

# Structure and Properties of Polybutadiene/Montmorillonite Nanocomposites Prepared by *In Situ* Polymerization

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**ABSTRACT:** Polybutadiene (PB)/Montmorillonite nanocomposites (NCs) were prepared by *in situ* polymerization through the anionic polymerization technique. The effects of treating method of organophilic MMT (OMMT), the type of OMMT, and the solvent used in polymerization were studied. The structure and properties of NCs were characterized using X-ray Diffraction (XRD), transmission electron micrograph (TEM), H-NMR spectrum, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The consumption of BuLi was varied with different treating methods. The molecular weight distribution of PB added with OMMT (DK1) was wide, and the molecular weight distribution became narrow when OMMT-DK1B and DK4 were added. OMMT did not disperse stably in cyclohexane, but could form a

homogeneous solution in toluene and xylene. XRD and TEM showed that exfoliated NCs were obtained by *in situ* polymerization through the anionic polymerization technique. From the H-NMR spectrum of PB and PB/OMMT NCs, it could be seen that the content of 1, 2 units of PB increased ~100%, while 1, 4 units decreased when 6.2 wt % of OMMT was added. The results of DSC and DMA indicated that  $T_g$  and  $T_{dc}$  were increased when compared with those of PB. Both storage modulus and loss modulus were increased with the addition of OMMT, and  $\tan \delta$  was decreased. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3615–3621, 2006

**Key words:** polybutadiene; montmorillonite; anionic polymerization; nanocomposites

## INTRODUCTION

Polymer/clay nanocomposites (NCs), which have special structure and morphology compared with that of conventional composites, have attracted much attention for their excellent properties, including mechanical properties, thermal properties, gas barrier properties, flame-retardant properties, and so on. Especially since Toyota Corp. reported the preparation of nylon 6/clay NCs in 1987,<sup>1</sup> this kind of NC has attracted great interest, both in industry and in academia. At present, reports about polymer/clay NCs mostly focus on the resin matrix, for example, nylon,<sup>1–4</sup> polystyrene,<sup>5–7</sup> poly(methyl methacrylate),<sup>8,9</sup> polypropylene,<sup>10,11</sup> etc., but many reports on rubber/clay NCs have appeared in recent years, for which the preparation methods usually are melt intercalation,<sup>12</sup> solution intercalation,<sup>13</sup> latex compounding,<sup>14,15</sup> etc. In the above preparation methods, the entropy of mixing will decrease during the intercalation of the rubber molecular chain into gallery of organophilic MMT (OMMT) because of the flexible long chain of rubber, resulting in a weak intercalation drive force, so problems

such as weak drive force and poor dispersion of montmorillonite in rubber matrix occur. Preparation of rubber/clay NCs by *in situ* polymerization can solve those problems *via* monomer molecules intercalating into the gallery space and polymerizing; however, this method is rarely used presently. Conventional rubbers such as BR, IR, and SBR are basically synthesized by the anionic polymerization technique, which requires rigorous reaction conditions, and thus it is difficult to realize the preparation of rubber/clay NC by *in situ* polymerization. This may limit the development of the preparation of rubber/clay NCs by *in situ* anionic polymerization and few reports are related to it.<sup>16–18</sup>

In this study, based on our previous work,<sup>16,17</sup> we have successfully synthesized Polybutadiene (PB)/OMMT NCs by *in situ* polymerization through the anionic polymerization technique, and the factors affecting the polymerization, the structure, and properties of rubber/OMMT NCs also were studied. Interesting results were obtained as seen subsequently.

## EXPERIMENTAL

### Materials

Organophilic MMT (OMMT) with trade name NAN-NOLIN DK1, DK1B, DK4 was supplied by Fenghong

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Clay Chemical Corp., China. It is a kind of OMMT that was ion-exchanged by a quaternary organic ammonium salt (length of ammonium increases from DK1 to DK4, possible lengths of ammonium are octyl, hexadecyl, octadecyl, trimethylammonium salts, respectively, based on analysis of IR) with a cation exchange capacity of 110 mequiv/100 g, and an average particle size is 25  $\mu\text{m}$  in the dry state. The butadiene was supplied by Beijing Yanshan Petrochemical Corp. The isoprene was supplied by Shanghai Jinshan Petrochemical Corp. BuLi was prepared in our laboratory.

