

Synthesis of Resol-Layered Silicate Nanocomposites by Reaction Exfoliation with Acid-Modified Montmorillonite

Hongsheng Wang, Tong Zhao, Yehai Yan, Yunzhao Yu

State Key Laboratory of Engineering Plastics, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 5 May 2003; accepted 27 August 2003

ABSTRACT: Resol-layered silicate nanocomposites were prepared by the intercalative polymerization of phenol and formaldehyde in the presence of acid-modified montmorillonite (HMMT). The nanocomposites were studied by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, dynamic mechanical analysis (DMA), and rheological measurements. The exfoliation of HMMT was promoted by the intragallery reactions catalyzed by protons in the galleries of the clay, whereas the

extragallery polymerization catalyzed by ammonia went on simultaneously. The nanocomposites showed higher glass-transition temperatures in the DMA diagram compared with the resol counterparts. The impact strength was improved significantly by the incorporation of the clay. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 791–797, 2004

Key words: clay; nanocomposites; TEM

INTRODUCTION

Polymer-layered silicate nanocomposites have drawn much research attention because of the ease of their preparation and their effectiveness in improving material properties.^{1–3} These composite materials can be produced either by melt intercalation or by *in situ* polymerization. The latter approach involves monomer intercalation and polymerization in the gallery of the host to effect the exfoliation of the clay, and the process is particularly convenient for thermoset-clay nanocomposites.⁴

The elementary layers of montmorillonite (MMT) are composed of an octahedral aluminum sheet sandwiched between two tetrahedral silica sheets. The stacking of the two-dimensional layers forms Van der Waals gaps, or galleries, which are occupied by cations to balance the charge deficiency that is generated by isomorphous substitution within the layers (e.g., Mg²⁺ for Al³⁺). The clay is usually organomodified with onium salts to facilitate dispersion and exfoliation in the polymer matrix.⁵ However, ionic or polar monomers can get into the interlayer of the pristine clay through ion exchange or can be driven there by the solvation of cations.^{6,7} Hydrophilic polymers show strong interactions with the clay through similar mechanisms.^{8–10}

Layered aluminosilicate provides a nanoscale host for polymerization; moreover, the structure of poly-

mers formed within clay galleries can be influenced.¹¹ Aniline was polymerized in the gallery of Cu²⁺ ion exchanged clay.^{12,13} The intercalative polymerization of styrene initiated by a living free-radical initiator anchored inside the galleries of layered silicate gave rise to polystyrene-silicate nanocomposites.¹⁴

Phenolic resins are prepared by the reaction of phenol or substituted phenol with aldehydes, especially formaldehyde, in the presence of an acidic or basic catalyst and are classified as novolac and resol. Byun et al. synthesized resol-type phenolic resin-layered silicate nanocomposites by melt intercalation with ω -amino acid modified MMT.¹⁵ Because the reactants are highly hydrophilic, the preparation of phenolic resin-MMT nanocomposites by the intercalative polymerization of pristine MMT is possible.

In a previous work,¹⁶ we reported that acid-modified montmorillonite (HMMT) can be used as a catalyst for the condensation of phenol and formaldehyde. The polymerization, catalyzed by protons inside the galleries, led to delamination of MMT, forming novolac-MMT nanocomposites.

When HMMT was introduced to the reaction systems of formaldehyde and phenol with ammonia as a catalyst, the intercalation and exfoliation of the layered silicate took place. In this article, we report the synthesis of resol-layered silicate nanocomposites with HMMT as the active clay.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na-MMT) with a cation exchange capacity of 1.0 mequiv/g (Zhangjiakou Clay

Correspondence to: T. Zhao (tzhao@infoc3.icas.ac.cn).

