

Nanocomposites from Phenolic Resin and Various Organo-Modified Montmorillonites: Preparation and Thermal Stability

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ABSTRACT: Phenolic resin (PF)/montmorillonite (MMT) nanocomposites have been successfully prepared using intercalative polymerization of resole-type phenolic resins in montmorillonites modified by octadecylamine (C18), benzyl-dimethylhexadecylammonium chloride (B2MH), benzyltriethylammonium chloride (B3E), and benzyldimethylphenylammonium chloride (B2MP). X-ray diffraction measurements and transmission electron microscope observations showed that clay platelets were partially exfoliated or intercalated after complete curing of the phenolic resins. The cured nanocomposites were named as modifier-MP (MP means montmorillonite-phenolic resin), for example, B3E-MP. Thermogravimetric analysis showed that thermal decomposition temperatures (T_d s) of the cured nanocomposites

B2MP-MP (826 K), B3E-MP (794 K), and B2MH-MP (783 K) were much higher than those of C18-MP (768 K) and cured phenolic resin (737 K). Therefore, thermal stability of the nanocomposites depends mainly on the chemical structure of the organic modifiers. B2MP-MP possesses the highest T_d since B2MP contains both benzyl and phenyl groups, followed with B3E-MP and B2MH-MP whose modifiers contain only one benzyl group. This is attributable to favorable interaction between phenolic resin and organic modifiers containing benzene rings. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5336–5343, 2006

Key words: nanocomposites; organoclay; resins; thermogravimetric analysis (TGA)

INTRODUCTION

Polymer/layered silicate nanocomposites are a relatively new class of materials with ultrafine phase dimensions and many researchers find them attractive due to their unexpected hybrid properties when compared to their micro- and macrocomposite counterparts and the pristine polymer matrix. These nanocomposites exhibit improved tensile strength and moduli,^{1–3} decreased thermal expansion coefficient,¹ decreased gas permeability,^{1–3} increased swelling resistance,⁴ enhanced ionic conductivity,^{5–7} flammability,^{8,9} and other physical or mechanical properties.^{10–23} The unprecedented mechanical properties of polymer/layered silicate nanocomposites were first demonstrated by Toyota research group using nylon as a polymer matrix. Since then, many polymer/layered silicate nanocomposites have been prepared for various thermoplastic and thermosetting polymers.

Phenolic resins today are indeed irreplaceable materials for selective high technology applications, offering high reliability under severe circumstances.

Because of their excellent ablative properties, structural integrity, thermal stability, and solvent resistance, phenolic resins are still widely used, especially in thermal insulation materials, molding compounds, foundry, wood products industry, coatings, and composite materials.²⁴ However, phenolic resin has been abandoned in the nanocomposite field even though it is the first synthesized resin in history and possess many advantages. The reason is that general phenolic resins have a three-dimensional structure even if the resin is not crosslinked.²⁵ Although the lamella of the layered silicate can be easily intercalated by linear polymers, this three-dimensional structure of phenolic resin makes it very difficult to intercalate in the layered silicate gallery.

To overcome this difficulty, Usuki et al.¹⁶ tried to synthesize phenolic resin/layered silicate nanocomposites by intercalative polymerization of phenolic resin with phenol and formaldehyde in the presence of oxalic acid and montmorillonite modified with 4-aminophenol hydrochloride. In addition, using linear novolac resin, Lee and Giannelis²⁵ were the first to prepare phenolic resin/clay nanocomposites by melt intercalation. Choi et al.^{26,27} prepared phenolic resin/layered silicate nanocomposites with intercalated or exfoliated nanostructures by melt intercalation using linear novolac and examined their

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mechanical properties and thermal stabilities. Wang et al.²⁸ synthesized phenolic/layered silicates nanocomposites by the condensation polymerization of phenol and formaldehyde catalyzed by *H*-montmorillonite. Up to now, only limited researches on resole-type phenolic resin/layered silicate nanocomposites via *in situ* polymerization of monomers have been published.^{29,30} For example, Wu et al. prepared phenolic resin/montmorillonite nanocomposites by suspension condensation polymerization and investigated their morphology.²⁹ But only two kinds of organic modified montmorillonite were adopted, and only assembled nanocomposites or little change in intercalated structures were observed.²⁹ However, thermal stability of resole-type phenolic resin/layered silicate nanocomposites have not been discussed so far.

