

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF ORGANOCLAY-MODIFIED POLYSULFONE/EPOXY INTERPENETRATING POLYMER NETWORK NANOCOMPOSITES

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Abstract Organoclay-modified hydroxylterminated polysulfone (PSF)/epoxy interpenetrating network nanocomposites (oM-PSF/EP nanocomposites) were prepared by adding organophilic montmorillonite (oMMT) to interpenetrating polymer networks (IPNs) of polysulfone and epoxy resin (PSF/EP) using diaminodiphenylmethane (DDM) as curing agent. The mechanical properties like tensile strength, tensile modulus, flexural strength, flexural modulus and impact properties of the nanocomposites were studied as per ASTM standards. Differential scanning calorimetry (DSC) analysis, dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) analysis showed that PSF was compatible with EP, and the glass transition temperature (T_g) of the oM-PSF/EP nanocomposites decreased with increasing the oMMT content. Water absorption tests showed that the PSF/EP interpenetrating networks and oMMT had synergistic effects on improvement in the water resistance of the oM-PSF/EP nanocomposites.

Keywords: Nanocomposites; Glass transition temperature; Impact strength; Interpenetrating networks (IPN); Polysulfone.

INTRODUCTION

Epoxy resins find many industrial applications in adhesives, construction materials, composites, laminates, coatings and aircraft and spacecraft industries owing to their high strength, low viscosity, low volatility and low shrinkage during cure, low creep and good adhesion to many substrates^[1–8]. However, the high level of formation of crosslinking during cure imparts brittle behavior, which limits their application in fields requiring high impact and fracture toughness, such as composites and coatings.

Therefore in the last few decades, much attention has been given to improve the thermal and mechanical properties of epoxy resins, especially making them tough. Engineering thermoplastics have been used to improve the fracture properties of epoxy resins, because thermoplastic modifiers are tough, ductile, chemically and thermally stable and have high T_g . It has been widely acknowledged that a great increase in toughness can be obtained by blending thermoplastics such as poly(ether imide) (PEI), poly(ether sulfone) (PES), poly(phenylene ether) (PPE), polysulfone, poly(ether ketone) (PEK) and so on^[9–23] with epoxy resins.

On the other hand, epoxy/organo layered silicate nanocomposites have attracted great interests from both scientists and industrialists in the recent years due to their remarkable improvement in mechanical properties, gas barrier properties, flammability resistance^[24–35] etc. But as to the toughness, the organo layered silicate/epoxy nanocomposites usually have only slightly improved toughness. The toughness of the hybrid nanocomposites is found to be greatly improved compared with the nanocomposites without liquid rubber and has only slightly negative impact to the stiffness. As high performance thermoplastics have intrinsic high T_g and better mechanical properties than liquid rubbers, hence, one can expect better mechanical properties of thermoplastics hybrid nanocomposites than those based on liquid rubber.

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Received July 30, 2007; Revised September 17, 2007; Accepted October 6, 2007

In the present investigation an attempt has been made to prepare thermoplastics modified epoxy hybrid nanocomposites using different ratios of nanoclays in hydroxyl terminated polysulfone modified diglycidyl ether of bisphenol-A type epoxy resin. The thermal, mechanical and morphological properties of hydroxyl terminated polysulfone modified DGEBA epoxy resin under conventional processing conditions were also discussed.

EXPERIMENTAL

Starting Materials

Epoxy resin (Diglycidylether of bisphenol A, DGEBA) LY556 having an epoxy equivalent of about 180–190, with viscosity of about 10 Pa·s and 4,4'-diaminodiphenylmethane (DDM), epoxy curing agent, were used as obtained from Ciba-Geigy Ltd., India. Bisphenol A based polysulfone ($M_w = 15000$, $T_g = 195^\circ\text{C}$) was supplied by Shauguang chemical factory, Shanghai, China was used as received. Cetyltrimethylammonium bromide (SRL, India) was used as received. Montmorillonite clay was purchased from Aldrich chemicals, USA.

Synthesis of Organophilic Nanoclay

15 g of the purified Na-montmorillonite clay was dispersed into 1200 mL of distilled water at 80°C . Cetyltrimethylammonium bromide, 5.7 g, in 300 mL distilled water was poured in the hot montmorillonite/water solution and stirred vigorously for 1 h at 80°C . A white precipitate formed, it was isolated by filtration and washed several times with a hot water/ethanol (1:1) mixture until no chloride was detected in the filtrate by adding one drop of 0.1 mol/L AgNO_3 solutions. The cetyltrimethylammonium ion exchanged montmorillonite was then dried for about two weeks at 75°C , ground with a mortar and pestle, and then the $< 50\ \mu\text{m}$ fraction was collected. The organophilic nanoclay was stored in a desiccator for further use.

Preparation of Organophilic Clay Filled Nanocomposites

Prior to curing, the epoxy resin was mixed with a desired amount of organophilic nanoclay at 70°C for 24 h. A stoichiometric amount of the curing agent 4,4'-diaminodiphenylmethane corresponding to epoxy equivalents was also added. The product was subjected to vacuum to remove the trapped air and then cast and cured at 140°C for 3 h. The castings were then post-cured at 200°C for 2 h and finally removed from the mould and characterized.

