

Polybenzoxazine/clay hybrid nanocomposites: influence of preparation method on the curing behavior and properties of polybenzoxazines

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Abstract

Several types of polybenzoxazine/clay hybrid nanocomposites have been prepared from organically modified montmorillonite (OMMT) and mono- or bifunctional benzoxazine, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa) or bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (Ba), respectively. OMMT was prepared by a cation exchange of montmorillonite (MMT) with ammonium salts of amines such as tyramine, phenylethylamine, aminolauric acid, and dodecyl amine. Polybenzoxazine/clay nanocomposites were prepared by two different methods, namely melt method and solvent method. Melt method employs the blending of benzoxazine and OMMT above the melting point of benzoxazine without solvent. In the solvent method, OMMT was dispersed in an organic solvent and then blended with benzoxazine. XRD measurements of the polybenzoxazine/clay hybrid nanocomposites showed that the blending method and the kind of solvent play crucial roles in the dispersion of OMMT in the polybenzoxazine matrix. DSC showed that the inclusion of any type of OMMT significantly lowered the curing exotherm of benzoxazines. The hybrid nanocomposites exhibited higher T_g values than the pristine resins. Dynamic and isothermal TGA clearly showed that the thermal stability was improved by the inclusion of clay. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polybenzoxazine; Montmorillonite; Melt method

1. Introduction

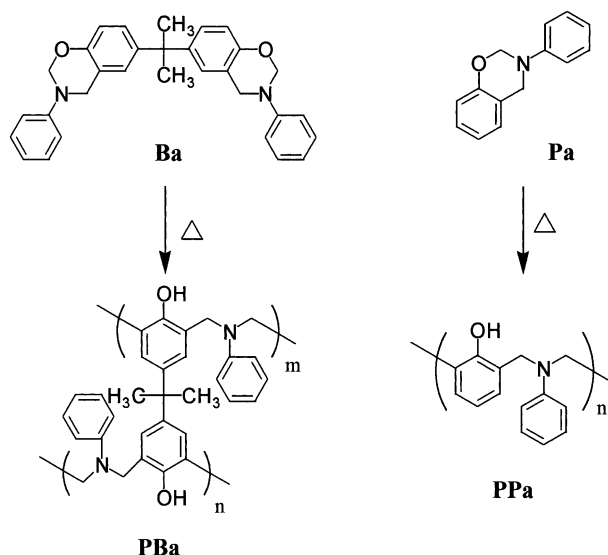
Polybenzoxazine is a newly developed thermoset resin with interesting properties. As a novel class of phenolic resins, it has been developed and studied to overcome the shortcomings of the traditional novolacs and resoles. Polybenzoxazine has excellent properties commonly found in the traditional phenolic resins such as heat resistance, good electrical properties, and flame retardance. Furthermore, polybenzoxazine has unique properties not found in the traditional phenolic resins such as excellent dimensional stability because of the ring-opening mode of polymerization, improved toughness, stable dielectric constant, and low moisture absorption. In addition, they can be synthesized from inexpensive raw materials, can be cured without strong acid or base catalyst, and do not release by-products during polymerization, thus being an attractive candidate for many applications [1–7].

Polymer–clay nanocomposite is a new class of composite materials, in which clay as a layered silicate is dispersed in nanoscale size in a polymeric matrix. Due to the nanoscale dispersion, when compared with the conventional fiber or

filler-filled composites, nanocomposites exhibit outstanding improvement on properties. These include the increasing of modulus, strength, thermal stability, solvent resistance and the decreasing of gas permeability and flammability [8–25]. The most widely used layered silicate for preparation of polymer–clay nanocomposite is montmorillonite (MMT).

MMT is a multilayer silicate mineral, in which galleries naturally exist inorganic cations, balancing the charge of oxide layers in a hydrophilic environment. The ion exchange of these cations with organic ammonium salts affords hydrophobic environment inside the galleries of organically modified MMT (OMMT) [15]. The resulting organophilic galleries of OMMT will enhance the compatibility with polymers [15], improve the dispersion of the silicate layers into the matrix [12] and assist the penetration of monomers and/or polymers into the galleries [22]. Also, organic ammonium salts can provide functional groups that can react or interact with the monomer or polymer to improve the interfacial strength between the reinforcement and the polymer matrix [18]. The dispersion of clay nanolayers and morphology of the nanocomposite depend on various factors, such as mixing method (melt or solvent), mixing temperature, solvent used, solvent concentration, the size of monomer or polymer, intercalation agent, ion exchange yield, mixing time and others.

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Scheme 1.

Recently, we successfully prepared polybenzoxazine/clay hybrid nanocomposites, in which introduction of OMMT led to a dramatic improvement on properties [25]. We employed melt method, which gave exfoliated OMMT nanocomposites. The melt method is sometimes difficult to fabricate, however, because of the high viscosity of the melt monomer and also because of the small difference in temperature between gelation point and melting temperature of the monomer. The addition of solvent will assist the intercalation and/or exfoliation process [18] and can improve the processability of benzoxazines/clay nanocomposites.

