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Synthesis and Characterization of Resol Type Phenolic Resin/Layered Silicate Nanocomposites

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Resol type phenolic resin/layered silicate nanocomposites (RPLSNs) are prepared by melt intercalation using various layered silicates such as sodium montmorillonite (MMT) and ω-amino acid modified montmorillonites (C3M, C6M, and C12M). The most hydrophilic MMT is the most compatible with the resol type phenolic resin (KL) at the beginning of cure due to the initial hydrophilicity of KL with many methylol groups. However, KL is deintercalated out of extragallery of MMT during the cure since the KL lose hydrophilicity by the depletion of methylol groups. It is found that the C6M has the best miscibility with KL at the entire cure stage. The KLC6M system has the best mechanical properties, due to the end-tethered structure formed by the reaction between the organic modifier (carboxylic acid) of C6M and the methylol group of KL, as well as the excellent dispersion of silicate layers. RPLSNs have similar thermal stability to the neat phenolic resin.

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] and flammability.[8−9] The unprecedented mechanical properties of polymer/layered silicate nanocomposites were first demonstrated by a group at the Toyota research center in Japan using nylon as a polymer matrix. Since then, many polymer/layered silicate nanocomposites have been synthesized for various thermoplastic and thermoset polymers.

Polymer melt intercalation is a relatively new and viable approach to synthesize polymer/layered silicate nanocomposite. This synthetic method involves the annealing, statically or under shear, of a mixture of polymer and layered silicate above the softening temperature of the polymer. During the annealing, polymer chains diffuse from the bulk into the interlayer or gallery of layered silicate.[10] Two types of polymer/layered silicate nanocomposites are possible. One is an intercalated nanocomposite that has a well-ordered multilayer alternating with a polymer/inorganic host layer expanded by intercalation of extended polymer chains, and the other is an exfoliated nanocomposite that is a disordered and homogeneous dispersion of silicates in a continuous polymer matrix.[11]

Phenolic resins are produced by the reaction of phenol with aldehyde and are classified as resol and novolac by synthetic conditions and curing mechanism.[12] It is very difficult to synthesize a phenolic resin/layered silicate nanocomposite, since phenolic resin has three-dimensional structure, even if it is not cross-linked.[13] To overcome this difficulty, Usuki et al.[14] tried to synthesize phenolic resin/layered silicate nanocomposite by intercalative polymerization of phenolic resin with phenol and formaldehyde in the presence of oxalic acid and montmorillonite modified with 4-aminophenol hydrochloride. Choi et al.[15,16] synthesized phenolic resin/layered silicate nanocomposites by the melt intercalation of linear novolac with intercalated or exfoliated nanostructures by melt intercalation using linear novolac. However, resol type phenolic resin has never been used in the polymer/layered silicate nanocomposite field because of difficulty in making linear resol type phenolic oligomers.

In this paper, we synthesized resol type phenolic resin/layered silicate nanocomposites by melt intercala-

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$HOOC–(CH_2)_{n-1}–NH_2$

n=3, β–alanine
n=6, 6–aminocaproic acid
n=12, 12-aminododecanoic acid

Figure 1. Chemical structure of ω-amino acids.

tion using a low molecular weight resol type phenolic resin and various layered silicates and investigated the effect of organic modifier on the morphology and mechanical properties of the nanocomposites.

Experimental Section

Materials. The partially water soluble resol type phenolic resin (KL) was obtained from Kolon Chemical Co. Ltd., and its commercial name is KSP20, which is a mixture of 85 wt % of phenolic resin and 15 wt % of water. Solid phenolic resin was recovered by precipitating the mixture in excess water and freeze-drying, followed by drying in a vacuum oven at room temperature for several days.

Sodium pristine montmorillonite (MMT), Kunipia-F with a cation exchange capacity of 119 mequiv/100 g, was purchased from Kunimine Co. β-Alanine, 6-aminocaproic acid, and 12-aminododecainoic acid were purchased from Aldrich and used for modifying MMT. All reagents were used without further purification. The chemical structure of ω-amino acids is shown in Figure 1.

