Mechanical and Thermal Properties of Phenolic Resin-Layered Silicate Nanocomposites Synthesized by Melt Intercalation

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ABSTRACT: Phenolic resin–layered silicate nanocomposites (PLSNs) were synthesized by melt intercalation with linear novolac resin (P1) and organosilicates such as montmorillonite modified by benzyldimethyloctadecylammonium (C18BM) and by bis(2-hydroxy-ethyl)methyl tallow ammonium (THEM). The PLSNs were prepared by a sequential process (IC) in which phenolic resin was melt-intercalated into organosilicate and subsequently cured with hexamethylenetetramine (HMTA). It was found from X-ray diffraction measurements that P1THEMIC nanocomposites showed better silicate dispersion than did P1C18BMIC nanocomposites, even though both systems had intercalated morphologies. The larger silicate gallery expansion in P1THEMIC nanocomposites was attributed to the strong hydrogen-bonding interaction between the phenolic resin and hydroxyl groups of the organic modifier of THEM. As they had better silicate dispersion, the P1THEMIC nanocomposites showed better mechanical properties than the P1C18BMIC nanocomposites. The thermal stability of the P1THEMIC nanocomposites was slightly increased or decreased, depending on the silicate content, relative to the neat phenolic resin. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2316–2321, 2003

Key words: phenolic resin; layered silicate; nanocomposite

INTRODUCTION

In recent years there has been considerable interest in polymer-layered silicate nanocomposites because their use has resulted in unexpected improvement in physical and mechanical properties, even with a small silicate content.[1–21] These enhanced properties of polymer-layered silicate nanocomposites are presumably a result of the nanometer size, large aspect ratio (100–1000), and large surface area (760 m^2/g) of the silicate.

Phenolic resin is one of the widely used thermosetting resins because of its excellent ablative property, structural integrity, thermal stability, and solvent resistance. However, phenolic resin–layered silicate nanocomposites (PLSNs) have remained relatively unexplored in the polymer-layered silicate nanocomposite field. This is because it is very difficult for phenolic resin to intercalate into the silicate gallery as a result of its three-dimensional structure and rigidity, even when uncured. To overcome these difficulties, Usuki et al.[22] tried to synthesize a PLSN composed of novolac resin and montmorillonite modified by 4-aminophenol hydrochloride via an intercalative polymerization method. In addition, using linear novolac resin, Lee and Giannelis[23] first tried to synthesize a PLSN via melt intercalation. However, they did not report data sufficient for understanding its morphology, curing behavior, and mechanical property of PLSN. Recently, Wang et al.[24] synthesized a PLSN by the condensation polymerization of phenol and formaldehyde catalyzed by *H*-montmorillonite. However, their system included only uncured nanocomposites, and no mechanical and thermal properties were provided.

In a previous study[25] we synthesized PLSNs via melt intercalation using linear novolac resin and various silicates including pristine montmorillonite and some organosilicates. We reported only the morphology and curing behaviors of PLSNs. In the current study we used various organosilicates different from those used in the previous study to synthesize PLSNs, and we examined their mechanical properties and thermal stabilities.

EXPERIMENTAL

Materials

Linear novolac resin (P1), KPH-F2002, was obtained from Nanokor Company, Ltd. Its specific characteris-

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tics were published elsewhere.[25] Hexamethylenetetramine (HMTA), purchased from Lancaster, was used as a curing agent for the phenolic resin. Pristine montmorillonite (PM), Kunipia-F, was purchased from Kunimine Company. Its cation exchange capacity was 119 meq/100 g. All chemicals were used without further purification.

Preparation of organically modified layered silicate

We used bis(2-hydroxy-ethyl)methyl tallow ammonium–modified montmorillonite (THEM), Cloisite 30B, obtained from Southern Clay Products, Inc. The tallow was composed of octadecyl chains and lower homologues. The approximate composition was 65% C_{18}, 30% C_{16}, and 5% C_{14}. Benzyldimethyloctadecylammonium-modified montmorillonite (C18BM) was prepared by ion exchange—3 g of PM was dispersed in 300 mL of deionized water and stirred for 1 day at room temperature. This suspension was stirred for 1 h at 85°C and then combined with 100 mL of the deionized water solution containing 4.284 mmol of benzyldimethyloctadecylammonium chloride (Aldrich). This mixture was continuously stirred at 85°C for 1 h. The cation-exchanged silicate was collected by filtration and subsequently washed with hot deionized water until a 0.1*N* $AgNO_3$ test indicated the absence of halide anions. The modified silicate was dried in a freezer-drier for 3 days and further dried in a vacuum oven at 80°C for several days. The dried organosilicate was ground to a powder (C18BM) and stored in a desiccator. The particle size of all the organosilicates used was less than 37 μm.