In this paper, we developed a new kind of polybenzoxazine/clay based on various types of OMMTs. We investigated the effect of preparation method and the effect of the type and content of OMMT on the properties of hybrid nanocomposites. We also examined the effect of the structures of monomer and polymer on the preparation and properties of hybrid nanocomposites. Monomers studied are bifunctional monomer, Ba, and monofunctional monomer, Pa, that leads to crosslinked PBa and linear PPa, respectively, as shown in Scheme 1 (structure of benzoxazine monomers and polymers).

2. Experimental

2.1. Materials

Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (Ba) and 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa) were kindly supplied by Shikoku Chemicals Co. and used as received. Kunipia-F, kindly supplied by Kunimine Ind. Co., is a Na-MMT with cation exchange capacity of 119 mequiv./100 g. Aminolauric acid and 2-phenylethylamine hydrochloride were used as received from Tokyo

Kasei Kogyo Co. Dodecylamine and hydrochloric acid (35%) were used as received from Kishida Chemical Co. Tyramine hydrochloride was used as received from Aldrich Chemical Co. Tetrahydrofuran (THF) and *N*-Methyl-2-pyrrolidinone (NMP) were purified by distillation over calcium hydride.

2.2. Preparation of OMMT

OMMT was prepared by cation exchange of MMT with organic ammonium salts in distilled water. The alkyl amines used for the cation exchange reaction were tyramine (Tyr), 2-phenylethylamine (Phe), aminolauric acid (LaA) and dodecylamine (Dod), as shown in Fig. 1. The OMMTs obtained were named Tyr-MMT, Phe-MMT, LaA-MMT, and Dod-MMT, respectively.

Modification of MMT by aminolauric acid is shown below as an example. Aminolauric acid ammonium chloride solution was prepared by the addition of 24.38 g of conc. HCl (234 mmol) to 50.39 g of aminolauric acid (234 mmol) in 2 l of distilled water. The mixture was stirred at 80°C until clear solution was obtained. To this solution a suspension of 150 g of MMT in 3 l of distilled water was added with mechanical stirring at 80°C. The stirring was continued for 5 h and the resultant white precipitate was collected by suction filtration. The filtrate was suspended in hot distilled water with mechanical stirring for 1 h and filtered. The washing process was repeated several times until no white precipitate of AgCl was formed by the addition of 0.1N AgNO₃ to certify the complete removal of any chloride ions. Finally, the precipitate was washed once with ethanol. The resulting OMMT was dried in vacuum at 80°C for 24 h.

Elemental analysis for Tyr-MMT: Anal. Calcd for (C₈H₁₂NO)_{0.3}Al₂Si₄O₁₀(OH)₂: C, 7.17%; H, 1.39%; N, 1.05%. Found: C, 6.25%; H, 2.07%; N, 1.07%. Elemental analysis for Phe-MMT: Anal. Calcd for (C₈H₁₂N)_{0.3}Al₂Si₄O₁₀(OH)₂: C, 7.26%; H, 1.41%; N, 1.06%. Found: C, 7.47%; H, 2.24%; N, 1.03%. Elemental analysis for LaA-MMT: Anal. Calcd for (C₁₂H₂₆NO₂)_{0.3}Al₂Si₄O₁₀(OH)₂: C, 10.17%; H, 2.30%; N, 0.99%. Found: C, 10.89%; H, 2.46%; N, 1.01%. Elemental analysis for Dod-MMT:

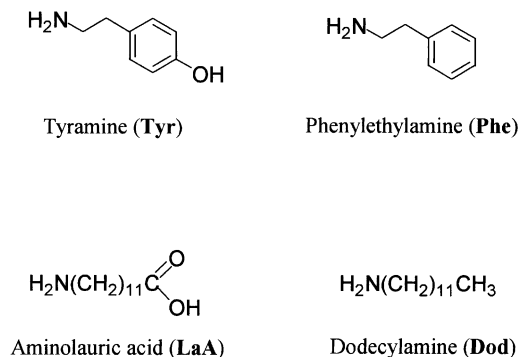


Fig. 1. Intercalation agents for OMMT preparation.

Anal. Calcd for $(C_{12}H_{26}N)_{0.3}Al_2Si_4O_{10}(OH)_2$: C, 10.39%; H, 2.50%; N, 1.01%. Found: C, 9.26%; H, 2.06%; N, 0.87%.

