Synthesis of Bismaleimide-Modified Novolac Resin/Clay Nanocomposites Using *p*-Phenylenediamine as Swelling Agent

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ABSTRACT: Sodium montmorillonite (Na–MMT) was swollen with protonated *p*-phenylenediamine, and the latter was converted to maleamic acid. Intercalation of the swelling agents was confirmed by FTIR, XRD, and TGA data. Exfoliation of the organoclay took place easily in the melt of the Bismaleimide-modified allylated novolac resin. It is remarkable that, as a result of layer delamination, introduction of 2 phr organoclay MAA–MMT brought in a rise in steady shear viscosity for over two orders of magnitude at low shear rates. Major improvement in thermal stability, flexural strength, and modulus was achieved by incorporation of the exfoliated clay layers, in contrast to the composite using pristine Na–MMT as reinforcement. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 466–474, 2005

Key words: clay; nanocomposites; rheology.

INTRODUCTION

Polymer/clay nanocomposites are of great interest since mechanical, thermal, and barrier properties can be improved significantly at very low inorganic loadings.[1,2] The most commonly used clay is the smectite mineral such as 2 : 1 layered silicate montmorillonite (MMT). The key to success in the preparation of polymer/clay nanocomposites is full exfoliation of the silicate platelets.

The elementary layers of MMT are composed of an octahedral alumina sheet sandwiched in between two tetrahedral silica sheets. Stacking of the two-dimensional layers forms Van der Waals gaps or galleries, which are occupied by cations, such as Na^+ and Ca^{2+}, to balance the charge deficiency that is generated by isomorphous substitution within the layers (e.g., Mg^{2+} for Al^{3+}). To facilitate intercalation of polymers or monomers, the clay is organomodified by exchanging the interlayer cations with organic cations, e.g., alkylammonium cations.[3,4]

Alternatively, swelling agent with functional groups that can react with the polymer was used as compatibilizer in the preparation of PET/clay nanocomposites.[5] Sufficient exfoliation of clay and strong adhesion of the polymer matrix were achieved. Tyan et al.[6] synthesized polyimide/clay nanocomposites using reactive organoclay and poly(amic acid). The reactive organic molecules (*p*-phenylenediamine) containing two amine groups were controlled in such a way that one of the amine groups formed an ionic bond with negatively charged silicates, and the other amine groups in the swelling agent are available for further reaction with poly(amic acid) containing dianhydride end groups. As a result, high modulus and thermally stable nanocomposites were obtained.

Layered silicates have been used in the synthesis of nanocomposites of thermoplastic as well as thermosetting matrices. Recently bismaleimide-modified novolac resins (BMAN) were developed in this laboratory.[7] They have good thermal and mechanical properties and can be processed by resin transfer molding technology. To achieve further improvement in the properties, we have tried to introduce MMT into this resin system.

In the present study, *p*-phenylenediamine (PDA) was used as the swelling agent for sodium–montmorillonite (Na–MMT) in the synthesis of BMAN/MMT nanocomposites. One amine group of PDA was converted into cation. Through ion exchanging, intercalation of the swelling agent to the clay was affected. The remaining amine group of the swelling agent was reacted with maleic anhydride to form maleamic acid. Organoclay thus obtained was easily exfoliated in the BMAN resin. Maleamic acid was converted into maleimide and copolymerized with BMAN upon curing.

EXPERIMENTAL

Materials

Sodium montmorillonite was purchased from Zhangjiakou Clay Mineral Corp. (China). The specific

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surface area was 700 m^2/g, and the cation exchange capacity (CEC) was 1.0 mEq/g. The clay was purified according to standard sedimentation methods.

p-Phenylenediamine was the analytic reagent obtained from Beijing Jinlong Chemical Reagents Corp. (Beijing, China). It was recrystallized from ethanol. Maleic anhydride (AR) was from Beijing Chemical Reagents Corp. (Beijing, China) and was used as received.

Bismaleimide-modified novolac resin was prepared in this laboratory. Its starting materials, phenol (CP) and formaldehyde (37% aqueous solution, CP), were from Beijing Organic Chemicals Factory (Beijing, China). Allyl chloride was obtained from Qilu Petrochemical Co. (Beijing, China) and used after distillation. 4,4'-Bismaleimidodiphenylmethane (BMI) was purchased from Fenguang Chemical Co., Ltd. (Honghu, China). It was a crystalline substance with a melting temperature of 154 ∼ 156°C.

Preparation of organo-MMT

PDA (1.08 g) was dissolved in 1,000 mL of 0.01*N* HCl, then 8.0 g Na–MMT was introduced, and the mixture was stirred at 60°C for 30 min. The solid was separated by filtration and washed repeatedly with distilled water, until chloride negative, tested with 0.1*N* AgNO$_3$ solution. The cake was dried at 80°C for 6 h in a vacuum oven. It was ground to pass a 300-mesh sieve. Treated MMT powder was thus termed PDA–MMT.

