Novel Polyether Polyurethane/Clay Nanocomposites Synthesized with Organicly Modified Montmorillonite as Chain Extenders

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ABSTRACT: A kind of novel polyether polyurethane (PU)/clay nanocomposite was synthesized using poly(tetramethylene glycol), 4,4′-diphenylmethane diisocyanate (MDI), 1,6-hexamethylenediamine, and modified Na^+-montmorillonite (MMT). Here, organicly modified MMT (O-MMT) was formed by applying 1,6-hexamethylenediamine as a swelling agent to treat the Na^+-MMT. The X-ray analysis showed that exfoliation occurred for the higher O-MMT content (40 wt %) in the polymer matrix. The mechanical analysis indicated that, when the O-MMT was used as a chain extender to replace a part of the 1,2-diaminopropane to form PU/clay nanocomposites, the strength and strain at break of the polymer was enhanced when increasing the content of O-MMT in the matrix. When the O-MMT content reached about 5%, the tensile strength and elongation at break were over 2 times that of the pure PU. The thermal stability and the glass transition of the O-MMT/PU nanocomposites also increased with increasing O-MMT content. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 6–13, 2006

Key words: montmorillonite; nanocomposites; polyurethane; intercalation; organoclay

INTRODUCTION

A nanocomposite is a kind of composite material having more than one solid phase with a dimension in the 1–20 nm range.[1–4] Recently, polymer/clay nanocomposites have attracted a great deal of attention. For example, polymer nanocomposites such as polyamide,[5–7] polyepoxy,[8,9] polystyrene,[10,11] poly(ethylene oxide),[12,13] polycaprolactone,[14] polyimide,[15–19] and polyurethane (PU),[20–26] with montmorillonite (MMT) or layered silicates have been developed. Because of the much stronger interfacial forces between the nanometer-sized domains, they exhibit many physical properties that are better, such as thermal, mechanical, and barrier properties, than those of conventional composites.

PU/clay nanocomposites were first reported by various groups.[20–27] They focused on the compatibility between organic clay and polyols and found that the MMT clay exchanged with long-chain onium ions (carbon number ≥ 12) had good compatibility. It was also found that the clay nanolayers were uniformly dispersed in the polymer matrix, nanolayer exfoliation had been achieved; and the mechanical properties and thermal stability of the PU/clay nanocomposites were increased.

The aim of this work was to design a new polyether PU nanocomposite based on organicly modified MMT (O-MMT) employed as chain extenders in the synthetic process. In our procedure, 1,6-hexamethylenediamine (carbon number < 12; double —NH_2 groups) was used as a swelling agent to treat Na^+-MMT and it was intercalated into clay nanolayers to form the O-MMT. Then, the O-MMT was used as a part of the chain extenders, replacing a part of the 1,2-diaminopropane to form PU/clay nanocomposites. Our research interest focused on the effect of the O-MMT content on the mechanical properties of the nanocomposites. The tensile stress, elongation at break, thermal stability, glass transition, and water absorption of the O-MMT/PU nanocomposites were investigated.

EXPERIMENTAL

Materials

MMT (Aldrich) with a cationic exchange capacity of 78.6 meq/100 g and 1,6-hexamethylenediamine (Tianjing Chemical Reagent Co.) were used as received. 4,4′-Diphenylmethane diisocyanate (MDI, Aldrich) and poly(tetramethylene glycol) (PTMEG, Mn = 2000, Aldrich) were dehydrated under a vacuum at 60°C for 24 h. Dimethylformamide (DMF; 99%, Tianjing Chem-

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ical Reagent Co.) and 1,2-diaminopropane (Shanghai Chemical Reagent Co.) were dried over calcium hydride for 2 days and then distilled under a vacuum.