2.3. Solvent method for the preparation of polybenzoxazines/clay hybrid nanocomposites

The solvent method was carried out as follows as an example for 5% inclusion of OMMT. OMMT (0.5 g) was tried to disperse in 20 ml of NMP (or THF) at 80°C for 1–2 h. OMMT dispersed homogeneously in NMP, but did not disperse homogeneously in THF. To the OMMT suspension, 9.5 g of Ba or Pa was added and stirred at 80°C for 3 h. The blends were casted on glass plate that was pre-treated with dichlorodimethylsilane. After drying at 60°C for 16 h, the films were cured at 100, 150, 200 and 240°C for 1 h each in air oven. The obtained polybenzoxazine/clay nanocomposites were transparent and red-wine colored with thickness ranging from 0.2 to 0.4 mm.

2.4. Melt method for the preparation of polybenzoxazines/clay hybrid nanocomposites

Hybrid nanocomposite was prepared by the melt method according to the reported method [25]. Ba and Pa were melted at 100 and above 60°C, respectively. Various amounts of powdery OMMT were slowly added to the melted monomers with mechanical stirring. To assist the well dispersion of OMMT in the monomer, small amount of methylene chloride was often added, especially for the high content of clay. After stirring for 4 h, films were cast and then cured similarly as above.

2.5. Measurements

IR spectra were obtained with JASCO spectrophotometer model FT/IR-420 using KBr disc. Differential scanning calorimetry was recorded using Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10°C/min under nitrogen. Thermogravimetric analysis (TGA) was determined with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 5°C/min under argon. Dynamic viscoelastic measurements were conducted on ORIENTEC Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at a frequency of 35 Hz at a heating rate of 4°C/min. XRD was measured using X-ray diffractometer, Rigaku, RINT2000 using $CuK\alpha$ radiation (30 kV, 20 mA). The experiments were performed in a 2θ range of 2–10°, with scan rate of 0.3°/min and scan step of 0.01°.

3. Results and discussion

3.1. Preparation of OMMT

MMT was modified with various ammonium salts

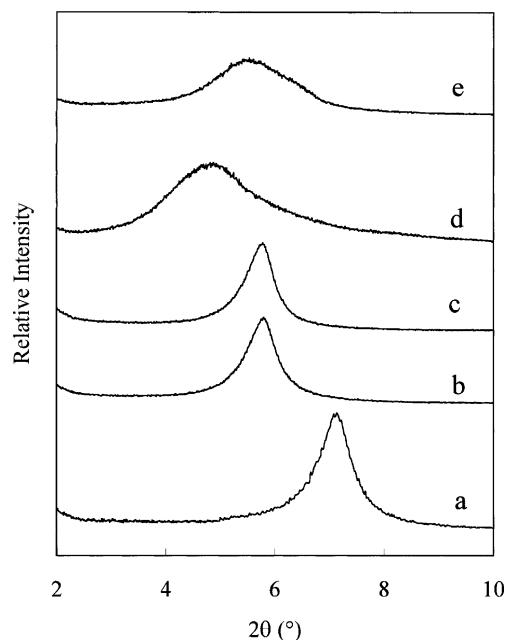


Fig. 2. XRD of (a) MMT and various OMMTs: (b) Tyr-MMT, (c) Phe-MMT, (d) LaA-MMT, (e) Dod-MMT.

according to the reported method [25]. The elemental analyses showed that satisfactory cation exchange were performed with any amines. The TGA of OMMT showed weight loss at 250–400°C due to the degradation of organic modifier. The amount of weight loss at the temperature range agreed well with the calculated amount of organic part in OMMT, which also showed that almost quantitative cation exchange was accomplished. The XRD patterns of MMT and various OMMTs are shown in Fig. 2. The diffraction peaks of MMT layers shifted to lower angles by the organo-modification. Accordingly, the original d -spacing of MMT (1.24 nm) increased to 1.52, 1.52, 1.83, and 1.59 nm for Tyr, Phe, LaA, and Dod, respectively. The calculated interlayer spacing of silicates expanded 2–3 times, as shown in Table 1. The interlayer spacing roughly correlated well with the length of the alkyl chains used for modification. Larger interlayer spacing should assist the penetration of benzoxazine monomers and exfoliation of nanocomposites by providing more hydrophobic environment.

Table 1
Interlayer spacing of MMT and OMMT modified with various organic modifiers

Code	Exchange cation	2θ (°)	d (001) (nm)	Interlayer spacing (nm)
MMT	Na^+	7.12	1.24	0.28
Tyr-MMT	$^+H_3N(CH_2)_2C_6H_4OH$	5.79	1.52	0.56
Phe-MMT	$^+H_3N(CH_2)_2C_6H_5$	5.78	1.52	0.56
LaA-MMT	$^+H_3N(CH_2)_{11}COOH$	4.83	1.83	0.87
Dod-MMT	$^+H_3N(CH_2)_{11}CH_3$	5.52	1.59	0.63

