

Preparation of Nanocomposites of Thermosetting Resin from Benzoxazine and Bisoxazoline with Montmorillonite

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Received 7 July 2005; accepted 19 September 2005

DOI 10.1002/app.23261

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermosetting resin from 2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) (PBO) and bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine)isopropane (BZ) was prepared, and it was found that the thermal property of the final resin was affected greatly by the content of PBO. The nanocomposite from the thermosetting resin from BZ and PBO (molar ratio of PBO to BZ, 0.8 : 1) (PBZ–PBO) and organically modified montmorillonite (OMMT) was prepared by melt method. Differential scanning calorimetry showed that on the introduction of OMMT, the onset curing temperature of the copolymerization of BZ and PBO decreased. The X-ray diffractometer and transmission electron micrograph characterization of the dispersion of OMMT in

the PBZ–PBO matrix suggested that exfoliation structure of OMMT was achieved. Dynamic mechanical analyses indicated that the nanocomposites exhibited much higher T_g values than the PBZ–PBO resin and pristine polybenzoxazine, and storage modulus of the nanocomposites was maintained up to higher temperature with the increasing OMMT content. Dynamic thermogravimetric analysis showed that the dispersion of clay nanolayers in the PBZ–PBO copolymer gave better thermal stability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4741–4747, 2006

Key words: benzoxazine; bisoxazoline; montmorillonite; nanocomposite

INTRODUCTION

Polymer–clay nanocomposite is a new class of composite material in which layered silicate as the reinforcing phase is dispersed in nanoscale size in a polymer matrix. Because of the nanoscale dispersion, when compared with pristine polymer matrix, the nanocomposites exhibit great improvement on many properties, and thus include the increase of tensile property, thermal stability, solvent resistance, and the decrease of the gas permeability, flammability, etc. Since the report of Nylon6/montmorillonite material from the Toyota research, considerable research efforts in recent years have been directed toward the synthesis and characterization of polymer–clay hybrids based on organically modified montmorillonite (OMMT). The study of OMMT nanocomposites has covered most polymeric systems reported.^{1–16}

The synthesis of benzoxazines and their application have been extensively investigated because of their superb properties compared with the traditional phenolic resins. Polybenzoxazine provides not only excellent properties of traditional phenolic, but also some

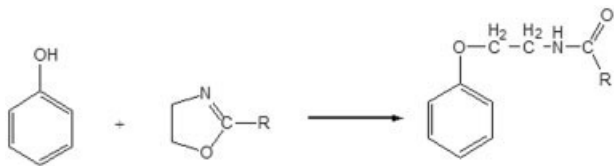
unique characteristics such as low moisture absorption, better static and dynamic mechanical property, and excellent dimensional stability due to the near-zero volumetric shrinkage during cure process. The cure of benzoxazine is in process through ring-opening oxazine rings without strong catalyst and produces no low molecular weight byproducts. In addition, the molecular design for the structure of benzoxazine monomers is easier, which is favorable for the development of high performance resin for various applications from various inexpensive raw materials.^{17–25}

The improvement of the properties of polybenzoxazine (PBZ) has been expected and required, and so, many studies have been undertaken. It was reported that toughness and thermal stability of PBZ improved when modified by rubber^{26,27} and epoxy,^{28,29} respectively. The mechanical property of PBZ was reinforced by glass-fiber³⁰ and carbon-fiber.^{31,32} Furthermore, PBZ/OMMT nanocomposites have attracted much attention. Because of the addition of OMMT, the curing temperature decreased observably compared with pure benzoxazine; storage modulus of the hybrid nanocomposites increased and T_g shifted to higher temperatures; and thermal stability also improved.^{33–38}

Oxazolines are five-membered heterocyclic compounds having one double bond, and that can react with carboxylic acid, anhydrides, aldehydes, epox-

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Contract grant sponsor: Committee of Natural Science Foundation of China; contract grant number: 50473041.