Maleic anhydride (1.0 g), PDA—MMT (5.0 g), and ethanol (30 mL) was added to a 100-mL beaker. The slurry was stirred for 12 h. After that, the volatile component was removed in a rotary evaporator. The residual was washed repeatedly with ethyl ether to remove free organic substances. The clay was ground to pass a 300-mesh sieve. The obtained powder was termed MAA–MMT.

Preparation of BMAN resins

The BMAN resin was prepared according to a method reported previously.[7] Thus novolac resin of number-average molecular weight 550 was allylated by reaction with allyl chloride. All phenolic hydroxyl groups were converted to allyl ether and, as a result of Claisen Rearrangement, each phenol ring was substituted by 0.17 allyl groups on average, estimated based on the integration of the ^{1}H-NMR signals. Next, 0.25 mol BMI for 1 mol of allyl group was introduced, and the mixture was heated at 140°C for 30 min under stirring to effect prepolymerization. After that, a clear BMAN resin was obtained.

Preparation of BMAN/MMT composites

BMAN resin (50 g) was melted at 140°C. MAA–MMT (1 g) was introduced, and the mixture was stirred at the same temperature for 15 min. The obtained dispersion was termed BMAN/MAA–MMT. For the preparation of specimens for transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) as well as for flexural tests, it was deaerated at 100°C in a vacuum oven, then cast in rectangular molds and cured at 170°C for 2 h, 200°C for 6 h, and 250°C for 6 h. Reactions responsible for the curing of BMAN resin are given in Scheme 1. Following the same procedure, the BMAN/Na–MMT composite (50 g BMAN resin with 1 g Na–MMT) was prepared.

Measurements

The BMAN/MMT blends were smeared on glass slides for the XRD studies. XRD analysis was performed on a Japan D/MAX.RB diffractometer (Rigaku, Tokyo, Japan) with Cu $\kappa\lambda$ radiation (λ = 0.154 nm) at a generator voltage of 40 kV and a generator current of 100 mA. The scanning was in 0.02° steps at a speed of 2°/min, beginning with 2θ value of 1.5°.

To study the microstructure, a piece of cured composite was embedded in epoxy resin (Epon828) in a capsule. The epoxy resin was cured with 11 phr of diethylenetriamine at 60°C for 48 h and microtomed into ultrathin sections. TEM pictures were taken on a Hitachi H-800 transmission electron microscope (Hitachi, Tokyo, Japan) using an acceleration voltage of 100 kV.

Thermal stability of cured composites was investigated by thermogravimetric analysis, performed on a NETZSCH 409 PC (NETZSCH, Selb, Germany) at a heating rate of 10°C/min in a nitrogen atmosphere. Dynamic mechanical analysis for the cured composites was performed on a NETZSCH DMA 242 C (NETZSCH, Selb, Germany) operated at a driving frequency of 1.0 Hz and a scanning rate of 5°C/min in a nitrogen atmosphere. The specimen geometry was of 15 mm × 3 mm × 2 mm.

Flexural tests for the composites were conducted on an Instron 1122 mechanic tester (Instron, Canton, MA) at a crosshead speed of 2 mm/min. The specimens were rectangular bars of 55 mm × 6 mm × 4 mm. For each composite material, five specimens were tested and the averaged values (standard deviation within parentheses) were reported.

Rheological measurements were carried out at 60°C on an ARES Rheometer (Rheometrics Scientific, Piscataway, NJ), in steady-shear mode with parallel plate geometry of plate diameter 25 mm and gap 1.0 mm.

