

Polybenzoxazine–montmorillonite hybrid nanocomposites: synthesis and characterization

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Abstract

Polybenzoxazine–clay hybrid nanocomposites were prepared from a polybenzoxazine precursor (**B-a**) and organically modified-montmorillonite (**OMMT**) as a type of layered silicates. **OMMTs** were prepared by surface treatment of montmorillonite (**MMT**) by octyl, dodecyl or stearyl ammonium chloride. The curing behavior of **B-a** in the presence of dispersed **OMMT** was followed by IR and DSC. DSC showed that the onset of the ring opening polymerization of pristine **B-a** started at 223°C. The ring opening polymerization of **B-a** in the presence of **OMMT** started at 177–190°C, however, suggesting the catalytic effect of the **OMMT** surface on the ring opening polymerization. DSC and IR indicated that the curing of **B-a** was completed by the end of the 230°C cure cycle. The dispersion of **OMMT** in the polybenzoxazine matrix was confirmed by XRD, which indicated the collapse of the registry of the **OMMT**. The absence of basal spacings diffractions of **OMMTs** from the XRD patterns suggests the dispersion of **OMMT** layers on the molecular level when the surface was pretreated with long chain surfactants like dodecyl or stearyl ammonium chloride. However, in case of **OMMT**, which was pretreated with short chain surfactants like octyl ammonium chloride, the intercalation of polybenzoxazine into the clay galleries occurred with a regularly stalked layered structure. Viscoelastic measurements showed that the T_g s of the hybrid materials were higher than that of the pristine resin. In addition, the storage moduli of the hybrid materials were maintained up to higher temperatures suggesting the reinforcement attained by **OMMT**. Isothermal and dynamic TGA showed that nanocomposites have delayed decomposition temperatures when compared with pristine polybenzoxazine indicating the enhancement in the thermal stability. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocomposites; Polybenzoxazine; Montmorillonite

1. Introduction

The interfacial adhesion between the polymer matrix and the reinforcing material plays an important role in determining the mechanical properties of a polymer composite. In conventional composites, the reinforcing material and polymer are combined on a macroscopic scale leading to microcomposites [1]. Thus, these composites usually have poor adhesion between the matrix and the reinforcing materials. A better interfacial bonding will impart better properties to a polymer composite such as interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance [2,3].

Nanocomposites are a class of composites in which the reinforcing phase dimensions are in the order of nanometers [4]. Because of their nanometer size characteristics nano-

composites possess superior properties than the conventional microcomposites due to maximizing the interfacial adhesion. Such improved properties can be attained in nanocomposites in which the building blocks are dispersed in a polymer matrix. Examples of the building blocks are nanoscale metal particles [5], silica nanotubes [6] and sheets of a ceramic like layered silicates [7].

Layered clays dispersed in a polymer matrix as a reinforcing phase are one of the most important forms of organic–inorganic hybrid nanocomposites [8–10]. Thus, smectite clays became good candidates for the preparation of organic–inorganic nanocomposites because they can be broken down into nanoscale building blocks. Nanostructured composites based on polymer and layered silicates typically exhibit properties far superior to those of separate components, which make them extremely interesting in the field of design and creation of new construction materials. Thus, since the discovery of the improved mechanical properties of nylon by reinforcing with exfoliated clay platelets [11], the general perception that clays act as low cost fillers in polymers has been changed

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because of their ability to enhance the properties of the final material. The preparation methods for the layered-silicate polymer nanocomposite can be classified into two ways. The first is the intercalation of a monomer into the interlayer galleries and subsequent heat treatment for polymerization [11–13]. The second is the direct intercalation of a preformed polymer into the layered silicates [14].

Extensive researches for preparations of polymer–clay nanocomposites have been investigated widely in order to obtain novel organic–inorganic nanocomposites with enhanced properties such as mechanical, thermal and fire resistance [15–17], and barrier properties [18–20]. The use of organically modified clays as precursors for preparation of nanocomposites has been studied into various types of polymer systems including nylon-6 [21–28], epoxy [29–37], polyimide [18–20,38], polyester [39], polyetherimide [16], polydimethylsiloxane [40], polypropylene [41], polyacrylamide [42], amine terminated acrylonitrile–butadiene rubber (ATBN) [14], polyurethane [43,44], poly(vinylpyrrolidone) [12], polypyrrol [45], polyaniline [46], polystyrene [13,47–49], polydiacetylene [50], polyacrylonitrile [51], poly(*p*-phenylenevinylene) [52], and poly(ethylene oxide) [53].