Scheme 1 Reaction of an oxazoline ring with a phenolic hydroxyl group.

ides, amines, and hydroxyl groups and so on.³⁹ So bisoxazolines can be used as the chain extender or crosslinking agent of polymer.⁴⁰ It was reported⁴¹ that phenolic resin, cured by bisoxazoline, had lower cure shrinkage and better toughness, while retaining high heat resistance, low flammability, and low smoke emission. The chain extending and crossing reaction of phenolic resin and bisoxazolines take advantage of the ring opening reaction of an oxazoline ring compound with a phenolic hydroxyl group, as shown in Scheme 1. Hajime et al.^{42,43} reported that the curing reaction of bisphenol A based benzoxazine (BZ) with bisoxazoline was that the ring opening of benzoxazine occurred, then the phenolic hydroxyl generated by it reacted with oxazoline. When there was some amount of oligomers in BZ, the heat and water resistance of the cure resin from BZ and bisoxazoline were better than that of the resin from neat BZ monomer.⁴³ But in the previous studies, the effect of bisoxazoline content on the property of the final resin has not been studied in detail. And the research of the modification of the thermosetting resin from benzoxazine and bisoxazoline by OMMT has not been reported.

In this article, we studied the effects of 2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) (PBO) content on the cure of pristine bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine)isopropane (BZ) monomer and on the thermal property of the final resin at the beginning. Then we chose the cure resin from BZ and PBO (molar ratio of PBO to BZ, 0.8 : 1) as the matrix, prepared the nanocomposite with OMMT by melt method. And the effect of the content of OMMT on the curing temperature of BZ and PBO blend was studied, and via step cure process, in the presence of OMMT, the curing behavior of the blend of BZ and PBO was also investigated. The dispersion of OMMT in PBZ–PBO matrix was confirmed by X-ray diffractometer (XRD) and transmission electron micrograph (TEM). Furthermore, the effect of OMMT on the dynamic mechanical property and the thermal stability of PBZ–PBO were studied.

EXPERIMENTAL

Materials

Bisphenol A (CR) was purchased from Haidian Xingxing Reagent Plant (Beijing, China), paraformaldehyde (AR) and aniline (AR) from Chemical Reagent

Institute (Tianjin, China), and OMMT from Zhejiang Fenghong Clay Chemical Industry (Zhejiang, China), 001 lattice spacing of it was 2.1–2.2 nm. 2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) (PBO) was purchased from Takeda Chemical Industries (Osaka, Japan). All reagents were commercially available compounds and were used as received without further purification.

Preparation of BZ monomer

BZ monomer was prepared from aniline, paraformaldehyde, and bisphenol A by using solvent method described in the previous study.¹⁷

Preparation of the blends of BZ and PBO

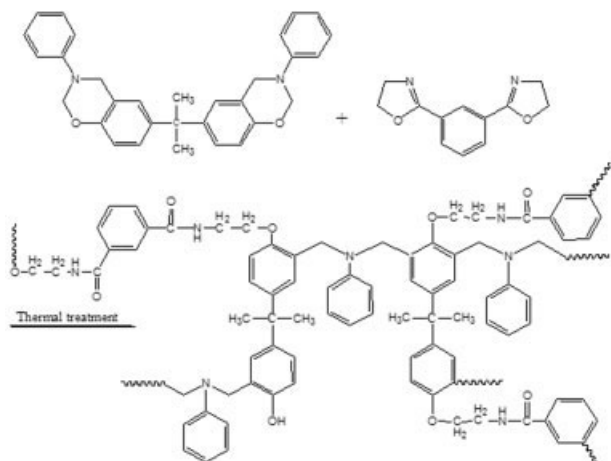
In the blends of BZ and PBO (BZ/PBO), the molar ratios of PBO to BZ were 0.2:1, 0.4:1, 0.6:1, 0.8:1, and 1:1, respectively. The procedure was as follows: In a 150-mL three-necked flask equipped with beater, condenser, and thermometer, a certain amount of PBO was added to 11.55 g (0.025 mol) BZ monomer, the temperature was gradually raised to 140°C, and the system was stirred until both PBO and BZ melt completely. The product was transparent light yellow solid.

Preparation of the mixtures of OMMT, BZ, and PBO

The mixtures of OMMT, BZ, and PBO were prepared by the melt method and the procedure is as follows: In a 150-mL three-necked flask equipped with beater, condenser, and thermometer, 11.55 g (0.025 mol) BZ monomer was melt at 110°C, then 4.32 g (0.02 mol) PBO and various amount of powdery OMMT were added to the melt. The mixture was kept stirring rigorously for 4 h to obtain the well dispersed mixture, then the temperature of the system was gradually raised to 140°C and stirred for 10 min to allow PBO melt completely. The mixtures were cast and cured in a mold at a specified temperature in the oven.