FTIR spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrometer (Wellesley, MA) using KBr pellets.
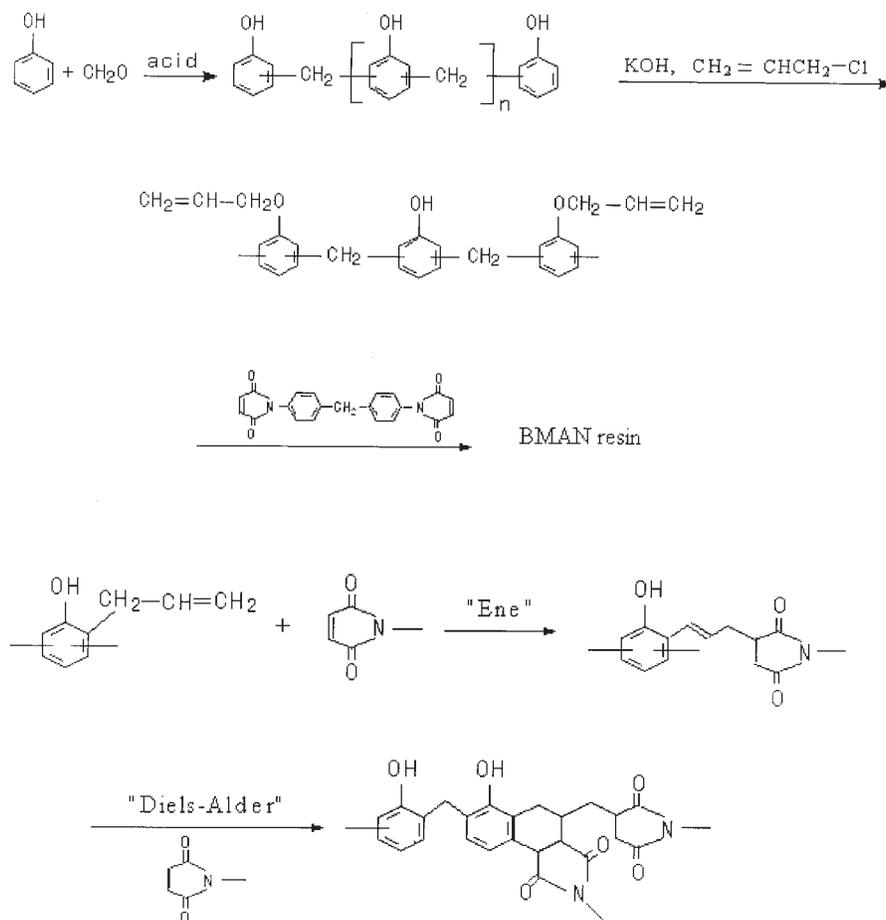
Scheme 1   Reactions responsible for the network formation of BMAN.

RESULTS AND DISCUSSION

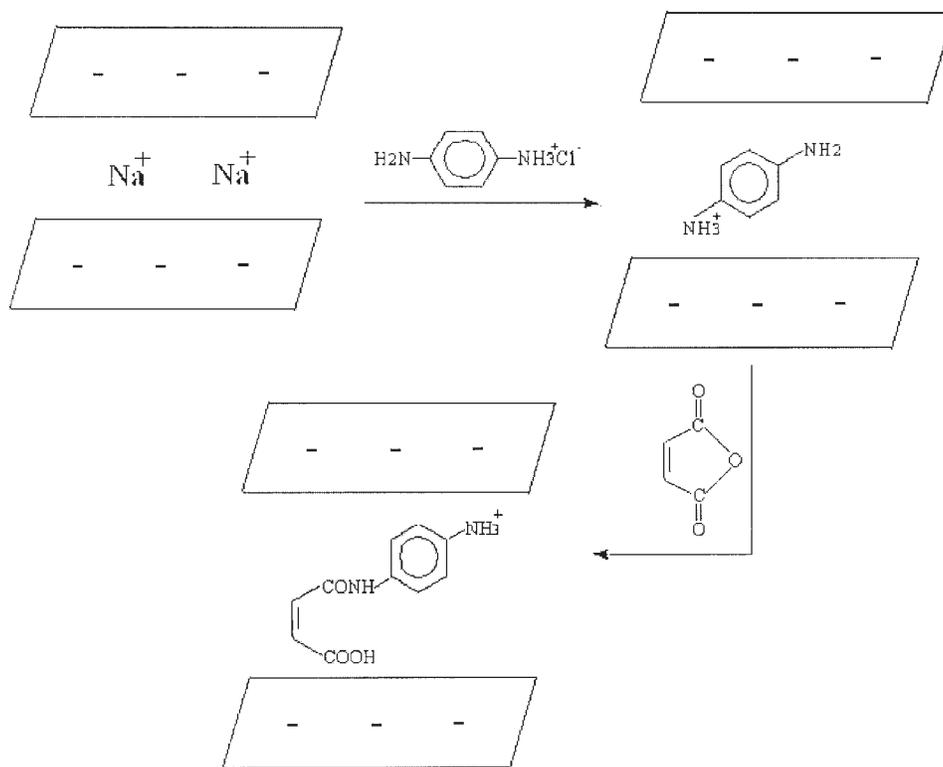### Intercalation of the swelling agent to MMT

To facilitate delamination of clay in the resin, PDA was used as swelling agent. One amino group of the molecule was neutralized with hydrochloric acid. Intercalation of PDA to Na–MMT took place as the cations in the gallery were exchanged by the protonated molecules, which formed ionic bonds with the negatively charged clay layer, as shown in Scheme 2. Subsequently, the other amino group of PDA reacted with maleic anhydride to form maleamic acid.