Polybenzoxazine has been recently developed and studied as a novel class of phenol resins to overcome the shortcomings of the traditional phenol resins [54–66]. It has excellent dimensional stability because of the ring opening cure process. Also, it can be synthesized from inexpensive raw materials and cured without strong acid as a catalyst. The present work is a part of our ongoing research for preparation of high performance polymer–clay nanocomposites capable of meeting the recent technological requirements. In an attempt to do so, in the current research we prepared high performance polybenzoxazine–clay nanocomposites with properties superior to that of pristine polybenzoxazine.

2. Experimental

2.1. Reagents

Kunipia-F, kindly supplied by Kunimine Ind. Co., is a Na-montmorillonite (**MMT**) with cation exchange capacity (CEC) of 119 meq/100 g. Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (**B-a**) as a polybenzoxazine precursor was kindly supplied by Shikoku Chemicals Co. and used as received. Octyl, dodecyl and stearyl amines were used as received from Tokyo Kasei.

2.2. Preparation of organically modified montmorillonite-type silicate

Organophilic montmorillonite (**OMMT**) was prepared using various alkyl ammonium salts according to the reported methods [18,20]. Modification of **MMT** by dodecyl ammonium chloride as an example was carried

out as follows. Dodecyl ammonium chloride solution was prepared by the addition of 4.17 g of conc. HCl (40 mmol) to 7.41 g of dodecylamine (40 mmol) in 1000 ml distilled water. The mixture was stirred at 80°C until a clear solution was obtained, indicating the formation of ammonium salt. To this solution a suspension of 20 g of **MMT** in 1000 ml of distilled water was added with mechanical stirring at 80°C. The stirring was continued for 5 h. The resulted white precipitate was collected by suction filtration. The precipitate was suspended in hot distilled water with mechanical stirring for 1 h to remove the adsorbed salts. This process was repeated several times until no chloride was detected in the filtrate when adding 0.1N AgNO₃. The precipitate was dried in a vented oven at 100°C for 3 days and then at 110°C under vacuum for 24 h.

2.3. Preparation of polybenzoxazine–**MMT** hybrids

B-a and **OMMT** were blended together in different weight ratios. The general procedure for preparation of the blends was carried out as follows: The **OMMT** was grained and sieved to separate sizes less than 63 μm. In 100 ml flask, **B-a** was melted and mechanically stirred at 100°C. To this melt the required ratio of **OMMT** was added portionwise. The mixture was mechanically stirred to achieve well dispersion of the **OMMT** in **B-a**. Small amount of methylene chloride was added to assist the dispersion of the **OMMT**. The mixture was heated at 120°C for 2 h under vacuum to remove the solvent and air bubbles. The mixture was free cast as a film on a glass plate with thickness in the range of 0.1–0.2 mm. The surface of the glass was pretreated by dichlorodimethylsilane before casting. The cast films were heated under vacuum at 120°C for 2 h and then cured at 150 and 180°C for 1 h each, and 200 and 230°C for 2 h each in a vented oven.

2.4. Measurements

IR spectra were obtained with JASCO spectrophotometer model FT/IR-420. 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 35 Hz at a heating rate of 4°C/min. Tensile properties were recorded with Imada Seisaku-sho Model SV-3 at a crosshead speed of 1 mm/min using films of 2 cm long. The tensile properties of each sample were determined from an average of at least five tests. XRD was measured using an X-ray diffractometer, Rigaku, RINT2000 using CuK α radiation and scanning rate of 0.3°/min.

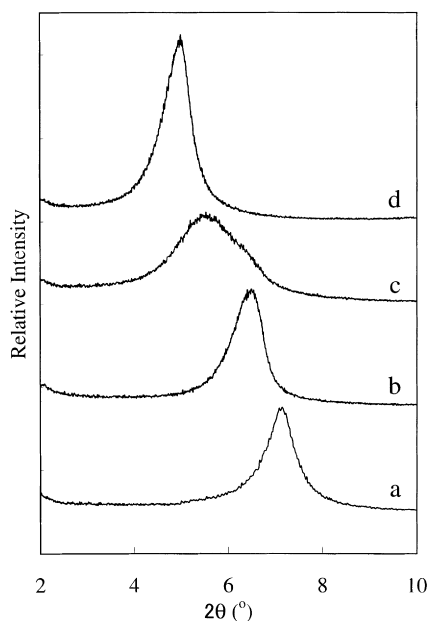


Fig. 1. XRD patterns of: (a) MMT; (b) octyl-MMT; (c) dodecyl-MMT; and (d) stearyl-MMT.

