

# Polybenzoxazine-Clay Hybrid Nanocomposites

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## Abstract

Polybenzoxazine-clay hybrid nanocomposites were prepared from a polybenzoxazine precursor (**B-a**) and organically modified-montmorillonite (**OMMT**). 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. XRD indicated the absence of the basal spacings diffractions of **OMMTs** from the XRD patterns of polybenzoxazine-clay hybrid nanocomposites suggesting the dispersion of **OMMT** layers on the molecular level. DMA showed that the Tgs of the hybrid materials were higher than that of the pristine resin. Also, the storage moduli of the hybrid materials were maintained up to higher temperature, suggesting the reinforcement attained by **OMMT**. Isothermal and dynamic TGA showed that nanocomposites have a delayed decomposition temperatures in compare with the pristine resin.

**Key words** Nanocomposites, Polybenzoxazine, Montmorillonite, Storage modulus, Thermal stability

## Introduction

Nanocomposite is a class of composites in which the reinforcing phase dimensions are in the order of nanometers [1]. Because of their nanometer size characteristics, nanocomposites possess superior properties than the conventional microcomposites due to maximizing the interfacial adhesion. Smectite clays dispersed in a polymer matrix as a reinforcing phase are one of the most important forms of organic-inorganic hybrid nanocomposites because they can be broken down into nanoscale building blocks [2]. Extensive researches for preparations of polymer-clay nanocomposites have been investigated widely in order to obtain novel nanocomposites with enhanced properties such as mechanical, thermal and fire

resistance [3,4], and barrier properties [5]. Polybenzoxazine has been recently developed and studied as a novel class of phenol resins to overcome the shortcomings of the traditional phenol resins [6-8]. It can be synthesized from inexpensive raw materials and cured without strong acid as a catalyst. In the current study, we prepared high performance polybenzoxazine-clay nanocomposites with properties superior to that of pristine polybenzoxazine.

## Experimental

### Preparation of polybenzoxazine-MMT nanocomposites

To the molten **B-a**, the required amount of **OMMT** prepared according to the reported method [5] was added portionwise. The mixture was

mechanically stirred to achieve well dispersion of the **OMMT** in **B-a**. The mixture was free cast as a film on a glass plate. The cast films were heated under vacuum at 120°C for 2h and then cured at 150°C and 180°C for 1h each, and 200°C and 230°C for 2h each in a vented oven.

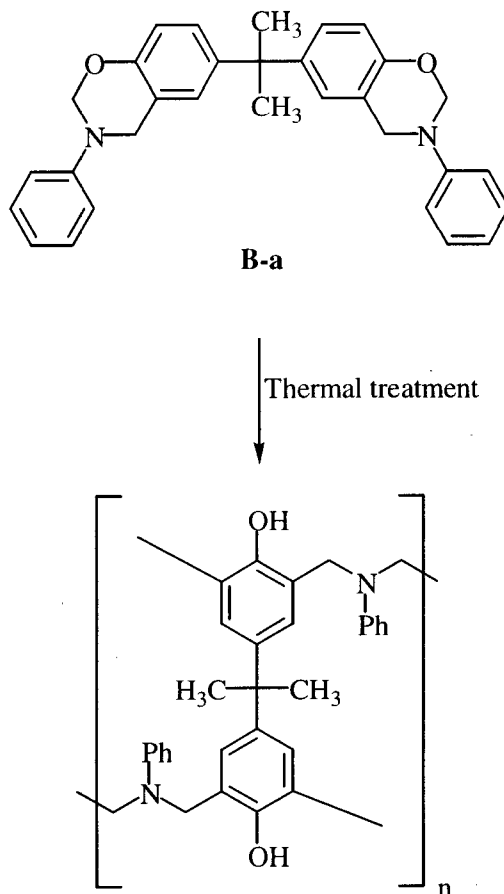
## Results and Discussion

### 1. Preparation of polybenzoxazine-MMT nanocomposites.

The surface modification of the **MMT** will render its surface having hydrophobic character. Thus, there will be hydrophobic environment into the **MMT** gallery surfaces to accommodate the hydrophobic **B-a** due to the compatibility between them.