The transformation is demonstrated by the changes in the FTIR spectra (Fig. 1). In the spectrum for Na–MMT, two strong bands at 1,091 and 1,040 cm^{-1} are due to stretching vibration of Si–O. The bands at 519 and 466 cm^{-1} are attributed to Al–O stretching and Si–O bending.[8] Appearance of the deformation band of benzene ring at 1,515 cm^{-1} in the spectrum for PDA–MMT indicates the intercalation of PDA. The absorption band at 1,633 cm^{-1} may result from both the bending vibration of –NH$_2$ and the stretching/deformation vibrations of the interlayer water. After reaction with maleic anhydride to form maleamic

acid, a new band at 1,703 cm^{-1} for the deformation of carbonyl group appeared, suggesting the chemical change in the gallery. The bands at 1,856 and 1,782 cm^{-1} for the anhydride did not appear in the spectrum for MAA–MMT.

According to the TGA data, the organic contents for PDA–MMT and MAA–MMT were 8.3 wt % and 14.3 wt %, respectively. It was estimated based on the cation exchange capacity of pristine Na–MMT that 83% of Na$^+$ cations were exchanged by the protonated PDA, and 96% of PDA molecules in the silicate layers were converted to maleamic acid.

After the treatment with swelling agents, the interlayer space expanded significantly as demonstrated by the X-ray diffraction patterns (Fig. 2). The interlayer distance d_{001} for Na–MMT was 1.25 nm, calculated according to the Bragg formula $\lambda = 2d\sin\theta$. The d_{001} spacing of 1.49 nm (diffraction peak $2\theta = 5.94°$) was found for PDA–MMT, indicating the intercalation of PDA molecules to the layered silicate. After reaction with maleic anhydride, the d_{001} spacing was further expanded to 1.59 nm (diffraction peak $2\theta = 5.56°$). The molecules of the swelling agent might be inclined in the gallery according to the d_{001} spacing.[3]

Scheme 2 Intercalation of MMT by the swelling agents.

Exfoliation of MMT in the BMAN resin

BMAN represents bismaleimide-modified allylated novolac resin. It turns to a melt of low viscosity on heating. Delamination of the organoclay MAA–MMT in the BMAN melt took place very easily: for example, after mechanically stirring for 15 min at 140°C, the 001 reflection peak of the clay completely disappeared in the XRD pattern [Fig. 3(c)], indicating the loss of structure registry of MMT layers. By contrast, for the BMAN/Na–MMT blend after a treatment at the same conditions, two reflection peaks were still present in the small angle region of the XRD trace [Fig. 3(a)]. It is
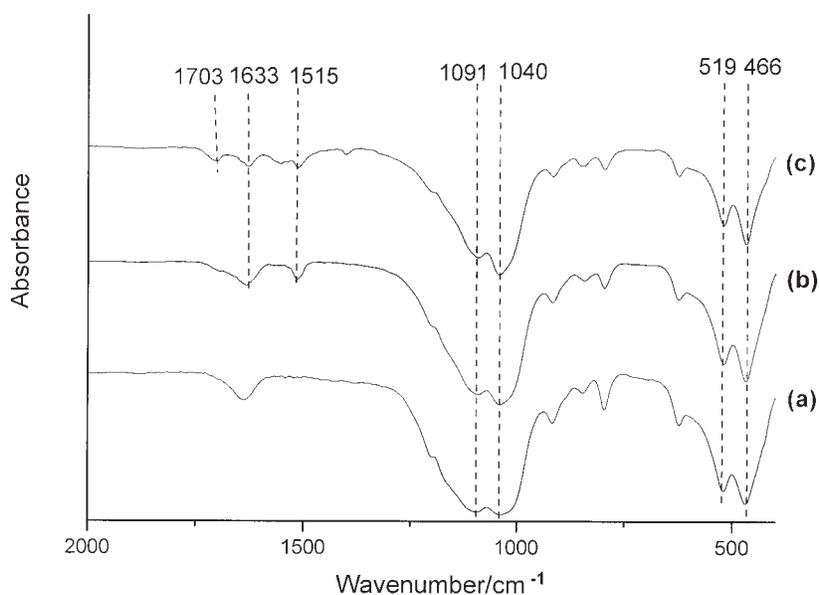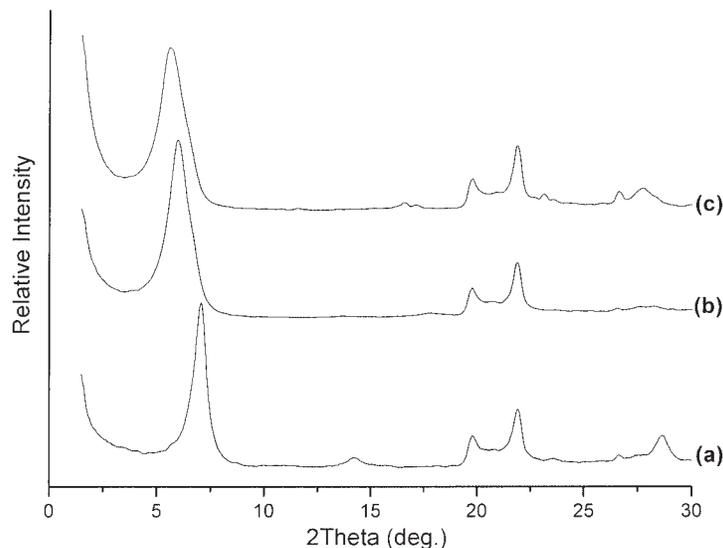

Figure 1 FTIR spectra for (a) Na–MMT, (b) PDA—MMT, and (c) MAA–MMT.