3. Results and discussion

3.1. Preparation of polybenzoxazine/montmorillonite nanocomposites

The modification of the hydrophilic **Na**-MMT surface layers to become hydrophobic is the initial stage to disperse **MMT** uniformly into polybenzoxazine matrix. As a result of this surface modification, the surface of the **MMT** will have a hydrophobic character [30,33]. Thus, there will be hydrophobic environment in the **MMT** gallery surfaces to accommodate the hydrophobic **B-a** due to the compatibility between them [37]. In our study, **Na**-MMT was surface treated with octyl, dodecyl, or stearyl ammonium chloride as organic bases or surfactants through ion exchange process to prepare organophilic **MMT** (**OMMT**). The inter-layer spacings were calculated from the X-ray diffraction (XRD) measurements shown in Fig. 1 and summarized in Table 1. It is clearly shown that the interlayer spacing increased with the increase of the size of surfactant: from 0.28 for **Na**-MMT to 0.40, 0.63, and 0.98 for octyl-MMT, dodecyl-MMT and stearyl-MMT, respectively.

B-a was blended with different weight ratios of **OMMT**. The cast films were cured at 150 and 180°C for 1 h each and

200 and 230°C for 2 h each. As a result of the thermal curing, ring opening of oxazine rings will occur, affording network structure of phenol resin as shown in Scheme 1 (preparation of polybenzoxazine). The resulting hybrid nanocomposites in the film form have thickness ranging from ca. 0.1–0.2 mm and all were transparent. The transparency of the hybrid nanocomposites comes from the nanoscale dispersion of the **MMT** particles in the polybenzoxazine matrix. The transparency, however, decreased with the increase of the content of **OMMT** due to aggregation [38].

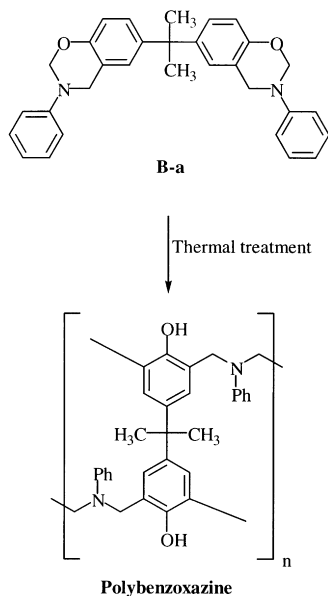
3.2. Curing behavior of polybenzoxazine–MMT hybrid nanocomposites

The curing behavior of **B-a** in the presence of **OMMT** was monitored by IR. Fig. 2 shows the IR spectra of **B-a** with 10% dodecyl ammonium modified **MMT** at different stages of curing. We see that the peaks at 952 and 1500 cm^{-1} due to the trisubstituted benzene ring, at 1233 cm^{-1} due to the asymmetric stretching of C–O–C, and at 1327 cm^{-1} due to CH_2 wagging receptively in benzoxazine structure have completely disappeared after the 230°C cure cycle. Whereas a new peak at 1489 cm^{-1} appeared due to the tetrasubstituted benzene ring mode suggesting that the ring opening of **B-a** affords polybenzoxazine [54]. Also, the IR spectra shows the vibration bands at 522 and 1042 cm^{-1} due to Si–O of **MMT** indicating the existence of a layered silicates framework in the hybrid polymer [67].