### Preparation of NCs

A certain amount of OMMT was dispersed into a mixture of toluene and butadiene (toluene/butadiene = 8/1). The mixture was first homogenized by stirring for 3 h. It was then preheated for 10 min at 50°C in a water bath before *n*-butyllithium was added as the initiator. The polymerization reaction was allowed to conduct for 3–6 h. The resulting composites were then poured into ethanol to yield white precipitates. These precipitates were filtered and dried under vacuum at 40°C.

### Characterization

The change in basal reflection of the NCs was measured using an X-ray diffractometer (D/max RB).  $\text{CuK}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) was used as an X-ray source, at a generator voltage of 40 kV and current of 100 mA. Diffraction angle was scanned from 1 to 10° at a rate of 2°/min. The basal spacing of MMT was estimated from the position of the (001) plane peak in the X-ray diffraction (XRD) pattern, using the Bragg's equation,  $d = \lambda/2 \sin \theta$ . For H-NMR analysis, a Bruker AVANCE400 NMR spectrometer was employed with a superconducting magnet and  $\text{CDCl}_3$  as solvent. Transmission electron micrograph (TEM) investigations were performed using a FEI Company TECNAI G220 TEM with a Cu filament operating at 200 kV, and freeze-cut slices.

Dynamic mechanical properties were measured using a TA 2980 DMA dynamic mechanical analyzer with Multi-Frequency Film-Tension Module. The specimens ( $1.5 \times 4.5 \times 20 \text{ mm}^3$ ) were cut from the center of the samples. A temperature sweep at 5°C/min was used, starting from -150 to 150°C at a frequency of 1 Hz. TA 2050 thermogravimetric analysis instrument was utilized for thermogravimetric analysis (TGA) investigation, using a temperature variation from ambient value to 550°C at a heating rate of 10 K/min under  $\text{N}_2$  protection. TA 2910M differential scanning calorimeter was employed for differential scanning calorimetry (DSC) analysis at a heating rate of 10°C/min for a scanning scope between -150 and 100°C.

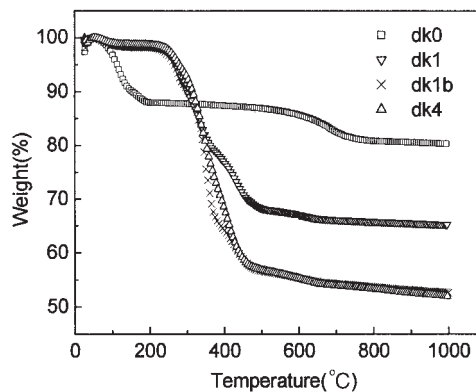


Figure 1 TGA spectrum for MMT and OMMT.

## RESULTS AND DISCUSSION

### Factors affecting the preparation of PB/OMMT NC

#### The effect of treating method of OMMT

The anionic polymerization requires high reaction conditions. The polymerization reaction can occur only in the absence of water and oxygen, and so it is necessary to purify the montmorillonite before the polymerization. It can be seen from Figure 1 that the weight loss of MMT occurs at two temperature areas: <200°C, loss of free water; 500–800°C, loss of bound water. The weight loss of OMMT occurs in three temperature areas: <200°C, loss of free water; 200–500°C, loss of interlayer water and organics; 500–800°C, loss of bound water.<sup>19</sup> Obviously, the free water can be eliminated under vacuum drying, but the interlayer water and the bound water cannot be eliminated totally, which will have effect on the polymerization reaction. At present, there is no effective and simple method to eliminate the interlayer water and the bound water. MAO was used in earlier works,<sup>20</sup> but MAO is not convenient for use and is too expensive. In this work, we used two methods to purify OMMT, and investigated the effect of treating method on the polymerization.