Preparation of Organophilic Clay Filled Hybrid Polysulfone Epoxy Nanocomposites

The hybrid polysulfone epoxy matrices were prepared by dissolving varying percentages (4 wt%, 8 wt% and 12 wt%) of bisphenol-A based polysulfone and tetra methyl ammonium hydroxide (TMAH) in a known amount (100 wt%) of epoxy resin with continuous stirring at 150°C for two hours. The hybrid matrix obtained was degassed under vacuum for half an hour and then cooled to 90°C . Then a desired amount of organophilic clay (1 wt%, 3 wt% and 5 wt%) was mixed with polysulfone modified epoxy resin at 80°C for 24 h. Then, a stoichiometric amount of curative 4,4'-diaminodiphenyl methane (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 h. The castings were then post cured at 200°C for 2 h and finally removed from the mould and characterized.

Test Methods

The IR spectra were recorded on a Perkin-Elmer (Model RX1) FTIR spectrometer with KBr pellets for solid samples. For viscous liquid samples, the measurements were carried out by placing the sample between two KBr pellets.

The tensile (stress-strain) properties were determined using INSTRON (Model 6025 UK) as per ASTM D 3039 at 10 mm/min cross-head speed using specimen with width of 25 mm, length of 200 mm and thickness of 3 mm. The flexural (strength and modulus) properties were measured (INSTRON, Model 6025 UK) as per ASTM D 790 using specimen with dimensions 3 mm in depth, 10 mm in width and 90 mm in length at 10 mm/min cross-head speed. The unnotched Izod impact strength of each sample was studied as per ASTM D 256. Five specimens were tested for each sample.

Glass transition temperature (T_g) of the samples was determined using a DSC Netzsch (TA instruments, USA) in the temperature range between 50°C and 250°C at a heating rate of 10 K/min in nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA instruments) at a heating rate of 10 K/min in nitrogen atmosphere. The heat deflection temperature of the samples was tested as *per* ASTM D 648-72. Dynamic mechanical behavior of the samples was measured using a DMA Netzsch 242 at a heating rate of 10 K/min from 30°C to 300°C.

X-ray diffraction patterns were recorded at room temperature by monitoring the diffraction angle 2θ from 10° to 70° as standard on a Rich Seifert (Model 3000) X-ray powder diffractometer. The diffractometer was equipped with a copper target ($\lambda = 0.15405$ nm) radiation using Guinier type camera employed as a focusing geometry and a solid-state detector. Curved nickel crystal was used as a monochromator. The step width (2θ scanning speed) used was 0.04 (°)/min.

The water absorption behavior of the samples was tested as per ASTM D 570. The cured specimens (dimensions: 60 mm square, 3 mm thick) were immersed in distilled water for 48 h. After the surface water was removed using a tissue paper the specimens were weighed to an accuracy of 0.001 g. Surface morphology of fractured surfaces of the samples was observed using a scanning electron microscope (SEM; JEOL JSM Model 6360). The fractured surface of the samples was coated with platinum before scanning.

RESULTS AND DISCUSSION

The formation of interpenetrating network of epoxy and polysulfone proceeds through the reaction between bisphenol A polysulfone (PSF) oligomer with large molar excess of epoxy resin in the presence of a catalyst, tetramethyl ammonium hydroxide (TMAH). The large excess of epoxy resin was used to endcap the polysulfone oligomers which essentially prevented further polymerization. An IR absorption for epoxide ring of epoxy resin appears at 914 cm^{-1} which is attributed to the stretching absorption of C—O in the epoxide ring, and this