The DSC of **B-a** was carried out to monitor the effect of the **OMMT** and the type of organic base used for the modification of the **MMT** surface on the curing of **B-a**. DSC thermograms of pristine **B-a** and **B-a** in the presence of 10 wt.% of dodecyl ammonium-MMT as an example are shown in Fig. 3. The onset of the exotherm due to the curing of the pristine **B-a** starts at 230°C with a maximum at 249°C (Fig. 3a). However, in the presence of dodecyl ammonium-MMT, the onset of the exotherm starts at 170°C with maximum at 214°C (Fig. 3b). This decrease in the onset of the ring opening polymerization by ca. 60°C is due to the acidic onium protons on the **MMT** surface which catalyzed the opening of the oxazine ring of the preintercalated **B-a** within the clay galleries. This behavior is somewhat similar to the self-polymerization of epoxy in smectite clays [33]. Moreover the broadening of the exotherm of the curing of **B-a** in the presence of **OMMT** than that of the

Table 1
Interlayer spacings of **MMT** modified with different organic cations

OMMT	Exchange cation	2θ (°)	d (001) spacings (nm)	Interlayer spacings (nm)
Na -MMT	Na^+	7.12	1.24	0.28
Octyl-MMT	$\text{C}_8\text{H}_{17}\text{NH}_3^+$	6.49	1.36	0.40
Dodecyl-MMT	$\text{C}_{12}\text{H}_{25}\text{NH}_3^+$	5.52	1.59	0.63
Stearyl-MMT	$\text{C}_{18}\text{H}_{37}\text{NH}_3^+$	4.54	1.94	0.98



Scheme 1.

pristine **B-a** suggests that the delay of the ring opening of **B-a** in the extra galleries than that of **B-a** in the intra-galleries of **OMMT**. The exotherm became smaller after curing at 180°C (Fig. 3c) and disappeared after the 230°C cure cycle (Fig. 3d).

Table 2 summarizes the results of the DSC of pristine **B-a** and that of **B-a** in the presence of **OMMTs**. **B-a** modified with different ratios of dodecyl-**MMT** was taken to study

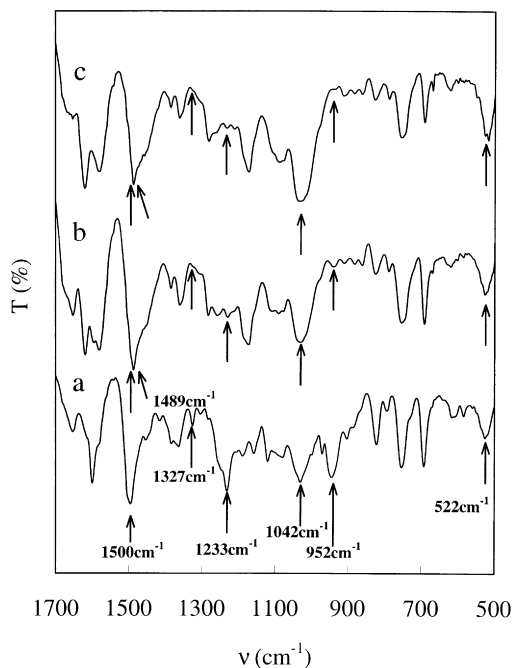


Fig. 2. IR spectra of **B-a**/dodecyl-**MMT** (10%) blend after thermal treatment at different temperatures: (a) 100°C/1 h; (b) 180°C/1 h; and (c) 230°C/2 h.

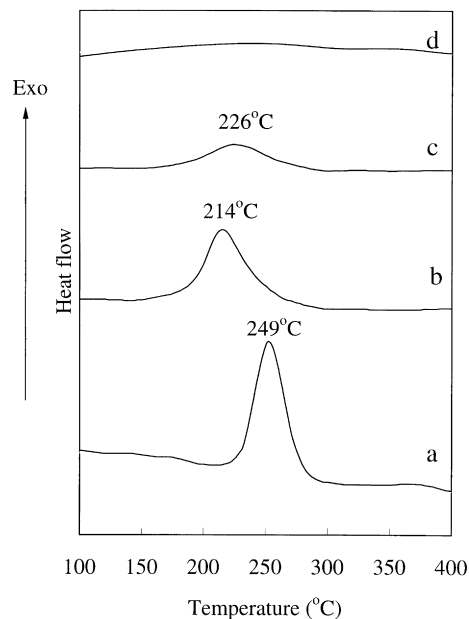


Fig. 3. DSC of: (a) pristine **B-a**; (b) **B-a**/dodecyl-**MMT** (10%) blend after thermal treatment at 100°C/1 h; (c) at 180°C/1 h; and (d) at 230°C/2 h.