In this work, we prepared resole-type phenolic resin/layered silicate nanocomposites using various organo-modified montmorillonites and investigated the effect of chemical structure of organic modifiers on the morphology and thermal stability of the nanocomposites.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na-MMT, Cloisite[®] Na⁺) was purchased from Southern Clay Products (Austin, TX), and the cation exchange capacity was 92.6 meq/100 g. Organic modifiers octadecylamine (CH₃(CH₂)₁₇NH₂, C18) and benzyldimethylphenylammonium chloride [C₆H₅CH₂N⁺(CH₃)₂C₆H₅Cl⁻, B2MP] were from Aldrich (Shanghai, China) and TCI (Tokyo, Japan), respectively. Benzyldimethylhexadecylammonium chloride (CH₃(CH₂)₁₅N⁺(CH₃)₂CH₂C₆H₅Cl⁻, B2MH) and benzyltriethylammonium chloride (C₆H₅CH₂N⁺(C₂H₅)₃Cl⁻, B3E) were purchased from Fluka (Buchs, Switzerland). Phenol, formaldehyde (37% aqueous solution), hydrochloric acid, and ammonia (NH₃ = 28 wt %) were analytical reagent (AR) grade. All reagents were used without further purification.

Preparation of organically modified MMT

For example, MMT (5 g) was dispersed in 400 mL of deionized water and stirred for 720 min at 353 K. A solution of 1.27 g of benzyltriethylammonium chloride (B3E) and 0.7 mL of concentrated hydrochloric acid (10N) in 80 mL deionized water was poured into MMT dispersed solution at 353 K in a 500 mL flask and stirred vigorously for 60 min. The treated MMT was washed repeatedly with a fresh 1:1 mixture of deionized water and ethanol, until no further AgCl precipitation is detected at titrating with 0.1N AgNO₃. The filter cake was dried in vac-

uum at 348 K for 3 days to obtain the benzyltriethylammonium chloride-modified MMT (B3E-M) and then pulverized in a mortar. Following the same procedures, octadecylamine-modified MMT (C18-M), benzyldimethylhexadecylammonium chloride-modified MMT (B2MH-M), and benzyldimethylphenylammonium chloride-modified MMT (B2MP-M) have also been synthesized and used as modified MMTs for nanocomposites preparation.

Preparation of phenolic resin/MMT nanocomposites

The desired amount of B3E-M (12 g, 10 wt % of total resin formulation) was mixed with phenol (80 g, 850 mmol), formaldehyde (77.2 g, 952 mmol) (P/F molar ratio 1 : 1.12, which had been optimized in our previous study) and ammonia (2.06 g, 4%) in a 250 mL three-necked glass reactor. The mixture became a semitransparent dispersion of B3E-M after stirring, which was then heated to 373 K and allowed to react for 150 min. The product was then dehydrated in vacuum using a rotary evaporator at about 328 K. Then it was completely dried in a vacuum oven at 318 K for 1 day to obtain the phenolic resin/MMT nanocomposite (B3E-MP). The cured nanocomposites were named as modifier-MP and MP means modified-montmorillonite and phenolic resin. Following the same procedures, phenolic nanocomposites composed of octadecylamine-modified MMT (C18-MP), benzyldimethylhexadecylammonium chloride-modified MMT (B2MH-MP), and benzyldimethylphenylammonium chloride-modified MMT (B2MP-MP) have also been prepared.

Before curing, the nanocomposite was charged into an aluminum plate and first treated in a vacuum oven at 323 K for 720 min to remove the trace volatile compounds. The curing procedures were subsequently conducted at 363 K for 60 min, 393 K for 60 min, 413 K for 60 min, 433 K for 60 min, and 453 K for 120 min. The cured specimens were used for thermogravimetric analysis (TGA) and transmission electron microscopy (TEM).

Measurements

X-ray diffraction (XRD) analysis was obtained using a Rigaku X-ray generator (Cu K α radiation with λ = 0.154 nm) at a generator voltage of 36 kV and a generator current of 26 mA. Scanning was performed at room temperature with a 2 θ range of 2°–10° and a scanning rate of 2°/min. Thermogravimetric analyzer was used to investigate the thermal stability of the cured nanocomposites. A typical sample weight was about 4–10 mg and the analysis was performed at a heating rate of 5–20 K/min from 363 to 1073 K in a nitrogen atmosphere.