Figure 2 Change of XRD patterns with intercalation of the swelling agents: (a) Na–MMT, (b) PDA—MMT, and (c) MAA–MMT.

indicative that Na–MMT was intercalated by the molecules in the BMAN resin rather than delaminated.[9]

To characterize the clay dispersion in the resin in a more quantitative way, rheometrical measurements were carried out. Viscosity of a fluid is related to the energy dissipation on flowing. Introduction of solid particles will bring in additional energy dissipation, and the increase in viscosity is depended on the volume fraction, the particle shape as well as the specific surface. For the study of polymer/clay nanocomposites, rheometrical methods have been applied.[10]

In Figure 4, steady shear viscosity at 60°C is plotted against shear rate for the BMAN resin and the blends with MMT. The neat BMAN resin was nearly a Newtonian fluid of viscosity $\sim$ 75 Pa.s since the resin was a mixture of low molecular weight substances. A moderate increase in viscosity was observed with the introduction of pristine Na–MMT. For the resin containing 2 parts by weight Na–MMT per 100 parts of BMAN resin (2 phr in abbreviation), the viscosity at low shear rates was increased to $\sim$ 260 Pa.s.

By contrast, the viscosity enhancing with introduction of MAA–MMT was tremendous. For example, incorporation of 2 phr MAA–MMT resulted in an increase in viscosity at low shear rates for over two orders of magnitude. The great increase in viscosity
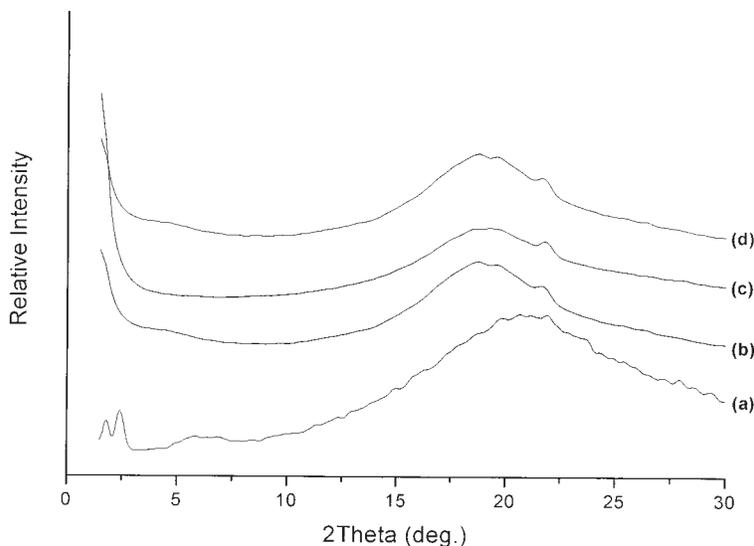
Figure 3 XRD patterns for (a) the BMAN/Na–MMT blend, (b) the BMAN/Na–MMT composite cured at 170°C for 2 h, (c) the BMAN/MAA–MMT blend, and (d) the BMAN/MAA–MMT composite cured at 170°C for 2 h.
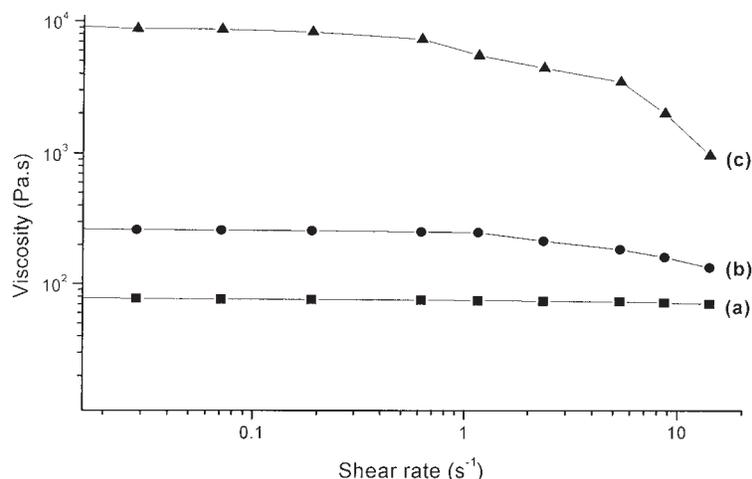
Figure 4 Viscosity versus shear rate at 60°C for (a) the neat BMAN resin, (b) the blend containing 2 phr Na–MMT, and (c) the blend containing 2 phr MAA–MMT.

was the consequence of well-delaminated clay and the high aspect ratio of the silicate sheets, and the firm bonding of the swelling agent to the platelets.