TABLE I
Compositions for the Preparation of Resol-Clay Composites and Neat Resol

	Phenol (g)	Formaldehyde, 37% aqueous solution (g)	Clay (g)	Ammonia, 28% aqueous solution (g)
Neat resol	100	103.5	—	5
HMMT3	100	103.5	HMMT, 3	5
HMMT5	100	103.5	HMMT, 5	5
HMMT10	100	103.5	HMMT, 10	5
Na-MMT5	100	103.5	Na-MMT, 5	5
Sole-HMMT5	100	103.5	HMMT, 5	—

Mineral Corp., Zhangjiakou, China) was purified according to a standard sedimentation method. Phenol, formaldehyde (37% w/w solution), hydrochloric acid, anhydrous ethyl acetate sodium sulfate, and ammonia ($\text{NH}_3 = 28 \text{ wt } \%$) were analytical reagent (AR) grade and were used without further purification.

Preparation of HMMT

HMMT was prepared through the ion exchange of Na-MMT with hydrochloric acid according to a previously reported method.¹⁶

Preparation of resol and resol-MMT composites

The compositions of the reaction mixtures are given in Table I. The calculated amount of HMMT was mixed with phenol and formaldehyde (phenol/formaldehyde molar ratio = 1:1.2) in a 500-mL, three-necked flask, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was heated to 65°C, and ammonia was added to start the polymerization. The temperature was increased to 80°C in 5 min, and the reaction continued at this temperature for about 2.5 h. The proceeding of condensation was monitored according to the change in the refractive index. Aliquots were taken and cooled to 25°C for refractive index measurements with a WYA-2D Abbey refractometer (Shanghai, China). The reaction was stopped when the refraction index reached 1.53. The product was then dehydrated *in vacuo* in a rotational evaporator at 80°C to a solid content of 90%. Following the previous method, we prepared both neat resol resin and resol-Na-MMT composites.

For the synthesis of the Sole-HMMT5 composite, a mixture of phenol, formaldehyde (phenol/formaldehyde molar ratio = 1:1.2), and HMMT was heated to 80°C in 15 min without the addition of ammonia, and the reaction continued at that temperature until the refraction index reached 1.53 (~12 h).

The resin was cast in rectangular molds, treated in a vacuum oven at 100°C for 2 h to remove the volatile compounds, and was then cured at 120°C for 2 h, 160°C for 2 h, and 180°C for 4 h. The cured specimens

were used for dynamic mechanical analysis (DMA) and impact tests.

To obtain samples for the Fourier transform infrared (FTIR) spectroscopy studies, we dissolved 2 g of Sole-HMMT5 composite in 20 g of ethyl acetate and then filtered the solution. The filtrate was dried with anhydrous sodium sulfate, and ethyl acetate was removed *in vacuo* in a rotational evaporator at 60°C. Following the previous method, we obtained the resin sample from the HMMT5 composite.

Measurements

X-ray diffraction (XRD) analysis was performed with a Japan D/MAX.RB diffractometer (Rigaku, Tokyo, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a generator voltage of 40 kV and a generator current of 100 mA. Scanning was in 0.02° steps at a speed of 2°/min, with a beginning 2θ value of 1.5°.

To study the dispersion of MMT in the composites, the fracture surfaces of the specimens were coated with gold. Scanning electron microscopy (SEM) micrographs were taken on a Hitachi S-530 electron microscope (Hitachi, Tokyo, Japan) at an operating voltage of 15 kV.

To study the microstructure, we embedded a powder sample of the cured composite in an epoxy resin Epon812 in a capsule and microtomed it into ultrathin sections. Transmission electron microscopy (TEM) pictures were taken on a Hitachi H-800 transmission electron microscope with an acceleration voltage of 100 kV.

DMA for the cured composites was performed on a PerkinElmer 7e DMA instrument (PerkinElmer, Wellesley, MA) operated at a driving frequency of 1.0 Hz and a scanning rate of 5°C/min in a nitrogen atmosphere. A sample geometry of 15 × 3 × 1.5 mm was used.

Impact tests for the composites were conducted on a CSI-137C manual pendulum impact tester (CSI, Newark, NJ). The specimens were rectangle bars 55 × 6 × 4 mm in size. Five specimens were tested for each composite material, and the highest, the lowest, and the mean values are reported.