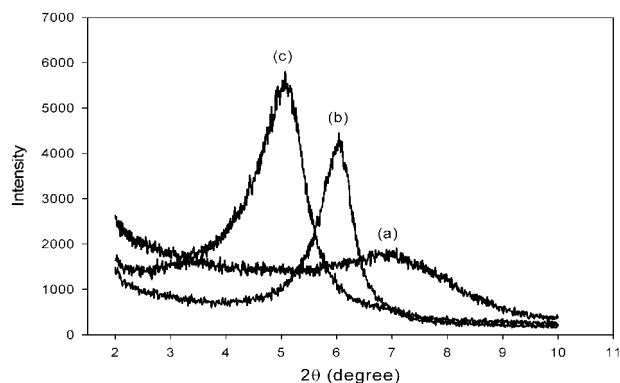


Figure 1 X-ray diffraction patterns of (a) PM, (b) B2MP-M, and (c) C18-M.

To study the microstructure of the nanocomposites, we embedded a sample of the cured composite in an epoxy resin (Epon 828) in a capsule and microtomed it into ultrathin sections. The morphologies of nanocomposites were imaged by TEM on 100 nm thick sections of the nanocomposite on a HF-2000 FE TEM with an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

In this work, *in situ* polymerization of monomers confined in molecule-sized space between silicate platelets were employed to prepare phenolic resin/MMT nanocomposites. The phenol and formaldehyde molecules were first absorbed into the gallery of the MMT and then polymerized *in situ*. Thus, the nanocomposite obtained is called “intercalated” if the phenolic resin was confined between the silicate layers. Both pristine and organo-modified layered silicates were employed for nanocomposites preparation. For the good dispersion of hydrophilic MMT in phenolic resin, sodium ions on its surface should be exchanged with organic ammonium ions through an ion exchange process to render the surface hydrophobic. Thus, the hydrophobic environment in the clay galleries can accommodate the hydrophobic phenolic resin matrix. In this work, we used C18, B2MH, B3E, and B2MP for the surface modification of MMT in the preparation of organoclay.

Morphology of modified MMTs and nanocomposites

XRD and TEM are the two frequently used and powerful tools to characterize the morphology of nanocomposites. The variations of the silicate-galleries spacing (d_{001}) and the dispersibility of layered silicate platelets in polymer/clay composites can be determined from XRD patterns, and TEM enables us to obtain a direct picture of the dispersion

of montmorillonite in the polymeric matrix. Figure 1 and Figure 2 show the XRD patterns of pristine montmorillonite (PM) and modified montmorillonites B2MP-M, C18-M, B3E-M, and B2MH-M. The d -spacings (d_{001}) of the nanocomposites are summarized in Table I. Clearly, organoclay nanocomposites always show larger d -spacing when compared to unmodified clay composite.

Generally, the pure montmorillonite exhibits a broad XRD peak and similar phenomenon was observed in PM.^{31–34} The basal spacing d_{001} for the PM was 1.26 nm, calculated according to the Bragg formula $\lambda = 2d \sin\theta$. The XRD patterns of PM, B2MP-M, and C18-M are shown in Figure 1. For B2MP-M the 2θ value of the 001 reflection is shifted from 7.01° to 6.04° after ion exchange, indicating that the basal spacing is expanded to 1.46 nm as the sodium cations in the interlayer galleries are replaced by B2MP. It is interesting that the XRD peaks sharpen after intercalation, suggesting increased ordering by exchanging with the organic modifiers. C18-M, B3E-M, and B2MH-M show similar results to B2MP-M and their d -spacings are 1.75, 1.61, and 2.02 nm, respectively, (Table I). According to the variations in d -spacing, possible arrangements of the modifiers within interlayer gallery of silicates can be proposed as Figure 3. The distance between adjacent clay layers can be easily estimated by deducting thickness of silicate layer (~ 0.9 nm) from d -spacing. For example, the distance between adjacent clay layers in C18-M (d -spacing = 1.75 nm) is 0.85 nm. However, the molecular length (from N atom to its farthest atom) of the modifier octadecylamine is about 2.11 nm, estimated from ChemDraw and PC Spartan Plus. Since this length is larger than the space between silicate layers, the C18 can be imaged as an oblique arrangement [Fig. 3(a)].^{35,36} This low layer spacing may also be owing to incomplete