Preparation of organophilic clay (O-MMT)

The MMT was first screened with a 300-mesh sieve to remove impurities. Then, 20 g of the screened MMT was gradually added to a previously prepared solution of 10.6 g of Na_2CO_3 dissolved in 200 mL of H_2O at 70°C, and the resultant suspension was vigorously stirred for 24 h. The treated MMT was then filtered and washed with deionized water until complete removal of CO_3^{2-} ions, which was insured by titrating with $0.1N$ $CaCl_2$. The filter cake was then dried at 70°C for 24 h in a vacuum ground, and screened with a 300-mesh sieve to obtain the Na-MMT.[28] Ten grams of the screened Na-MMT was gradually added to a previously prepared solution of 1,6-hexamethylenediamine (12.5 g) dissolved in 1000 mL of $0.01N$ HCl at 70°C. The resulting suspension was vigorously stirred for 6 h. Then, this white precipitate was isolated by filtration, suspended in 400 mL of hot water, and stirred for 2 h. To insure complete removal of chloride ions, the precipitate was washed repeatedly until no further formation of AgCl was detected after the addition of $0.1N$ $AgNO_3$ to the washing water. The product was finally filtered and dried *in vacuuo* at 80°C for 24 h, ground, and screened with a 300-mesh sieve to obtain the organoclay.[29]

Synthesis of PU/clay nanocomposites

Preparation of pure PU

Five grams of MDI and 19.5 g of PTMEG at a molar ratio of 2 : 1 were dissolved in DMF solvent, and then the whole solution was mixed under a nitrogen atmosphere for 2 h at 90°C to form a prepolymer. Then, 0.74 g of 1,2-diaminopropane was gradually added to the prepolymer with vigorous stirring at room temperature for 4 h to complete the reaction (Scheme 1). The PU films were formed by casting the solution onto glass plates and then removing the solvent in a vacuum at 70°C for 36 h.[30]

Preparation of PU/clay nanocomposites

The procedure of synthesizing the PU prepolymer was as in the previous section, but different amounts of O-MMT (1,2, and 3 wt %, etc.) were mixed with 20 mL of DMF and then added to the prepolymer with vigorous stirring at room temperature for 2 h. Subsequently, 0.74 g of 1,2-diaminopropane was gradually added to the mixture with vigorous stirring for 4 h to complete the reaction (Scheme 2). The PU/clay films were obtained in the same way as the PU films.[30]

Polymer recovery from PU/clay nanocomposites

Toluene (10 mL) was added to 1 g of the synthesized PU/clay while stirring for 2 h at room temperature. Then, 20 mL of a 1% LiCl solution in DMF was gradually added to the suspension. The mixture was stirred for 48 h to perform the reverse ion-exchange reaction, and then the solution was centrifuged at 10,000 rpm for 2 min. The supernatant liquid after centrifugation was poured into methanol and the resulting solid was filtered and dried *in vacuuo*.[29,30]

Characterization

X-ray diffraction (XRD) measurements were performed with a D/Max-2400 Rigaku diffractometer with Ni-filtered Cu K_α radiation (λ = 1.5418 Å). The scanning rate was 2°C/min over a range of 2θ = 2–15°. The molecular weights of the polymer were determined with a Waters 2695-2410 gel permeation chromatography (GPC) system with DMF as the solvent. The calibration curves for GPC were obtained by using polystyrene standards.

Differential scanning calorimetry (DSC) was performed with a DSC822E under a N_2 atmosphere with a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer 7 Series thermal analysis system at a scanning rate of 10°C/min in a nitrogen atmosphere. The tensile properties of the sample were tested with an Instron mechanical tester (model DY-35) at a crosshead speed of 500 mm/min. The I-shaped specimens were prepared with a 4-mm width, 16-mm length, and 0.2-mm thickness. For each datum point, five samples were tested and the average value was taken.