Rheological measurements were carried out at 30°C on a DSR200 dynamic rheometer (Scientific Rheometrics, Piscataway, NJ) in steady-shear mode with par-

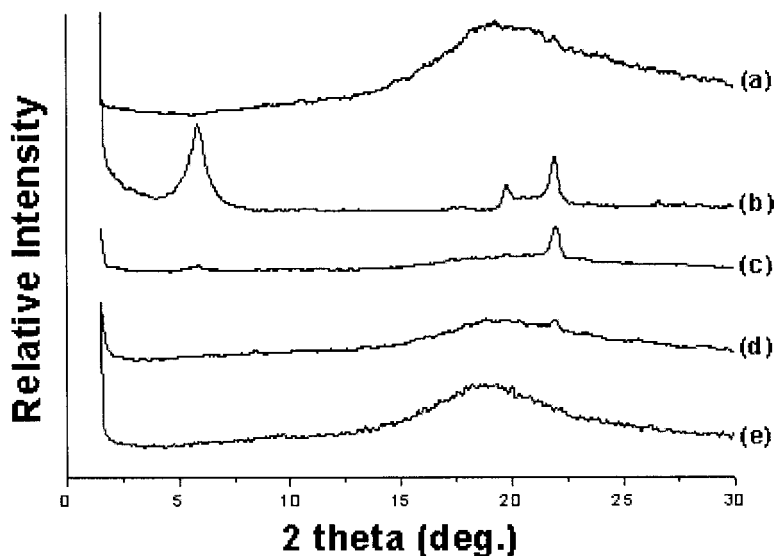


Figure 1 XRD patterns for (a) the neat resol resin after dehydration, (b) HMMT, (c) HMMT5 after reaction at 80°C for 1 h, (d) HMMT5 after reaction at 80°C for 2.5 h and (e) the product after dehydration.

allel plate geometry, a plate diameter of 25 mm, and a gap of 0.5 mm.

FTIR spectra for the HMMT5 composite, the neat resol, and the resin samples from Sole-HMMT5 and HMMT5 were recorded with a PerkinElmer 2000 FTIR spectrometer with KBr pellets.

RESULTS AND DISCUSSION

Exfoliation of the clay

The status of clay exfoliation was monitored by XRD deflection. When HMMT was at low concentrations, it

was easy to delaminate in the reaction system. XRD patterns for the HMMT5 system are shown in Figure 1. The interlayer distance (d_{001}) for HMMT was 1.54 nm, calculated according to the Bragg formula ($\lambda = 2d \sin \theta$). The intensity of the 001 reflection peak decreased progressively as the reaction went on. After 2.5 h of reaction, the 001 reflection peak disappeared completely, indicating delamination of the clay. The XRD pattern of the neat resol resin is also shown in Figure 1 for comparison.

The change of XRD patterns with reaction time for HMMT3 was similar to that for HMMT5 (Fig. 2). For

