Morphology and Curing Behaviors of Phenolic Resin-Layered Silicate Nanocomposites Prepared by Melt Intercalation

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The melt intercalation and curing behavior of phenolic resin (P1) were investigated by use of layered silicates, such as pristine montmorillonite (PM), dodecylammonium-modified montmorillonite (C12M), octadecylammonium-modified montmorillonite (C18M), benzyldimethyloctadecylammonium-modified fluorohectorite (C18BH), and hexamethylenetetramine (HMTA), as curing agents. It was found by X-ray diffraction that the uncured phenolic resin was intercalated into PM, C18M, and C18BH. Cured phenolic resin-layered silicate nanocomposites were prepared by two methods: one was the sequential process of intercalation and curing (IC, the suffix of sample code), and the other was the simultaneous process of mixing and curing (MC). The intercalated structures were preserved in cured P1C18BH but not in cured P1C18M, i.e., the phenolic resin intercalated in C18M was deintercalated when it was cured. It was suggested that the intercalated structure of P1C18BH was more stable in the curing process than that of P1C18M due to chemical affinity derived from the favorable interaction between the phenolic resin and intercalant-containing benzene ring. Transmission electron micrographs showed that a splitted-stacked structure was formed in the samples of P1PMMC and P1PMIC, indicating the phenolic resin did not intercalate the PM. Conclusively, the modification of layered silicate and the resulting interaction between organic modifier and phenolic resin played an important role in determining the stable nanostructure and the final morphology of phenolic resin-layered silicate nanocomposite.

Introduction

Recently, organic−inorganic nanocomposites have stimulated great interest in many researchers due to their unexpected hybrid properties derived from the unique combination of each component. One of the promising nanocomposite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of layered structures, which belong to the general family of 2:1 layered silicates.[1] Their structures consist of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The silicate layers are coupled through relatively weak dipolar and van der Waals forces.[2] The Na^+ or Ca^{2+} residing in the interlayers can be replaced by organic cations such as alkylammonium ions via an ion-exchange reaction to render the hydrophilic layered silicate organophilic. Additionally, the alkylammonium cations could provide functional groups that can react with the polymer or initiate polymerization of monomers to improve the strength of the interface between the inorganic and the polymer.[3]

Experimental work on these materials has generally shown that virtually all types and classes of polymer-layered silicate nanocomposites lead to new and improved properties when compared to their micro- and macrocomposite counterparts and the pristine polymer matrix. The nanocomposites exhibit improved tensile strength and moduli,[4−7] decreased thermal expansion coefficient,[4] decreased gas permeability,[4−7] increased swelling resistance,[8] enhanced ionic conductivity,[9−11] and flammability.[12,13] The enhanced properties of polymer-layered silicate nanocomposites are presumably due to the nanoscale structure of the hybrids, the large aspect ratio (100−1000) of the layered silicate, and large

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surface area (760 m^2/g) able to contact with the polymer matrix to a great extent.

The unprecedented mechanical properties of polymer-layered silicate nanocomposites were first demonstrated by a group at the Toyota research center in Japan using nylon nanocomposites.[14−16] Since then, many polymer-layered silicate nanocomposites have been synthesized, including those with the polymers, poly(ϵ-caprolactone),[17] polyacrylonitrile,[18] poly(methyl methacrylate),[19−24] polyaniline,[25−27] polypyrrole,[28] polyimide,[7,29] polystyrene,[30,31] nylon 6,[3,6,32] polypropylene,[33] poly(ethylene oxide),[34−38] poly(*p*-phenylenevinylene),[39] and epoxy.[4,40]

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.[41]

However, phenolic resin has been abandoned in the nanocomposite field even though it is the first synthesized resin in history and has many advantages. The reason is that general phenolic resin has a three-dimensional structure even if the resin is not cross-linked. This three-dimensional structure of phenolic resin makes it very difficult to intercalate in the layered silicate gallery because the lamella of the layered silicate can be easily intercalated by linear polymers.

To overcome the structural problem of phenolic resin, Usuki et al.[42] tried to synthesize the phenolic resin-layered silicate nanocomposite via intercalative polymerization. They obtained a composite material composed of novolac resin and montmorillonite by reaction between phenol and formaldehyde in the presence of oxalic acid and montmorillonite modified with 4-aminophenol hydrochloride.