Preparation of the cured resins from BZ and PBO (PBZ–PBO) and nanocomposites of PBZ–PBO and OMMT (PBZ–PBO/OMMT)

Both the PBZ/PBO copolymers and the PBZ–PBO/OMMT nanocomposites were obtained by heating the mixtures at above 160°C for 1 h, 180°C for 2 h, 200°C for 1 h, and 220°C for 1 h in an air oven.



Scheme 2 Curing reaction of BZ with PBO.

Measurement

IR spectra were obtained with Nicolet-60SXB spectrophotometer using KBr disc. Differential scanning calorimetry (DSC) was recorded by using a PerkinElmer DSC, operating at a heating rate of 10°C/min under nitrogen. X-ray measurements were done with Rigaku D/MAX2500 VBZ+/PC XRD, using $\text{CuK}\alpha$ radiation and scanning rate of 3°/min. Transmission electron micrograph (TEM) was obtained with a Hitachi H-800-1 TEM, using an acceleration voltage of 200 kV. Dynamic mechanical analyses (DMA) were conducted on Rheometri Scientific™ DMTA V at 1 Hz at a heating rate of 3°C/min, and the dimensions of the sample was $25 \times 5 \times 1 \text{ mm}^3$. Thermogravimetric analysis (TGA) was obtained with TOSHIBA Netzsch 209C thermogravimetric analyzer at 10°C/min under nitrogen.

RESULTS AND DISCUSSION

Effect of PBO on the curing and the properties of the cured resin of BZ

As Hajime et al. reported,⁴³ in the curing progress of BZ monomer and PBO, the ring opening of benzoxazine occurred, and then the phenolic hydroxyl groups generated by the ring opening polymerization reacted with oxazoline ring as shown in Scheme. 2.

In the blends, the molar ratios of PBO to BZ were 0, 0.2 : 1, 0.4 : 1, 0.6 : 1, 0.8 : 1, and 1 : 1, respectively. The curing process of the PBO/BZ blend was investigated by DSC and the results were summarized in Table I. The DSC of each blend had single exotherm, as shown in Figure 3(b). Compared with pure BZ monomer, the curing temperature of blends of PBO and BZ with different molar ratio had little change. The onset curing temperature was about 225–232°C and the maximum 240–247°C. This suggested that the ring opening of BZ and the reaction of phenolic hydroxyl groups

TABLE I
DSC of BZ–PBO Blends with Different Molar Ratios

Composition				Exotherm		
BZ		PBO		Onset	Maximum	Amount
(g)	(mmol)	(g)	(mmol)	(°C)	(°C)	(J/g)
11.55	(25)	–	–	232	247	675
11.55	(25)	1.08	(5)	226	239	289
11.55	(25)	2.16	(10)	226	240	222
11.55	(25)	3.24	(15)	227	240	246
11.55	(25)	4.32	(20)	229	242	237
11.55	(25)	5.40	(25)	228	244	209

with PBO proceed rapidly in the curing process of the blends. The content of PBO has little influence on the cure of pristine BZ monomer.

The thermal properties of the copolymer of BZ and PBO (PBZ–PBO) were studied by using DMA. The result of DMA of PBZ–PBO with different molar ratio is shown in Figure 1. With the increase of the PBO content, the T_g values of the PBZ–PBO obtained from both the maximum of loss modulus (E'') and $\tan \delta$ had the same tendency. T_g increased with the increase of molar ratio of PBO to BZ at first and reached a maximum when the ratio was 0.4 : 1, then decreased when the molar ratio increased continually. The reason of these behaviors could be that two competition factors affected the performance of the copolymer. One was the increase of chemical crosslink density of BZ due to the introduction of PBO. The other was that the weakening of the force of hydrogen bonds, because with the increase of the content of PBO, the number of phenolic hydroxyl groups generated by the reaction of ring opening of oxazine ring in the copolymer decreased because it reacted with PBO. It was reported¹⁷ that in the polymer of BZ monomer, there were a lot of hydrogen bonds, which came from phenolic hydroxyls,