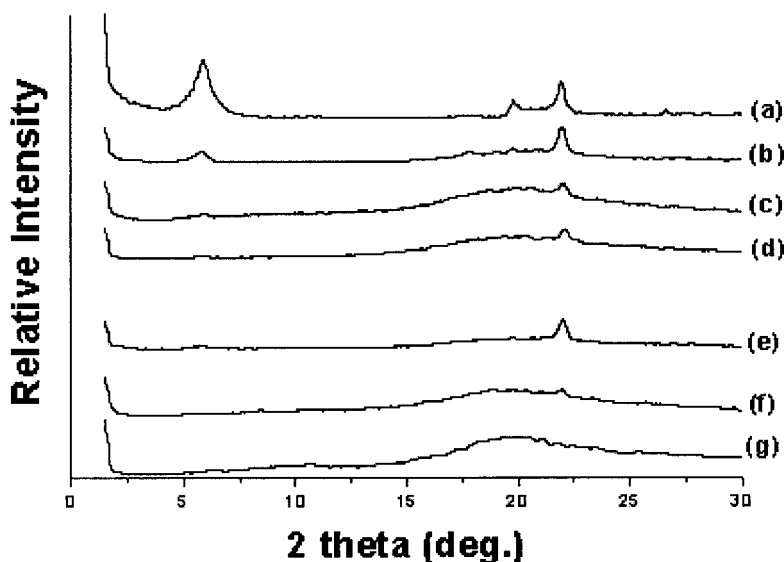


Figure 2 XRD patterns for (a) HMMT, (b) HMMT10 after reaction at 80°C for 1 h, (c) HMMT10 after reaction at 80°C for 2.5 h, (d) the product after dehydration, (e) HMMT3 after reaction at 80°C for 1 h, (f) HMMT3 after reaction at 80°C for 2.5 h, and (g) the product after dehydration.

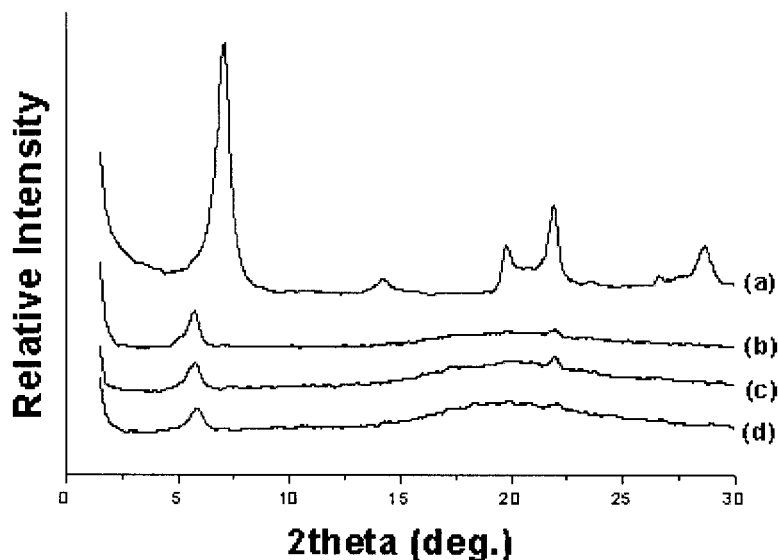


Figure 3 XRD patterns for (a) Na-MMT, (b) Na-MMT5 after reaction at 80°C for 1 h, (c) Na-MMT5 after reaction at 80°C for 2.5 h, and (d) the product after dehydration.

HMMT10, however, a weak 001 reflection peak remained after 2.5 h of reaction (Fig. 2), indicating that complete exfoliation was not achieved.

Pristine Na-MMT delaminated less easily in the reaction system. The change in XRD patterns for the Na-MMT5 system is shown in Figure 3 for comparison. As the reaction started by addition of the catalyst, the 2θ value for the 001 reflection was shifted from 7.12 to 5.80°, corresponding to expansion of the basal spacing from 1.24 to 1.52 nm. The angle and the intensity of 001 reflection remained unchanged until the end of the reaction. That is, exfoliation did not take place.

Dispersion of the layered silicate

SEM studies were carried out to examine the difference in the dispersion of the clay in the HMMT10 and

HMMT5 composites. In the HMMT10 composite [Fig. 4(a)], particles of about 2 μm in diameter were visible. By comparison, no clay particles could be seen with SEM in the HMMT5 composite [Fig. 4(b)].

The microstructure of the HMMT5 composite was studied by TEM. In the micrograph (Fig. 5), the dark lines in the picture represent the clay layers, and the gray clouds represent the resol matrix. The average distance between clay layers was around 20 nm. This was in agreement with XRD results: when the 001 deflection disappears in the XRD pattern, the basal distance of regular stacking should exceed 8.8 nm.¹⁷

According to XRD and SEM studies, we believe that HMMT3 and HMMT5 were exfoliated nanocomposites, whereas the clay in HMMT10 was not completely exfoliated.