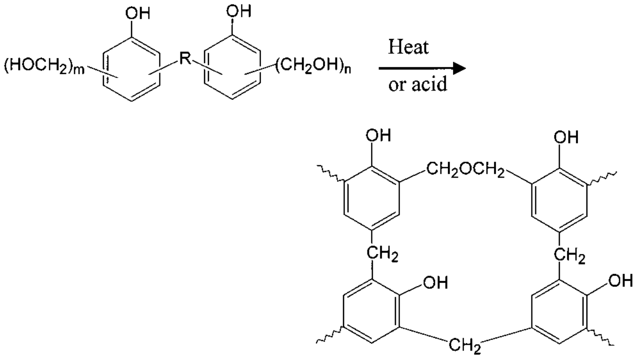
Preparation of ω-Amino Acid Modified Montmorillonite. ω-Amino acid modified montmorillonite was prepared by the method of Usuki et al.[17] MMT (5 g) was dispersed in 400 mL of deionized water for 1 day. An aqueous solution of 12 mmol of ω-amino acids, 1.2 mL of concentrated hydrochloric acid, and 100 mL of deionized water was poured into MMT dispersed solution at 85 °C in a 1000 mL three-neck flask and stirred vigorously for 1 h. The product was filtered and washed several times with 500 mL of hot water until chloride ion was not detected by $AgNO_3$. The filter cake was freeze-dried for 2 days, followed by drying in a vacuum at 100 °C for 4 days and then crushed in a mortar. Following the above method, β-alanine modified MMT (C3M), 6-aminocaproic acid modified MMT (C6M), and 12-aminododecainoic acid modified MMT (C12M) were prepared and used as modified MMTs.

Synthesis of Resol Type Phenolic Resin/Layered Silicate Nanocomposite (RPLSNs). Solid KL resin and layered silicates (1∼5 wt %) were mixed mechanically in a mortar and cured at 110 °C for 1 h, followed by curing at 130 °C for 1 h on a hot press. To investigate the nanostructure with the cure time, RPLSNs were cured at 110 °C for 1−60 min and heat-treated further at 110 °C for 60 min followed by curing at 130 °C for 60 min. Nanocomposites were named as KLC*x*M*n*, where *x* is the number of carbons in the ω-amino acid and *n* is the weight fraction of the layered silicate.

Measurements. The molecular weight of the KL resin was determined by gel permeation chromatography (GPC). GPC measurement was performed on a Waters WISP 712 instrument with a Shodex linear HT 800column, using tetrahydrofuran as a solvent. The injection volume was 200 μL and its run time was 30 min.

Matrix assisted laser desorption ionization/time of flight/mass spectroscopy (MALDI/TOF/MS) measurement was performed on a Kratos Kompact MALDI II (Kratos, England). The N_2 laser wavelength was 337 nm, and the accelerated voltage for time-of-flight (TOF) mass spectrometer was 20 kV. The sample was dissolved in methanol, and the matrix solvent was 2,5-dihydroxybenzoic acid.

X-ray diffraction spectra were obtained using a Rigaku X-ray generator (Cu Kα radiation with $\lambda = 0.15406$ nm, 40 kV, 80 mA) at room temperature. The diffractograms were scanned in the 2θ range of 2°∠10° at a rate of 2°/min.



m, n = 0, 1, or 2 ; R= $–CH_2–$ or $–CH_2OCH_2–$

Figure 2. Schematic illustration of the reaction mechanism and chemical structure of resol type phenolic resin.

The morphology of RPLSN was imaged using a transmission electron microscope (TEM) on carbon-coated 100 nm thick sections of the nanocomposite on a Philips CM-20 transmission electron microscope at an accelerating voltage of 160 kV.

FT-IR spectroscopy was used to observe the reaction between KL resin and ω-amino acid. Infrared spectra on KBr pellets were the average of 5−20 scans taken at 4 cm^{-1} resolution on a FT-IR spectrometer (Bomem-MB 100 model).

The mechanical properties of RPLSNs were measured with an Instron tensile tester (model 4201) according to ASTM 638-94 at room temperature. At least, five specimens were tested and the mean values were reported.