The water absorption measurements of pure PU and PU/clay nanocomposites were carried out according to the specifications of ASTM D 570, and the test specimens were cut in the shape of 76.2 × 25.4 × 1 mm. The specimens were dried in a vacuum at 80°C for 24 h, cooled in a desiccator, and then immediately weighed with 0.001-g precision to get the initial weight (W_0). Subsequently, the conditioned specimens were entirely immersed in a container of deionized water maintained at 25 ± 0.2°C for 24 h, taken out of the water, and the surface water removed with a dry cloth. Then, the specimens were weighed immediately to ascertain the final weight (W_1). The percentage of increased weight of the samples was calculated with 0.01% precision by using the formula $(W_1 - W_0)/W_0$.[24]

RESULTS AND DISCUSSION

Polymer synthesis

In Schemes 1 and 2 the synthetic process and one simplified chemical structure of PU and O-MMT/PU are reported. As shown in Scheme 1, in the first step
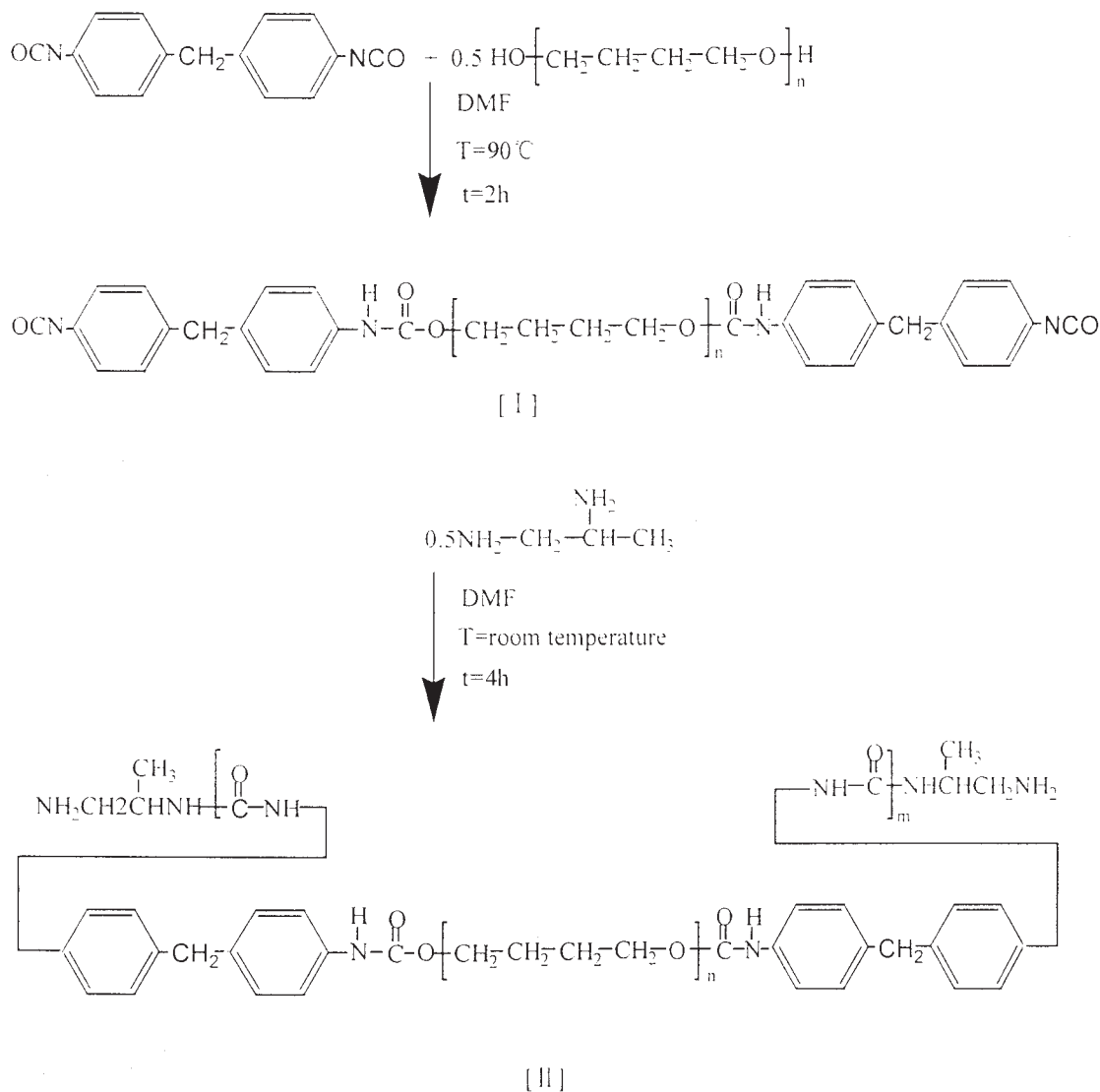
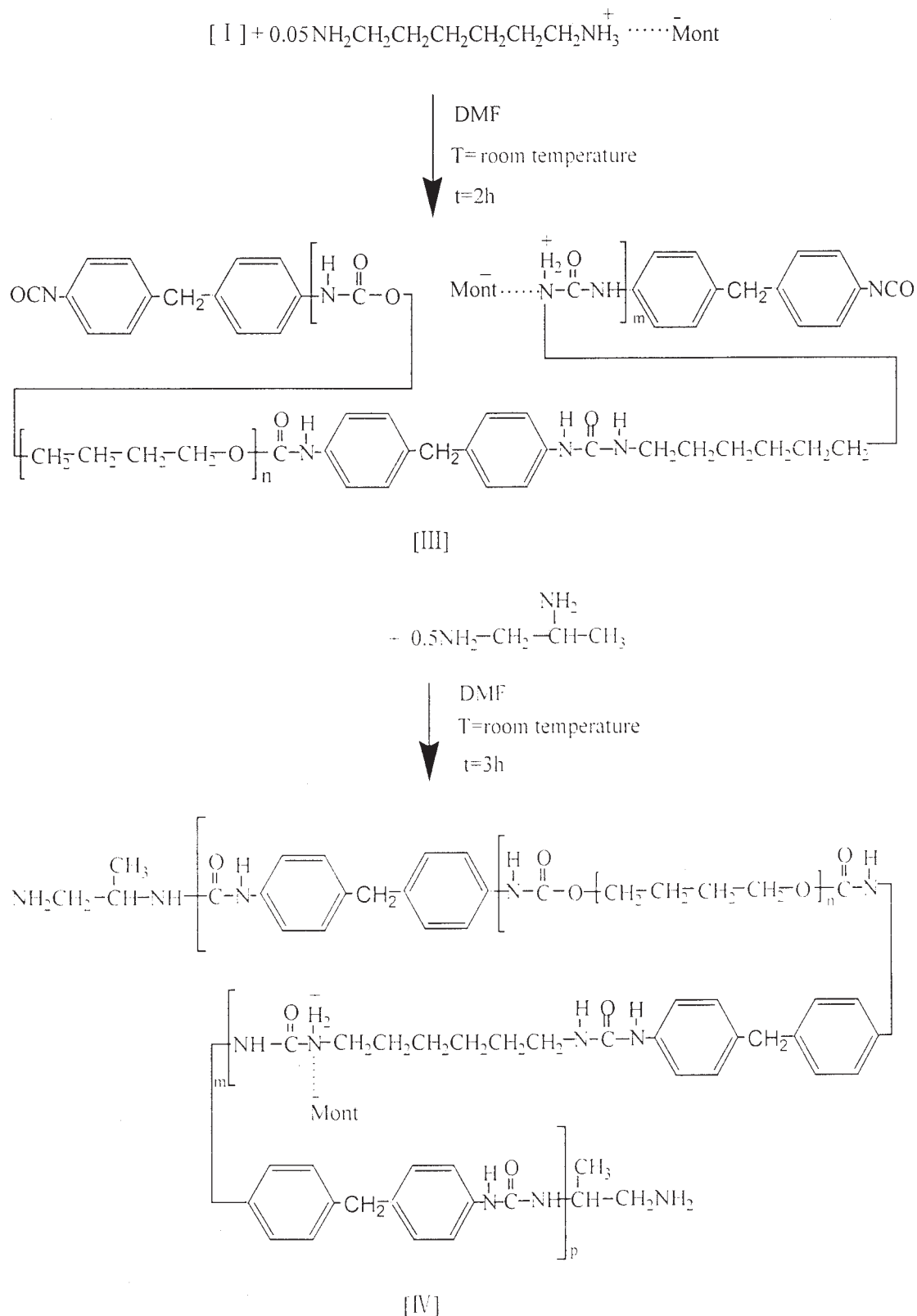**Scheme 1**   The reaction pattern that was followed to obtain the PU segments.