The first method was to dry montmorillonite directly at 60°C. Table I shows the weight change of OMMT under different drying time. It can be seen that the weight of OMMT did not change beyond 48 h of drying. OMMT prepared by this method was used to synthesize PI/OMMT (DK4) NC by *in situ* polymerization.

Targetted  $M_n$  was  $10^5$ , and the  $M_n$  of the sample was  $10.2 \times 10^4$ ,  $M_w/M_n = 1.08$ . This drying method is very simple, but only the free water can be eliminated and the consumption of BuLi is very high. The wastage of BuLi used on OMMT can be calculated by the following formula:

$$B_{\text{mmt}} = B_g - B_p - B_s$$

TABLE I  
Weight of DK1B at Different Drying Time

Time (h)	Weight (g)
0	20.898
3	20.844
7	20.836
17.5	20.835
25.5	20.830
46	20.823
48	20.821
53	20.821
65	20.821
73	20.821

$B_{\text{mmt}}$  is the wastage of BuLi used on OMMT;  $B_{\text{g}}$  is the total consumption of BuLi;  $B_{\text{p}}$  is the consumption of BuLi by initiating polymerization;  $B_{\text{s}}$  is the wastage of BuLi used on the reaction system, which relates to monomer, solvent, and impurity in the reaction vessel. The results are shown in Table II.

Table II shows that the wastage of BuLi used on DK0 was much higher than that used on OMMT, indicating that there is much more impurity in DK0 (mostly water), but the modified OMMT, with the decreased interlayer polarity and increased organophilic, because of ion exchange, resulted in decreasing interlayer free water. Additionally, the ion exchange reaction may partially destroy bound water, reducing the constituted water content and is demonstrated by TGA. Figure 1 reveals that the weight loss rate of OMMT, below 300°C and during the range of 500–800°C, is less than that of MMT. Furthermore, the addition of intercalation agent may decrease the adsorption of oxygen in the interlayer gallery.

The second method was dipping the OMMT in toluene, and then evacuating to eliminate water and oxygen further. Through this method we have prepared the PB/OMMT (DK1B) NC successfully. The designed  $M_n$  was  $10^5$ , and the sample of  $M_n$  was  $9.2 \times 10^4$ ,  $M_w/M_n = 1.06$ . The wastage of BuLi used on OMMT in polymerization was 0.43–0.55 mmol/g OMMT, which was half of the wastage used in the first method, indicating that the second method can eliminate the interlayer water. But intercalation agent may be partly taken off during the dipping in toluene, resulting in a change of the microenvironment of the interlayer gallery. Figure 2 shows that interlayer spac-

TABLE II  
Wastage of BuLi Used on OMMT

OMMT	$B_{\text{mmt}}$ (mmol/g)
DK0	4.657
DK1	1.355
DK1B	1.143
DK4	1.065

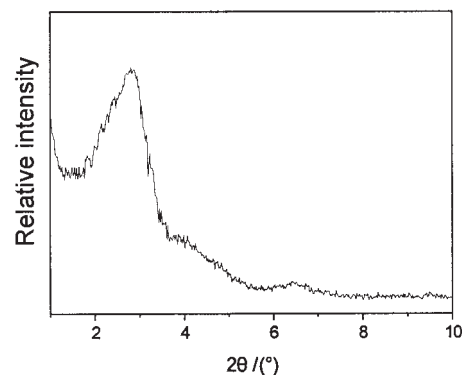


Figure 2 XRD patterns of OMMT (DK1B) treated by second method.

ing of treated OMMT (DK1B) by the second method increases a little compared with that of untreated OMMT (diffraction peak is 2.89°, the corresponding interlayer spacing is 3.05 nm, and the interlayer spacing of untreated OMMT is shown in Table III), indicating the removal of intercalation agent. Because the second method consumed less BuLi, following polymerizations adopted this method to treat OMMT.