Synthesis of phenolic resin–layered silicate nanocomposites

Phenolic resin and organosilicates (1–5 wt % relative to phenolic resin) were mixed and subsequently annealed in a vacuum at 140°C for 2 h. These uncured phenolic resin–layered silicate nanocomposites (PLSNs) have been designated as P1C18BM and P1THEM. To measure the intercalation kinetics with X-ray diffraction, a sample was prepared on a glass slide by annealing at a temperature in the range of 120°C–160°C for 5 min–2 h. In all cases, the phenolic resin and organosilicates were kept in a vacuum before use.

The annealed PLSNs were cured with 10 wt % HMTA relative to phenolic resin (i.e., 90:10 phenolic resin/HMTA) at 140°C for 1 h, followed by curing at 180°C for 1 h on a hot press. The cured phenolic resin and PLSNs synthesized by the sequential process of intercalation and curing were named P1C (phenolic resin cured) and P1C18BMIC and P1THEMIC, respectively.

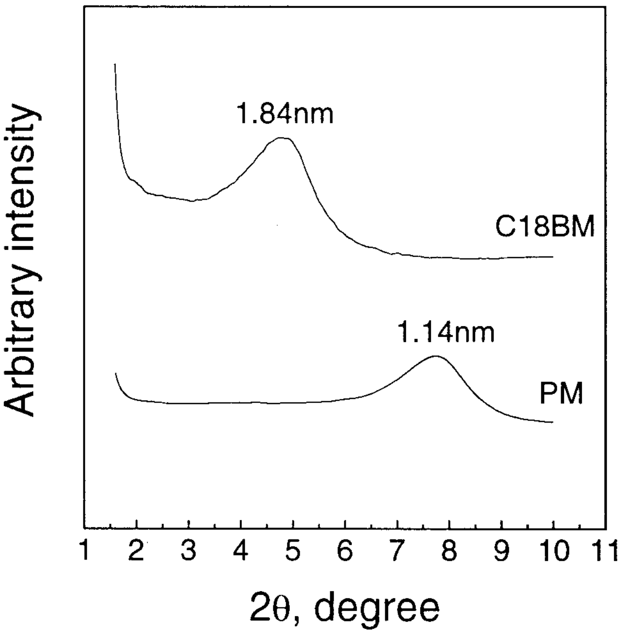

Figure 1 X-ray diffraction patterns of C18BM and PM.

Measurements

X-ray diffraction spectra were obtained using a Rigaku X-ray generator (Cu Kα radiation with $\lambda = 0.15406$ nm) at room temperature in a 2θ range of 2°–10° at a rate of 2°/min.

Tensile test specimens were prepared by molding in a dumbbell-shaped molder on a hot press. Each sample was cured at 140°C for 1 h, followed by curing at 180°C for 1 h. Tensile tests were performed at room temperature on an Instron tester (model 4201) according to ASTM Standard D 638-94. At least seven specimens were tested for each set of samples, and the mean value is reported. For comparative purposes, we include the X-ray data and mechanical properties of P1C18MIC containing octadecylammonium-modified montmorillonite prepared in the previous study.[25]

To investigate the thermal stability of PLSNs, a thermogravimetric analyzer (TGA; Du Pont Model 2100) was used. The analysis was performed at a heating rate of 10°C/min in a nitrogen atmosphere. TGA was also sued to determine the organic content of each organosilicate.

RESULTS AND DISCUSSION

Organically modified layered silicate

Figure 1 shows the X-ray diffraction patterns of C18BM and PM. C18BM shows the basal reflection peak at a lower angle than that of PM, indicating the organosilicate C18BM was successfully prepared by ion exchange. Thermogravimetric analysis showed that C18BM had a total organic content of 27 wt %. THEM had a similar organic content to C18BM.