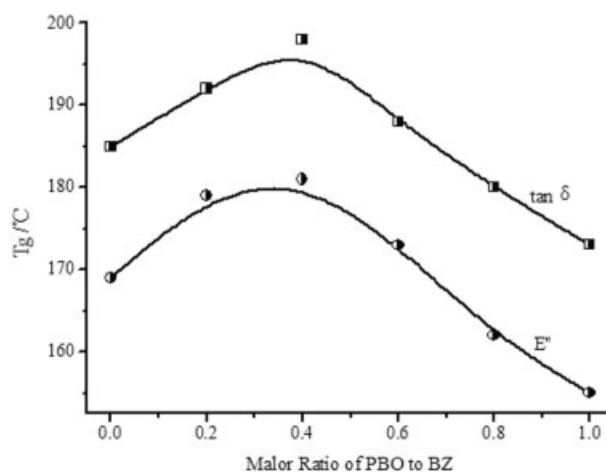


Figure 1 Effect of molar ratio of PBO to BZ on the T_g of PBZ–PBO.

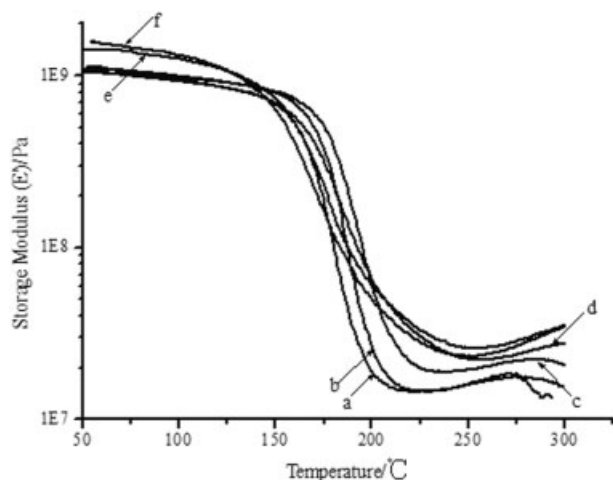


Figure 2 DMA of PBZ-PBO with different molar ratio of PBO to BZ: (a) 0 : 1; (b) 0.2 : 1; (c) 0.4 : 1; (d) 0.6 : 1; (e) 0.8 : 1; and (f) 1 : 1.

and the phenolic hydroxyl and the nitrogen atom caused the enhancement of both inter- and intramolecular force. So in the PBZ-PBO, with the increase of PBO content, the chemical density of crosslink increased and the number of phenolic hydroxyls decreased and the force of hydrogen bonds weakened; when the molar ratio of PBO to BZ was less than 0.4:1, the main factor affecting the property of copolymer was the former, and when the ratio was more than 0.4:1, the factor was the latter.

Furthermore, the initial storage modulus (E') at lower temperature increased from about 1.07 to 1.12, 1.09, 1.43, and 1.65 Gpa when the molar ratio of PBO to BZ were 0.2 : 1, 0.4 : 1, 0.8 : 1, and 1 : 1 respectively, as shown in Figure 2. The E' was maintained constant up to about 150°C. The reason should be the increase in the chemical crosslink density of BZ due to the introduction of PBO.⁴³

Effect of OMMT on the curing behavior and thermal properties of the cured resin from BZ and PBO (PBZ-PBO)

As reported,^{42,43} when the molar ratio of PBO to BZ was 1 : 1, there was a small amount of PBO that could not react with phenolic hydroxyl group, and so, there could be some PBO molecule without or partially reacting in the PBZ-PBO, which may affect the property of the final cure resin. But with the increase of the PBO loading, the flowability of the BZ-PBO blend became better at 140–150°C, which was helpful in molding. Therefore, in our research, the copolymer with 0.8–1 molar ratio of PBO to BZ was chosen as the matrix resin, and the effect of OMMT on the curing behavior and thermal properties was studied.

Curing behavior of the mixture of OMMT, BZ, and PBO (BZ-PBO/OMMT)