#### The effect of the type of OMMT

The XRD patterns of MMT and OMMT are shown in Figure 3. It can be seen that the diffraction peak (d001) of OMMT shifted to a small angle. The interlayer spacing is calculated by Bragg's equation and the results are shown in Table III.

Table III shows that the interlayer spacings of modified DK1, DK1B, and DK4 increases by 0.51, 1.62, and 2.08 nm, respectively, compared with that of MMT, indicating that the interlayer spacing is increased with the increasing length of carbon chain of the intercalation agent. PB, PI/OMMT NCs were prepared by *in situ* polymerization. A different type of OMMT has a different effect on the molecular weight distribution of

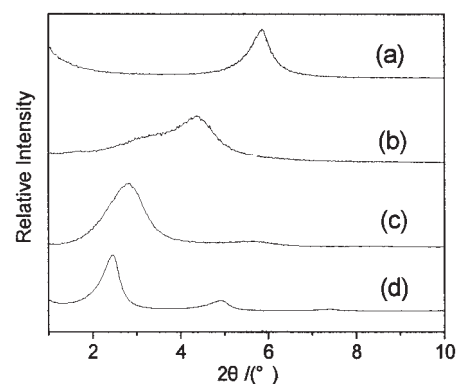


Figure 3 XRD patterns of MMT and OMMT [(a) DK0; (b) DK1; (c) DK1B; (d) DK4].

**TABLE III**  
Diffraction Angle and Basal Spacing of MMT and OMMT

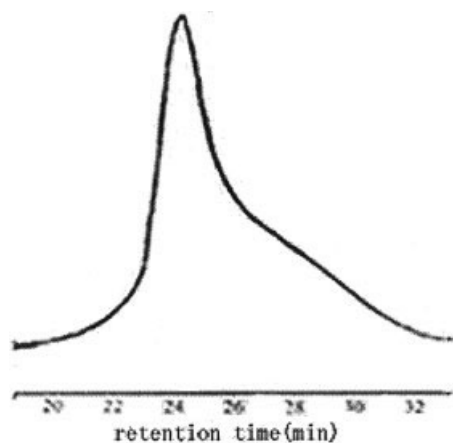
MMT and OMMT	Diffraction angle $2\theta$ ( $^{\circ}$ )	Basal spacing (nm)
DKO	5.86	1.51
DK1	4.38	2.02
DK1B	2.82	3.13
DK4	2.46	3.59

polymer. For example, the molecular weight distribution of the sample with DK1 added is very wide: the  $M_w/M_n$  of PI/OMMT (DK1) NC increases to 2.22, and the GPC curve has serious tailing phenomena (see Fig. 4, the synthesis mechanism of PI and PB NCs is similar, and thus one can take the GPC curves of PI NC as an example), indicating that there was chain termination or chain transfer during the polymerization. But the molecular weight distribution of the sample with DK1B or DK4 added is rather narrow, for instance, PB/OMMT (DK1B) NC is 1.06 and PB/OMMT (DK4) NC is 1.09.

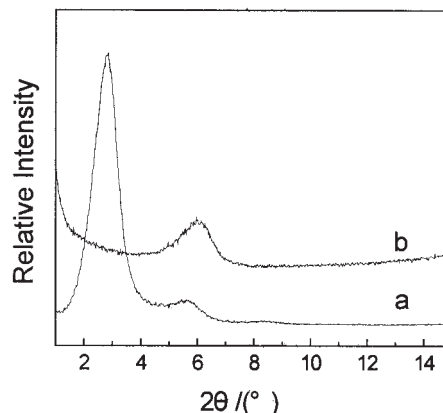
The tailing phenomena may result from the impurity content of OMMT. The interlayer gallery of DK1 is small, so it's hard to eliminate impurities residing in the galleries, which results in the low-molecular weight polymer, forming the tail of the GPC curve. However, the interlayer spacings of DK1B and DK4 are large, and the impurity in the galleries is easy to eliminate, and so there are few reactive species terminated; therefore, there is less effect on the molecular weight distribution. Table II shows that the consumption of BuLi used on DK1 is more than that used on DK1B and DK4, which also indicates that there is much more impurity in DK1.