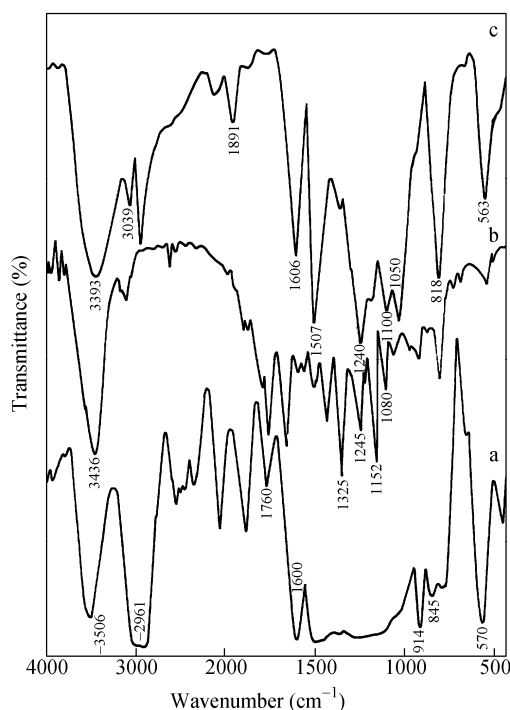
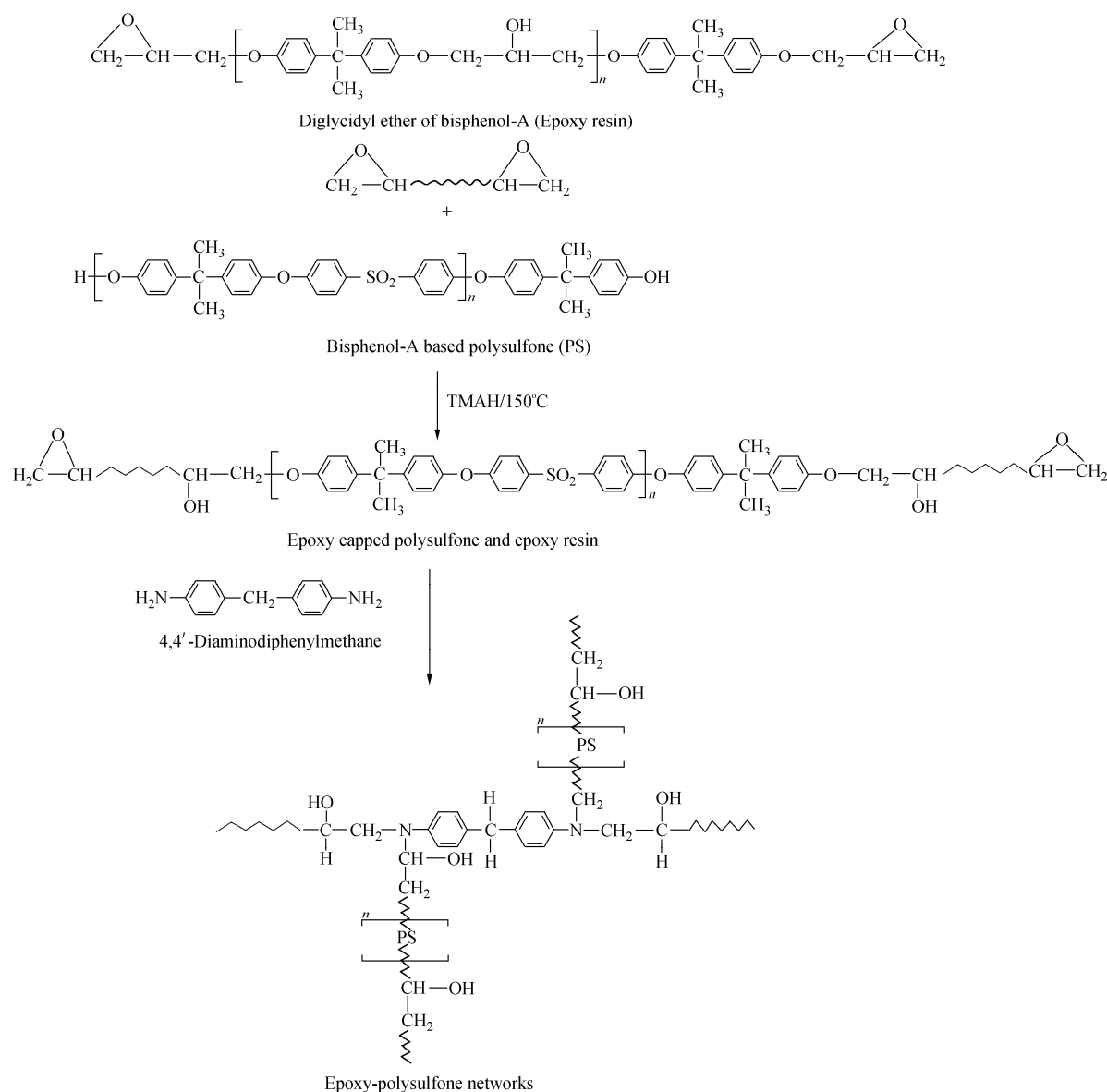


Fig. 1 FTIR spectra of (a) unmodified epoxy, (b) polysulfone prepolymer and (c) polysulfone modified epoxy system

absorption clearly disappears after curing at 120°C (Fig. 1). The formation of IPN in epoxy and polysulfone systems is due to reactions of (i) hydroxyl groups of PSF with amino groups of curative (DDM) and (ii) hydroxyl groups of PSF with epoxy groups of epoxy resin. The intensity of IR absorption peaks observed for oxirane of epoxy (Fig. 1a) is very high at the beginning stage of the reaction. As the reaction proceeds, the intensity of the peak for oxirane ring of epoxy disappears (Fig. 1c) after the completion of the reaction. This confirms the reaction between epoxy and polysulfone and the formation of interpenetrating polymer network structure (IPN) (Scheme 1).



Scheme 1 Formation of polysulfone modified epoxy-DDM interpenetration polymer network

Tensile Properties

The values of tensile strength of unmodified epoxy, organophilic montmorillonite clay filled epoxy and polysulfone modified epoxy nanocomposites are presented in Table 1. The introduction of 4%, 8% and 12% polysulfone into epoxy resin enhances the tensile strength to an insignificant extent. The marginal improvement

may be explained due to the inherent rigid aromatic molecular structure of polysulfone and the formation of interpenetrating network between epoxy and polysulfone. The values of tensile modulus obtained for the unmodified epoxy and epoxy modified with polysulfone exhibit similar trend as observed in the case of tensile strength.