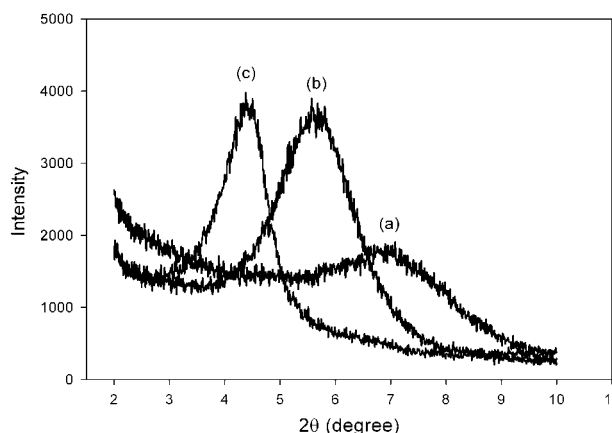


Figure 2 X-ray diffraction patterns of (a) PM, (b) B3E-M, and (c) B2MH-M.

TABLE I
X-ray Peak Position and d -Spacing (d_{001}) of
Pure Clay and Organoclays

Sample	2θ (deg)	d -Spacing (nm)
PM ^a	7.01	1.26
C18-M	5.06	1.75
B2MH-M	4.38	2.02
B3E-M	5.30	1.61
B2MP-M	6.04	1.46

^a PM: pristine montmorillonite.

exchange with octadecylamine modifier. Similarly, the molecular length of B2MH (1.86 nm) is larger than the space between layers in B2MH-M (1.12 nm), oblique arrangement of intercalated B2MH between silicate layers is also proposed as in Figure 3(b). However, the molecular lengths of modifier B3E (0.50 nm) and B2MP (0.51 nm) are much shorter than intercalated spaces between layers of their corresponding organoclays B3E-M (0.71 nm) and B2MP-M (0.56 nm), respectively. Therefore, more than one layer but less than two layers arrangements of these modifiers are estimated in Figures 3(c,d). The interactions between phenolic resin and the modified clays, result mainly from the strong dipolar interaction and especially the strong hydrogen-bonding interaction between the organic clay and amine groups of the modifiers (or —OH groups of the phenolic resins).^{10,23,37,38} The preparation of exfoliated nanocomposite necessitates the clay layers to assume an efficient swelling, which leads to better dispersion. When the basal spacing between the layers is small (i.e., between 1.5 and 3.0 nm), the nanocomposite is termed “intercalated.” If the spacing is sufficiently large, the nanocomposite is termed “exfoliated.” An increase in the basal spacing between the layers is related to an increase of the degree of exfoliation.

Curing behavior of the nanocomposites

The curing of phenolic resin is usually carried out by the thermally initiated crosslinking of the phenyl ring by the methylene bridges. Since curing changes the molecular structure of phenolic resin, it possibly affects the morphology of the nanocomposites. To investigate the influence of curing on the morphology of the nanocomposites we studied their XRD patterns. Several kinds of diffractogram patterns have been found in different types of clay composites.³⁹ The nanostructure is considered to be exfoliated only if the characteristic diffraction peak of the modified clays ($2\theta = 4.38^\circ$ – 6.04°) disappears after curing. When characteristic peak decreases in intensity or shifts to low angle after curing, the nanostructure is considered to be intercalated. And the system is immiscible when the characteristic peak is intact

after curing. Therefore, the structural order of the silicates is mainly indicated by the variations in the intensity and shape of the basal reflections, which is mostly attributed to polymer intercalation. Increased order is shown by a decrease in band width and *vice versa*. Figure 4 presents XRD patterns for C18-MP, B2MH-MP, B3E-MP, and B2MP-MP (MP represents composites from MMT and phenolic resin). The characteristic peaks of C18-M, B3E-M, and B2MP-M disappear completely after curing, indicating exfoliation in the process of curing. Although B2MH-MP shows similar structures to other nanocomposites before curing, it exhibits a broad peak at $2\theta = 5^\circ$ – 6° after curing. This means that during curing some galleries collapse or the intercalated phenolic resins de-intercalate, leading to the contraction of interlayer spacing. Therefore, the nanocomposites whose modifiers expanded clay layers less (C18-M, B3E-M, and B2MP-M; d -spacing = 1.46–1.75 nm) led to exfoliation after curing. On the contrary, the nanocomposite (B2MH-M) with greater d -spacing (2.02 nm) resulted in some collapsed structure after curing. Unfortunately, the mechanism of this abnormal phenomenon has not been elucidated so far, but the structure of the organic modifier should play an important role.