the effect of the **OMMT** content on the temperature of the ring opening polymerization. It was found that the onsets of the ring opening polymerization started at 188–190°C with a maxima at ca. 214°C regardless of the content of dodecyl-**MMT**. This suggests that the clay content had no effect on the initiation temperature of the ring opening. In case of **MMT** modified with stearyl the onset of ring opening polymerization was at 177°C, which is a little lower than in case of modification with dodecyl ammonium chloride. This may reflect the high degree of dispersion of stearyl-**MMT** into polybenzoxazine matrix in comparison with dodecyl-**MMT**. We can conclude from these results that the clay surface acted as a catalyst to initiate the ring opening, and there is no sharp difference in the onset of the exotherms with change the type of surfactant or amount of **OMMT**.

3.3. X-ray diffraction analyses of polybenzoxazine-**OMMT** nanocomposites

XRD is a powerful technique to follow the dispersion of **OMMT** in the polybenzoxazine matrix before and after curing [37], and is useful in judging the nature of polybenzoxazine-**OMMT** hybrid nanocomposites either **MMT** is intercalated or exfoliated. As has been reported, the diffractions in the range of $2\theta = 3\text{--}9^\circ$ indicate either an intercalated hybrid or an immiscible system [39]. The XRD of polybenzoxazine-**MMT** hybrids was measured and the results are summarized in Table 3. In the nanocomposite in which the **MMT** surface was pretreated with octyl ammonium salt, the diffraction at $2\theta = 6.49^\circ$ shifted to $2\theta = 5.04^\circ$ with a shoulder at $2\theta = 6.9^\circ$ (Fig. 4) corresponding to a basal spacing of 1.75 nm. This increase in the basal

Table 2
DSC of **B-a** and **B-a/OMMT** blends

Code	OMMT		Treatment temperature (°C)	Exotherm		
	Type	Content (wt.%)		Onset (°C)	Maximum (°C)	Amount (cal/g)
B-a	–	0	100	223	249	79
Ia	Dodecyl-MMT	5	100	189	214	66
Ib	Dodecyl-MMT	10	100	188	214	70
IIb	Dodecyl-MMT	10	180	198	226	31
IIb	Dodecyl-MMT	10	230	–	–	–
Ic	Dodecyl-MMT	20	100	190	214	68
IIIa	Stearyl-MMT	2.5	100	177	213	73

Table 3
Interlayer spacings and properties of polybenzoxazine–OMMTs nanocomposites obtained by heat treatment at 230°C/1 h

Code	OMMT	OMMTs content (wt.%)	2θ (°)	d (001) spacings (nm)	Interlayer spacings (nm)	Remarks
I	Octyl-MMT	5	5.04	1.75	0.79	Intercalation
Ia	Dodecyl-MMT	10	–	–	–	Exfoliation
Ib	Dodecyl-MMT	20	3.37 & 5.96	2.62 & 1.48	1.66 & 0.52	Intercalation ^a
IIIa	Stearyl-MMT	2.5	–	–	–	Exfoliation
IIIb	Stearyl-MMT	5	–	–	–	Exfoliation
IIIc	Stearyl-MMT	10	–	–	–	Exfoliation
IIId	Stearyl-MMT	20	2.24, 4.72 & 5.47	3.94, 1.87 & 1.62	2.98, 0.91 & 0.66	Intercalation ^a

^a Nanocomposites of high content of OMMT may have mixed morphology, i.e. exfoliation morphology in addition to intercalation.

spacing suggests the intercalation of polybenzoxazine into the MMT galleries. However, when the MMT surface was pretreated with longer chain surfactants such as dodecyl or stearyl ammonium salt, there were no peaks attributable to the basal spacing on XRD patterns of nanocomposites having up to 10 wt.% of OMMT (Figs. 5 and 6). This

suggests the disorder and loss of structure registry of the MMT layers. Thus, the clay tactoids are considered to be exfoliated and the 0.96 nm-thick MMT layers dispersed at the molecular level into polybenzoxazine matrix. This collapse in the lattice structure is due to the migration of **B-a** into the clay galleries upon heating due to the presence