There are two types of phenolic resins: i.e., novolac and resol types of resin. Novolac resin is almost unable to cross-link without a curing agent and can be obtained as a linear structure by adopting a low mole ratio of F/P (formaldehyde/phenol) and controlling pH. These characteristics of novolac resin allow it to form a nanocomposite with the thermoset resin with success. Lee and Giannelis[43] first synthesized a phenolic resin-layered silicate nanocomposite via melt intercalation. However, their report is not sufficient enough to understand the morphology and curing behaviors of phenolic resin-layered silicate nanocomposites.

In this paper, we focus on the effect of modification of layered silicate and the resulting interaction between the modifiers preoccupied in organosilicate and phenolic resin and on the morphology and curing behavior of phenolic resin-layered silicate nanocomposite prepared by melt intercalation.

Experimental Section

Materials. Linear novolac resin (P1), KPH−F2002, was obtained from Kolon Chemical Co. Ltd. Its number-average molecular weight, weight-average molecular weight, and polydispersity index were 724, 1515, and 2.09, respectively. Hexamethylenetetramine (HMTA) purchased from Lancaster was used as a curing agent for the phenolic resin. All the chemicals used in this study were used without further purification.

To investigate the effect of modifier in a layered silicate, we used pristine and various organically modified layered silicates. Natural sodium pristine montmorillonite (PM) and dodecylammonium-modified montmorillonite (C12M), octadecylammonium-modified montmorillonite (C18M), and synthetic benzyldimethyloctadecylammonium-modified fluorohectorite (C18BH) used in this study were obtained from Nanocor Inc. The cation exchange capacity (CEC) values of PM and C18BH were 108 and 150 mequiv/100 g, respectively. CEC values of C12M and C18M were the same as that of PM. The ideal formulas of sodium montmorillonite and lithium fluorohectorite are $Na_{0.90}[Al_{3.10}Mg_{0.90}](Si_{8.0})O_{20}(OH)_4$ and $Li_{1.30}[Mg_{4.70}Li_{1.30}](Si_{8.0})O_{20}(OH,F)_4$, respectively. All the layered silicates were used as received and their particle sizes were below 37 μm.

Synthesis of Phenolic Resin-Layered Silicate Nanocomposites. Fine particles of phenolic resin (95 wt %) and layered silicates (5 wt %) were mechanically mixed and placed on glass slides. The mixtures were subsequently annealed in a vacuum at a temperature range of 120∼160 °C for 5 min∼2 h. The uncured phenolic resin-layered silicate nanocomposites (PLSNs)

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were referred to as P1PM, P1C12M, P1C18M, and P1C18BH from the above names of phenolic resin and layered silicates.

The PLSNs were again pulverized mechanically and cured with HMTA of 10 wt % relative to the phenolic resin (i.e., phenolic resin/HMTA = 90/10) 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 that were synthesized by the sequential process of intercalation and curing were named as P1C (phenolic resin cured), P1PMIC, P1C18MIC, and P1C18BHIC, respectively.

Phenolic resin, layered silicates (PM, C18M, and C18BH), and HMTA were mixed mechanically at the same time with the same composition of P1PMIC, etc., and cured at 140 °C for 1 h followed by curing at 180 °C for 1 h on a hot press. The samples were named as P1PMMC, P1C18MMC, and P1C18BHMC.

Also, the P1C18MMC and P1C18MIC samples were cured at 120 °C for 5 or 10 min to investigate the effect of curing temperature and time on their nanostructures.

Measurements. X-ray diffraction spectra were obtained on a Rigaku X-ray generator (CuKα radiation with $\lambda = 0.15406$ nm) at room temperature. A sample was prepared in the form of film on a glass slide. The diffractograms were scanned in a 2θ range of 2−10° at a rate of 2°/min.

FTIR spectroscopy was used to observe the curing behavior of phenolic resin and the structures of PLSNs. Infrared spectra on KBr pellets were averaged over 20 scans taken at 4 cm^{-1} resolution on a FTIR spectrometer (Bomem 102 model).

The curing behaviors of phenolic resin and PLSNs were observed with a differential scanning calorimeter (DSC; Du Pont model 910 thermal analyzer) under nitrogen atmosphere. A typical sample weight was about 10 mg and the scan speed was 10 °C/min.