The resin containing MMT exhibited shear thinning at shear rates above 1 s^{-1}. This behavior can be accounted for by orientation of the silicate layers under shearing.

Microstructure of the BMAN/MAA—MMT nanocomposites

Although the XRD patterns and the rheological data demonstrated a great difference in dispersion states after melt blending between the BMAN/MAA–MMT system and the BMAN/Na–MMT system, the cured composites of both systems did not show any 001 reflection in the XRD patterns [Figs. 3(b) and (d)]. It seems that one cannot differentiate an exfoliated composite from an intercalated composite according to only the XRD patterns.

To characterize the microstructure of the BMAN/ clay composites, TEM studies were carried out. In Figure 5 TEM micrographs of the BMAN composites containing 2 phr MAA–MMT and 2 phr Na–MMT are shown. It is seen that, in the BMAN/MAA–MMT composite, many exfoliated silicate layers (darker lines) of thickness about 1 nm, along with some thicker platelets, are dispersed in the polymer matrix. The space between silicate layers appears to range from 10 to 30 nm. By contrast, fewer exfoliated clay layers and more multiples are present in the picture for the BMAN/Na–MMT composite.

Based on the results of rheometrical studies and the TEM results we would say that the BMAN/MAA–MMT composite was basically of the exfoliated type and the BMAN/Na–MMT composite was of the par-tially exfoliated type, as classified by Lan and Pinnavaia.[11]

Transitions and thermal properties of the BMAN/MMT composites

The DMA diagrams for the BMAN resin, the composite containing 2 phr Na—MMT, and the composite containing 2 phr BMAN/MAA–MMT are given in Figure 6. The glass transition temperatures (T_g) according to the peak of the tan δ curve for the BMAN resin, the BMAN/Na–MMT composite, and the BMAN/MAA–MMT nanocomposite are 405, 403, and 408°C, respectively. Since the BMAN resin had an extremely high T_g value by itself, incorporation of MMT did not cause a further increase in T_g.

It is noteworthy that the layered silicate can bring in an improvement in storage modulus in the glass region, and the exfoliated clay is obviously much more effective. Incorporation of 2 phr MAA–MMT resulted in an enhancement of the storage modulus of 27% over that of BMAN.

To study the effect of MMT nanolayers on the thermal stability of the BMAN resin, TGA was carried out. Thermograms for the BMAN resin, the composite containing 2 phr Na—MMT, and the composite containing 2 phr BMAN/MAA–MMT are given in Figure 7.