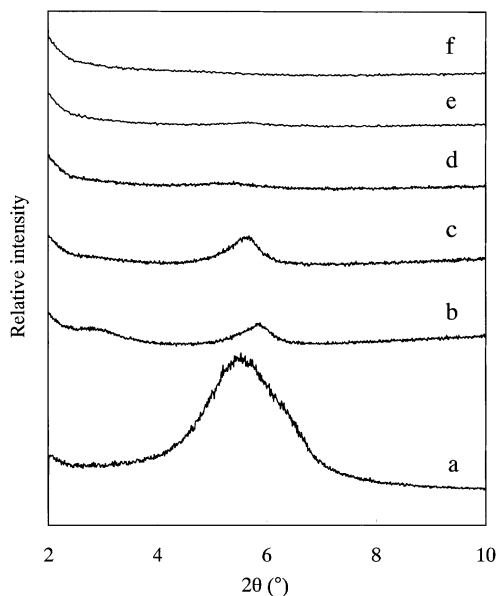


Fig. 3. XRD of (a) Dod-MMT and Ba/Dod-MMT (95/5) prepared by (b) solvent-method in THF after 100°C/1 h, (c) solvent-method in THF after 240°C/1 h, (d) solvent-method in NMP after 100°C/1 h, (e) solvent-method in NMP after 240°C/1 h, (d) melt method after 100°C/1 h.

3.2. Preparation of polybenzoxazine/clay hybrid nanocomposites

We used two methods for the preparation of benzoxazine/clay nanocomposites: melt method and solvent method. Melt method has great advantage industrially because it does not use solvent. Solvent method, on the other hand, has an advantage in easy processability because of the low viscosity, and suitable for preliminary study in small scale. Fig. 3 shows the XRD of Dod-MMT (Fig. 3a) and Ba/Dod-MMT hybrids with 5% of Dod-MMT prepared by various methods. Solvent method afforded intercalated or exfoliated nanocomposites depending on the solvent used for preparation. When THF was used as solvent, a small peak remained at $2\theta = 5.82^\circ$ (Fig. 3b) and at 5.62° (Fig. 3c), showing that complete exfoliation was not achieved. When NMP was used as solvent, however, the peak has almost completely disappeared, showing that exfoliation of OMMT was achieved (Fig. 3d and e). This reflects that dispersion of OMMT is much better in NMP and gives stable suspension than in THF. This shows that mixing solvent plays an important role on the dispersion of clay layers in the resulting composite. Melt method gave exfoliated structure, as shown in Fig. 3f, as was reported previously [25].

The effect of OMMT content on dispersion was examined by XRD. The 2 and 5% inclusion of Tyr-MMT gave exfoliated composites by the solvent method using NMP (Fig. 4b). Other OMMTs also showed the same XRD patterns. But, small peak was observed in case of 10% addition, suggesting that complete exfoliation was not achieved at high OMMT content (Fig. 4c). In case THF was used as solvent, completely exfoliated nanocomposites was not

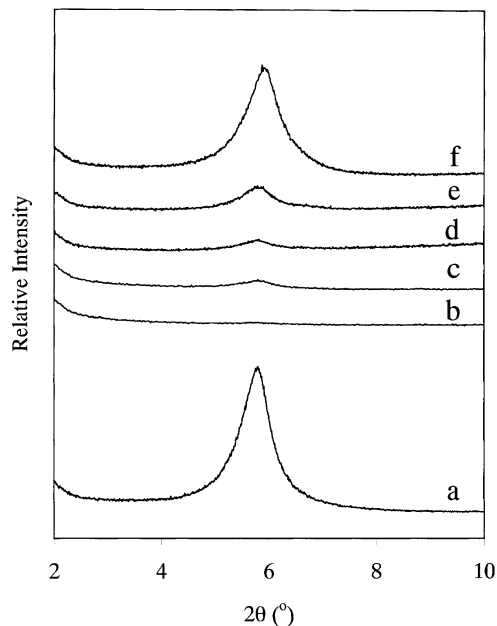


Fig. 4. XRD of (a) Tyr-MMT and PBa/Tyr-MMT at various OMMT content using solvent method; (b) 5%(NMP), (c) 10%(NMP), (d) 2%(THF), (e) 5%(THF), (f) 10%(THF).

obtained even at 2 and 5% of clay loading (Fig. 4d and e), and aggregation was significant at 10% of clay loading (Fig. 4f).