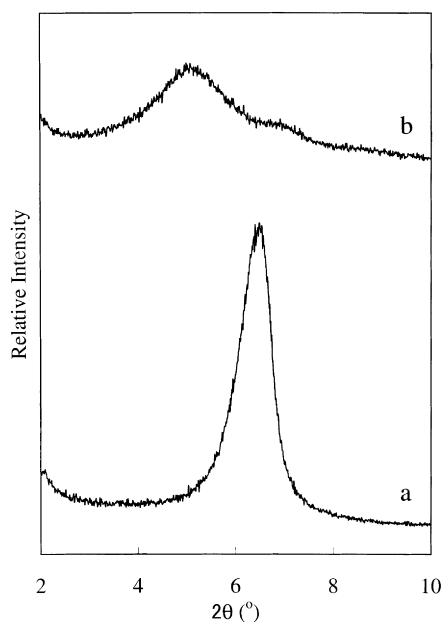


Fig. 4. XRD patterns of: (a) octyl-MMT; (b) polybenzoxazine–octyl-MMT (5%) after 230°C/2 h.

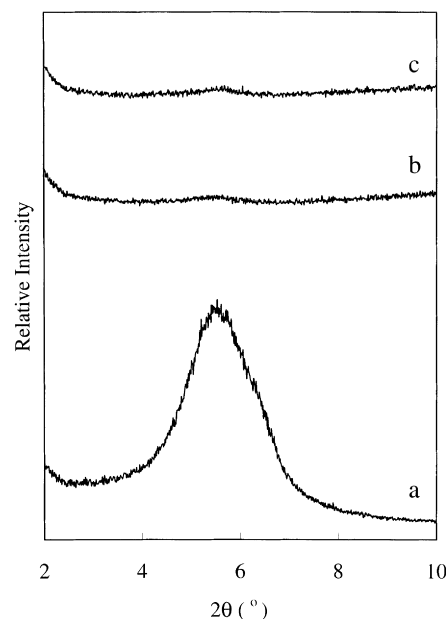


Fig. 5. XRD patterns of: (a) dodecyl-MMT; (b) polybenzoxazine–dodecyl-MMT (10%) after 120°C; (c) polybenzoxazine–dodecyl-MMT (10%) after 230°C/2 h.

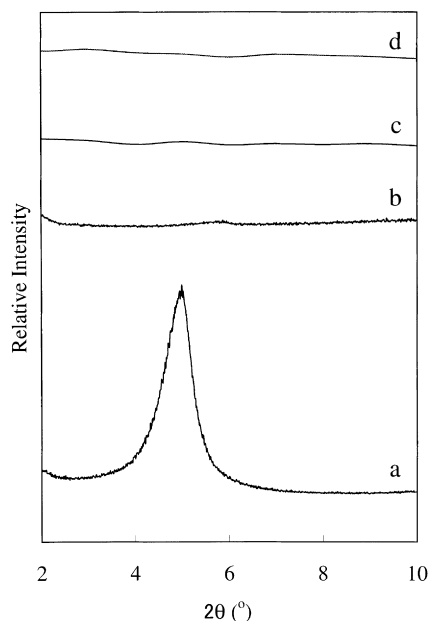


Fig. 6. XRD patterns of: (a) stearyl-MMT; (b) polybenzoxazine-stearyl-MMT (10%) after 120°C; (c) polybenzoxazine-stearyl-MMT (10%) after 180°C; and (d) polybenzoxazine-stearyl-MMT (10%) after 230°C/2 h.

of enough hydrophobicity to accommodate more monomers than in case of octyl ammonium treated-MMT which led to the collapse of the lattice structure of MMT [30]. The behavior of **B-a** in the presence of dispersed OMMT is somewhat similar to the behavior of epoxy resin in the presence of OMMT [37].

In case of high loading of polybenzoxazine with stearyl modified-MMT (20 wt.%), there were diffractions

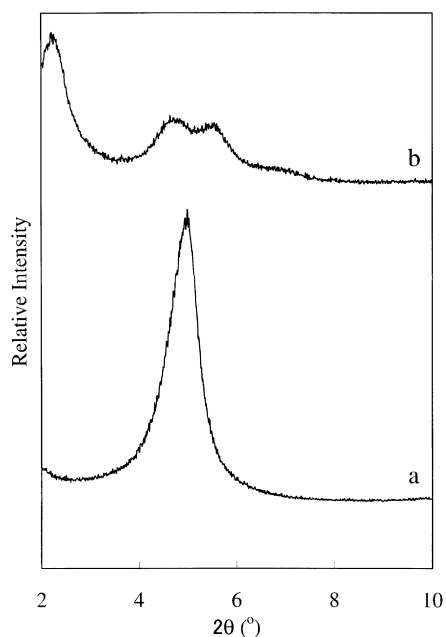


Fig. 7. XRD patterns of: (a) stearyl-MMT; and (b) polybenzoxazine-stearyl-MMT (20%) after 230°C/2 h.