**B-a** was blended with different weight ratios of **OMMT**. 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. The resulted hybrid nanocomposites in the film form have thickness ranging from ca. 0.1 ~ 0.2 mm and all were transparent. The transparency, however, decreased with the increase of the content of **OMMT** due to aggregation.

The curing behavior of **B-a** in the presence of **OMMT** was monitored by IR. IR spectra of **B-a** with 10% dodecyl ammonium modified **MMT** showed that the peaks at 952 and 1500  $\text{cm}^{-1}$  due to the trisubstituted benzene ring, at 1233  $\text{cm}^{-1}$  due to the asymmetric stretching of C-O-C, and at 1327  $\text{cm}^{-1}$  due to  $\text{CH}_2$  wagging receptively in benzoxazine structure are completely disappeared after the 230°C cure cycle. Whereas a new peak at 1489  $\text{cm}^{-1}$  appeared due to tetrasubstituted benzene ring mode suggesting the ring opening of **B-a** to afford polybenzoxazine. Also, the IR spectra shows the vibration bands at 522 and 1042  $\text{cm}^{-1}$  due to Si-O of **MMT** indicating the existence of layered silicates framework in



Scheme 1. Preparation of polybenzoxazine

the hybrid polymer. 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.1. The onset of the exotherm due to the curing of the pristine **B-a** starts at 230°C with maximum at 249°C (Fig. 1a). However, in the presence of dodecyl ammonium-**MMT**, the onset of the exotherm starts at 170°C with maximum at 214°C (Fig. 1b). 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. Exotherm became smaller after curing at 180°C (Fig. 1c) and disappeared after 230°C cure cycle (Fig. 1d). Also from the DSC study, it was found that clay content has no effect on the initiation temperature of the ring opening. In case of

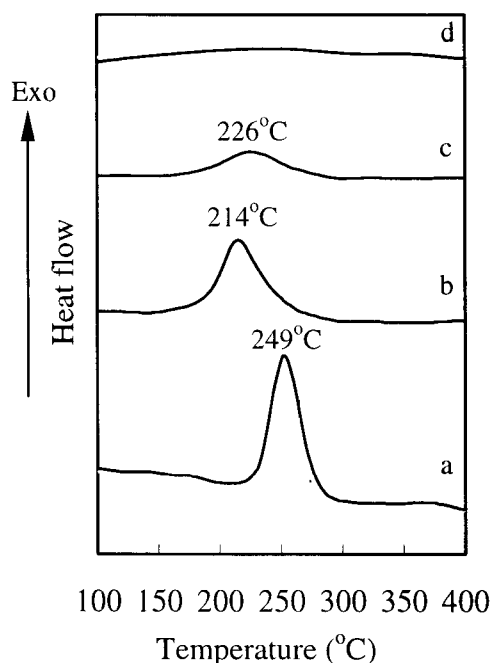


Fig. 1: DSC of a; pristine B-a, b: B-a/dodecyl-MMT (10%) blend after thermal treatment at 100°C/1h, c; at 180°C/1h and d; at 230°C/2h.