3.3. Curing behavior of the hybrid nanocomposite

The curing behavior of benzoxazines was followed by IR and DSC analysis. Fig. 5 shows IR of Ba/Tyr-MMT (95/5) after various curing stages. Decrease of characteristic

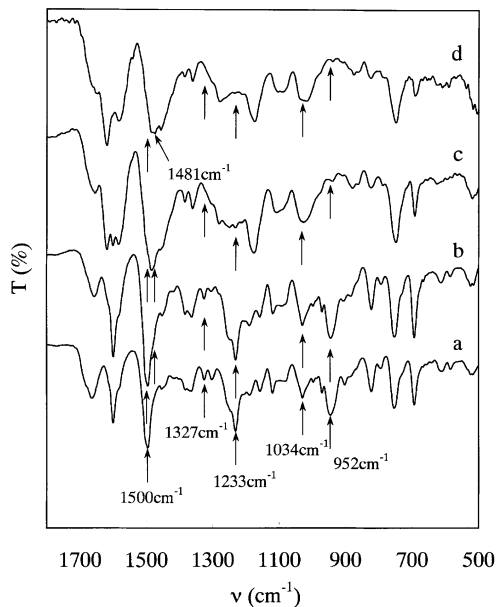


Fig. 5. IR spectra of Ba/Dod-MMT (95/5) after different curing temperatures: (a) 100°C/1 h, (b) 150°C/1 h, (c) 200°C/1 h, (d) 240°C/1 h.

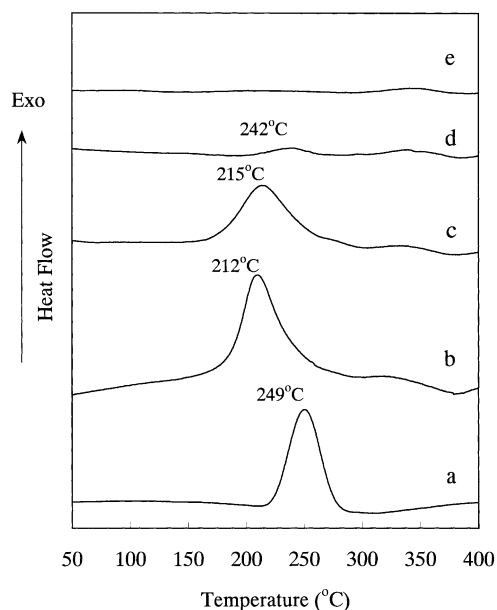


Fig. 6. DSC of (a) Ba and Ba/Tyr-MMT (95/5) using solvent method (NMP) after treatment at (b) 100°C/1 h, (c) 150°C/1 h, (d) 200°C/1 h, (e) 240°C/1 h.

absorption bands of benzoxazines with higher cure temperature was observed at 952, 1500 (trisubstituted benzene), 1233 (ether linkage) and 1327 cm^{-1} (CH₂ of benzoxazine ring). While, tetra-substituted mode at 1481 cm^{-1} increased [2,4,25]. The absorption at 1034 cm^{-1} present in all stages is attributed to Si–O in MMT layers.

Curing behavior of Ba–clay blends were studied by DSC. As an example, DSC of Ba and Ba/Tyr-MMT (95/5) at various curing stages is shown in Fig. 6. The pristine Ba showed an exotherm with onset and max at 210 and 249°C, respectively (Fig. 6a). The introduction of Tyr-MMT decreased the onset and the maximum for ca. 30°C (Fig. 6b). Also, LaA-MMT shifted the exotherm to lower temperature range as shown in Table 2. The decrease of the exotherm temperature is believed to be the catalytic effect of the acidic onium protons inside clay galleries on the ring opening polymerization of benzoxazines [25]. The

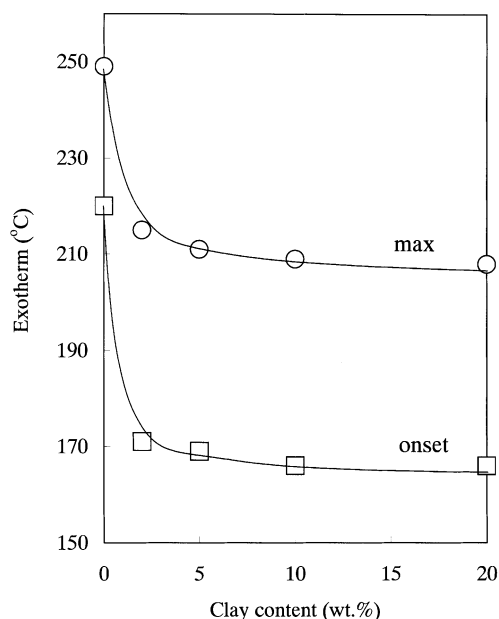


Fig. 7. Effect of clay content on the onset and maximum of exotherm temperature of Ba/Tyr-MMT (solvent method, NMP) after 100°C/1 h.

decrease of temperature for ring opening polymerization was also observed in the case of epoxy resin [21]. The exotherm of benzoxazines became small after the higher curing temperature and finally disappeared, suggesting that polymerization of benzoxazine was finished after the cure at 240°C for 1 h.