#### The effect of solvent

The degree of dispersion of OMMT in the solvent has a direct effect on its dispersion in the NCs, and so it is



**Figure 4** GPC curves of PI/DK1 NC (2.5 wt%).



**Figure 5** XRD patterns of DK1B (a) and PB/DK1B composites (b).

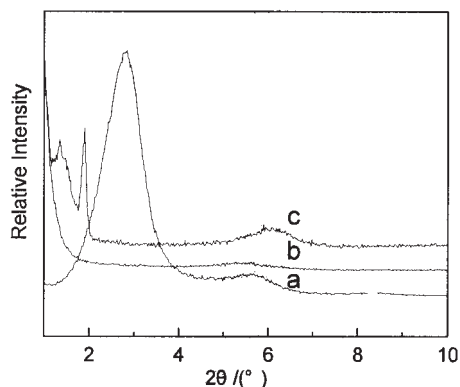
very important to choose the appropriate solvent. Montmorillonite is highly polar, although, after treating MMT by intercalation agent, ammonium salt intercalated into interlayer gallery, MMT became organic and organophilicity of OMMT increased, which is favorable for dispersing in solvent, but yet there is still a certain extent of polarity in OMMT, so it's better to disperse OMMT in polar solvent. Furthermore, the literature<sup>21</sup> also reported that the OMMT can form a uniform dispersion in polar solvent. If one chose cyclohexane as solvent, the experiment demonstrated that OMMT had poor dispersion in it, obvious demixing can be observed, and Figure 5 shows the XRD patterns of PB/OMMT (DK1B, 2.5 wt %) NC, with cyclohexane as solvent. It can be seen that the diffraction peaks of OMMT and NCs are 2.82 and 5.96 $^{\circ}$ , the corresponding interlayer spacing are 3.13 and 1.48 nm, respectively, indicating that the PB chains did not intercalate into the interlayer gallery and *in situ* polymerization did not occur; therefore, the cyclohexane is not suitable to be used as solvent.

Both toluene and xylene have weak polarity, and so they have better dispersion ability for OMMT. The experiments demonstrated that OMMT could form stable emulsions either in toluene or in xylene, and so both the types of solvent can be used in the preparation of PB/OMMT NCs.

#### Structure of PB/OMMT NC

##### Intercalation structure of PB/OMMT NCs

The XRD patterns of OMMT and the corresponding NC are shown in Figure 6. The figure shows that the diffraction angles of OMMT (DK1B) (curve a) alone and the OMMT in the NC (curve c) are 2.82 and 1.34 $^{\circ}$ , respectively, and the corresponding interlayer spacings are 3.13 and 6.59 nm. It was obvious that the spacing was increased for butadiene intercalated into