The morphologies of PLSNs were imaged by transmission electron microscopy (TEM) on 100 nm thick sections of the nanocomposite coated with carbon on a Philips CM-20 transmission electron microscope at an accelerating voltage of 160 kV.

Results and Discussion

Synthesis of Phenolic Resin-Layered Silicate Nanocomposites (PLSNs). To facilitate the intercalation of phenolic resin into the silicate, the mixture of phenolic resin and silicate was annealed in a vacuum above T_g (about 60 °C) of uncured phenolic resin. X-ray diffraction patterns of PLSNs annealed at various temperatures with time are illustrated in Figure 1. Also, in Table 1, the dispersibility of layered silicates in phenolic resin and *d* spacing (d_{001}) of PLSNs are summarized. As shown in Figure 1a, the (*001*) reflection peak of pristine P1PM (before annealing) shifts to a lower angle after annealing at 120 °C for 1 h. No further intercalation occurs even if the annealing temperature and period increase. The difference of *d* spacing between pristine and annealed P1PM is 3.3 Å, which suggests that the monolayer of phenolic resin might be intercalated in the pristine montmorillonite gallery.

In general, polymer does not intercalate into layered silicate because the layered silicate is hydrophilic and the polymer is generally hydrophobic. So layered silicate is modified with alkylammonium, which confers hydrophobicity. However, some polymers with a hydrophilic structure such as poly(ethylene oxide) would be easily intercalated in pristine layered silicate without modification with alkylammonium chain.[44,45] It is likely that the hydroxyl groups in phenolic ring probably contribute

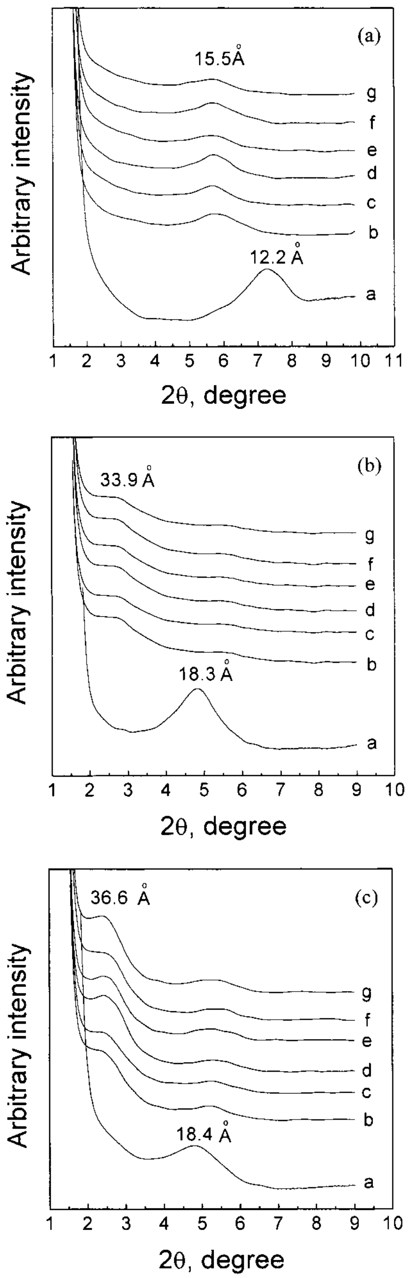

Figure 1. X-ray diffraction patterns of (a) P1PM, (b) P1C18M, and (c) P1C18BH as a function of intercalation temperature and time: traces a, mixture of phenolic resin and layered silicate before heating; traces b, 120 °C for 1 h; traces c, 120 °C for 2 h; traces d, 140 °C for 1 h; traces e, 140 °C for 2 h; traces f, 160 °C for 1 h; and traces g, 160 °C for 2 h.

Table 1. Dispersibility of Layered Silicates in Phenolic Resin and *d* Spacings (d_{001}) of PLSNs

		2θ (deg)/*d* spacing (Å)		
sample	intercalation/-immiscible	pristine sample	annealed sample	difference of *d* spacing (Å)
P1PM	intercalation	7.27/12.2	5.70/15.5	3.3
P1C12M	immiscible	6.49/13.6	5.93/14.9	1.3
P1C18M	intercalation	4.82/18.3	2.60/33.9	15.6
P1C18BH	intercalation	4.80/18.4	2.41/36.6	18.2

the intercalation into pristine montmorillonite due to its interaction with hydroxyl or oxygen groups of layered silicate through hydrogen bonding like other systems.[46,47] The morphology of P1PM will be discussed again in the following morphology section as to whether the phenolic resin is really intercalated into the gallery of pristine montmorillonite.