Results and Discussion

Characterization of Resol Type Phenolic Resin (KL) and ω-Amino Acid Modified MMT. In general, most polymers with linear and flexible structures can intercalate into the silicate gallery more easily than the polymer with the three-dimensional structure for the preparation of polymer/layered silicate nanocomposites. The linear novolac type phenolic resin can be obtained under weak acidic condition (pH 4−6) with an excess of phenol to formaldehyde and divalent metal salts such as Zn, Mg, Cd, Pb, Cu, Co, and Ni, preferably acetates.[18] However, resol resins have structural peculiarities that are due to the polyfunctionality of phenol, i.e., more than one reactive site for aromatic substitution reaction, and the excess of formaldehyde. These structural peculiarities may cause resins to be too bulky to synthesize a nanocomposite. Figure 2 shows the schematic illustration of the reaction mechanism of resol type phenolic resin. Resol type phenolic resins have reactive methylolphenols.[19] As the cure of resol type phenolic resin commences by heating or acidification, molecular weight advancement occurs, leading to an insoluble, chemically stable, mechanically rigid, and cross-linked structure. Consequently, the molecular weight of resol type phenolic resin could be an important factor to synthesize resol type phenolic resin/layered silicate nanocomposite. The lower the molecular weight of the resol type phenolic resin, the easier it penetrates through the silicate gallery.

To investigate the molecular weight of KL prepolymer, we used GPC and MALDI-MS. Its number average molecular weight, weight average molecular weight, and

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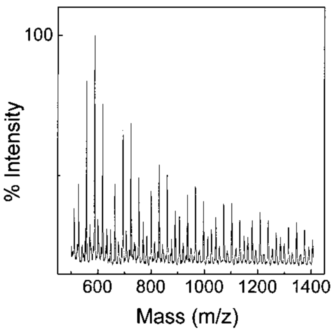

Figure 3. MALDI-MS spectrum of phenolic prepolymer.

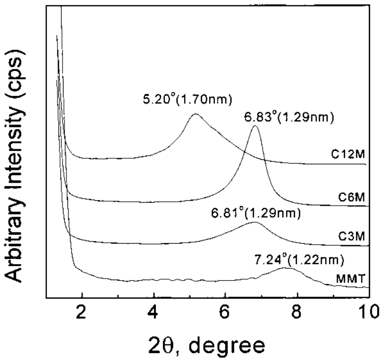

Figure 4. X-ray diffraction patterns of (a) MMT, (b) C3M, (c) C6M, and (d) C12M.

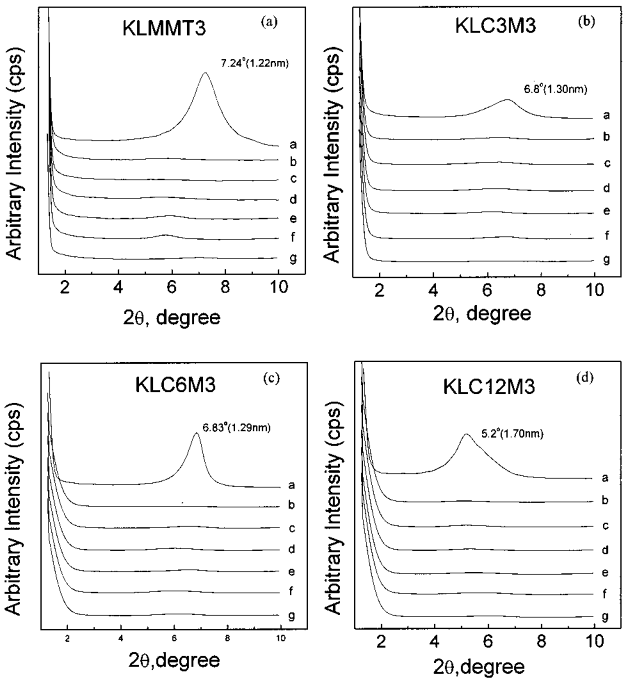

Figure 5. X-ray diffraction patterns of (a) KLMMT3, (b) KLC3M3, (c) KLC6M3, and (d) KLC12M3 as a function of curing time: a, 0 min; b, 1 min; c, 5 min; d, 10 min; e, 30 min; f, 60 min at 110 °C, and g, curing at 110 °C for 1 h followed by curing at 130 °C for 1 h.

polydisperse index are 1026, 2473, and 2.41, respectively. MALDI-MS is a soft ionization technique developed by Karas and Hillenkamp[20] and has been found to be an invaluable tool for the characterization of synthetic polymer.[21−22] Figure 3 shows the MALDI-MS spectrum of KL. It clearly demonstrates the presence of a series of prepolymers when the molar mass is in the range of 600−1200.[19] Consequently, we confirm from ^{13}C NMR study that KL has many low molecular weight prepolymers and very hydrophilic methylol groups.[19]