Table 1. Mechanical properties of unmodified epoxy, organo clay filled epoxy and organo clay filled polysulfone modified epoxy nanocomposites

Epoxy/Polysulfone/Clay composition	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
100/00/00	61.2	2713.4	104	1753.9	98.3
100/00/01	66.3	3052.6	115.3	1986.3	103.9
100/00/03	74.2	3342.5	119.2	2152.5	114.8
100/00/05	88.5	3897.5	129.6	2282.2	130.7
100/04/00	61.8	2723.2	105.7	1772.8	122.0
100/08/00	62.3	2736.9	106.3	1794.3	132.9
100/12/00	63.1	2752.6	107.1	1824.2	146.1
100/08/01	64.7	2912.4	110.3	1923.4	140.6
100/08/03	69.6	3245.6	118.4	2105.2	148.7
100/08/05	76.8	3452.8	128.7	2234.8	153.4

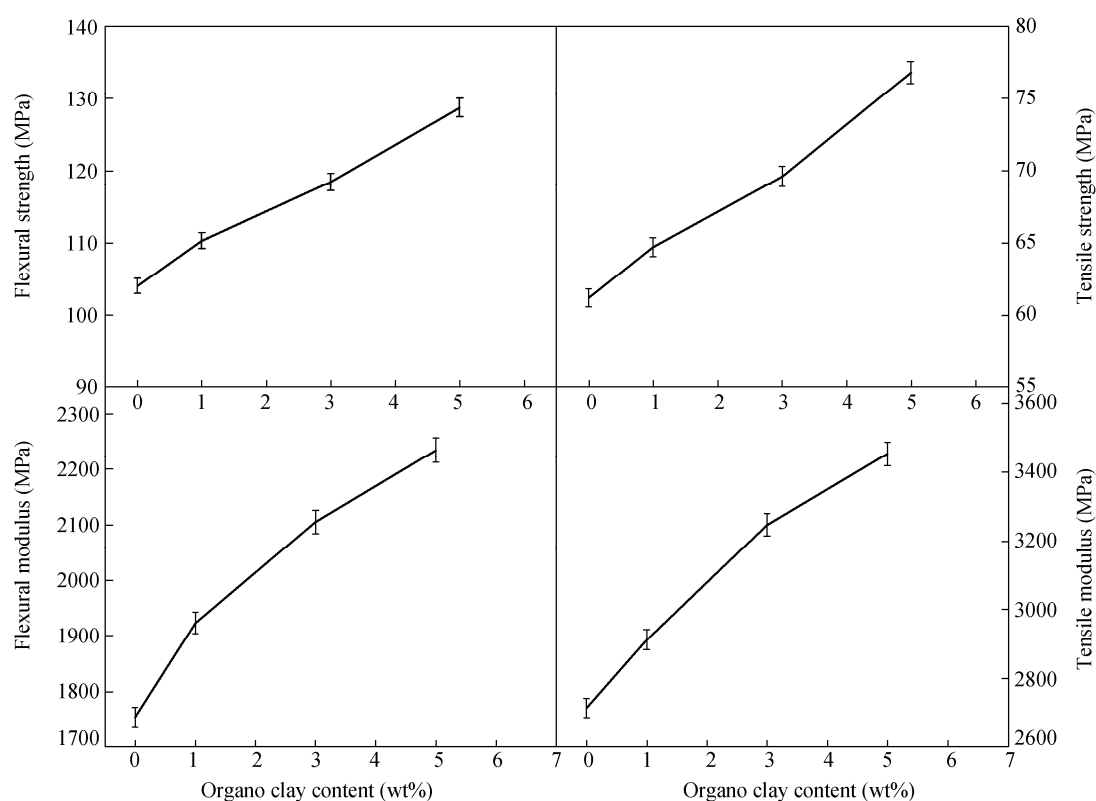


Fig. 2 Effect of organo-clay content on tensile and flexural properties of epoxy and polysulfone (8%)-epoxy systems

The tensile properties of nanocomposites formed from organo modified MMT clay were measured to determine the effect of interfacial properties on reinforcement. The tensile properties of organo clay filled polysulfone modified epoxy nanocomposites increases gradually according to the concentration of polysulfone and organo clay (Fig. 2). XRD results indicate that all the clay nanolayers are fully exfoliated, and the matrix is

completely cured. It is observed that the introduction of 5% organo clay into modified epoxy matrices enhances the tensile properties to an appreciable extent. For example the value of tensile strength of unfilled polysulfone (8%) modified epoxy system is 62.3 MPa, whereas 5% organo clay filled polysulfone modified epoxy system is 76.8 MPa.