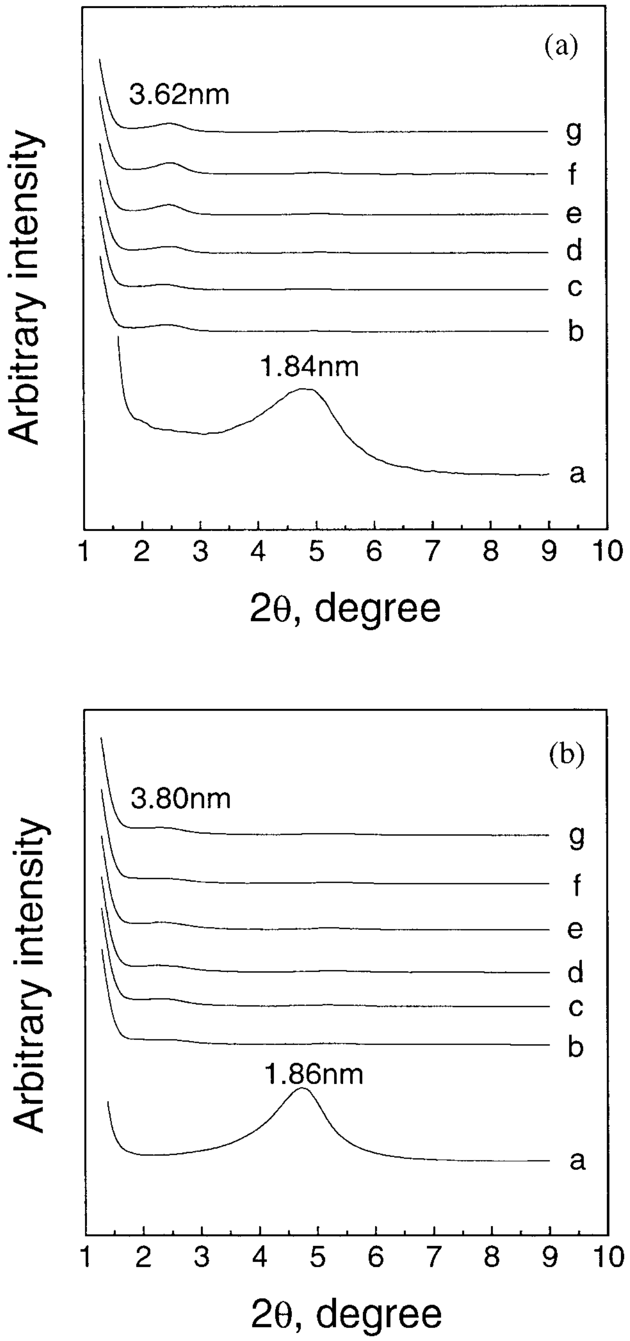

Figure 2 X-ray diffraction patterns of (a) P1C18BM and (b) P1THEM at various temperatures with time: trace a, pristine organoclay (C18BM and THEM, respectively); trace b, 120°C for 1 h; trace c, 120°C for 2 h; trace d, 140°C for 1 h; trace e, 140°C for 2 h; trace f, 160°C for 1 h; trace g, 160°C for 2 h (silicate content = 5 wt %).

Synthesis of phenolic resin–layered silicate nanocomposites

To investigate the effects of annealing temperature and time on the morphology of phenolic resin–layered silicate nanocomposites (PLSNs), X-ray diffraction spectra were obtained at various temperatures with time (Fig. 2). In Table I the X-ray diffraction peak positions and *d* spacings are illustrated. The *d* spacing was calculated using the Bragg equation with the peak position. As shown in Figure 2(a), the basal reflection peak of pristine C18BM shifted to a lower angle upon annealing at 120°C for 1 h. This indicates that intercalated nanocomposites were formed through melt intercalation. No additional change in the diffraction peak was observed in the overall features, even if the annealing temperature and period increase. In our previous study[25] we used fluorohectorite modified with the same organic modifier as that of C18BM. Comparing the X-ray results between the two nanocomposites, we found that the kind of silicate did not have much of an effect on the intercalated morphology of the phenolic resin nanocomposites. P1THEM showed intercalation behavior similar to P1C18BM at that annealing temperature and time, but its diffraction peaks were slightly broader relative than those of P1C18BM [Fig. 2(b)]. It is noted that P1THEM had the largest gallery expansion (Table I). Gallery expansion was in this order: P1THEM (1.94 nm) > P1C18BM (1.78 nm) > P1C18M (1.56 nm). It is well known that the organic modifier of a silicate plays a key role in the intercalation of polymeric chain into the silicate gallery. The organic modifier makes the hydrophilic silicate organophilic. In this way a favorable interaction with the generally hydrophobic polymer can be induced. From a thermodynamic consideration, it can compensate for the thermodynamic barrier derived from entropy loss of polymer confined in the silicate gallery by attaining a gain in entropy upon gallery expansion to accommodate the diffusing polymeric chain. Phenolic resin has many hydroxyl groups that can be acceptors or donors in the hydrogen-bonding interaction. In addition, the organic modifier of THEM has hydroxyl groups. Thus, the largest gallery expansion in P1THEM nanocomposites can be attributed to the most favorable interaction between phenolic resin and the organic modifier arising from the strong hydrogen bonding. Other polymer–organosilicate nanocomposites also showed better silicate dispersion and sometimes exfoliation, resulting from the strong dipolar interaction and especially the strong hydrogen-bonding interaction.[1,14,21,26]