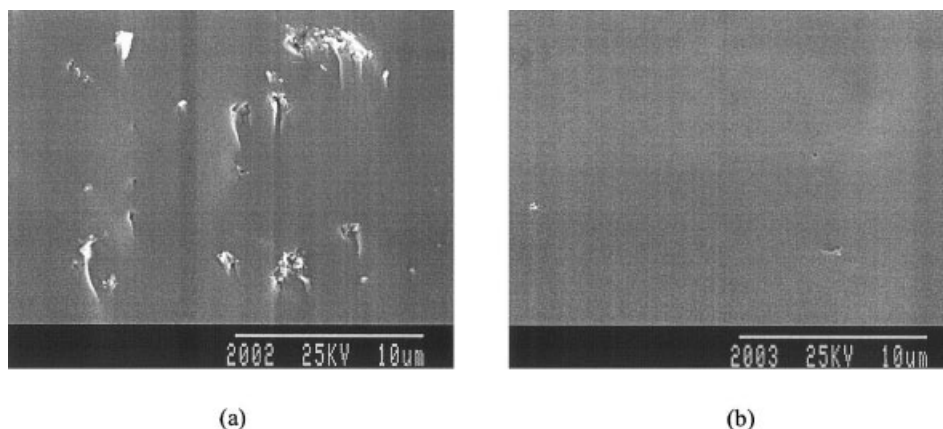


Figure 4 SEM micrographs for (a) HMMT10 and (b) HMMT5.

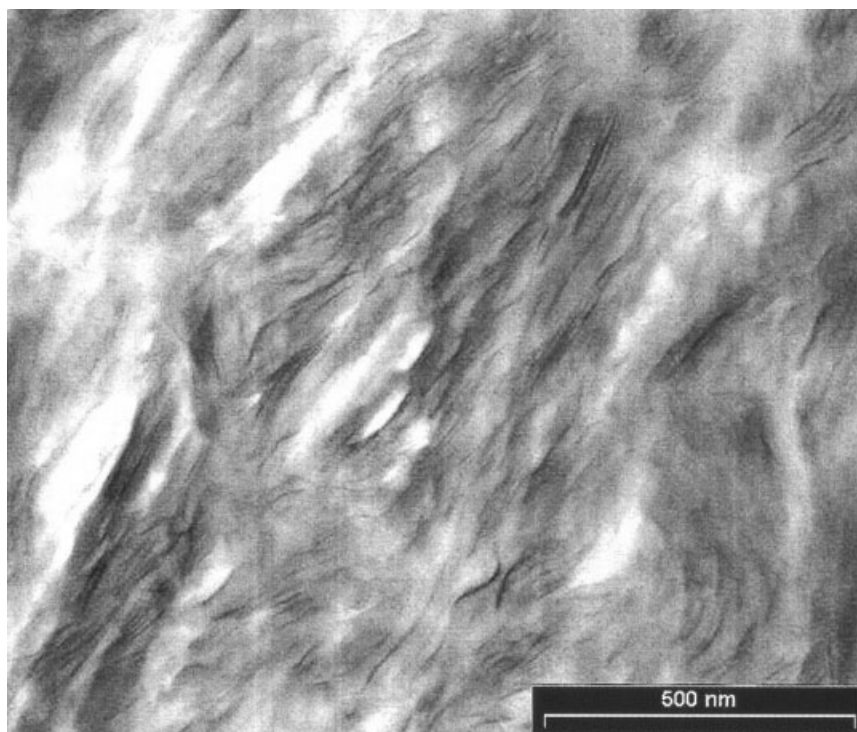


Figure 5 TEM micrograph for HMMT5.

Rheological studies

In the preparation of resol and the HMMT3, HMMT5, HMMT10, and Na-MMT5 composites, the condensation degree of the resin was similar according to the refraction index (1.53 at 25°C), and the solid contents were controlled to be in the range 90.1–90.3 wt %. The rheological behavior of the resin was influenced by the inorganic phase in different ways.