The (*001*) reflection peak of pristine P1C18M shifts to a lower angle by about 2.2° as shown in Figure 1b (the difference of *d*-spacing between pristine and annealed P1C18M = 15.6 Å) after annealing even at low temperature and for a short time, suggesting the intercalation of P1 into the C18M gallery with an opening of more than bilayers of phenolic resin. However, phenolic resin and C12M are almost immiscible as illustrated in Table 1 although C12M is modified silicate with alkylammonium (X-ray diffraction peak is not shown here), which indicates that the C12M is not sufficiently organophilic to make intercalation of phenolic resin. Probably, the modified silicate becomes more hydrophobic to increase the miscibility of phenolic resin and layered silicate by increasing the alkylammonium chain length. Lan and Pinnavaia[48] reported that longer alkylammonium chains facilitate the formation of the nanocomposites in the epoxy and montmorillonite system. Phenolic resin intercalates well into C18BH as in the P1C18M system, considering the shift of the (*001*) reflection peaks to a lower angle in Figure 1c. The P1C18BH shows a slightly larger gallery expansion (18.2 Å) than P1C18M, with a gallery expansion of 15.6 Å. It may be suggested that phenolic resin intercalates more into C18BH than into C18M because phenolic resin with benzene rings has a more favorable interaction with modifier containing benzene ring.

P1C18M and P1C18BH show much less intense and broader reflection peaks (Figure 1b,c) than the parent organosilicates. This behavior indicates that the layered silicates are highly disordered even though they are not fully exfoliated.

For the above three intercalated systems, i.e., P1PM (which will be discussed more in the following section Morphology of PLSNs), P1C18M, and P1C18BH, the optimum intercalation temperature is determined to be 140 °C.

To investigate the intercalation rate over time, P1PM, P1C18M, and P1C18BH were intercalated at 140 °C. The (001) reflection peak of P1C18BH shifts to a lower angle only at 5 min and remains almost constant after 5 min as shown in Figure 2. P1PM and P1C18M show similar intercalation kinetics to P1C18BH. Thus, it is suggested that since the intercalation process of phenolic resin into layered silicate is very fast, the simultaneous process of mixing and curing of phenolic resin would be possible instead of the sequential process of intercalation of phenolic resin into layered silicate gallery and then curing. The comparison of morphologies of these two methods will be discussed in the following section. The intercalation rate of phenolic resin is so fast that the annealing is fixed at 140 °C for 2 h in order to ensure full intercalation.

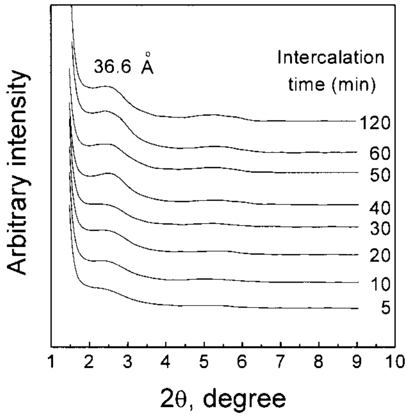

Figure 2. X-ray diffraction patterns of P1C18BH intercalated at 140 °C as a function of intercalation time.

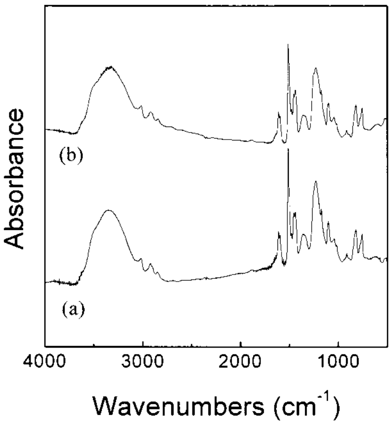

Figure 3. FTIR spectra of (a) phenolic resin and C18M mixture before annealing (pristine P1C18M) and (b) annealed P1C18M with the intercalated structure.