Figure 4 shows the X-ray diffraction patterns of pristine MMT and modified silicates. The basal spacings of MMT, C3M, C6M, and C12M are 1.22, 1.29, 1.29, and 1.70 nm, respectively, which is similar to Usuki et al.'s results.[17] The alkyl chains of C3M and C6M would be arranged parallel to the silicate surface, while that of C12M would be tilted to the silicate surface by 21.5° on the basis of the basal spacings. Also, Usuki et al. suggested that the carboxyl (−COOH) end group of the ω-amino acid should combine with the oxygen (−O−) group of the silicate surface through hydrogen bonding. To obtain nylon/layered silicate nanocomposite, they reported that the chemical attraction between ω-amino acid and ϵ-caprolactam should be stronger than the hydrogen bonding between the −COOH end group of the ω-amino acid and silicate surface. It can be easily expected that the hydrophilicity of the layered silicate decreases as the alkyl chain length of modifier increases, MMT > C3M > C6M > C12M.

Synthesis of Resol Type Phenolic Resin/Layered Silicate Nanocomposites (RPLSNs). Figure 5 shows X-ray diffraction patterns of RPLSNs as a function of cure time during the cure at 110 °C for 1 h followed by postcuring at 130 °C for 1 h (silicate content = 3 wt %). The condensation reaction of resol type phenolic resin could be affected by the cure temperature. As the temperature increases, the curing reaction rate becomes faster and the vitrification occurs in a shorter time.[24] The vitrification is defined as the phase change time when the glass transition temperature (T_g) and the reaction temperature of polymer are the same. After the vitrification, the mobility of the polymer chains is abruptly reduced and the reaction becomes diffusion-controlled. After all, to fabricate RPLSNs successfully, the reaction rate should be sufficiently low in order that low molecular prepolymers of phenolic resin have enough time to be intercalated into the silicate gallery. As shown in Figure 5, regular registry of layered silicate is completely destroyed within 1 min at 110 °C, indicating that silicate layers are exfoliated. But a small and broad (001) reflection peak appears during cure, indicating that some of the exfoliated silicates layers are restacked. Due to the high hydrophilicity of the silicate, water molecules are usually present between layers as well as cations to counterbalance with the negative charges of the silicate.[25] The change in degree of hydration could contribute in part to the changes observed in the weak peak position. When the same heating condition (110 °C for 1 h followed by 130 °C for 1 h) is applied to the MMT and ω-amino acid modified MMT, there is no peculiar change in the peak position; i.e., there is little effect of water molecules and decomposition of the alkyl chain. So we could suggest that the

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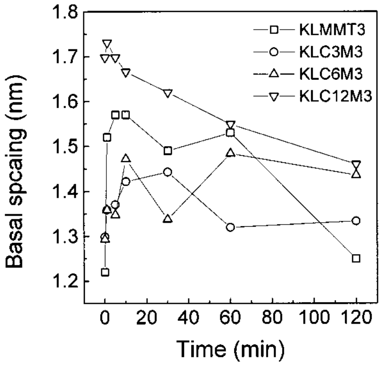

Figure 6. Basal spacings of RPLSNs cured at 110 °C as a function of curing time. The basal spacing at 120 min corresponds to with the RPLSNs cured at 110 °C for 1 h followed by curing at 130 °C for 1 h.

shift of peak position to a lower angle should be mainly attributed to the reaction and interaction of phenolic resin with silicates.