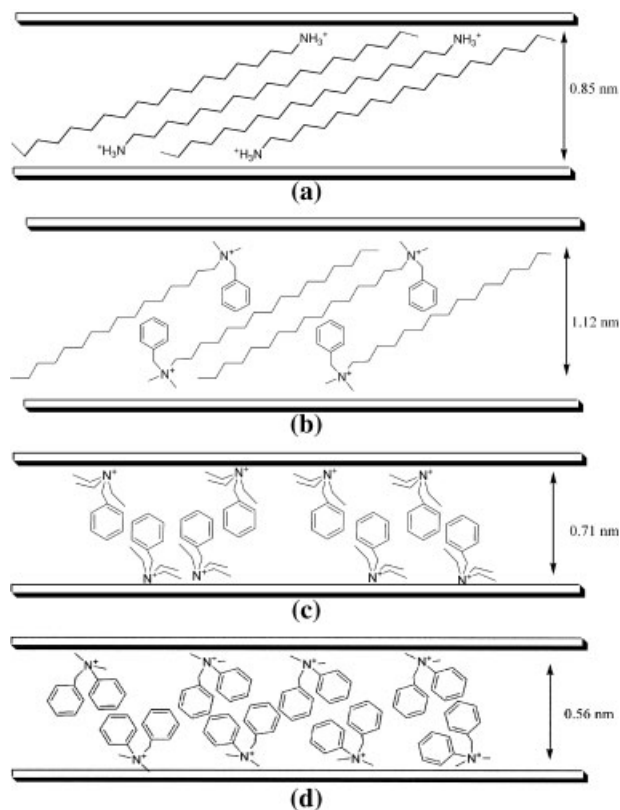


Figure 3 Proposed arrangements of organic modifiers within layered silicates: (a) C18-M, (b) B2MH-M, (c) B3E-M, and (d) B2MP-M.