corresponding to the basal spacing (Fig. 7). Similar diffraction patterns were observed for high loading dodecyl modified MMT (Table 3). These diffractions suggest the formation of intercalated nanocomposites with regularly stalked layered silicates when content of dodecyl or stearyl modified-MMT increased.

3.4. Viscoelastic and thermal properties of nanocomposites

The dynamic mechanical properties were recorded (Fig. 8) for polybenzoxazine-stearyl-MMT hybrid nanocomposites. As can be judged from the maxima of the loss modulus, the glass transition temperature (T_g) of the nanocomposites shifted to higher temperature in comparison with pristine polybenzoxazine. The pronounced effect of the layered silicate is the broadening of the glass transition region judging from the peaks of the loss moduli (E'') and the increase of the storage modulus (E') in the transition region by the increase of the content of the layered silicate. The increase of the storage modulus can be attributed to maximizing the adhesion between the polymer and layered silicate surfaces because of nanometer size, which restricts segmental motion near the organic inorganic interface. The changes in the density of the packing of polymer chains results in the modification of the conformation and orientation of chain segments in the neighborhood of the inorganic surface [1]. These results of dynamic mechanical analysis suggest the improvement in thermal properties by incorporation of MMT.

Dynamic thermogravimetric analyses (TGA) were recorded for stearyl-MMT based nanocomposites to monitor the effect on the thermal properties of the MMT

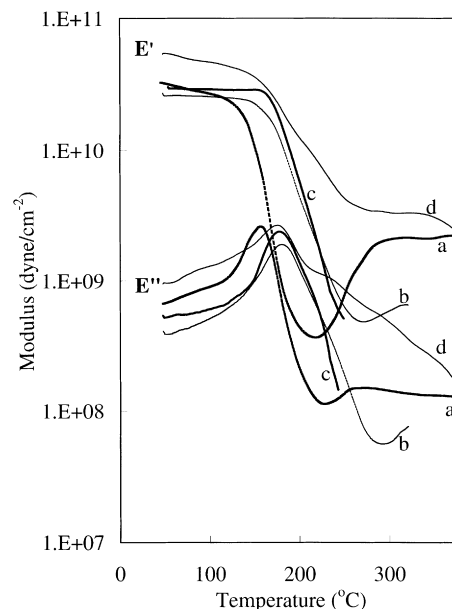


Fig. 8. Dynamic mechanical analyses of polybenzoxazine-stearyl-MMT nanocomposites with various stearyl-MMT content: (a) 0%; (b) 2.5%; (c) 10%; and (d) 20%.

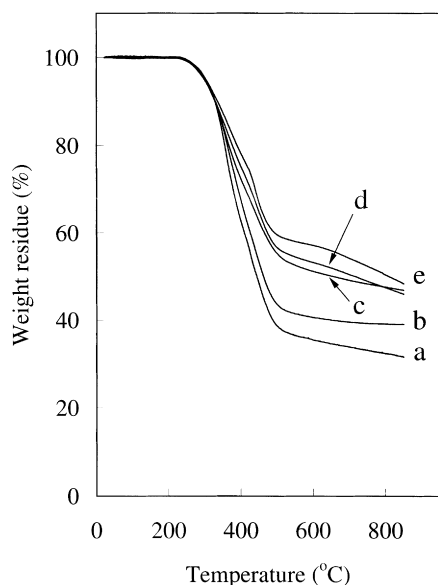


Fig. 9. TGA of polybenzoxazine–stearyl-MMT nanocomposites with various stearyl-MMT content after thermal treatment at 230°C/2 h: (a) 0%; (b) 2.5%; (c) 5%; (d) 10%; and (e) 20%.

nanolayers dispersed in the polybenzoxazine matrix. The results of TGA shown in Fig. 9 were converted into weight residue at different temperatures versus clay content (Fig. 10). The onset of the degradation of the nanocomposites was little improved by the incorporation of the MMT due to the initial decomposition of the organic base used for surface treatment of MMT. This initial decomposition occurred at the same temperature range like polybenzoxazine. However, we can see that only very small amount of clay is effective to improve the weight residues for nano-