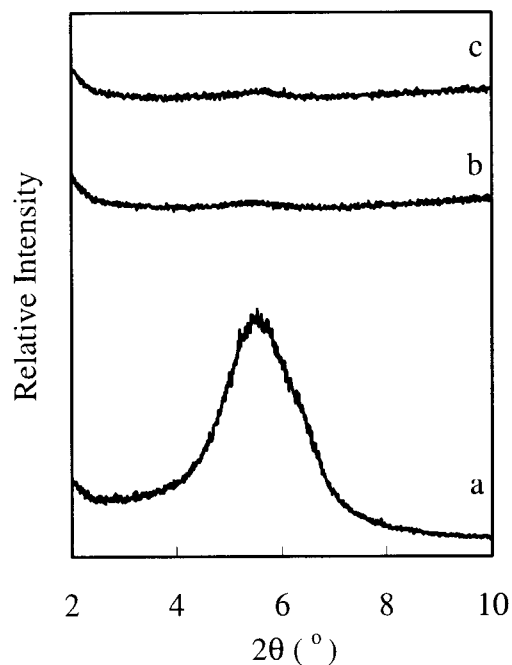


Fig. 2: XRD patterns of a; dodecyl-MMT, b; polybenzoxazine-dodecyl-MMT (10%) after 120°C, c; polybenzoxazine-dodecyl-MMT (10%) after 230°C/2h

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 compare with dodecyl-MMT.

XRD indicated that nanocomposite in which MMT surface was pretreated with octyl ammonium salt has diffraction at  $2\theta = 6.49^\circ$  shifted to  $2\theta = 5.04^\circ$  with a shoulder at  $2\theta = 6.9^\circ$  corresponding to a basal spacing of 1.75 nm. This increase in the basal spacing suggests the intercalation of polybenzoxazine into the MMT galleries. However, when 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 (Fig. 2).

This suggests the disorder and loss of structure registry of the MMT layers. This collapse in the lattice structure is due to the migration of B-a into the clay galleries upon heating due to the presence 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.

In case of high loading of polybenzoxazine with stearyl modified-MMT (20wt. %), there were diffractions corresponding to the basal spacing suggesting the formation of intercalated nanocomposites with regularly stalked layered silicates when content of dodecyl or stearyl modified-MMT increased.

## 2. Viscoelastic and Thermal Properties of Nanocomposites.

The dynamic mechanical properties were recorded for polybenzoxazine-

stearyl-MMT hybrid nanocomposites. 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. 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** nanolayers dispersed in the polybenzoxazine matrix. Only very small amount of clay is effective to improve the weight residues for nanocomposites. The char yield at 800°C increased by ca. 20% with 5% **MMT** content in nanocomposite. As can be seen from these results, the thermal stability of the nanocomposites was improved by the presence of dispersed **MMT** nanolayers in compare 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.

Also, isothermal TGA at 300°C/2h (Fig. 3) show that the nanocomposites have a delayed decomposition compared with the pristine polybenzoxazine due to the homogeneous distribution of the silicate sheets into polybenzoxazine matrix and consequently improved the thermal properties.

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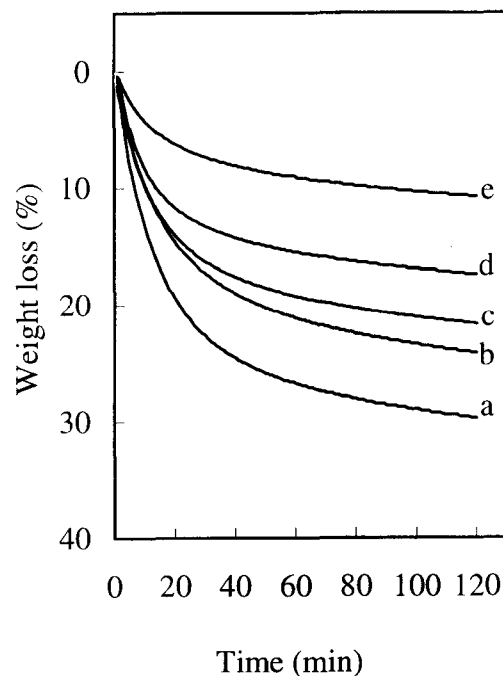


Figure 3. Isothermal TGA of polybenzoxazine-stearyl-MMT nanocomposites with various stearyl-MMT content at 300°C. a; 0 %, b; 2.5%, c; 5%, d; 10%, and e; 20%.

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