Figure 6 shows the change of basal spacing of each RPLSN calculated from the (001) reflection peak position with the cure time in Figure 5. In the case of KLMMT3, the basal spacing increases by about 0.4 nm in 10 min at a given temperature. It is noted that the degree of initial gallery expansion of KLMMT3 is higher than those of the other RPLSNs, but the initially increased basal spacing decreases continuously to the original value. In the case of KLC3M3, the tendency of basal spacing change is similar to that of KLMMT3, except that the initial gallery expansion is smaller than that of KLMMT3. However, the basal spacing change of KLC6M3 is different from that of KLC3M3. Its initial gallery expansion is similar to that of KLC3M3, but it does not decrease, even though it is fully cured. The fully cured KLC6M3 has a basal spacing of 1.47 nm, which indicates that the basal spacing increases by about 0.2 nm when compared to the original silicate. KLC12M3 shows only a decrease in the basal spacing continuously with the cure time. These behaviors can be explained by the following. MMT is the most hydrophilic among layered silicates and KL prepolymer is also hydrophilic; thus, their compatibility at the beginning of the cure would be superior. In fact, the initial gallery expansion of KLMMT3 is the largest. But as the cure goes on, KL loses its hydrophilicity to become hydrophobic, due to the depletion of the methylol groups, which makes KL and MMT immiscible and phenolic resin deintercalated. Contrary to MMT, the modified silicate is somewhat incompatible with the hydrophobic cured KL resin. Thus, it is considered that there is an optimum compatibility between KL and the layered silicates. The miscibility window can be controlled by the alkyl chain length of ω-amino acid, the organic modifier of silicate. From the results of the change in basal spacing in Figure 6, it seems that C6M is the most compatible with KL during the entire cure, because the deintercalation of phenolic resin occurs less than for the others. Figure 7 shows the X-ray diffraction patterns of KL6CM as a function of silicate content. As the silicate content increases, the (001) reflection peak is more distinctive, which indicates that the amount of intercalated or stacked silicate increases. The other RPLSN systems show similar behaviors. The morphology of nanocomposite is confirmed by the X-ray diffraction pattern with transmission electron microscopy (TEM). TEM micrograph verifies the partially exfoliated structure of KLMMT3 in Figure 8. Individual layers, oriented perpendicular to the sample surface, appear as dark lines with thickness around 1 nm and with lateral size around 200−500 nm. Primary particles consist of stacks of parallel elementary sheets (lamellae) with an average of about 10 sheets per particle. The figure shows completely exfoliated silicate layers of about 1 nm thickness but also some stacked silicate layers with about 10−20 nm thickness, consisting of about 2−10 parallel silicate layers. Some stacked parts are formed at the primary particle, having a gallery with relatively small basal spacing due to relatively less intercalation of KL resin. Some portions in Figure 8 show the face-to-edge structure of the silicate layers and the expanded face-to-face structure over 10 nm caused by destroying the initial stacked face-to-face structure of silicate layers. The RPLSNs with 3 wt % of silicate are seen to have the partially exfoliated nanostructure rather than the completely exfoliated one.

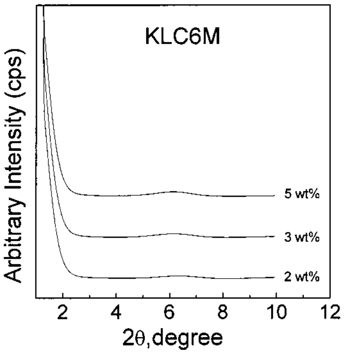

Figure 7. X-ray diffraction patterns of (a) KLMMT, (b) KLC3M, (c) KLC6M, and (d) KLC12M cured at 110 °C for 1 h followed by curing at 130 °C for 1 h as a function of silicate content.

Figure 8. TEM micrographs of KLMMT3 cured at 110 °C for 1 h followed by curing at 130 °C for 1 h (silicate content = 3 wt %).

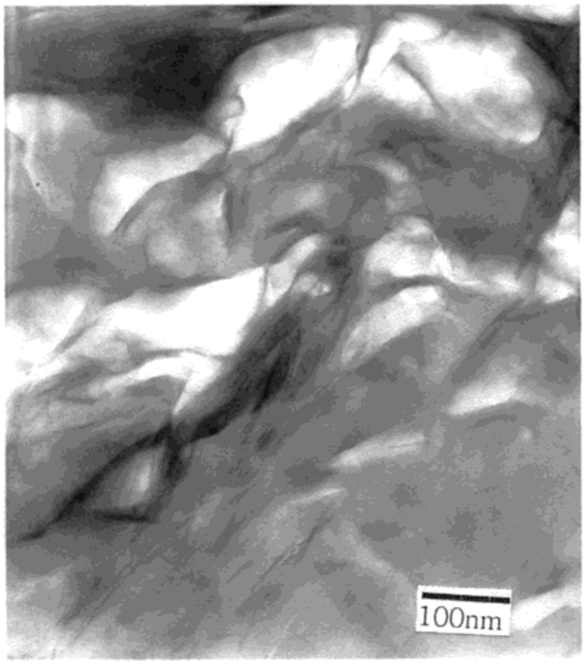

Figure 9. TEM micrographs of KLC6M5 cured at 110 °C for 1 h followed by curing at 130 °C for 1 h (silicate content = 5 wt %).