Flexural Properties

The introduction of 4%, 8% and 12% polysulfone (by wt%) into epoxy resin enhances the flexural strength to an insignificant extent, as compared with that of unmodified epoxy system, due to the formation of interpenetrating polymer network (IPN) composed of the epoxy and linear polysulfone with flexible molecular skeleton. The values of flexural modulus also follow the similar trend. The flexural properties of the unmodified epoxy, organophilic montmorillonite clay filled epoxy and polysulfone-epoxy nanocomposite are presented in Table 1. The introduction of organo clay into polysulfone modified epoxy system has significant effect on flexural properties (Fig. 2). This may be due to the efficient interaction results between organoclay and polysulfone modified epoxy matrix.

Impact Strength

The introduction of polysulfone into epoxy resin improves the impact strength to an appreciable extent when compared with that of unmodified epoxy system. The incorporation of 4%, 8% and 12% polysulfone into epoxy systems enhances the values of impact strength by 24.1%, 35.2% and 48.6% respectively. This is due to the formation of entangled network structure developed due to the unsaturated active sites of polysulfone toughened epoxy system. This may also be explained due to the chain lengthening by the introduction of polysulfone and formation of flexible IPN structure within the system. Further the presence of ether linkage in the polysulfone skeleton is also responsible for the enhancement for values of impact strength due to its free molecular rotation.

The values of impact strength of organo clay filled polysulfone modified epoxy nanocomposites are increased appreciably according the concentration of organo clay (Fig. 3). The improvement of both toughness and strength in the case of the exfoliated nanocomposites is attributed due to the plasticizing effect of the dangling (surfactant) chains in the polymer matrix and reinforcement effect of the clay nanolayers^[36]. The nanolevel reinforcement of organophilic modified montmorillonite clay into polysulfone epoxy systems hinders the molecular mobility with improvement of mechanical properties.

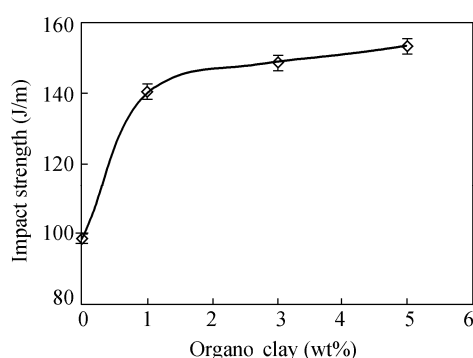


Fig. 3 Effect of organo-clay content on impact strength of epoxy and polysulfone-epoxy systems

Glass Transition Temperature

The polysulfone modified epoxy hybrids prepared are transparent at ambient temperature, and no evidence of phase separation is found. Further the single value of T_g observed for polysulfone modified epoxy system suggests that the hybrid is chemically bonded homogeneous product of amorphous nature. The value of glass transition temperature of epoxy system is decreased marginally when polysulfone is incorporated. The incorporation of polysulfone raised the viscosity of the system, which could result in an incomplete curing

reaction due to the steric hindrance under the curing condition^[37]. The thickening effect of polysulfone is also an important factor which gives rise to the reduction in the crosslinking density and consequent chain lengthening of polysulfone skeleton and hence the molecular flexibility occurs at low temperature.

The glass transition temperature of filled polysulfone epoxy nanocomposites is decreased gradually according to the concentration of organo clay. This may be due to catalyzed homopolymerization of epoxy during swelling period by alkylammonium cation or a plasticizing effect of unreacted resin or hardener monomers or the increase in free volume of hybrid systems^[38-40]. The T_g values of nanocomposites are found to be lower than that of the original matrix systems. The lower relaxation strength or higher crosslinking may be due to the exfoliation of the polymer molecules between the organo clay layers which greatly reduce their molecular mobility. This can be confirmed by XRD and mechanical studies, since the relaxation strength is associated with molecular mobility.

The incorporation of polysulfone into epoxy resin improves its thermal stability and enhances the degradation temperature according to its percentage concentration (Fig. 4). The presence of polysulfone 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 the unmodified epoxy system. The formation of interpenetrating network between polysulfone and epoxy also delays the degradation temperature of the systems.

The degradation temperature of organophilic nanoclay incorporated epoxy systems and organophilic nanoclay incorporated polysulfone toughened epoxy systems are related with increasing nanoclay concentration. It is observed that the degradation temperature increases with increasing nanoclay concentrations, as observed in the case of polysulfone toughened epoxy systems, and this is due to the plasticization of crosslinked epoxy networks formed between clay layers by hydrocarbon chains of alkylammonium ions present in the organophilic nanoclay (Fig. 5). Further, this enhancement on thermal stability is due to the presence of clay layers which act as barriers to minimize the permeability of volatile degradation products from the polysulfone-epoxy clay nanocomposites.