PTMEG reacted with MDI at a 0.5 molar ratio of PTMEG/MDI to form isocyanate-terminated pre-PU. In the second step a stoichiometric amount of 1,2-diaminopropane was used as a chain extender to produce PU. Correspondingly, as reported in Scheme 2, O-MMT was used as a chain extender to produce O-MMT/PU nanocomposites in the second step. Finally, in the third step of the reaction 1,2-diaminopropane was added; lead to the formation of the O-MMT/PU nanocomposites with the O-MMT content varying regularly from 0 to 50 wt %.

Structural characterization

The XRD patterns of the MMT and the O-MMT are shown in Figure 1. The first diffraction peaks at 2θ = 7.04 and 6.30°, corresponding to a spacing of MMT and O-MMT platelets of 1.255 and 1.403 nm, respec-

tively, indicated that the silicate layer galleries in the MMT were intercalated by 1,2-diaminopropane. The second diffraction peaks were at 2θ = 8.38° and the peak of MMT was weaker than that of O-MMT, indicating that the silicate layer galleries in the MMT were also intercalated at 2θ = 8.38°. The X-ray patterns of PU, PU5, PU10, PU20, PU30, and PU40 are shown in Figure 2. It is obvious that in the XRD patterns of PU/clay nanocomposites the peaks at 2θ = 6.30 and 8.38° were all totally absent. Such results suggested the exfoliation of the clay platelets in the polymeric matrix.[24–30]

Therefore, it can be concluded that the reaction scheme adopted gave rise to nanocomposites in which the silicate layers was intercalated (or exfoliated). When the clay weight fraction reached high content (O-MMT = 40.0 wt %), the MMT platelets were dispersed in the polymer matrix.

$$[\ \text{I}\ ] + 0.05\,\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{+}{\text{NH}}_3 \cdots\cdots \overset{-}{\text{Mont}}$$

DMF

T= room temperature

t=2h

[III]

$$-\ 0.5\,\text{NH}_2{-}\text{CH}_2\overset{\underset{|}{\text{NH}_2}}{-}\text{CH}{-}\text{CH}_3$$

DMF

T=room temperature

t=3h

[IV]

Scheme 2 The reaction pattern that was followed to obtain the PU/clay segments.

The number-average molecular weight (M_n) and polydispersity (D) of PU, O-MMT/PU nanocomposites, and recovered PU from organoclay/PU nano-composites at different chain extender ratios are given in Figure 3. It was found that the M_n and D values were strongly affected by the addition of O-MMT.
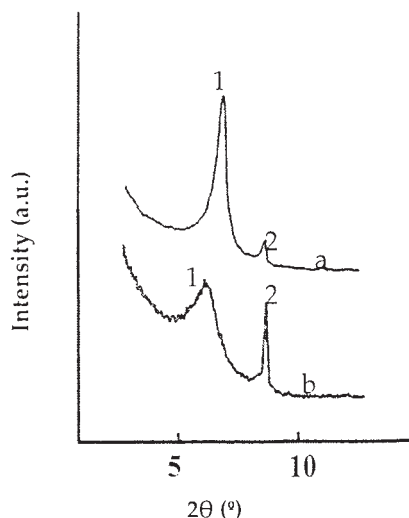
Figure 1 XRD patterns of (a) montmoriilonite and (b) organomodified montmorillonite.

Compared to the pure PU, the M_n and D of 1%, 5%, and 8% O-MMT/PU showed only a slight change at different chain extender ratios. In addition, the M_n values of those nanocompsites were higher than that of pure PU. Such results suggested that the mechanical properties of 1%, 5%, and 8% O-MMT/PU nanocomposites were better than that of pure PU. The thermal properties of those nanocompsites were higher than that of pure PU[31] and are presented and discussed in the following.