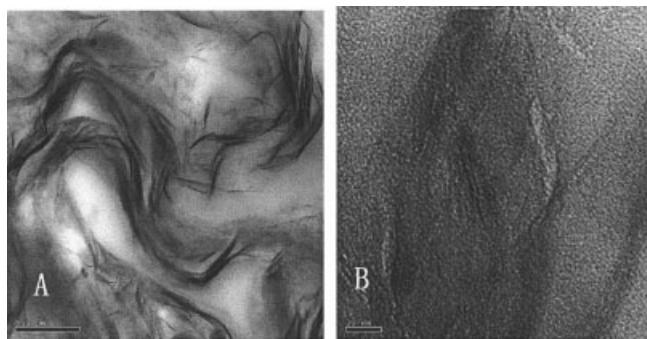


**Figure 6** XRD patterns of OMMT and PB/DK1B NC [(a) OKIB; (b) 6.2 wt%; (c) 2.1 wt%].

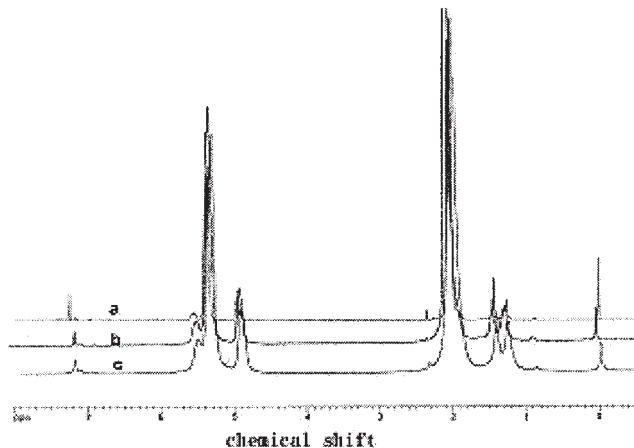
the gallery space, which enabled the *in situ* polymerization and the PB/OMMT NC with intercalated structure was obtained. When the content of DK1B increased to 6.2 wt % (curve b), there was no obvious diffraction angle observed in the XRD, indicating that montmorillonite layers were exfoliated in the polymer matrix and formed exfoliated NC.

#### Phase morphology of PB/OMMT NCs

The TEMs of PB/OMMT NCs are shown in Figure 7. The white area is rubber matrix and the black area is montmorillonite layer. It can be seen from Figure 7(a) that the montmorillonite layers are dispersed in the PB matrix randomly. The interface between PB and montmorillonite layer is a little hazy and the bundles of layers are in a contorted condition, which indicates that there is a strong interfacial force between PB and montmorillonite layer. Further magnification [Fig. 7(b)] shows that montmorillonite layers are entirely exfoliated into monolayer structure and the layers are distorted, arranged in no order. The results show that the butadiene monomers intercalated into interlayer gallery polymerize and convert into PB, which resulted in increasing the interlayer spacing, and the quantity of heat energy released during the polymer-



**Figure 7** TEM patterns of PB/DK1B NC (6.2 wt%).



**Figure 8** H-NMR patterns of PB (a) and PB/OMMT-DK1B NC [(b) 2.1 wt%; (c) 6.2 wt%].

ization further weakened the interaction among the montmorillonite layers, leading to the exfoliation of the layers. The results obtained by TEM are consistent with the analysis of XRD.

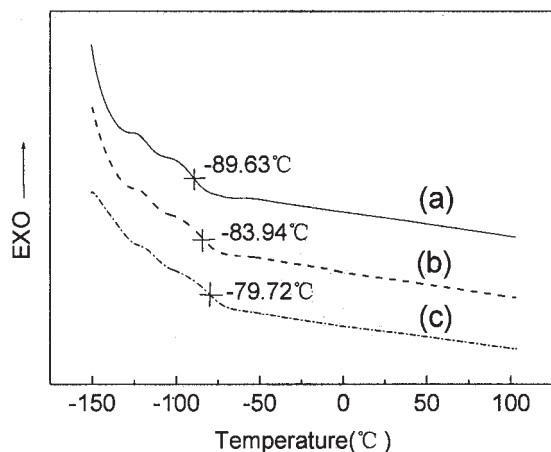
#### Microstructure of PB/OMMT NCs

The H-NMR patterns of PB and corresponding NCs are shown in Figure 8. In Figure 8, 4.0–6.0 ppm was PB double bonds: 4.8–5.01 ppm was 1, 2 units and 5.36–5.4 ppm was superposition of 1, 4 units and 1, 2 units. The contents of 1, 2 units and 1, 4 units of PB and the corresponding NC were calculated by the method of area integration according to H-NMR patterns, and the results are shown in Table IV.