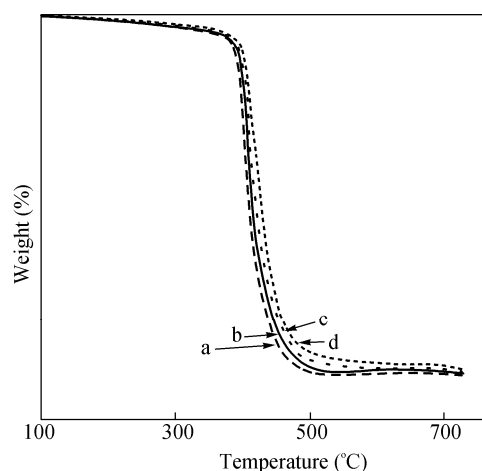


Fig. 4 TGA curves of epoxy and polysulfone-epoxy systems
a) Unmodified epoxy; b) 4%; c) 8%; d) 12% polysulfone-epoxy systems

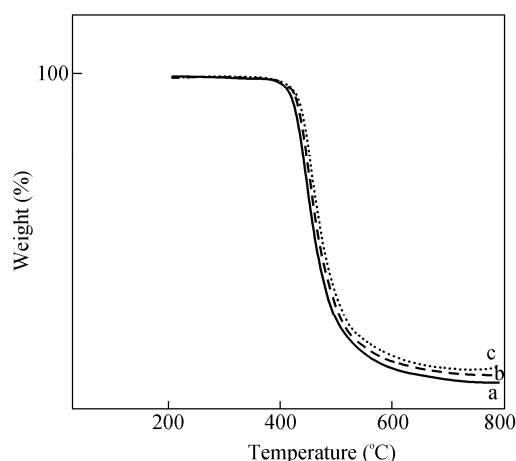


Fig. 5 TGA curves of organo clay modified polysulfone-epoxy systems
a) 1%; b) 3%; c) 5% organo clay modified polysulfone (8%) epoxy systems

Dynamic Mechanical Analysis

A plot of $\tan\delta$ as a function temperature is shown in Fig. 6. The loss tangent is a sensitive indicator of cross-linking. At temperatures above T_g damping decreases with increase in cross-linking. The DMA curves of unmodified epoxy, organo clay filled polysulfone modified epoxy clay nanocomposites at a heating rate of

10 K/min from 30°C to 300°C are presented in Fig. 6. It is observed from the figure that the introduction of organo clay shifts the glass transition temperature towards the lower temperature with reducing the intensity of the $\tan\delta$. The intercalation of the polymer molecules between the clay layers greatly reduces their molecular mobility and in turn decreases the intensity of the $\tan\delta$, since the relaxation peak height is associated with molecular mobility.

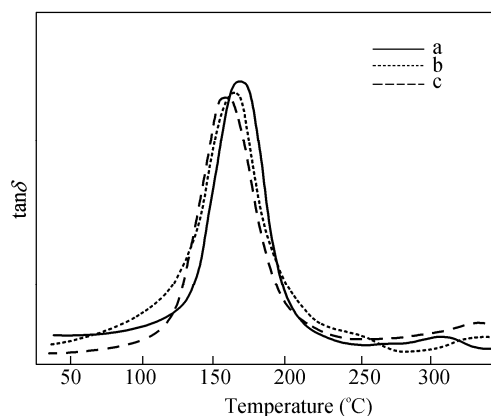


Fig. 6 Variation of $\tan\delta$ as a function of temperature
a) Unmodified epoxy; b) Organo clay filled epoxy;
c) Organo clay filled polysulfone modified epoxy systems

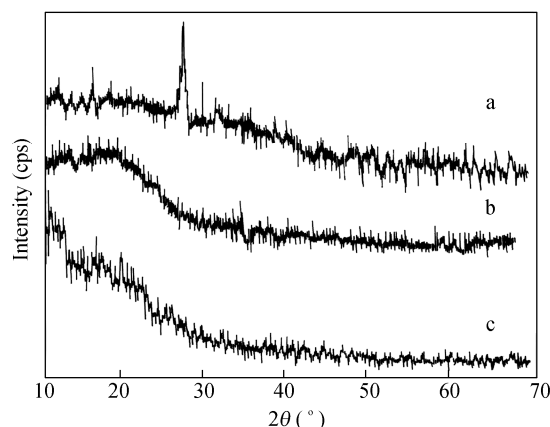


Fig. 7 XRD patterns of (a) montmorillonite clay,
(b) organo clay (5%) filled epoxy and (c) organo
clay (5%) filled polysulfone modified epoxy

X-ray Diffraction Analysis

XRD measurements were made to evaluate the spacing between the silicate layers in the organoclay filled hybrid PSF/EP nanocomposites. Bragg's Law ($n\lambda = 2d\sin\theta$) was used to compute the crystallographic spacing (Fig. 7). The XRD patterns of organoclay filled PSF/EP-epoxy systems suggested the formation of exfoliated nano hybrids (Fig. 7c). The clay layers are evenly dispersed throughout the epoxy matrix^[41, 42]. This is due to the compatibility of polysulfone-epoxy resin with the layered silicates, and the PSF-epoxy chains penetrate into the gallery and expand the nano size to some extent^[43]. From Figs. 7(b) and 7(c), it is observed that the 001 reflections of the clay is absent in the cured product indicating the delamination of the crystal structure of clay, which in turn confirms the formation of exfoliated nanocomposites^[39, 44]. It is also evident that the swelling period of clay in epoxy resin influences the formation of nanocomposites. Longer the swelling time favors the delamination of the clay^[39]. The introduction of nanoclay into a matrix system has significant effect on mechanical properties. The addition of nanoclay to the unmodified matrix increases the mechanical properties to an appreciable extent. The increase in mechanical strength is attributed to the formation of nanocomposites.