It is seen that the decomposition onset temperature was not influenced by incorporation of the clay. However, a significant improvement in the weight retention above 450°C can be achieved by incorporation of the clay. The char yields at 900°C were 30.2, 34.5, and 37.2% for the BMAN resin, the BMAN/Na–MMT composite, and the BMAN/MAA–MMT composite, respectively. The MMT layers worked as barriers to reduce the per-
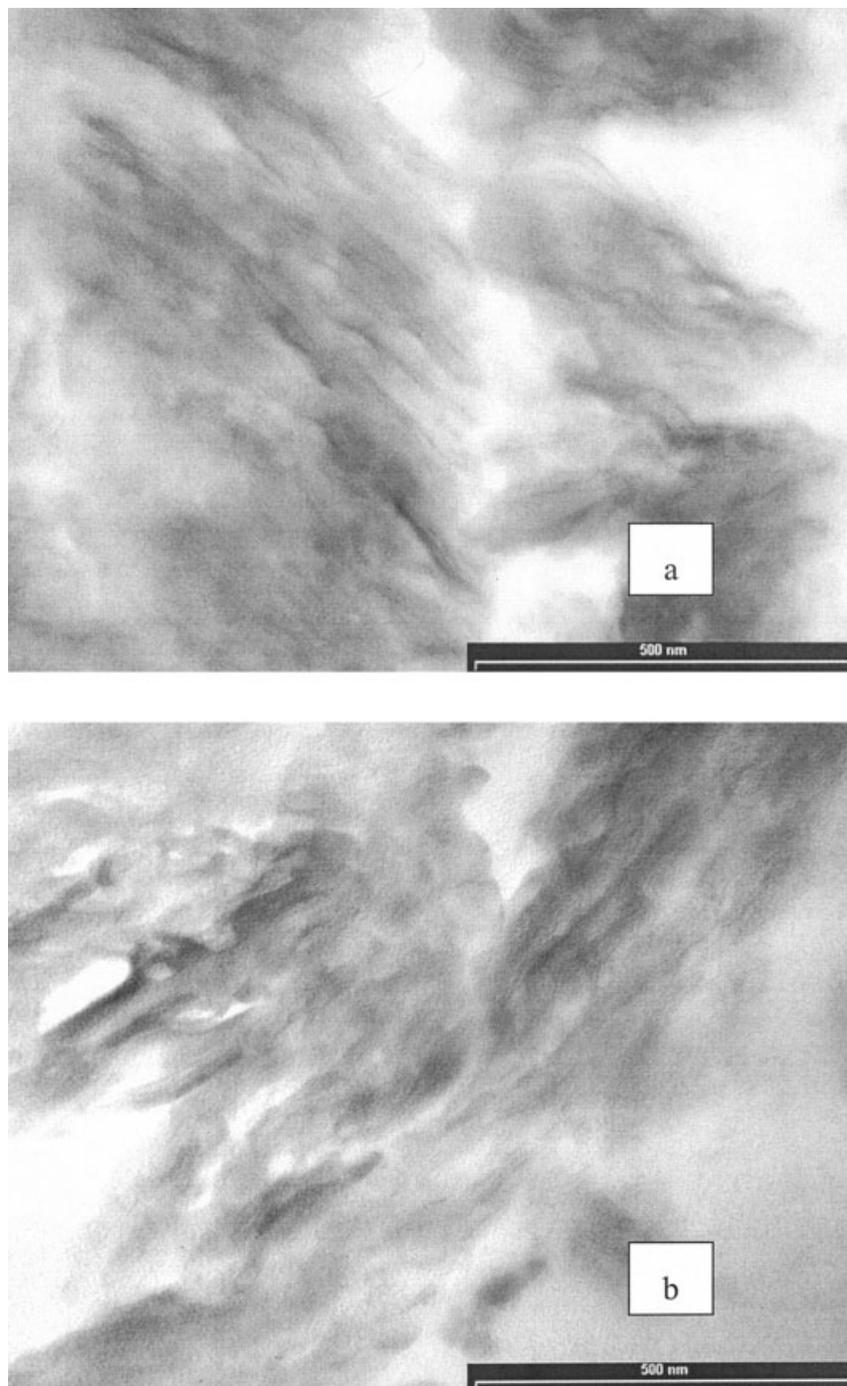
Figure 5 TEM micrograph for the cured BMAN composites (a) containing 2 phr MAA–MMT and (b) containing 2 phr Na–MMT.

meability of the volatile degradation products out of the material.

Mechanical properties of the BMAN/MAA—MMT nanocoposites

For mechanical tests, only specimens of the composites containing 2 phr clay were used. Preparation of void-free specimens containing more MAA–MMT

was unsuccessful because the viscosity was too high for complete deaeration.