In Figure 6, viscosity is plotted against shear stress for the resol resin and the composites. In the second Newtonian region, the viscosity for the neat resin was 34 Pa s. For the resin containing 3 g of HMMT (HMMT3) and 5 g of HMMT (HMMT5) per 100 g of phenol, the viscosity value increased to 1248 and 210 Pa s, respectively. As the clay content was further increased to 10 g per 100 g of phenol (HMMT10), the

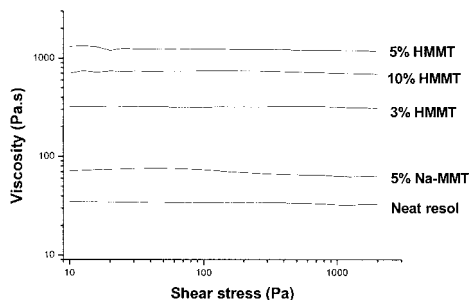


Figure 6 Viscosity versus shear stress for the neat resol, HMMT3, HMMT5, HMMT10, and Na-MMT5.

viscosity did not increase further. In fact, the viscosity of HMMT10 was lower than that of HMMT5. This could be attributed to the low exfoliation degree of the clay in HMMT10.

The incorporation of Na-MMT did not result in a significant increase in viscosity. The viscosity was 71 Pa s for the blend containing 5 g of Na-MMT per 100 g of phenol (Na-MMT5). Obviously, the exfoliation degree of the clay was very low in Na-HMMT5.

Mechanism of the exfoliation of HMMT

The great difference in the exfoliation behavior between HMMT and the pristine Na-MMT could be accounted for by the different modes of interactions with substances in the reaction systems. The exfoliation of HMMT was closely related with the catalytic activity for the condensation of phenol and formaldehyde.

According to the XRD data, the interlayer distance of MMT was expanded from 1.24 to 1.54 nm as the sodium cations were exchanged by protons in the form of H_3O^+ .¹⁶ With an MMT layer thickness of 0.96 nm taken into account, the remaining space corresponded to two water-molecule layers.¹⁸ As phenol and formaldehyde diffused into the clay galleries, condensation proceeded at the place under the catalysis of protons. As the polymerization inside the galleries progressed, the layers were pushed gradually apart and eventually delaminated, leading to the formation of the nanocomposites.

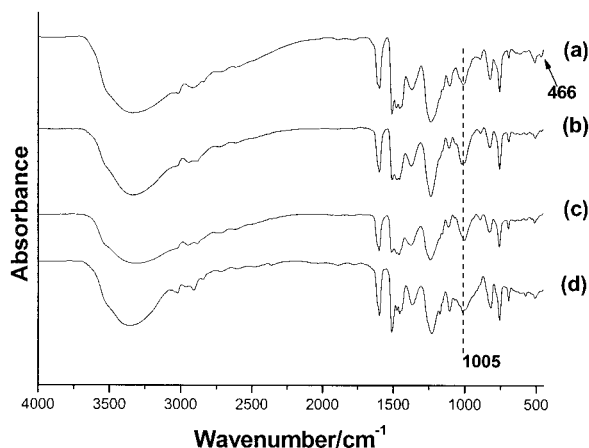


Figure 7 FTIR spectra for (a) HMMT5, (b) the neat resol, (c) the resin separated from HMMT5, and (d) the resin separated from Sole-HMMT5.

To illustrate the catalytic activity of HMMT, a Sole-HMMT5 composite was prepared without an external catalyst. The FTIR spectrum for the resin separated from Sole-HMMT5 was very similar to that of the neat resin (Fig. 7). The band at 1005 cm^{-1} was characteristic of the hydroxymethyl groups.¹⁹ HMMT is a solid-state acid in nature; therefore, hydroxymethyl groups could exist. The spectrum for the HMMT5 composite was also similar to that of the neat resin, except for the band at 466 cm^{-1} , because of the Si—O bending of the clay in the composite.²⁰

In the synthesis of resol-HMMT composites, ammonia was used as the catalyst. The extragallery reactions catalyzed by ammonia and the intragallery reactions catalyzed by protons should have proceeded simultaneously. The intragallery reactions were important for the exfoliation of the clay. In the case of Na-MMT, the

intragallery reactions seemed unfavorable. Because the clay layers of Na-MMT were negatively charged, the hydroxides were not able to get into the gallery.