The figures show that the microstructure of PB changes a lot: the content of 1, 2 units is increased dramatically with the increasing loading of OMMT, from 17 to 21.1%, twice as much as that of pure PB. This reveals that montmorillonite acts not only as a reinforcing, but also a polar modifier. For anionic polymerization amine-compounds as polar modifier are used extensively, intercalation agents ammonium salts used on OMMT contain amine group also, and so ammonium salts, may play the role of a polar modifier. This finding indicates that the addition of montmorillonite influences the polymerization mechanism

**TABLE IV**  
Microstructure of PB/OMMT NC

Sample	OMMT content (wt%)	Microstructure unit and content (%)	
		1, 2 unit	1, 4 unit
PB		11.6	88.4
NC1	2.1	17.0	83.0
NC2	6.2	21.1	78.9



**Figure 9** DSC patterns of PB and PB/DK1B NC [(a) PB; (b) 2.1 wt%; (c) 6.2 wt%].

and changes the microstructure of polymers. The particular mechanism needs to be investigated in further research.

### Properties of PB/OMMT NC

#### $T_g$ of the NCs

The DSC patterns of PB and the corresponding NC are shown in Figure 9.

The  $T_g$  values are increased with increasing addition of OMMT: the  $T_g$  is increased from  $-89.6$  (pure PB) to  $-83.9^\circ\text{C}$ , at a loading of 2.1 wt % OMMT; when the loading increases to 6.2 wt %,  $T_g$  is increased to  $-79.7^\circ\text{C}$ , increasing  $10^\circ\text{C}$  compared with pure PB. The  $T_g$  represents the extent of the movement of chain segments. Because OMMT layers are dispersed in polymer matrix at the nanoscale, there is a strong interfacial force between layers and polymer chains, which confines the movement of chain segments, resulting in the increasing  $T_g$ , and the extent of confinement is enhanced with the increasing loading of OMMT, and so the  $T_g$  is increased dramatically.

#### TGA analysis of the NCs

The TGA curves of PB and the corresponding NC are shown in Table IV. The marked temperature ( $T_{dc}$ ) is the fastest weight loss temperature that represents the heat resistance of the NC. Table V reveals that the  $T_{dc}$  of the NC is increased with the increasing content of OMMT.

At the loadings of 2.1 and 6.2 wt % OMMT, the corresponding  $T_{dc}$  are 462 and  $475^\circ\text{C}$ , respectively, 3 and  $16^\circ\text{C}$  higher than pure PB. Table IV shows that the weight loss temperature of NC is higher than that of pure PB, and is increased with the increasing loading of OMMT. In the beginning decomposition step, the

weight loss temperature of NCs increases gradually, but in the process of decomposition, the weight loss temperature increases dramatically, resulting from a change in process of weight loss. In general, the weight loss first occurs at polymer chains that are not combined with the OMMT layer, and that kind of chain is the same as the chain of pure PB, and so the weight loss temperature does not change significantly at first. When NCs decompose to some extent, because of the dispersion in nanoscale and the strong interfacial mutual interaction between PB and OMMT layer, the NCs possess excellent thermal stability in the OMMT layer, and thus the weight loss temperature increased greatly.

#### Dynamic mechanical properties of NCs

The dynamic mechanical analysis (DMA) curves of PB and PB/OMMT (DK1B) NC are shown in Figure 10. It is clear that the  $T_g$  of NC is about  $10^\circ\text{C}$  higher than that of PB, consistent with the DSC analysis. Storage modulus and loss modulus are increased dramatically, while  $\tan \delta$  is decreased.

The interfacial interaction is strong because of good dispersion of the OMMT layers in PB of the nanoscale, and the layers act as like crosslinking points, which results in markedly reinforcing and increasing storage modulus of NCs. The decreasing  $\tan \delta$  is the result of the strong mutual interaction between PB and OMMT that decreases the interfacial slide and relaxation, resulting in decreasing lag.

### CONCLUSIONS

PB/OMMT NC was successfully prepared by *in situ* polymerization through the anionic polymerization technique. The consumption of BuLi varied with different treating methods; and the method of drying directly consumed twice as much as that of the method of solvent substitution. The molecular weight distribution of the NC with OMMT (DK1) added was wide, but the distribution was rather narrow with DK1B or DK4 added. OMMT did not stably disperse in cyclohexane, but can form a homogeneous solution either in toluene or in xylene. XRD and TEM revealed that the exfoliated

**TABLE V**  
TGA Temperature ( $^\circ\text{C}$ ) of PB and PB/OMMT-DK1B NC

	$T_0$	$T_{20}$	$T_{50}$	$T_{80}$	$T_{dc}$
PB	357	450	465	481	459
2.1 wt%	358	451	468	486	462
6.2 wt%	359	457	471	491	475

$T_0$ , initial decomposition temperature;  $T_{20}$ , 20% weight loss temperature;  $T_{50}$ , 50% weight loss temperature;  $T_{80}$ , 80% weight loss temperature;  $T_{dc}$ , weight loss central temperature.