The TEM micrograph of KLC6M5 with 5 wt % of silicate shows more stacked silicate particles (Figure 9) relative to the KLMMT3 with 3 wt % of silicate. The low molecular weight prepolymer can play an important role in determining the morphology of RPLSN at the beginning of cure. As the silicate content increases, it is difficult for phenolic resin to penetrate through the gallery of layered silicate due to the limited amount of low molecular weight prepolymer, which results in the formation of more stacked particles. Choi et al.[15,16] reported another formation mechanism of the stacked silicate particles, even at low silicate content, wherein novolac type phenolic resin is deintercalated out of extragallery to react with curing agent.

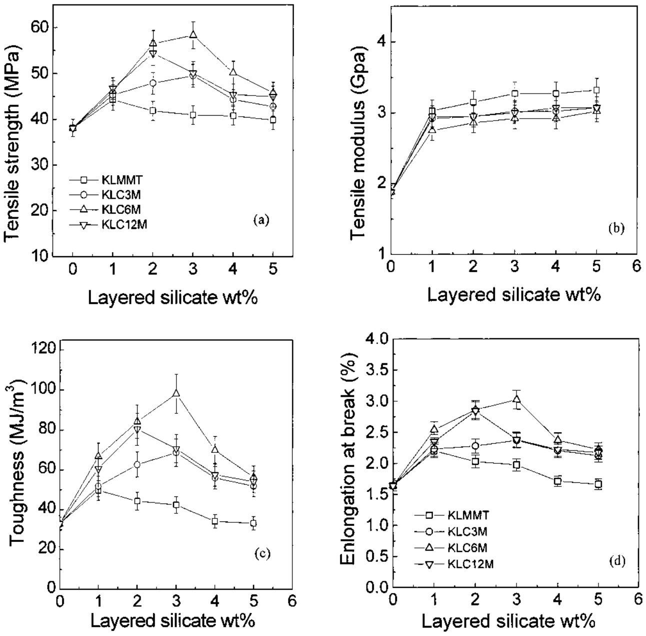

Figure 10. Mechanical properties of RPLSNs cured at 110 °C for 1 h followed by curing at 130 °C for 1 h as a function of silicate content: (a) tensile strength, (b) tensile modulus, (c) toughness, and (d) elongation at break. Mechanical properties at 0 wt % indicate the mechanical properties of neat phenolic resin.

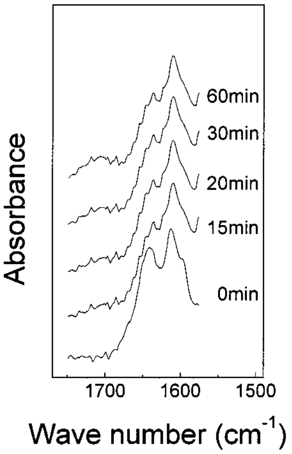

Figure 11. FTIR spectra of the reaction of phenolic resin with the organic modifier of C6M at 130 °C as a function of time.