Transitions and mechanical properties

DMA curves for the neat resol and the resol-HMMT composites are shown in Figure 8. Because the segment motion of the polymer was restricted by the inorganic component,^{21–23} the glass-transition temperature (T_g) of the composites shifted to higher temperatures. The T_g , measured by the $\tan \delta$ peak temperature, increased from 255°C for the neat resol to 315°C for the composite HMMT5. The HMMT10 composite showed a T_g at 310°C , close to that for the HMMT3 system. It is likely that only the exfoliated clay layers were effective in increasing the T_g . In the HMMT10 composite, the concentration of exfoliated clay layers was low because a part of the space was occupied by nonexfoliated clay particles, which were ineffective.

The impact strengths of the neat resol, HMMT5, and HMMT10 were 5.7 kJ/m^2 (averaged from five specimens with values ranging from 5.4 to 6.0), 8.7 kJ/m^2 (range = 8.5–9.0), and 7.9 kJ/m^2 (range = 7.4–8.3), respectively. The impact strength of the resol-HMMT composites showed an optimum value with the HMMT5 nanocomposite; a 53% improvement over that of the neat resol was achieved. The impact strength of the HMMT10 composite was inferior compared to that of the HMMT5 nanocomposite. The results indicate that the delamination of the clay was essential to the mechanical properties of the composites. Exfoliated clay layers with a very high aspect ratio were effective in improving the impact strength of the resol.

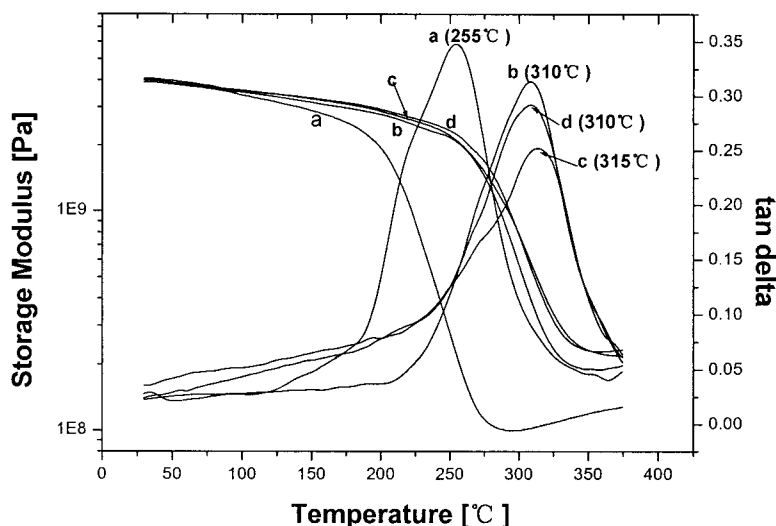


Figure 8 DMA for (a) the neat resol, (b) HMMT3, (c) HMMT5, and (d) HMMT10.

CONCLUSIONS

Resol-layered silicate nanocomposites were synthesized by the intercalative polymerization of phenol and formaldehyde in the presence of HMMT. Intragallery reactions catalyzed by protons and the extragallery polymerization catalyzed by ammonia went on simultaneously. The intragallery reactions were essential to the delamination of the clay. In the composites containing 3 and 5 parts HMMT per 100 parts phenol, the clay was completely exfoliated. As the concentration of HMMT was increased to 10 parts, full exfoliation was not achieved. The exfoliated clay layers were effective in increasing the T_g and improving impact strength. The HMMT5 nanocomposite was optimum for these properties.

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