In the presence of OMMT, the curing behavior of the blend of BZ and PBO was monitored by using IR and DSC. From the results of IR, it was found that the absorption at 950 and 1500 cm^{-1} assigned to the trisubstituted benzene ring, at 1233 cm^{-1} due to the asymmetric stretching of C—O—C, and at 1327 cm^{-1} assigned to CH_2 wagging receptively in benzoxazine structure gradually decreased in the all curing cycles and disappeared after 220°C cure stage. While one new peak at 1483 cm^{-1} due to the tetra-substituted benzene ring appeared after the curing cycle of 160°C/1 h, and it was suggested that the ring opening of BZ monomer; the other new absorption at 1620 cm^{-1} assigned to the amide group also appeared after 160°C cure stage, and it was indicated that PBO reacted with the phenolic hydroxyl groups that generated by the ring-opening of benzoxazine ring. It also demonstrated that the amide groups generated by the ring-opening of oxazoline ring could not be associated with the curing reaction, because the resonance effect of amide group could lessen the nucleophilicity of nitrogen and the reactivity of the secondary amine group to oxazoline ring was lower than that of phenolic hydroxyl group.⁴³ Furthermore, the absorption at 516 and 1028 cm^{-1} due to Si—O of OMMT present in all cycle indicating the existence of a layered silicates framework in the mixture.

The DSC curves of the mixture of BZ-PBO/OMMT (100/5) at different curing stages is shown in Figure 3. With the comparison of Figure 3(a,b), it could be seen that in the presence of OMMT, the exotherm of BZ-PBO shift to lower temperature range. The reason for the decrease of curing temperature was the catalytic

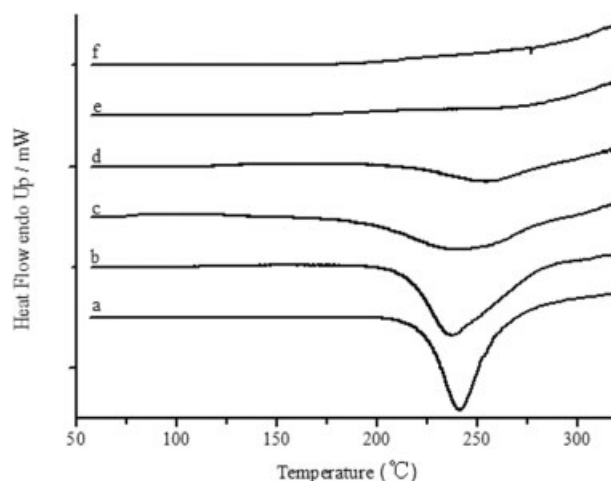


Figure 3 DSC of (a) BZ-PBO (molar ratio of PBO to BZ, 0.8:1) and BZ-PBO/OMMT (100/5) mixture at different curing cycle: (b) untreated; (c) 160°C/1 h; (d) 180°C/2 h; (e) 200°C/1 h; and (f) 220°C/1 h.

TABLE II
DSC of BZ, BZ-PBO (Molar Ratio 1 : 0.8) and BZ-PBO/OMMT Blends

	OMMT content (wt %)	Exotherm		
		Onset (°C)	Maximum (°C)	Amount (J/g)
BZ	–	232	247	675
BZ-PBO	–	229	242	237
BZ-PBO/OMMT-A	1	220	238	233
BZ-PBO/OMMT-B	2	220	238	243
BZ-PBO/OMMT-C	3	221	238	267
BZ-PBO/OMMT-D	4	220	237	256
BZ-PBO/OMMT-E	5	220	237	279

effect of the acidic onium protons inside clay galleries on the ring opening polymerization of benzoxazine.^{34–38} The exotherm of BZ-PBO/OMMT (100/5) mixtures became smaller and smaller in the all cure stages, and finally disappeared; and the exotherm amount continually decreased in the curing process and the amount became zero finally after 220°C curing cycle, indicating that the cure reaction of the system was finished after the cure at 220°C for 1 h.

The effect of the OMMT content on the cure reaction of BZ-PBO was studied by DSC and the result is summarized in Table II. It was found that in the existence of OMMT, the onset curing temperature of BZ-PBO decreased for about 10°C and when the OMMT content increased from 1 to 5%, the onset had insignificant change. It was suggested that only small amount of clay was enough to lower the onset curing temperature. However, it was also found that the maximum curing temperature decreased slightly in the presence of OMMT. The reason could be that in the system there were two kinds of curing reactions: one was the polymerization of benzoxazine, the other was the ring opening of oxazoline; OMMT had catalytic effect on the former, but for the latter, the effect of OMMT was little and reaction temperature should be the main factor. Moreover, compared with the pristine BZ-PBO blend, with the clay content increased, the exotherm amount of BZ-PBO/OMMT became higher, which indicated more complete cure process.