The influence of clay content on the polymerization of benzoxazines was monitored using Tyr-MMT. Large shift of exotherm to lower temperature range was clearly observed. The effect of clay content on the temperature of exotherm maximum is summarized in Fig. 7. The addition of 2 wt% Tyr-MMT decreased the onset to 192°C and maximum to 215°C. The large decrease of the exotherm temperature of Ba at only 2% of loading and only the slight decrease at higher loading suggest that only a small amount of clay is enough to lower the curing temperature of benzoxazines. Similar results are observed in Ba/LaA-MMT hybrid (Table 3). This behavior may be correlated

Table 2
DSC study of Ba and Ba/OMMT (95/5) at various curing stages

Code	Thermal treatment (°C/1 h)	Exotherm		
		Onset (°C)	Max (°C)	Amount (cal/g)
Ba	–	220	249	80
Ba/Tyr-MMT	100	189	212	79
	150	180	215	63
	200	207	242	6
	240	–	–	0
Ba/LaA-MMT	100	179	210	70
	150	182	216	50
	200	235	255	1
	240	–	–	0

Table 3
DSC study of Ba and Ba/OMMT at various clay contents after 100°C/1 h

Code	OMMT content (wt%)	Exotherm		
		Onset (°C)	Max (°C)	Amount (cal/g)
Ba	–	220	249	80
Ba/Tyr-MMT	2	192	215	77
	5	189	212	79
	10	177	209	64
	20	170	207	66
		2	191	212
Ba/LaA-MMT	5	179	210	70
	10	171	207	69
	20	163	200	61

with the dispersion of OMMT, which did not exfoliate completely at high content.

The effect of clay modifier on the polymerization behavior of Ba and Pa was followed by DSC. The results are summarized in Table 4. The addition of any type of OMMT lowered the maximum of exotherm for Ba almost uniformly to 209–212°C. The cure onset of Ba also lowered ca. 20–30°C in the presence of 5 wt% OMMT. There is a slight tendency that longer modifier (Dod and LaA) decreased the exotherm temperature more than the shorter modifier (Tyr and Phe). In case of Pa, the addition of OMMT modified with short aromatic amines (Tyr and Phe) lowered the onset by ca. 30°C and maximum temperature by ca. 40°C. The inclusion of OMMT modified with longer aliphatic amines (Dod and LaA) lowered the onset by ca. 40°C and the max by ca. 55°C. This difference in lowering of exotherm temperature by the organic modifier is considered to come from the difference in the gallery height of OMMT. The longer aliphatic modifier expanded the clay galleries more than the shorter aromatic modifier, which assisted the dispersion of OMMT into the matrix and allowed the monomers to penetrate easily into the galleries, especially for the smaller Pa.

It is also noted that the smaller the size of benzoxazine molecule, the higher the effect of OMMT on curing

behavior. The effect of clay addition on Pa is much larger than on Ba. The smaller Pa is easier to penetrate into the clay galleries and the amount of Pa molecules in contact with catalytic clay surface should be larger than the bigger Ba molecule.

Organic modifier can provide functional groups that can react or interact with the monomer or polymer, such as phenolic group of Tyr-MMT and carboxylic acid of LaA-MMT. Phenolic compounds with free *ortho* and *para* position can initiate polymerization of benzoxazines [1,26]. Carboxylic groups also can act as catalyst for benzoxazines [27]. However, as summarized in Table 4, the difference of functionality of clay modifier did not give any significant effect on the curing behavior of benzoxazines. Thus, the acidic onium protons on the clay surface have much more predominant effect as catalyst than clay functionalities.

3.4. Dynamic mechanical analysis of polybenzoxazine/clay nanocomposite

Fig. 8 shows the dynamic mechanical analysis (DMA) of Ba/Tyr-MMT at various clay contents. The addition of clay into polymers increased the glass transition temperatures (T_g) of the hybrid nanocomposite. The T_g of pristine PBA (150°C) obtained from the maximum of loss modulus (E'')

Table 4
DSC study of benzoxazines and benzoxazines/clay (95/5) with different OMMT types after 100°C/1 h

Code	OMMT content (wt%)	Exotherm		
		Onset (°C)	Max (°C)	Amount (cal/g)
Ba	–	220	249	80
Ba/Tyr-MMT	5	189	212	79
Ba/Phe-MMT	5	187	212	74
Ba/LaA-MMT	5	179	210	70
Ba/Dod-MMT	5	175	209	79
Pa	–	221	230	63
Pa/Tyr-MMT	5	180	199	60
Pa/Phe-MMT	5	180	200	59
Pa/LaA-MMT	5	167	191	66
Pa/Dod-MMT	5	161	188	62