Morphology

The scanning electron micrographs of the organophilic montmorillonite clay filled epoxy nanocomposite and polysulfone modified epoxy nanocomposites are shown in Fig. 8. The micrograph of unmodified epoxy shows a smooth glassy fracture surface with cracks in different places. This indicates the brittle nature of the unmodified epoxy, which shows its poor impact strength (Fig. 8a). The fractured surface of polysulfone modified epoxy system also revealed smooth and homogeneous microstructure. The efficient interaction between polysulfone and epoxy resin and consequent IPN formation may be the cause for the development of homogeneous morphology (Fig. 8b). The micrograph of fractured surface of organo clay filled epoxy nanocomposite shows that the clay layers are not occupying the full volume, because the large regions of pure matrix are visible. Further, the clay layers are separated over the whole of the matrix (Fig. 8c).

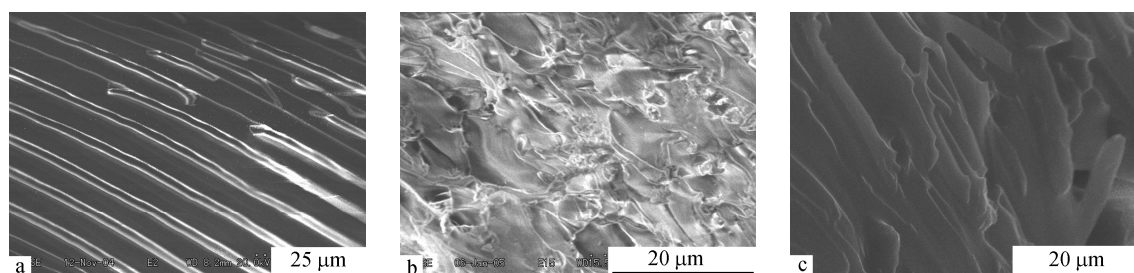


Fig. 8 SEM photographs of epoxy and polysulfone modified epoxy

a) Unmodified epoxy; b) Organo clay (5%) filled epoxy; c) Organo clay (5%) filled polysulfone (8%) modified epoxy

The percentage water absorption of unmodified epoxy, polysulfone oligomer toughened epoxy and organophilic clay filled polysulfone oligomer toughened epoxy nanocomposites are presented in Table 2. The incorporation of organophilic clay into both epoxy and polysulfone oligomer toughened epoxy systems reduces the percentage water uptake. This is due to the fact that the decrease in permeability influenced by the exfoliated nanocomposites structure.

Table 2. Heat distortion temperature and glass transition temperature of unmodified epoxy, organo clay filled epoxy and organo clay filled polysulfone modified epoxy nanocomposites

Epoxy/ Polysulfone/Clay composition	Heat distortion temperature (°C)	Glass transition temperature (°C)	Water absorption (%)
100/00/00	153	165	0.1201
100/00/01	151	163	0.1109
100/00/03	148	160	0.1086
100/00/05	145	155	0.0876
100/04/00	152	163	0.1176
100/08/00	149	161	0.1102
100/12/00	146	160	0.1068
100/08/01	142	156	0.0967
100/08/03	137	150	0.0752
100/08/05	132	145	0.0615

CONCLUSIONS

Organophilic MMT clay filled polysulfone toughened epoxy hybrid nanocomposites were developed. The thermal properties of polysulfone toughened epoxy and organophilic clay filled PSF-epoxy systems have been compared with those of unmodified epoxy systems, and a decreasing trend with PSF was observed whereas thermal stability was increased with increasing PSF content. The mechanical studies inferred that the incorporation of hydroxyl terminated polysulfone oligomer into epoxy resin improved the impact strength with slight increase in the tensile and flexural strength, whereas the incorporation of organophilic clay increased the stress-strain properties greatly according to its percentage content, along with much improvement in impact strength. The XRD patterns of organophilic clay filled hybrid PSF-epoxy systems suggested the formation of exfoliated nanocomposites to which the drastic improvement in mechanical behavior could be attributed. The fractured surfaces of the organophilic clay and polysulfone oligomer toughened epoxy system showed the presence of homogeneous microstructures. So, the hybrid matrix systems developed in the present work can be used to fabricate advanced composite components with better performance and enhanced longevity for engineering and aerospace applications.