The dispersion of OMMT in the cured resin from BZ and PBO

XRD was a powerful technique to judge the nature of polymer-OMMT nanocomposites: either montmorillonite was intercalated or exfoliated and the diffraction in the range of $2\theta = 3\text{--}9^\circ$ indicated either an intercalated or an immiscible system. Figure 4 shows the XRD curves of OMMT and PBZ-PBO/OMMT nanocomposites with different clay loading in the region of $2\text{--}10^\circ$. Figure 4(a) showed that the diffraction peak of OMMT was at 4.20° and the basal spacing was

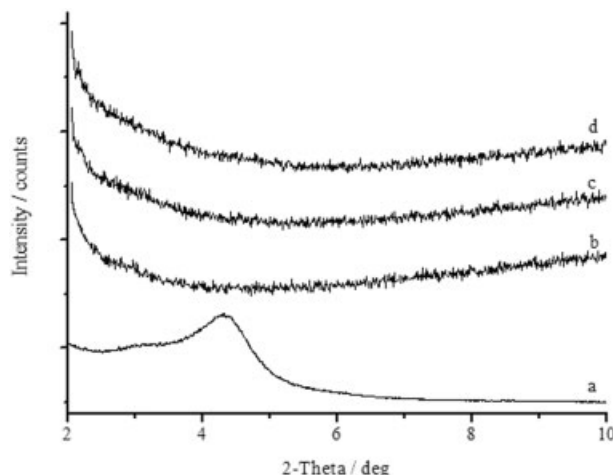


Figure 4 XRD of (a) OMMT and BZ-PBO/OMMT nanocomposite at various OMMT content: (b) 1%; (c) 3%; and (d) 5%.

2.10 nm. Compared with OMMT, diffraction of clay layers in the PBZ-PBO matrix had almost completely disappeared. This suggested that the basal spacing of OMMT in the nanocomposites was more than 4.41 nm, and it meant exfoliation structure of OMMT was achieved and disorder and loss of structure registry of the montmorillonite layers had occurred. Therefore, the XRD analysis indicated that because of the good compatibility of OMMT, BZ, and PBO, BZ monomer and PBO could successfully immigrate into the interlayer of the OMMT, and when the temperature was



Figure 5 TEM micrograph of PBZ-PBO/OMMT nanocomposite (clay content 3%).

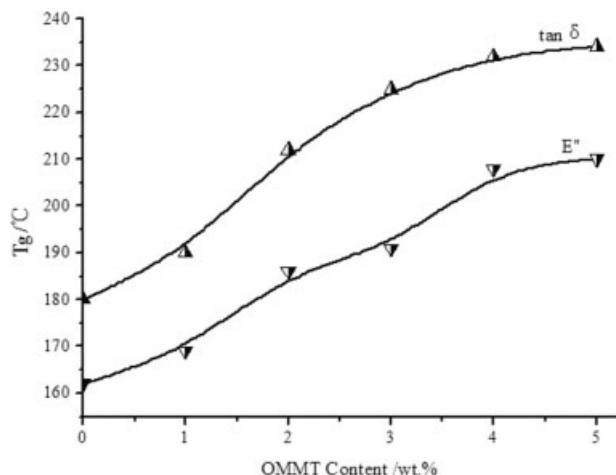


Figure 6 Effect of OMMT content on the T_g of PBZ-PBO/OMMT nanocomposites.

raised, the polymerization of BZ and the ring-opening reaction of oxazoline occurred, which led to the collapse of lattice structure of OMMT.

TEM of the PBZ-PBO/OMMT nanocomposite is shown in Figure 5. The white lines are the silicate layers that dispersed well in the matrix, and OMMT had an almost exfoliated structure, which in agreement with the disappearance of diffraction of 001 lattice spacing of OMMT in the matrix observed by XRD.