Physical properties

DSC study

The thermal properties of pure PU and O-MMT/PU nanocomposites were studied by DSC, and these results are shown in Table I. The glass-transition temperatures of the O-MMT/PU nanocomposites were between −58 and −61°C, being nearly identical to that of pure PU at −61.5°C (Table I). The effect of O-MMT dispersed on the free volume of PU was insignificant in influencing the glass-transition temperature of pure PU. The pure PU exhibited two broad endothermic transitions at higher temperature (endo 1 and endo 2) and a tiny exothermic transition high (100°C). The O-MMT/PU nanocomposites had only one broad endothermic transition (endo 1) at higher temperature than the pure PU (endo 1). This trend might be explained by the idea that there were two phases in the polymer matrix. Endo 1 in the pure PU identified with the disruption of soft segment/hard segment bonds or disruption of short-range order within the hard segment microdomains. In addition, endo 2 was related to the breakup of interurethane hydrogen bonds.[32] When O-MMT was used as a chain extender to replace

a part of the 1,2-diaminopropane, the MMT was dispersed in the polymer matrix. The chain motions of the polymer molecules in these silicate layers were barred and limited. The crystallizability of O-MMT/PU nanocomposites was reduced and endo 2 disappeared in the O-MMT/PU nanocomposites.[33] These results can be interpreted by the intercalative behavior of the polymer as shown in Figure 2.

TGA study

The TGA of pure PU and O-MMT/PU nanocomposites is shown in Figure 4. In the temperature range from 250 to 650°C, the O-MMT/PU nanocomposites displayed higher thermal resistance than that of pure PU (Fig. 4). The explaination for this could be that the chain motions of the polymer molecules in these silicate layers were barred and limited, and the thermal properties of the O-MMT/PU nanocomposites increased. The more polymer molecule chains that were attached in the intercalation, the higher the thermal capability was.[34]