Figure 3 shows no distinct difference of overall features between pristine and annealed P1C18M in the FTIR spectra. It indicates that the overall structure of intercalated phenolic resin in the layered silicate gallery does not change significantly when compared to the bulk phenolic resin. P1PM and P1C18BH system also show similar behavior.

Curing Behavior of Phenolic Resin. In general, novolac resins are thermally cured by adding a methylene cross-linker, hexamethylenetetramine (HMTA) or paraformaldehyde, and changes to insoluble and infusible products. The product properties depend on synthesis and operating conditions. Specifically, the curing process is responsible for many physical and mechanical characteristics of PLSNs and is important and essential for the improvement of their properties.

In this study, the curing behavior of phenolic resin with HMTA was investigated at various curing temperatures by an in situ method with FTIR. In Figure 4, the spectrum at 25 °C indicates a simple mixture of P1 and HMTA. A broad peak around 3200−3700 cm^{-1} corresponds to the −OH stretching. Small peaks around 3060 and 2900 cm^{-1} are associated with the −CH stretching of the phenolic ring and −CH stretching of methylene ($-CH_2-$) bridges between phenolic rings, respectively. A signal at 1610 cm^{-1} is the characteristic for the elongation of the aromatic ethylene bond (C=

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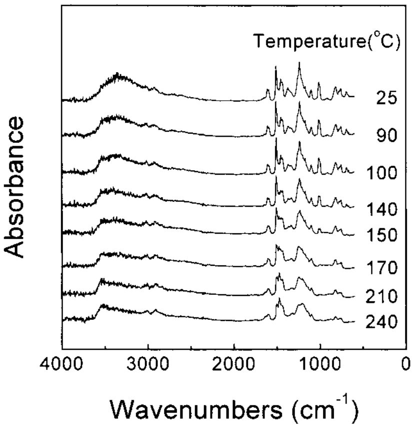

Figure 4. FTIR spectra of curing behaviors of phenolic resin at various temperatures.

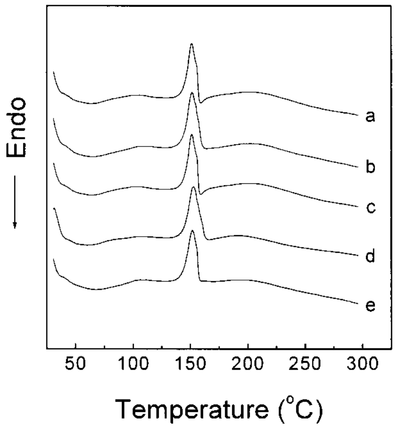

Figure 5. DSC thermograms of curing behavior of phenolic resin and PLSNs with HMTA: trace a, phenolic resin; trace b, P1PM; trace c, P1C12M; trace d, P1C18M; and trace e, P1C18BH.

C). The regions of 753−794, 820−855, and 912−917 cm^{-1} can be assigned to *ortho* and *para* substitution and ring deformation of a phenolic ring, respectively. The band at 1500 cm^{-1} is assigned to a phenolic ring substituted at the *ortho* or *para* positions. At 90 °C the intensity of the band at 1500 cm^{-1} starts to decrease, suggesting the depletion of mono- and disubstituted phenolic rings due to the initiation of cross-linking. Upon elevation of the temperature above 90 °C, the intensity of the band at 1500 cm^{-1} decreases further but abruptly at 140−150 °C. In this temperature range, the curing reaction of phenolic resin may be most prominent. As more phenolic resin is cured, the −OH peaks around 3700−3500 cm^{-1} become broadened and the phenolic ring deformation peaks in the regions of 753−794, 820−855, and 912−917 cm^{-1} decrease in intensity. Probably, these phenomena are attributed to the difficulty of phenolic ring deformation when it is highly cured.

Curing Behaviors of PLSNs. By DSC, the effect of curing on the intercalation morphology of phenolic resin is investigated. DSC thermograms for PLSNs at the heating rate of 10 °C/min are illustrated in Figure 5. The phenolic resin with HMTA is cured in a broad range of temperature. Curing starts from about 60−70 °C and continues until 270−275 °C. Especially, a very strong exotherm is seen at 150 °C, indicating the very vigorous curing reaction related to the abrupt decrease in band intensity at 1500 cm^{-1} in Figure 4. In Figure 5, phenolic resin and PLSNs show almost identical curing behavior. Messersmith and Giannelis[4] observed a strong exotherm in the presence of organosilicates in the curing behavior of intercalated epoxy resin cured with benzyldimethylamine when compared to unfilled epoxy resin cured with the same curing agent. They suggested from the strong exotherm on DSC thermograms that the organosilicates played a catalytic role in the base-catalyzed homopolymerization of epoxy. In our systems, organosilicates probably do not play a catalytic role in curing of phenolic resin since the exothermic peaks are almost identical for all the samples as shown in Figure 5.