To investigate the intercalation kinetics, P1THEM was annealed at 140°C with time. The basal reflection

TABLE I
X-ray Peak Positions and *d* Spacings (d_{001}) of PLSNs

Sample	Pristine sample 2θ (deg)/d spacing (nm)	Annealed sample 2θ (deg)/d spacing (nm)	Differences of d spacing (nm)
P1C18M[25]	4.82/1.83	2.60/3.39	1.56
P1C18BM	4.80/1.84	2.42/3.62	1.78
P1THEM	4.76/1.86	2.35/3.80	1.94

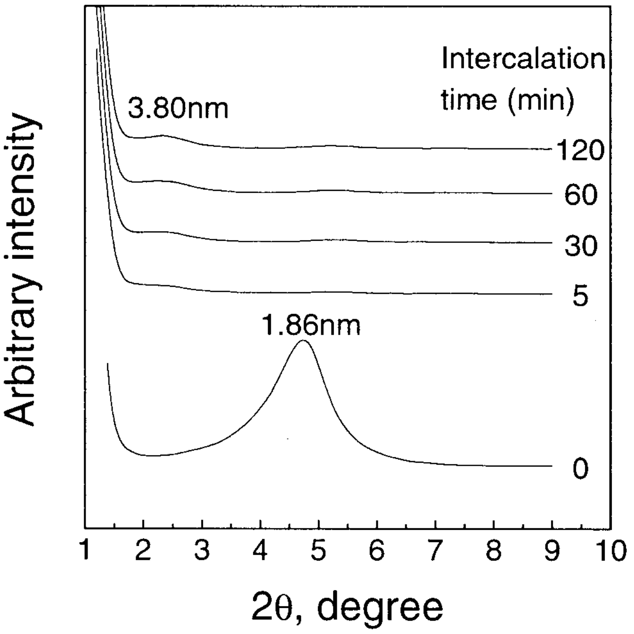

Figure 3 X-ray diffraction patterns of P1THEM intercalated at 140°C as a function of intercalation time (silicate content = 5 wt %).

peak of P1THEM shifted to a lower angle within 5 min and remained in almost the same position over 5 min, as shown in Figure 3. The P1C18BM nanocomposites showed intercalation kinetics similar to P1THEM. These behaviors indicate a very fast diffusion of phenolic resin into the silicate gallery to intercalate.

Figure 4 shows X-ray diffraction spectra of P1THEM systems before and after curing. P1THEM showed almost no change in the peak position and only a slight peak broadening when cured. This behavior means that the initial intercalated morphology of P1THEM was stable against curing and that the curing process more slightly induced disorder of the silicate layers but not exfoliation. The cured P1C18BMIC nanocomposites also had a similar intercalated X-ray peak position to the uncured P1C18BM. However, P1C18MIC showed an X-ray peak shifting to a higher angle relative to the uncured P1C18M, indicating the deintercalation of phenolic resin out of the silicate gallery during the curing process to form a kind of conventional composite.[25]