Dynamic mechanical analysis of PBZ-PBO/OMMT nanocomposites

Figure 6 showed the result of the DMA of PBZ-PBO/OMMT nanocomposites at different clay loading. It was found that the introduction of OMMT increased the glass transition temperatures (T_g) of the nanocomposites obviously, and with the increase of the OMMT content, the T_g of the nanocomposites also increased. The values of T_g obtained from both the maximum of loss modulus (E'') and $\tan \delta$ had similar tendency. The T_g of pristine PBZ-PBO matrix obtained from $\tan \delta$ was 180°C, and increased to 234°C at 5% OMMT con-

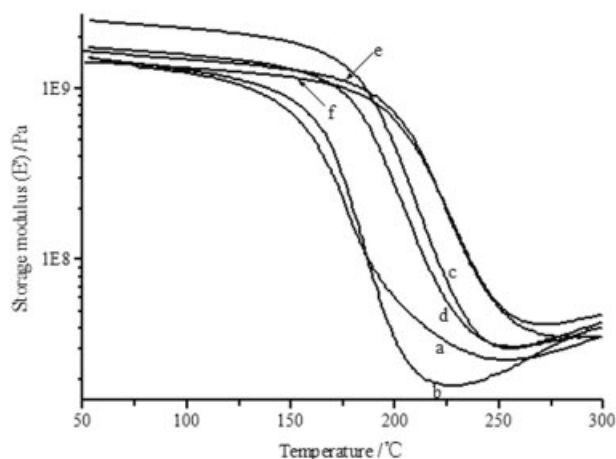


Figure 7 DMA of PBZ-PBO/OMMT nanocomposites with different OMMT content: (a) 0%; (b) 1%; (c) 2%; (d) 3%; (e) 4%; and (f) 5%.

tent, which was much higher than that of the neat polybenzoxazine.

The initial storage modulus (E') of PBZ-PBO/OMMT nanocomposites was increased with increase in clay content, as shown in Figure 7. With the introduction of OMMT, the initial storage modulus (E') of the PBZ-PBO matrix at lower temperature increased from about 1.43 to 1.52, 2.52, 1.74, and 1.65 GPa at 1, 2, 3, and 4% clay loading, respectively. Compared with the pristine PBZ-PBO, E' of nanocomposites was maintained constant to higher temperature by the increase of OMMT content.

These behaviors should contribute to the increase in the adhesion between the polymer and OMMT surfaces because of nanometer size, which restricted segmental motion of the polymer near the organic-inorganic interface.

Thermogravimetric analysis of PBZ-PBO/OMMT nanocomposites

The effect of the OMMT on the thermal property of PBZ-PBO/OMMT nanocomposites was monitored by

TABLE III
Effect of OMMT Content on the Weight Residue of PBZ-PBO/OMMT Nanocomposites at Different Temperature

OMMT content (wt %)	Weight residue at different temperatures				
	300°C	400°C	500°C	600°C	700°C
BZ	96.8	69.5	43.1	35.6	34.4
BZ-PBO	97.5	78.4	46.4	38.7	36.6
BZ-PBO/OMMT	98.1	78.5	46.3	38.3	36.3
	99.3	81.5	48.7	41.4	39.6
	98.9	80.0	49.8	42.5	40.9
	99.5	81.9	49.4	42.4	40.9
	99.0	82.3	53.7	45.6	43.7

dynamic TGA. The result of TGA was converted into weight residue at different temperatures versus clay content summarized in Table III.

With the introduction of OMMT, it was found that both the initial decomposition temperature and weight residues of nanocomposite were increased, which meant that the thermal stability of PBZ-PBO/OMMT was improved. And with the increase of clay loading, the improvement became more and more obvious. The char yield of neat PBZ-PBO copolymer at 700°C was 36.6%, and with 5% OMMT content in nanocomposite, the char yield increased to 43.7%. It was suggested that due to the montmorillonite nanolayers, which acted as barriers to minimize the permeability of volatile degradation products out from the material, the thermal properties of the nanocomposite enhanced. Furthermore, compared with the pristine polybenzoxazine, the improvement of PBZ-PBO/OMMT nanocomposite at various clay contents was significant, the reasons of the behavior should be the complete exfoliation structure of OMMT and increase in the crosslink density due to the reaction of PBO and phenolic hydroxyl groups.

CONCLUSIONS

The content of PBO has little influence on the cure temperature of BZ monomer, but affected the thermal property of the final copolymer greatly.

A novel nanocomposite of the thermosetting resin from benzoxazine and bisoxazoline and OMMT was prepared by using melt method. With the inclusion of OMMT, the curing temperature of BZ/PBO blend decreased. The exfoliated structure of the PBZ-PBO/OMMT nanocomposites was characterized with XRD and TEM. With the increasing OMMT content, storage modulus of the nanocomposites was maintained up to higher temperature and T_g increased. The thermal stability of the nanocomposites also improved with the inclusion of OMMT.