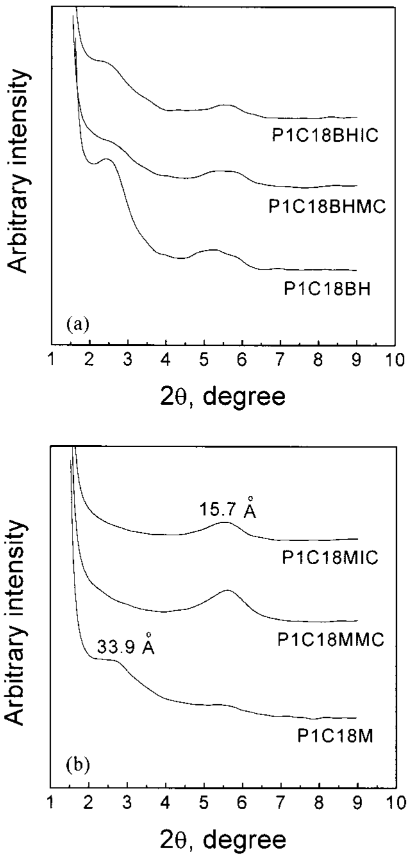

Figure 6. X-ray diffraction patterns of PLSNs before and after curing at 140 °C for 1 h followed by curing at 180 °C for 1 h: (a) P1C18BH system and (b) P1C18M system.

The effect of curing on the nanostructure of PLSNs is investigated by use of X-ray diffraction patterns of PLSNs cured at 140 °C for 1 h followed by curing at 180 °C for 1 h. In Figure 6, P1C18BH shows a broad reflection peak but no peak shift after curing with HMTA when compared to the uncured state, regardless of preparation method of PLSNs (i.e., MC and IC). The P1PM system shows similar behavior to the P1C18BH system. It suggests that the curing process of phenolic resin does not affect the intercalated structures. However, according to Messersmith and Giannelis,[4] the organosilicate galleries intercalated with epoxy resin were delaminated when the nanocomposite was cured with benzyldimethylamine, but they were not delaminated when the nanocomposite was cured with the primary and secondary amines. Thus, the choice of curing agent for a thermosetting resin is critical in determining the intercalated and/or delaminated nano-

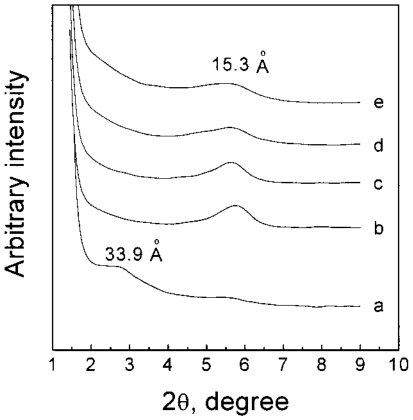

Figure 7. X-ray diffraction patterns: trace a, P1C18M; trace b, P1C18MMC cured at 120 °C for 5 min; trace c, P1C18MMC cured at 120 °C for 10 min; trace d, P1C18MIC cured at 120 °C for 5 min; and trace e, P1C18MIC cured at 120 °C for 10 min.

structures of layered silicate nanocomposites. In our phenolic resin and HMTA system, no further intercalation or exfoliation occurs, probably since HMTA has a ring structure at the initial state and it is very difficult to intercalate into the layered silicate gallery. Also, the P1C18BHIC shows no difference in nanostructure from the P1C18BHMC (Figure 6), suggesting that the intercalation rate of phenolic resin is comparable to or faster than the curing rate of phenolic resin. If the above suggestion is really true, the PLSNs can be synthesized simply by the simultaneous process of mixing and curing.