REFERENCES

- 1 May, C.A. and Tanaka, G.Y., "Epoxy Resin Chemistry and Technology", Marcel Dekker, New York, 1973, p.44
- 2 Bauer, R.S., "Advances in Chemistry", American Chemical Society, Washington, D.C., 1979, p.114
- 3 Akutsu, U., Inoki, M., Daicho, N., Kasashima, Y., Srirashish, N. and Marushima, I., J. Appl. Polym. Sci., 1998, 69: 1737
- 4 Vabrik, Y., Czajlik, I., Tury, G., Rusznak, I., Ille, A. and Vig, A., J. Appl. Polym. Sci., 1998, 68: 111
- 5 Lin, M.S., Liu, C.C. and Lee, C.T., J. Appl. Polym. Sci., 1999, 72: 585
- 6 Li, Y., Shen, S., Liu, Y. and Gao, J., J. Appl. Polym. Sci., 1999, 73: 1799
- 7 Deng, B.L., Hu, Y.S., Chen, L.A., Chiu, W.Y. and Wu, T.R., J. Appl. Polym. Sci., 1999, 74: 229
- 8 Kaji, M., Nakahara, K. and Endo, T., J. Appl. Polym. Sci., 1999, 74: 690
- 9 Bucknell, C.B. and Gilbert, A.H., Polymer, 1989, 30: 213
- 10 Lestriez, B., Chapel, J.P. and Gérard, J.F., Macromolecules, 2001, 34: 1204
- 11 Gan, W., Yu, Y., Wang, M., Tao, Q. and Li, S., Macromolecules, 2003, 20: 7746
- 12 Bonnet, A., Pascault, J.P., Sautereau, H., Rogozinski, J. and Kranbuehl, D., Macromolecules, 2000, 10: 3833
- 13 Bonnet, A., Pascault, J.P., Sautereau, H. and Camberlin, Y., Macromolecules, 1999, 25: 8524
- 14 Pethrick, R.A., Hollins, E.A., McEwan, I., MacKinnon, A.J., Hayward, D. and Cannon, L.A., Macromolecules, 1996, 29(15): 5208
- 15 Wang, M., Yu, Y.F., Wu, X.G. and Li, S., Polymer, 2004, 45: 1253
- 16 Su, C.C. and Woo, E.M., Polymer, 1995, 15: 2883
- 17 Husang, P., Zheng, S., Huang, J. and Guo, Q., Polymer, 1997, 22: 5565
- 18 Mimura, K., Ito, H. and Fujioka, H., Polymer, 2000, 41: 4451
- 19 Rajasekaran, R. and Alagar, M., Int. J. Polym. Mater., 2007, 56(9): 911
- 20 Kim, B.S., Chiba, T. and Inoue, T., Polymer, 1995, 36(1): 43
- 21 Xie, X. and Yang, H., Mater. Des., 2001, 22: 7
- 22 Mimura, K., Ito, H. and Fujioka, H., Polymer, 2000, 41: 4451
- 23 Inoue, T., Prog. Polym. Sci., 1995, 20: 119
- 24 Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y. and Kurauchi, T., Mater. Res., 1993, 8: 1185
- 25 Yano, K., Usuki, A. and Okada, A., J. Polym. Sci., Part A: Polym. Chem., 1997, 35: 2289
- 26 Gilman, J.W., Kashiwagi, T. and Lichtenhan, J.D., SAMPE J., 1997, 33: 40
- 27 Vaia, R.A., Price, G., Ruth, P.N., Nguyen, H.T. and Lichtenhan, J.D., Appl. Clay Sci., 1999, 15: 67
- 28 Someya, Y. and Shibata, M., Polymer, 2005, 46(13): 4891
- 29 Osman, M.A., Rupp, J.E.P. and Suter, U.W., Polymer, 2005, 46(5): 1653
- 30 Yei, D.R., Kuo, S.W., Fu, H.K. and Chang, F.C., Polymer, 2005, 46(3): 741
- 31 Choi, Y.S., Xu, M. and Chung, I.J., Polymer, 2005, 46(2): 531
- 32 Zhang, Z., Zhang, L., Li, Y. and Xu, H., Polymer, 2005, 46(1): 129
- 33 Yalcin, B. and Cakmak, M., Polymer, 2004, 45(19): 6623
- 34 Loo, L.S. and Gleason, K.K., Polymer, 2004, 45(17): 5933
- 35 Yei, D.R., Kuo, S.W., Su, Y.C. and Chang, F.C., Polymer, 2004, 45(8): 2633
- 36 Wang, Z. and Pinnavaia, J.T., Chem. Mater., 1998, 10: 1820
- 37 Zheng, S., Zhang, N., Luo, X. and Ma, D., Polymer, 1995, 36: 3609
- 38 Kornmann, X., Lindberg, H. and Berglund, A., Polymer, 2001, 42: 1303
- 39 Dinakaran, K. and Alagar, M., Polym. Adv. Technol., 2003, 14: 574
- 40 Hussain, M., Varley, R.J., Mathys, Z., Cheng, B. and Simon, G.P., J. Appl. Polym. Sci., 2004, 91: 1233
- 41 Salahuddin, N.A., Polym. Adv. Technol., 2004, 15: 251
- 42 Fu, X.A., and Qutubuddin, S., Polym. Eng. Sci., 2004, 44: 345
- 43 Chen, C.G. and Curliss, D., Nanotechnology, 2003, 14: 643
- 44 Miyagawa, H., Drzal, L.T. and Carsello, J.A., Polym. Eng. Sci., 2006, 46: 452