The flexural properties of the BMAN/MAA–MMT composite are given in Table I along with those of the BMAN/Na–MMT for comparison. It is seen that 42% improvement in flexural strength and 38% improvement in the modulus over that of the neat BMAN resin were achieved. By contrast, the
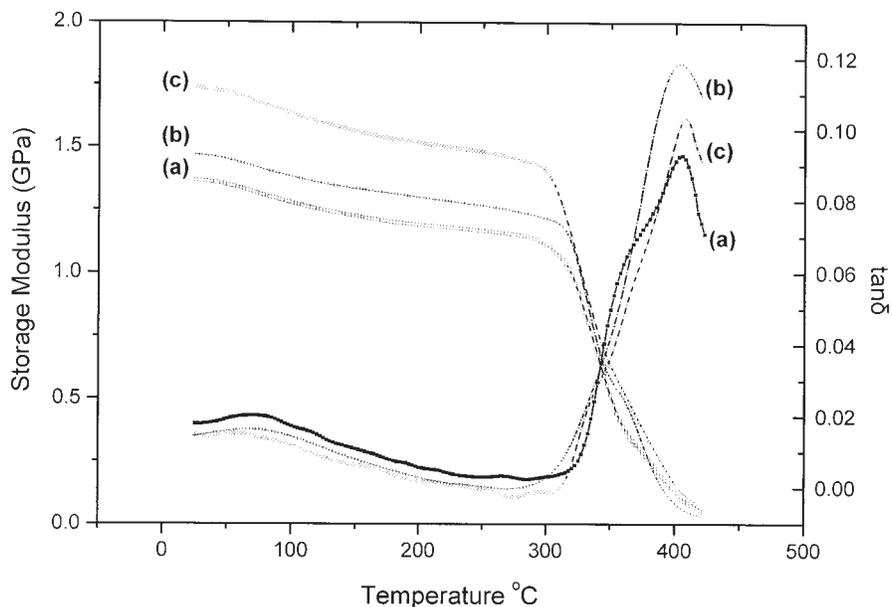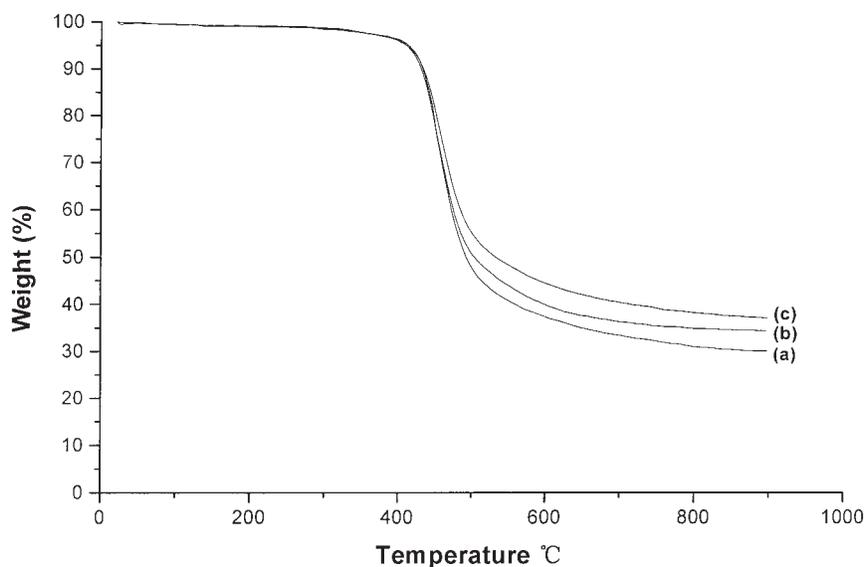
Figure 6 DMA diagrams for (a) the BMAN resin, (b) the composite containing 2 phr Na–MMT, and (c) the composite containing 2 phr MAA–MMT.

improvement in mechanical properties by Na–MMT was marginal. It can be concluded that exfoliation of the clay layer is essential for obtaining nanocomposites of superior mechanical properties, and the swelling agent, which increases the interaction between the clay layer and the matrix resin, may make a contribution also.

CONCLUSION

Protonated *p*-phenylenediamine can be used as swelling agent for sodium–montmorillonite to facil-

itate delamination in the bismaleimide-modified allylated novolac resin. It is converted to maleamic acid by the reaction with maleic anhydride in the gallery of the layered silicate. The d_{001} spacing is expanded by intercalation of the swelling agents. Delamination of the organo-MMT in the resin gives rise to a tremendous increase in viscosity. Major improvements in thermal stability, mechanical strength, and stiffness can be achieved by incorporation of the exfoliated clay nanolayers.

Figure 7 TGA curves for the cured resins: (a) the BMAN resin, (b) the composite containing 2 phr Na–MMT, and (c) the composite containing 2 phr MAA–MMT.

TABLE I
Properties of BMAN/MMT Composites

Sample code	T_g (°C)	Flexural strength (MPa)[a]	Flexural modulus (MPa)[a]
BMAN	405	55.1 (5.7)	2,876.0 (143.9)
BMAN/Na–MMT	403	57.9 (7.1)	3,666.7 (351.4)
BMAN/MAA–MMT	408	78.7 (12.0)	3,979.2 (164.9)

[a] Values in parentheses are SD.

References

1. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem Polym Chem 1993, 31, 2493.
2. Giannelis, E. P. Adv Mater 1996, 8, 29.
3. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. Chem Mater 1995, 7, 2144.
4. Ke, Y. C.; Lu, J. K.; Yi, X. S.; Zhao, J.; Qi, Z. N. J Appl Polym Sci 2000, 78, 808.
5. Imai, Y.; Nishimura, S.; Abe, E.; Tateyama, H.; Abiko, A.; Yanaguchi, A.; Aoyama, T.; Taguchi, H. Chem Mater 2002, 14, 477.
6. Tyan, H. L.; Liu, Y. C.; Wei, K. H. Chem Mater 1999, 11, 1942.
7. Yan, Y. H.; Shi, X. M.; Liu, J. G.; Zhao, T.; Yu, Y. Z. J Appl Polym Sci 2002, 83, 1651.
8. Chen, G. M.; Liu, S. H.; Chen, S. J.; Qi, Z. N. Macromol Chem Phys 2001, 202, 1189.
9. Kornmann, X.; Berglund, L. A.; Sterte, J.; Giannelis, E. P. Polym Eng Sci 1998, 38, 1351.
10. Krishnamoorti, R.; Vaia, R. A.; Giannelis, E. P. Chem Mater 1996, 8, 1728.
11. Lan, T.; Pinnavaia, T. J., Chem Mater 1994, 6, 2216.