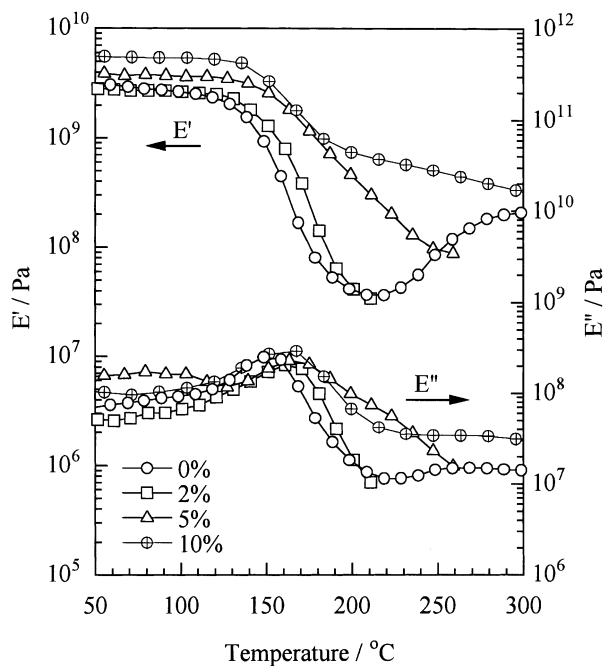


Fig. 8. Viscoelastic analysis of (a) PBa and PBa/Tyr-MMT prepared by solvent method (NMP) cured at 240°C/1 h for various clay contents: (b) 98/2, (c) 95/5, (d) 90/10.

increased to 163 and 167°C by the addition of 2 and 5 wt% of OMMT, respectively, as shown in Fig. 9. The T_g values then started to decrease slightly at 10 wt% of clay loading. The T_g values obtained from $\tan \delta$ had the same tendency. The decrease of T_g is considered to be associated with the incomplete exfoliation of silicate layers.

Increasing the clay content also increased initial storage modulus (E') at room temperature from ca. 3 to 4.2 GPa and 5.6 GPa at 5 and 10% clay loading, respectively. The

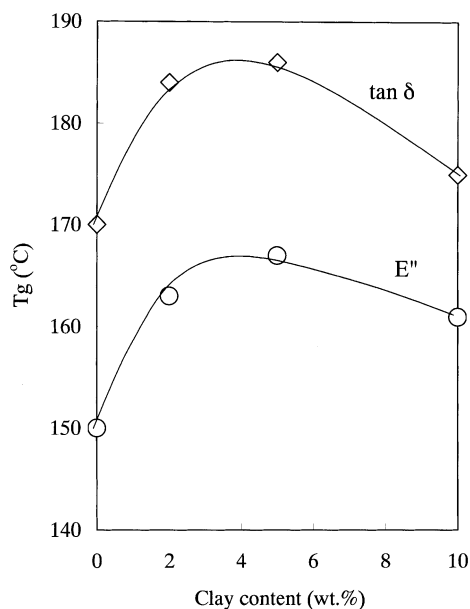


Fig. 9. T_g of PBa/Tyr-MMT at various clay contents.

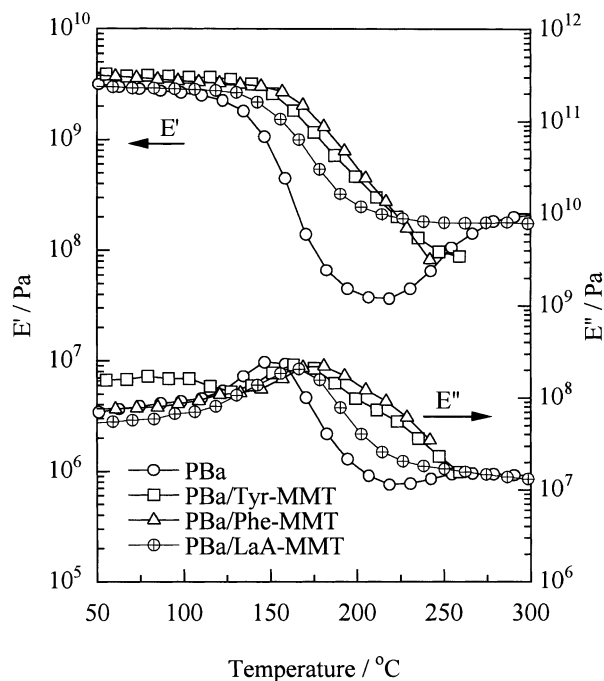


Fig. 10. Viscoelastic analysis of (a) PBa and various PBa/clay (95/5) prepared by solvent method (NMP): (b) Tyr-MMT, (c) Phe-MMT, (d) LaA-MMT (95/5) after 240°C/1 h.

storage modulus was maintained constant up to higher temperatures by the increase of clay content. This behavior can be attributed to the effect of restriction of segmental motion of the polymer near the organic–inorganic interface, due to the increased adhesion obtained between the polymer and OMMT surface [25].