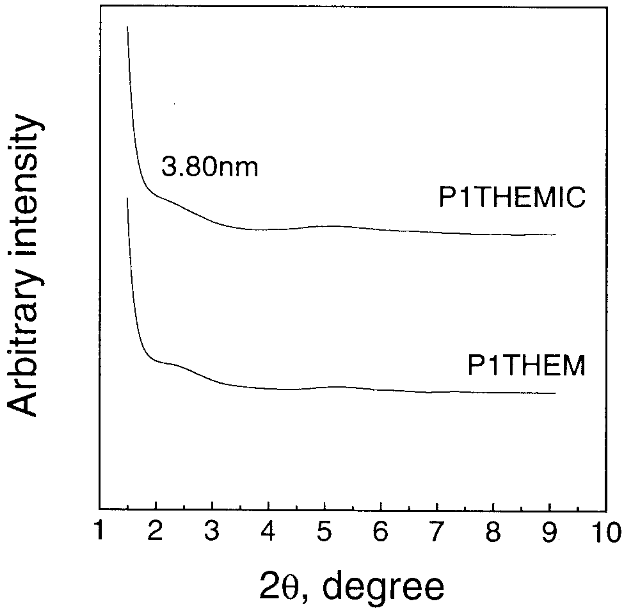

Figure 4 X-ray diffraction patterns of P1THEM systems before and after curing at 140°C for 1 h followed by curing at 180°C for 1 h (silicate content = 5 wt %).

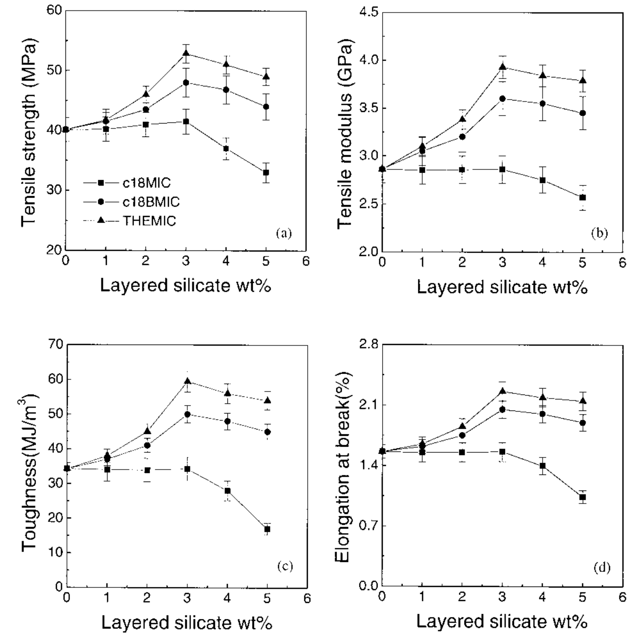

Figure 5 Mechanical properties of various PLSNs cured at 140°C for 1 h followed by curing at 180°C for 1 h as a function of silicate content: (a) tensile strength, (b) tensile modulus, (c) toughness, and (d) elongation at break (0 wt % is neat phenolic resin).

Mechanical properties of PLSNs

Figure 5 shows the tensile properties of PLSNs. For all the tensile properties, P1C18MIC showed almost no increase in mechanical property because of its poor silicate dispersion. This system showed even lower mechanical properties than the neat phenolic resin over 3 wt % of silicate content. In contrast, P1C18BMIC and P1THEMIC showed steep increases in mechanical properties up to 3 wt % of silicate content. They showed increases in tensile strength of 20% and 32%, respectively, at 3 wt % of silicate content when compared to the neat phenolic resin, as shown in Figure 5(a). Their tensile moduli were 1.26 and 1.37 times higher, respectively [Fig. 6(b)], showing even higher increases in toughness (46% for P1C18BMIC

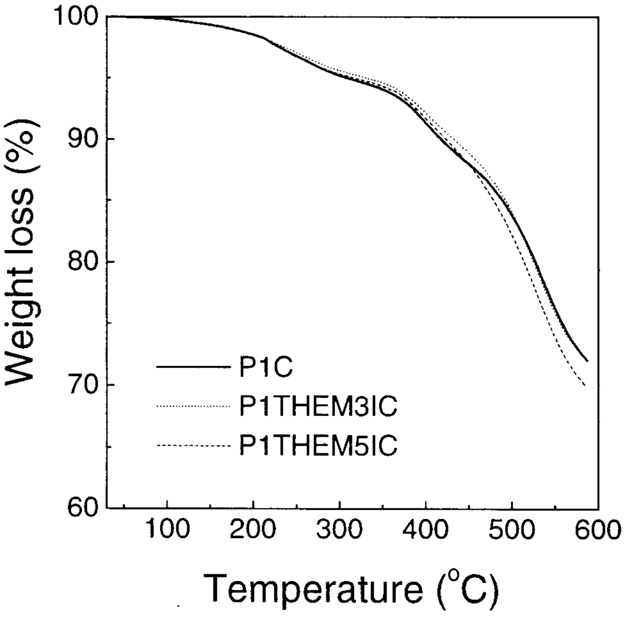

Figure 6 TGA thermograms of phenolic resin and P1THEMIC nanocomposites with various silicate contents cured with HMTA at 140°C for 1 h followed by curing at 180°C for 1 h. Numbers in the legend indicate silicate content.

