).
- [32] Musto P., Mariuscelli E., Ragosta G., Russo P., Scarinzi G.: An interpenetrated system based on a tetrafunctional epoxy resin and a thermosetting bismaleimide: Structure-properties correlation. *Journal of Applied Polymer Science*, **69**, 1029–1042 (1998).
- [33] Crivello J. V.: Polyimidothioethers. *Journal of Polymer Science, Part A: Polymer Chemistry*, **14**, 159–182 (1976).
- [34] Lüders G., Merker E., Raumbach H.: Polymerisation von n-substituierten Maleimiden in Epoxidverbindungen, 1. Die Angewandte Makromolekulare Chemie, **182**, 135–151 (1990).
- [35] Musto P., Mariuscelli E., Ragosta G., Russo P., Scarinzi G.: An interpenetrated system based an tetrafunctional epoxy resin and a thermosetting bismaleimide: Structure-properties correlation. *Journal of Applied Polymer. Science*, **69**, 1029–1042 (1998).
- [36] Zheng S., Zhang N., Luo X., Ma D.: Epoxy resin/poly(ethylene oxide) blends cured with aromatic amine. *Polymer*, **36**, 3609–3613 (1995).