Mechanical Properties of RPLSNs. The mechanical properties of RPLSNs are shown in Figure 10. Up to 2 or 3 wt %, the mechanical properties increase significantly but decrease steadily at higher silicate content except for tensile modulus. Tensile modulus increases up to 1 wt % but reaches up to about 3GPa over 1 wt % of silicate for all the RPLSNs. The tensile modulus seems to be independent of the modification of MMT. The KLMMT system shows a slight increase in mechanical properties when compared to RPLSNs with the modified MMT. Although MMT is dispersed well in the matrix, the miscibility with cured KL is not as good, so the deintercalation of KL results in stacked silicate particles. In the gallery of stacked silicate of KLMMT system, there is almost no phenolic resin, since the final basal spacing is very similar to the original basal spacing (Figure 6). These stacked particles can generate a significant defect for the improvement of the mechanical property of the KLMMT system. The RPLSNs with ω-amino acid modified MMT seem to have more improved mechanical properties than the KLMMT system, because they have very well dispersed clay layers and the end-tethered structures. The end-tethered structure could be formed by the condensation reaction between the carboxyl group (−COOH) of the ω-amino acid and the methylol group of the phenolic resin. Figure 11 shows the FTIR spectra of KLC6M with time at 130 °C. Two sharp peaks at 1645 and 1620 cm^{-1} correspond to the non-hydrogen-bonded and hydrogen-bonded C=O in carboxylic acids. The carbonyl signal of the ester linkage appears at a high frequency (1710 cm^{-1}) within 15 min,[26] as a result of the reaction between carboxyl acids of organophilic layered silicate and methylol groups of phenolic resin. The KLC6M system shows the most improvement in mechanical properties, while KLC3M and KLC12M have similar mechanical properties. Tensile strength, toughness, and elongation at break of KLC6M with 3 wt % of silicate increase 1.53, 2.98, and 1.84 times when compared to

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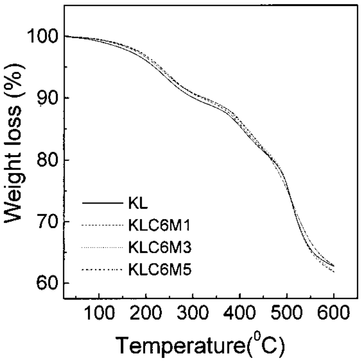

Figure 12. TGA thermograms of phenolic resin (KL) and KLC6M cured at 110 °C for 1 h followed by curing at 130 °C for 1 h as a function of silicate content.

the neat phenolic resin, respectively. Thus, the highest improvement in the mechanical properties of the KLC6M system is attributed to the end-tethered structure as well as the homogeneous dispersion of silicate layers due to the good miscibility of C6M in comparison with C3M and C12M having more stacked silicates, i.e., defects. The improved elasticity can be attributed to the plasticizing effect of the organic modifier of layered silicate, which contributes to the dangling chain formation, as well as to the conformational effect on the polymer at the silicate−matrix interface.[27] Some researchers suggested that the improved toughness for nanocomposites based on polyamide 12[28] and epoxy[29] were attributable to the microvoid formation inside the stacked silicate layers and strong prevention of the microvoid propagation. The reason the mechanical properties decreased at high silicate content (>4 wt %) is probably due to the defect of stacked silicate particle[30] or dangling chain formation.[31]

Thermal Stability of RPLSN. Figure 12 shows TGA thermograms of pristine phenolic resin and KLC6M system as a function of silicate content. The KLC6M system has only slightly increased thermal stability when compared to the neat phenolic resin. The other RPLSN systems show similar behaviors. It seems that the silicate layers do not play a significant role in enhancing the thermal stability of phenolic resin, since the phenolic resin itself has a good thermal stability. Consequently, the RPLSNs with the modified silicates exhibit significantly improved mechanical properties, keeping the original thermal stability of phenolic resin.

Conclusions

We have synthesized resol type phenolic resin/layered silicate nanocomposite (RPLSNs) using various layered silicates by melt intercalation. From the GPC and MALDI-MS, resol type phenolic resin with a hydrophilic methylol group has prepolymers having molecular weight low enough to be inserted in the silicate gallery. X-ray diffraction and TEM show that RPLSNs have partially exfoliated nanosturctures. But some stacked silicate particles are formed by deintercalation of phenolic resin during the cure. Of various silicates, the C6M is the most compatible with phenolic resin at the entire cure stage and the KLC6M system does not show the deintercalation of the phenolic resin. The mechanical properties of the RPLSNs are improved more significantly than pristine phenolic resin, even if a very small amount of silicate has been used. The mechanical properties of the RPLSNs with ω-amino acid modified MMT (KLC3M, KLC6M, KLC12M) are better than that of the KLMMT system. This is because the RPLSNs have an end-tethered structure formed by the reaction of the carboxylic acid of the organic modifier with the methylol group of the phenolic resin. The KLC6M system has shown the best mechanical properties due to the excellent dispersion of silicate layers as well as the good interfacial adhesion between phenolic resin and silicate. The RPLSNs have similar thermal stability to the neat phenolic resin.

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