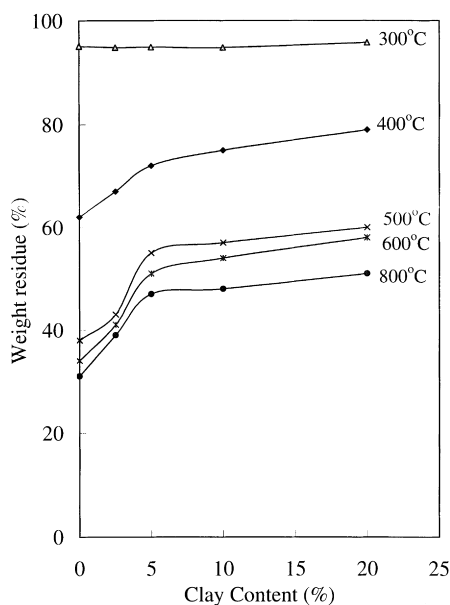


Fig. 10. Effect of stearyl-MMT content on the weight residue at different temperature.

composites (Fig. 10). The char yield at 800°C increased by ca. 20% with 5% MMT content in the nanocomposite. As can be seen from these results, the thermal stability of the nanocomposites was improved by the presence of dispersed MMT nanolayers in comparison with the pristine polybenzoxazine. This enhancement in the thermal properties is due to the presence of the MMT nanolayers, which acted as barriers to minimize the permeability of volatile degradation products out from the material [68].

In addition, isothermal TGA were measured to give more evidence about the improvement of the thermal stability of polybenzoxazine in the presence of MMT. Fig. 11 shows the isothermal TGA at 300°C for 2 h. As clearly seen, the nanocomposites show a delayed decomposition compared with the pristine polybenzoxazine due to the homogeneous distribution of the silicate sheets into the polybenzoxazine matrix and consequently improved the thermal properties of the nanocomposites as explained before.

4. Conclusion

1. Novel hybrid organic–inorganic nanocomposites from polybenzoxazine–MMT were successfully prepared from the polybenzoxazine precursor (**B-a**) and OMMT.
2. DSC showed that the onset of the ring opening of **B-a** in the presence of OMMT to form polybenzoxazine–OMMT nanocomposites occurred at relatively low temperatures in comparison with pristine **B-a** suggesting the catalytic effect of the OMMT surface on the ring opening polymerization.
3. XRD of the formed nanocomposites indicated that the exfoliation of the OMMT on the molecular level

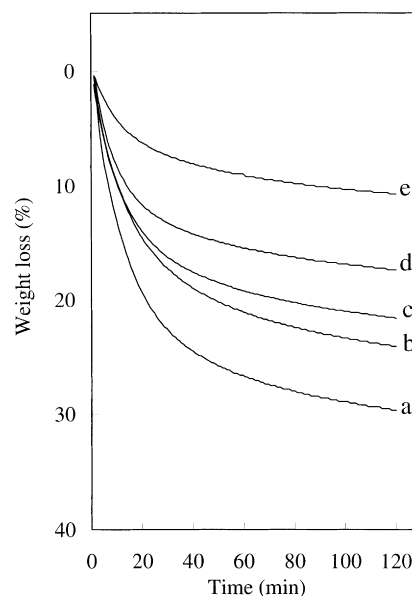


Fig. 11. Isothermal TGA of polybenzoxazine–stearyl-MMT nanocomposites with various stearyl-MMT content at 300°C: (a) 0%; (b) 2.5%; (c) 5%; (d) 10%; and (e) 20%.

occurred when the surface was pretreated with long chain surfactants.

4. The storage moduli of the hybrid materials were increased with increase in the content of the MMT in the polybenzoxazine matrix suggesting the encountered reinforcement especially above T_g . T_g s of the hybrid materials were higher than that of the pristine resin.
5. Isothermal and dynamic TGA showed that the nanocomposites have higher thermal stability in comparison with pristine polybenzoxazine. The char yields increased with the increase of the MMT content. The evaluation of the mechanical properties of the nanocomposites, and study of using reactive surfaces modified-MMT and other higher aspect ratio layered silicates are being carried out.

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