References

- Peter, C. L.; Zhen, W.; Thomas, J. P. *Appl Clay Sci* 1999, 15, 11.
- Jeffrey, W. G. *Appl Clay Sci* 1999, 15, 31.
- Michael, A.; Philippe, D. *Mater Sci Eng R Rep* 2000, 28, 1.
- Kojima, Y.; Usaki, A. *J Polym Sci Part A: Polym Chem* 1993, 31, 1755.
- Messersmith, P. B.; Giannelis, E. P. *Chem Mater* 1994, 6, 1719.
- Carrado, A. K. *Clays Clay Miner* 1996, 14, 506.
- Zhu, Z. K.; Yin, J. *J Appl Polym Sci* 1999, 73, 2063.
- Fu, X.; Qutubuddin, S. *Mater Lett* 2000, 42, 12.
- China, I. J.; Thomas, T. A.; Kim, H. C. *Polymer* 2001, 42, 5947.
- Ajit, R.; Nandika, A. D.; Bruce, G. *Polymer* 2002, 43, 3759.
- Yang, S. M.; Chen, K. H. *Synth Met* 2003, 135, 51.
- Ma, J.; Xu, J.; Ren, J. *Polymer* 2003, 44, 4619.
- Wang, S. F.; Hu, Y.; Zong, R. *Appl Clay Sci* 2004, 25, 49.
- Leslie, S. L.; Karen, K. G. *Polymer* 2004, 45, 5933.
- Maged, A.; Osman, J. E. P. R.; Ulrich, W. S. *Polymer* 2005, 46, 1653.
- Xin, N.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1994, 32, 921.
- Ishida, H.; Allen, D. J. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
- Shen, S. B.; Ishida, H. *J Appl Polym Sci* 1996, 61, 1595.
- Ishida, H.; Krus, C. M. *Macromolecules* 1998, 31, 2409.
- Wan, X. B.; He, J. B.; Xu, N. *Chem J Chin Univ* 2002, 22, 506 (in Chinese).
- Ishida, H.; Sanders, D. P. *Macromolecules* 2000, 33, 8149.
- Agag, T.; Takeichi, T. *Macromolecules* 2001, 34, 7257.
- Shen, S. B.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1999, 37, 3257.
- Gu, Y. *Thermosetting Resin* 2002, 17, 31 (in Chinese).
- Agag, T.; Takeichi, T. *Macromolecules* 2003, 36, 6010.
- Jang, J.; Seo, D. *J Appl Polym Sci* 1998, 67, 1.
- Ishida, H.; Yu, H. L. *Polym Polym Compos* 2001, 9, 121.
- Ishida, H.; Allen, D. J. *Polymer* 1996, 37, 4487.
- Rimdsut, S.; Ishida, H. *Polymer* 2000, 41, 7941.
- Ishida, H.; Low, H. Y. *J Appl Polym Sci* 1998, 69, 2559.
- Jang, J.; Yang, H. *J Mater Sci* 2000, 35, 2297.
- Jang, J.; Yang, H. *Compos Sci Technol* 2000, 60, 457.
- Ishida, H. *Mater Res Innovat* 2001, 4, 187.
- Yu, D. S.; Shi, Z. X.; Xu, R. W. *Chem Chin Univ* 2002, 23, 2188 (in Chinese).
- Shi, Z. X.; Yu, D. S.; Wang, Y. Z. *Eur Polym J* 2002, 38, 727.
- Shi, Z. X.; Yu, D. S.; Wang, Y. Z. *J Appl Polym Sci* 2003, 88, 194.
- Agag, T.; Takeichi, T. *Polymer* 2000, 41, 7083.
- Takeichi, T.; Zeidam, R.; Agag, T. *Polymer* 2002, 43, 45.
- John, A. F. *Chem Rev* 1971, 71, 483.
- Yasuo, S. *J Polym Sci Part A: Polym Chem* 1989, 27, 2749.
- Culbertson, B. M.; Tiba, O.; Deviney, M. L. U.S. Pat. 4,430,491 (1984).
- Hajime, K.; Akihiro, M.; Kiichi, H. *J Appl Polym Sci* 1999, 72, 1551.
- Hajime, K.; Shuuichi, T.; Akihiro, M. *J Appl Polym Sci* 2001, 79, 2331.