and 73% for P1THEMIC) and elongation at break (31% and 45%, respectively) than the neat phenolic resin [Fig. 6(c,d)]. These increases in all the tensile properties would be unusual in a conventional composite system. They may be partly a result of the reinforcement of the silicate layers in the phenolic matrix at the nanometer level and partly a result of the high aspect ratio and large surface area being able to contact with the phenolic resin. Wang et al.[16] reported that the improvement in tensile strength and modulus was directly attributable to the reinforcement of silicate layers and that the improved elasticity might be attributed in part to the plasticizing effect of the organic modifier of layered silicate, which contributes to the dangling chain formation in the epoxy matrix, as well as to the conformational effect on the polymer at the silicate–matrix interface. Some researchers[17,27,28] suggested that the improvement in toughness in polyamide 12-, acrylic copolymer- and epoxy-layered silicate nanocomposites could be attributed to microvoid formation inside the stacked silicate layers and to strong prevention of microvoid propagation. Even though various models have been suggested to explain the increase in the toughness and elasticity of polymer–silicate nanocomposites, the reason for each nanocomposite system is still unclear. It is noted that P1THEMIC showed the highest tensile properties for the entire silicate content range. The best silicate dispersion in P1THEMIC led to the highest mechanical properties, confirming the importance of the strong hydrogen-bonding interaction between phenolic resin and the organic modifier of THEM.

All the PLSNs have maximum mechanical properties at a silicate content of 3 wt %. Yang et al.[18] reported that both tensile strength and elongation at break decreased at montmorillonite contents above 5 wt %, which might have been caused by the aggregation of montmorillonite. Chen et al.[19] suggested that the lower tensile strength of polyurethane nanocomposites with a 5% organoclay content relative to that of the unfilled polyurethane was probably a result of the high organic modifier content. Wang et al.[20] attributed the decrease in tensile strength and modulus of epoxy–magadiite nanocomposites with magadiite content greater than 11.6% to dangling chain formation. In our system phenolic resin existed in the silicate gallery, and the curing agent HMTA coexisted with a part of the phenolic resin remaining unintercalated out of the silicate gallery before curing. Thus, the HMTA had to be intercalated into the silicate gallery to react with the phenolic resin uniformly in and out of the silicate gallery. However, the silicate layers and the preintercalated phenolic resin prevented the HMTA, residing initially extragallery, from diffusing intragallery. Furthermore, the increase in viscosity of the nanocomposites with silicate content can make the diffusion of HMTA intragallery more difficult. Using curing kinetics, we verified quantitatively the retardation effect of the silicate layers on the curing (especially postcuring at 180°C). These effects lowered the tensile properties of PLSNs with a silicate content of more than 3 wt %. It seems that 3 wt % is a critical value in intercalated PLSN. We discuss the curing kinetics in detail in another article.

Thermal stabilities of PLSNs

Thermal stabilities of PLSNs were investigated using TGA. Figure 6 shows the TGA thermograms of neat phenolic resin and P1THEMIC nanocomposites. The numbers in the legend indicate silicate contents (for example, the "3" in P1THEM3IC indicates 3 wt % of silicate content). Both neat phenolic resin and PLSNs were thermally degraded in three steps, a typical feature of the degradation process of phenolic resin. P1THEM3IC showed slightly improved thermal stability, but P1THEM5IC decreased relative to neat phenolic resin (P1C). The decrease in thermal stability with silicate content was not clear. However, it might be related to the decreased mechanical properties of P1THEMIC nanocomposites with more than 3 wt % silica content.

CONCLUSIONS

We investigated morphologies, mechanical properties and thermal stabilities of PLSNs synthesized by melt intercalation. P1C18BM and P1THEM systems had intercalated nanostructures that were stable against the curing process. However, the P1C18M system showed an unstable nanostructure against the curing process, resulting in deintercalation of phenolic resin out of the silicate gallery and formation of a conventional composite. The P1THEM system had a higher gallery expansion than did any other system, which was attributed to the strong hydrogen-bonding interaction between phenolic resin and the organic modifier of THEM. The P1THEMIC having the best silicate dispersion had the highest mechanical properties. Depending on the silicate content, P1THEMIC nanocomposites showed slightly improved or decreased thermal stability compared to that of the neat phenolic resin.

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