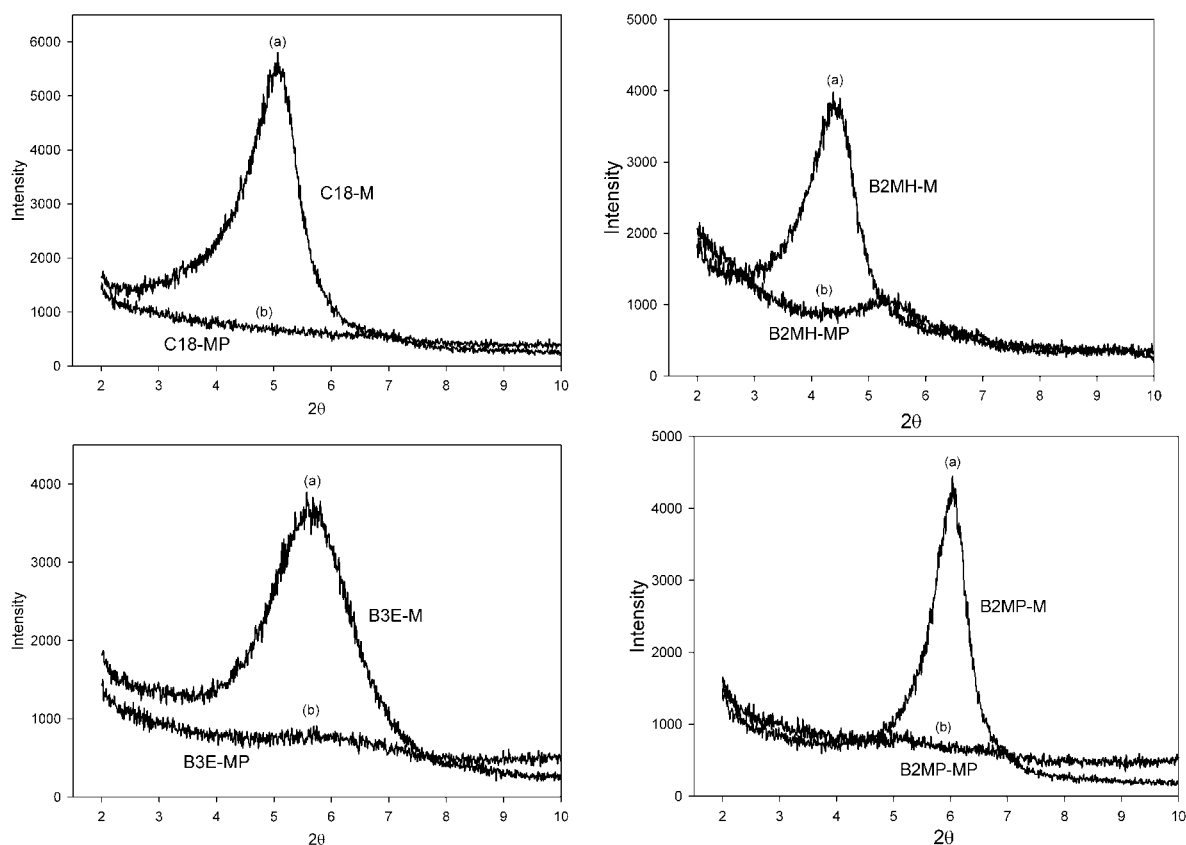


Figure 4 X-ray diffraction patterns of (a) modified montmorillonites and (b) cured phenolic resin/montmorillonite nanocomposites. Curing conditions: 363 K for 3.6×10^3 s, 393 K for 3.6×10^3 s, 413 K for 3.6×10^3 s, 433 K for 3.6×10^3 s, and 453 K for 7.2×10^3 s.

TEM studies were carried out to examine the dispersion of the clay layers in the final composite. Typical TEM photographs for the B3E-MP and B2MP-MP nanocomposites after curing are displayed

in Figure 5. The dark lines in the picture represent the clay layers, and the gray clouds represent the phenolic resin matrix. The distance between adjacent dark lines is mostly in the range of 5–10 nm. The

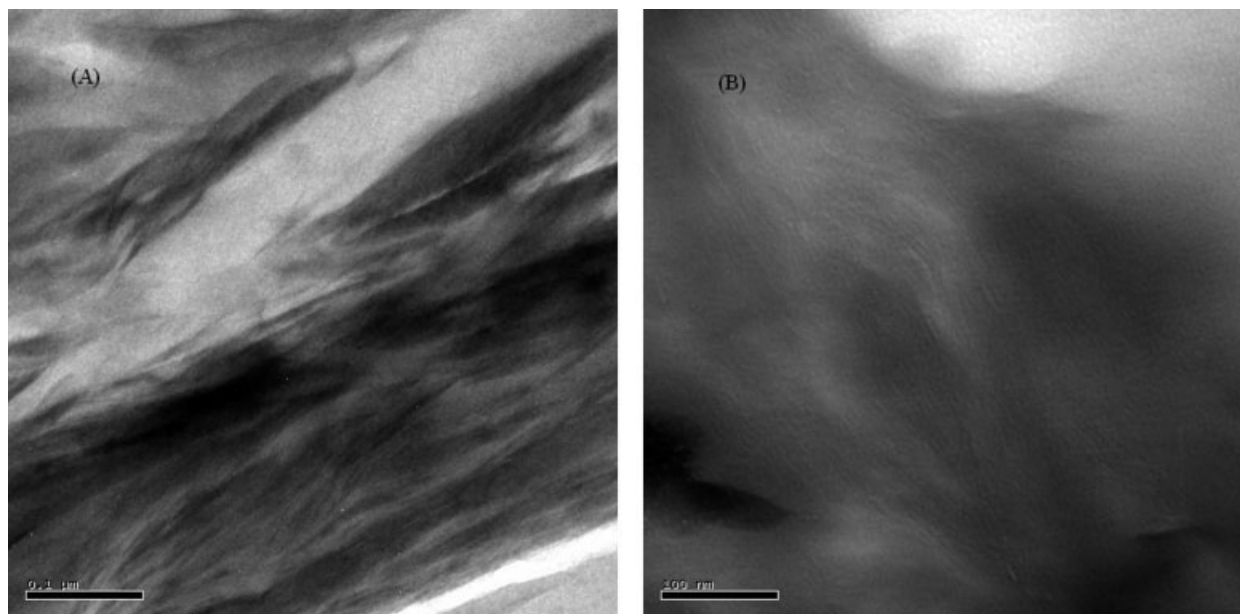


Figure 5 TEM images of the cured (A) B3E-MP and (B) B2MP-MP.