Unlike the P1PM and P1C18BH systems, the X-ray diffraction patterns of P1C18M system show a strikingly different feature. The (*001*) reflection peaks of P1C18MMC and P1C18MIC shift to a higher angle as shown in Figure 6b, indicating the deintercalation of intercalated phenolic resin during the curing process and/or the collapse of expanded silicate gallery by the phenolic resin cured in extragallery. The rearrangement of the alkylammonium chain in the silicate gallery results in the reduction of *d*-spacing values from 18.3 Å before curing to 15.7 Å. It is suggested that the C18M intercalated by phenolic resin is more unstable than C18BH deintercalated on curing. Doh and Cho[49] observed that the organically modified montmorillonite with an alkylammonium chain containing a benzene ring was dispersed well in styrene monomer and concluded that as the structural affinity between styrene monomer and organic group of organosilicate increased, the dispersibility of organosilicate became higher. Generally, it is known that the penetration of monomers into the lamellae of organosilicate can be facilitated by the attractive forces between the organosilicate interlayers and the free monomer molecules. The solvation efficiency of the organosilicate with monomer depends not only on the nature of the organic group intercalated in the layered silicate but also on the chemical structure of the monomer used.[50] Thus, the more stable characteristics of intercalated phenolic resin in P1C18BH than in P1C18M during the curing process are probably due to the chemical affinity, i.e., the favorable interaction between the intercalated phenolic resin and the benzyldimethyloctadecylammonium within C18BH. Other systems also show a gallery contraction. Lan et al.[29] reported a contraction of silicate gallery when polyamic acids were imidized at 300 °C. They explained that the contraction was attributed to the thermal decomposition of alkylammonium chain in the gallery during imidization process. Messersmith and Giannelis[17] also observed the reduction of *d*-spacing when ϵ-caprolactone was polymerized in layered silicate. They suggested that the decrease in layer spacing followed the ring opening of lactone in the monomer, which produced a monolayer of fully collapsed poly(ϵ-caprolactone) chains.

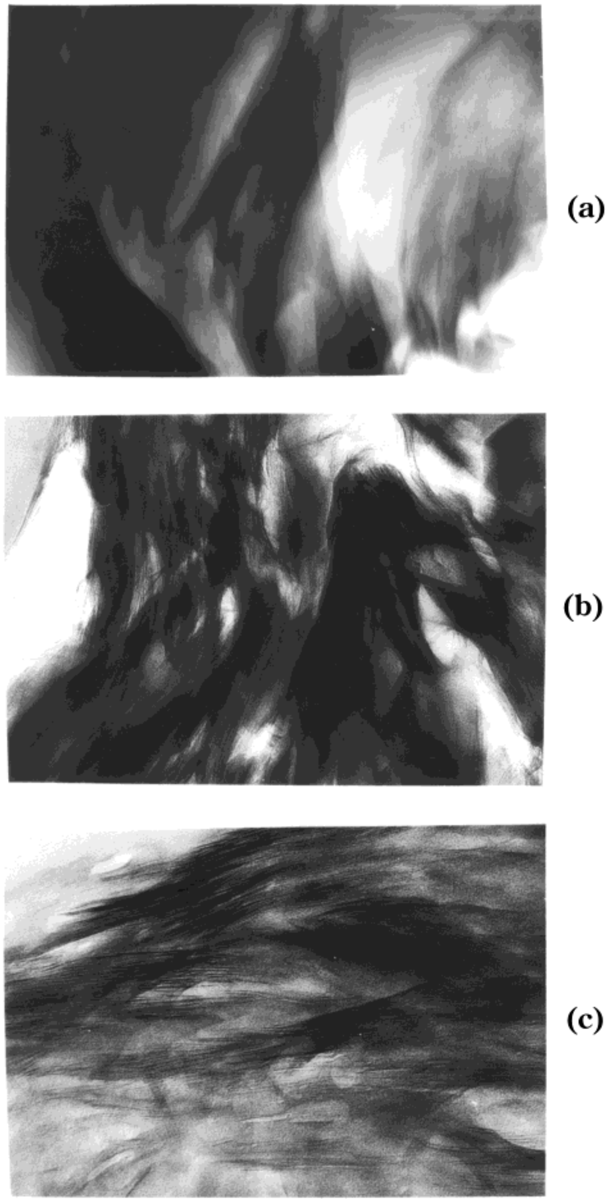

Figure 8. TEM micrographs of (a) P1PMIC, (b) P1C18MIC, and (c) P1C18BHIC cured at 140 °C for 1 h followed by curing at 180 °C for 1 h.