Fig. 10 shows the DMA of Ba with various types of OMMT at 5% of clay loading. The inclusion of any kind

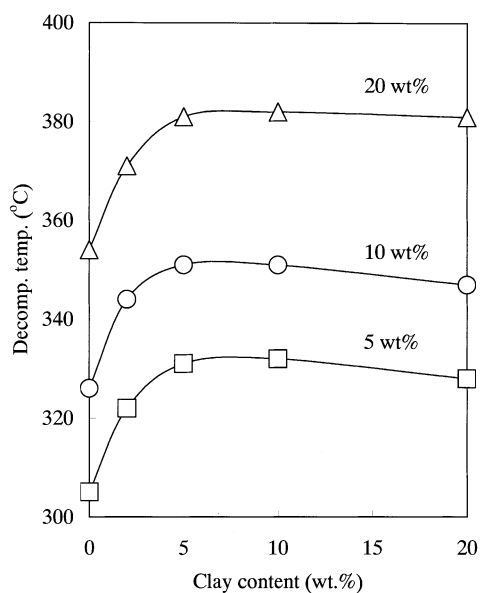


Fig. 11. Weight loss temperatures of PBa/Tyr-MMT prepared by solvent method (NMP) at various clay contents.

Table 5
TGA results of PBA-clay nanocomposites

Sample	OMMT		Weight loss temperature (°C)		Char yield (%)
	Wt%	Type	5 wt%	10 wt%	
PBa	0	Tyr-MMT	300	330	34
Ia	2	Tyr-MMT	321	343	36
Ib	5	Tyr-MMT	331	352	45
Ic	10	Tyr-MMT	331	351	46
Id	20	Tyr-MMT	342	348	50
II	5	Phe-MMT	330	351	45
III	5	LaA-MMT	338	361	43
IV	5	Dod-MMT	306	340	42

of the OMMTs shifted the T_g of benzoxazines to higher temperatures by 15–25°C. There was no appreciable difference in improvement of T_g among the organic modifier.

3.5. Thermal stability of polybenzoxazines/clay hybrid nanocomposites

TGA of PBa/clay hybrids was studied to examine the effect of clay content and the degree of dispersion on the thermal stability of polybenzoxazine. TGA of Ba/Tyr-MMT with various clay content prepared by solvent method using NMP clearly showed a tendency that the inclusion of clay led to an improvement on the thermal stability of the resin from the temperatures of 5 and 10% weight loss (Fig. 11). The improvement is significant at relatively low clay loading and reaches maximum at around 5% loading, as was found in the enhancement in T_g . This proves that just a few part of clay is enough to improve the thermal stabilities of benzoxazines. When THF was used as solvent in the

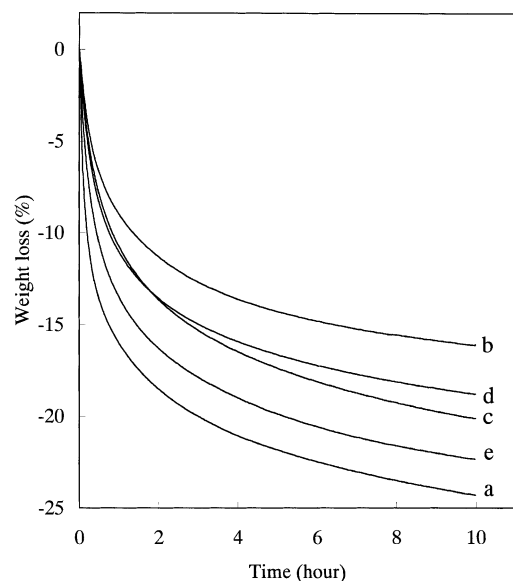


Fig. 12. Isothermal TGA of (a) PBA and various PBA/clay nanocomposites: (b) Tyr-MMT, (c) Phe-MMT, (d) LaA-MMT, (e) Dod-MMT (95/5) after 240°C/1 h.

same system, the weight loss temperatures did not improve by the inclusion of clay. This shows that complete exfoliation has significant effect on improving the thermal stability.

Dynamic TGA of Ba with various types of clay is summarized in Table 5. The thermal stability of Ba was improved by the inclusion of any kind of OMMT. Isothermal TGA of Ba with various types of clay is shown in Fig. 12, which also shows that inclusion of any kind of OMMT is effective to improve the thermal stability. Among the OMMT, aromatic modifiers were more effective than the aliphatic modifier.

4. Conclusions

A new kind of polybenzoxazine/clay nanocomposites based on various types of OMMTs was successfully prepared by melt method and solvent method. Morphology depended on the method and solvent used for preparation. In the melt method and in the solvent method using NMP as a solvent, a complete exfoliation of clay nanolayers into polybenzoxazine matrix was achieved. But the solvent method using THF did not completely exfoliate clay layers. The curing temperatures of benzoxazines lowered by the OMMT loading, suggesting the catalytic effect of clay surface on the ring opening polymerization of benzoxazines. The effect of OMMT on curing behavior of benzoxazines is mainly affected by the onium ions inside the clay galleries, and did not depend so much on the type of functional group of modifier. Storage modulus of the hybrid nanocomposite increased and T_g shifted to higher temperatures with the addition of clay. Thermal stability also increased with the introduction of clay. The effect of clay was most significant at around 2–5 wt% of inclusion for the improvement of various properties.

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