results suggest that silicate layers have been partially exfoliated by the phenolic resin. It is noteworthy that many clay layers are curved in the images. This flexibility of the layers is due to very low thickness and very large aspect ratio of the clay platelets, as also noticed by Krishnamoorti et al. in their TEM images.⁴⁰ Comparing to previous study of Wu et al., the mechanisms of action for these nanocomposites are suggested as following. First, the organo-modified silicates are swelled and expanded by the monomers (phenol and formaldehyde) and catalyst (ammonia). Then *in situ* polymerization of the monomers further expands or exfoliates the layered silicates. Finally, after heat curing treatments the modified silicates are partially exfoliated.

Thermal stability of the nanocomposites

Figure 6 shows that the TGA thermograms of the cured phenolic resins and their nanocomposites up to 1073 K. The decomposition temperature (T_d), which is defined as the temperature at 10% weight loss and residual weight of nanocomposites at 1073 K are summarized in Table II. Clearly the thermal stability of phenolic resins ($T_d = 737$ K) are enhanced by the incorporation of 15 wt % (to phenol) modified montmorillonites (>768 K), especially the nanocomposites containing MMT treated with quarternary ammonium containing benzene ring. The B2MP-MP, in which the modifier (B2MP) contains both benzyl and phenyl group, shows the highest T_d at 826 K. The T_d s of B3E-MP and B2MH-MP, in which both the modifiers (B3E and B2MH) possesses a benzyl substituent, are 794 and 783 K, respectively. This can be attributed to enhanced chemical affinity between the phenolic resin and the montmorillonites treated

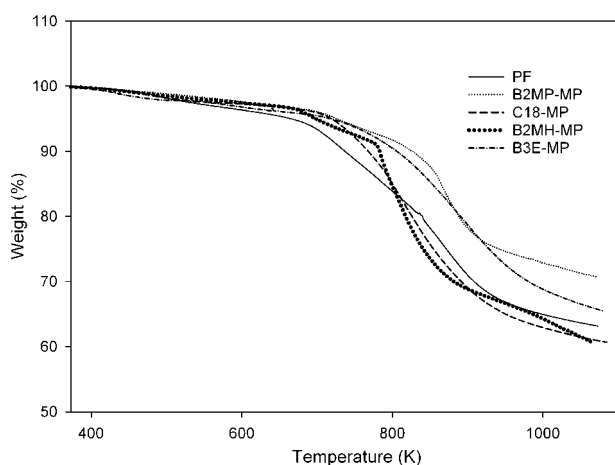


Figure 6 TGA thermograms of phenolic resin and nanocomposites with various modified montmorillonites cured at 363 K for 3.6×10^3 s, 393 K for 3.6×10^3 s, 413 K for 3.6×10^3 s, 433 K for 3.6×10^3 s, and 453 K for 7.2×10^3 s.

TABLE II
Decomposition Temperatures (T_d) and Residual Weight of Phenolic Resin and Nanocomposites

Sample	T_d (K) ^a	Residual weight (wt %)
PF ^b	737	63.1
C18-MP	768	60.9
B2MH-MP	783	60.0
B3E-MP	794	69.0
B2MP-MP	826	70.7

^a The decomposition temperature (T_d) at a 10% weight loss.

^b PF: cured phenolic resin.

with modifiers containing benzene groups. The favorable interaction leads to exfoliation and homogeneous distribution of the silicate platelets in phenolic resin matrix.