In general, as the curing temperature increases, the curing rate increases. Thus, the collapse of the layered silicate gallery in the case of P1C18M may be caused by the high curing rate of phenolic resin (recall the curing at 140 °C) and the deintercalation of phenolic resin in the silicate to react with the bulk HMTA. It

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can be expected that if the curing rate is lowered by decreasing the curing temperature, the intercalated structure of P1C18M will be preserved. To confirm this postulate, P1C18M was cured at a lower temperature, 120 °C rather than 140 °C. Also, to lower the degree of cure, the curing time selected was short, 5 or 10 min. X-ray diffraction patterns of P1C18M cured at 120 °C are shown in Figure 7. It is again observed that the (*001*) reflection peaks of P1C18M shift to a higher angle, indicating that the C18M intercalated by phenolic resin is still unstable even though the curing temperature and the curing rate are lower than 140 °C. It is found that the deintercalation rate of phenolic resin during curing is very fast like the intercalation rate.

Morphology of PLSNs. P1PM and P1C18BH still had the intercalated nanostructure when they were cured with HMTA, but P1C18M did not. To confirm the hybrid structures, the morphology of PLSNs cured was observed by transmission electron microscopy. TEM micrographs of PLSNs cured with HMTA at 140 °C for 1 h followed by curing at 180 °C for 1 h are shown in Figure 8. In the TEM micrographs, the dark lines are the intersections of the silicate layers of about 10 Å thickness. In Figure 8a, some splitting of stacked layered structures is shown as a dark portion, indicating that P1PMIC has only a splitting of stacked layered structures but not an intercalated structure. Okada et al.[51] also reported that nylon 6 is not intercalated into pristine montmorillonite but intercalated into organically modified montmorillonite. Thus, in Figure 1a, the shifting of (*001*) reflection peaks to a lower angle when compared to PM is probably due only to the splitting of stacked silicate layers. It is noted that the (*001*) reflection peaks of P1PM remain at the same position before and after curing. In the above section, phenolic resin intercalated into C18M was deintercalated out of extragallery when cured. The stacked silicate layers and some intercalated dark portion are seen in Figure 8b. The stacked part of P1C18M may be formed by restacking of silicate layers during gallery contraction. Some parts of phenolic resin intercalated in C18M could not be deintercalated out of extragallery in cure and preserved the intercalated structure. However, P1C18BHIC has a well-intercalated nanostructure as shown in Figure 8c. The distance between the dark lines is in the range of 16−22 Å. These values are almost identical to the results of X-ray diffraction peaks, about 18.2 Å from Table 1 [recall that the (*001*) reflection peaks of P1C18BH before and after curing were almost identical]. It is found that the preparation method of PLSNs, i.e., IC or MC, does not affect the morphology.

In conclusion, P1C18BHMC and P1C18BHIC have an intercalated structure, and P1C18MMC and P1C18MIC have a partly intercalated structure and a partly stacked structure, and P1PMIC and P1PMMC have only a split-stacked structure. The kind of layered silicate, such as montmorillonite, fluorohectorite, etc., can affect the morphology of a nanocomposite due to the different ionic strength, aspect ratio, size, and chemical composition. In this study, however, it is probably most important that the modifier has a constituent that can favorably interact with phenolic resin. It is suggested that the modifier benzyldimethyloctadecylammonium, with a benzene ring, favorably interacts with phenolic resins containing benzene rings. More experiments on this matter are underway. The modifiers of organosilicates clearly affected not only the curing behavior but also the final morphology of PLSNs.

Conclusions

In this study, we investigated the effect of modifiers of organosilicate on the curing behaviors and final morphology of phenolic resin-layered silicate nanocomposite prepared by melt intercalation. P1C18BHMC and P1C18BHIC had an intercalated morphology and P1C18MMC and P1C18MIC had a partly intercalated morphology. P1PM system had only a split-stacked morphology. Especially, it was found that the P1C18M system had a very unstable nanostructure when cured, showing that the phenolic resin intercalated in C18M was deintercalated out of extragallery during the curing process.

In conclusion, the modification of layered silicate and the resulting interaction between organic modifier and phenolic resin played an important role in determining the stable nanostructure and final morphology of phenolic resin-layered silicate nanocomposite.

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