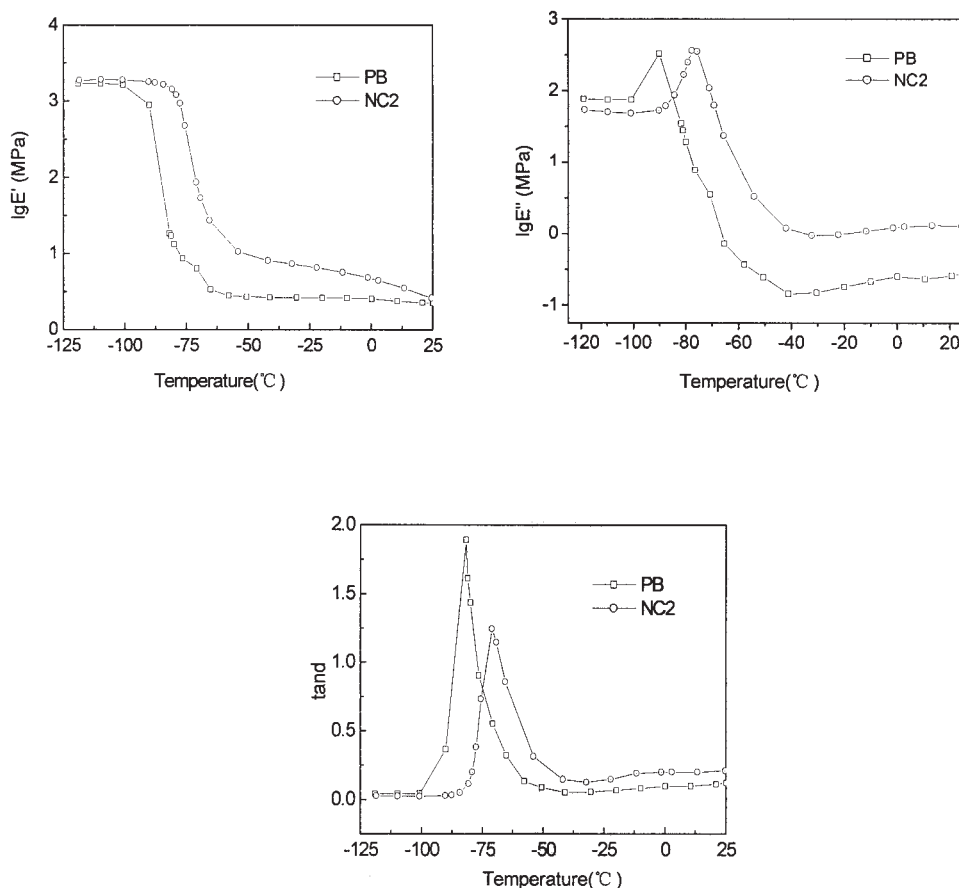


Figure 10 DMA measurements for PB and PB/OMMT NC (6.2 wt%).

PB/OMMT NC was prepared by *in situ* polymerization through anionic polymerization. The addition of OMMT changed the content of the microstructure of PB greatly. The content of 1, 2 units approximately doubled at a loading of 6.2 wt % OMMT. The  $T_g$  and thermal stability of NC increased dramatically compared with those of PB alone. When the content of OMMT was 6.2 wt %,  $T_g$  and  $T_{dc}$  increased at 10 and 16°C, respectively. Both the storage modulus and loss modulus increased greatly, and  $\tan \delta$  was decreased.

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