Moreover, silicates are also known for its excellent thermo-oxidative stability to provide a retarding effect on the thermal degradation of the organic component of the nanocomposites. Therefore, the MMT should also enhance heat resistance of the phenolic resins of the nanocomposites. Accordingly, as shown in Figure 5, the weight residues of B2MP-MP and B3E-MP exceed 69% and higher than that of the phenolic resin (PF: 63.1%) at 1073 K under nitrogen. However, the residual weight of B2MH-MP (60%) and C18-MP (60.9%), both of which contains long alkyl chains in their intercalated modifiers, are lower than that of PF. This suggests that tertiary amine modifiers containing long alkyl chain tend to depress the residual weight of the nanocomposites.

The TGA thermograms of cured B2MH-MP, B3E-MP, and B2MP-MP under different heating rate have also been measured and shown in Figure 7. It is obvious that the decomposition temperatures decreased with increasing heating rate. For example, the decomposition temperature of B3E-MP reduces from 794 to 764 K by changing the heating rate from 5 to 20 K/min. However, among these three nanocomposites, the lowest decomposition temperature occurs at 755 K (for B2MH-MP at a heating rate of 5 K/min) which is still larger than cured phenolic resin (737 K) at a heating rate of 20 K/min. Therefore, thermal stability of phenolic resin can be significantly improved by organo-modified montmorillonites.

CONCLUSIONS

In this study, we prepared four modified montmorillonites using octadecylamine (C18), benzyl-dimethylhexadecylammonium chloride (B2MH), benzyl-triethylammonium chloride (B3E), and benzyl-dimethylphenylammonium chloride (B2MP) as organic modifiers. Phenolic resin/layered silicate nanocom-

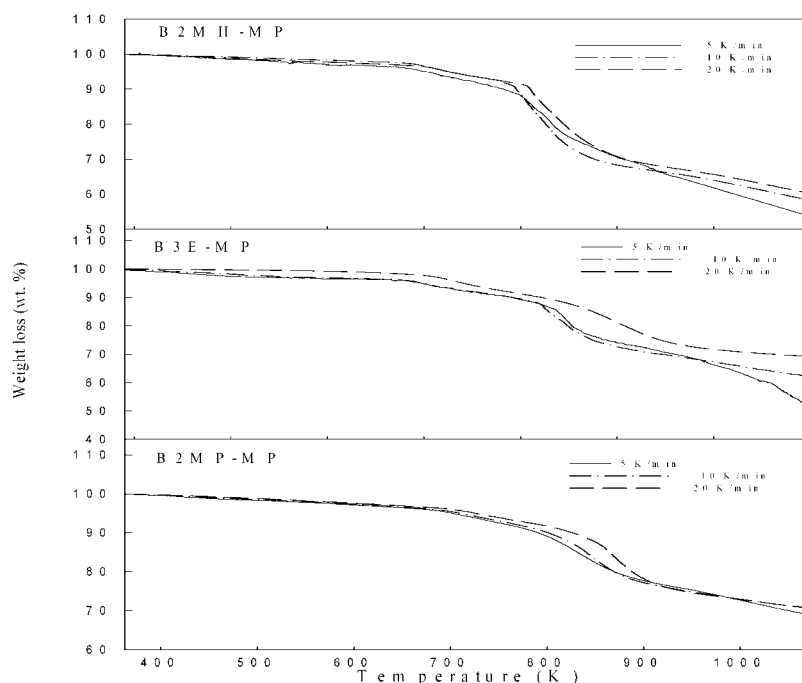


Figure 7 TGA thermograms of cured nanocomposites under different heating rate.

posites were prepared by the intercalative polymerization of phenol and formaldehyde in the presence of the modified montmorillonites. Exfoliation of the clay layers was confirmed crystallographically by the disappearance of the 001 deflection in the XRD patterns. TEM images also showed that in B3E-MP and B2MP-MP the silicate layers were partially exfoliated and dispersed uniformly in the phenolic resin. All nanocomposites showed improved thermal stability as compared to that of the neat phenolic resin. For example the T_{d5} of C18-MP, B2MH-MP, B3E-MP, and B2MP-MP (768–826 K) are much higher than that of the cured phenolic resin (737 K). The nanocomposites made of MMT modified by benzyl-containing modifiers exhibited T_{d5} higher than 783 K, among them the highest one is from B2MP-MP which contains both benzyl- and phenyl groups. This has been attributed to their similar structures to phenolic resin that promote the exfoliation and uniform distribution of MMT. The modifiers of montmorillonites clearly affected not only the curing behavior but also the final morphology of nanocomposites.

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