Stress–strain behavior

The experimental results of the effect of the O-MMT content on the tensile mechanical properties of the nanocomposites are shown in Figure 5. It was found that the O-MMT content had a remarkable effect on the mechanical properties of the nanocomposites. As shown in Figure 5, both the tensile strength and the elongation at break of the O-MMT/PU increased with the increasing of O-MMT content in the range of 1–5 wt %. When the O-MMT content was in the range of
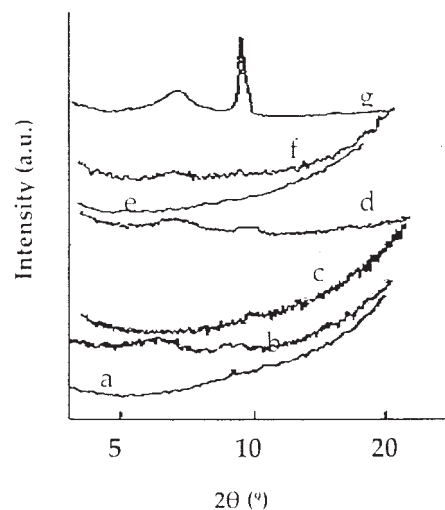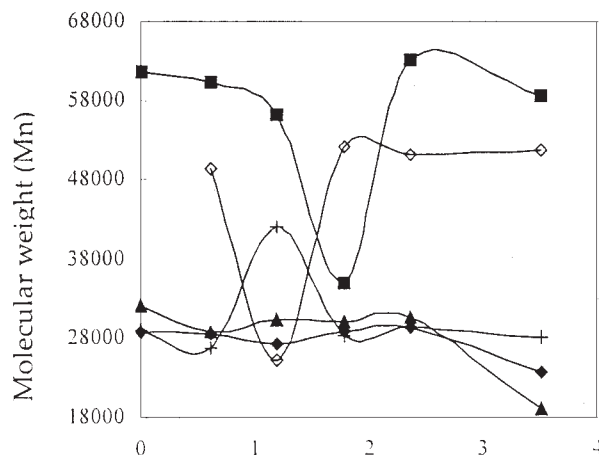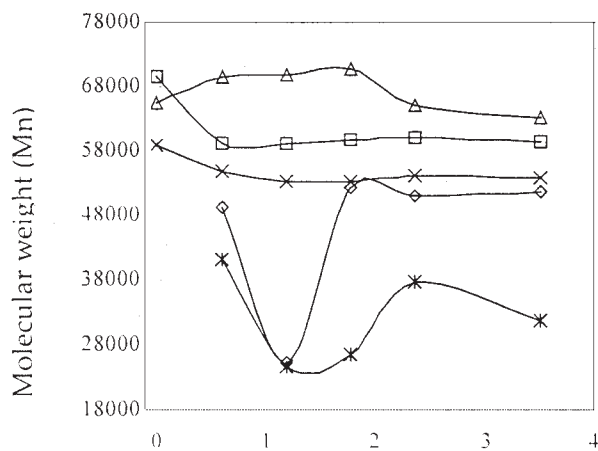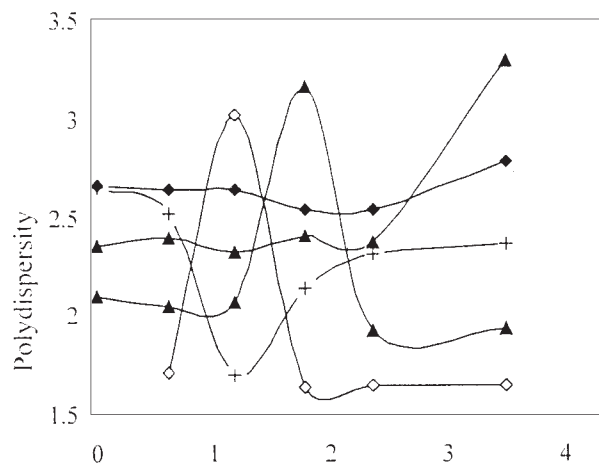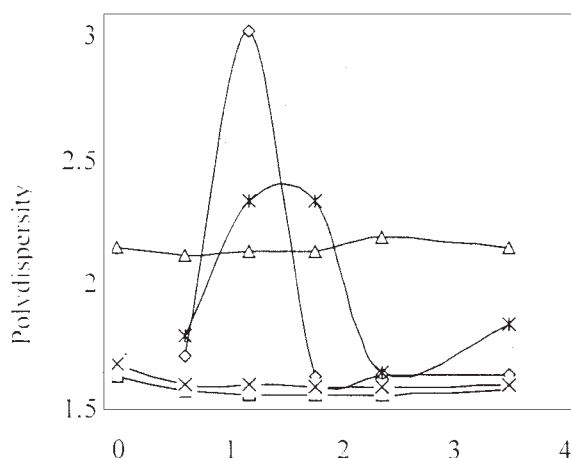

Figure 2 XRD patterns of PU and O-MMT/PU nancomposites: (a) PU, (b) 5% O-MMT/PU, (c) 10% O-MMT/PU, (d) 20% O-MMT/PU, (e) 30% O-MMT/PU, (f) 40% O-MMT/PU, and (g) 50% O-MMT/PU.

a

b

Figure 3 (a) The number-average molecular weight (M_n) and (b) polydispersity of PU and O-MMT/PU at different chain extender ratios.

1–8%, the tensile strength and the elongation at break were higher than that of pure PU. Compared to the pure PU, the tensile strength and the elongation at break of the 5 wt % O-MMT content were increased by more than 157 and 145%, respectively. When the O-MMT content was higher than 5 wt %, both the tensile strength and the elongation at break of the O-MMT/PU decreased.

All of these results could be explained by the M_n of the pure PU and the nanometer O-MMT layers. When

the O-MMT content was in the range of 1–8%, the M_n of the O-MMT/PU nanocomposites was higher than that of pure PU and the nanocomposites possessed better mechanical properties. When the O-MMT content attained the range of 8–40 wt %, the M_n of the O-MMT/PU nanocomposites was lower and the D of O-MMT/PU nanocomposites was higher than that of pure PU and the tensile strength and the elongation at break of the O-MMT/PU decreased.[35] When the O-MMT content was higher than 40 wt %, the O-MMT

TABLE I
**Endothermic Transitions and Water Absorption of Pure PU and O-MMT/PU Nanocomposites**

| O-MMT content (wt %)	$T_g{}^a$ (°C)	Endo 1 peak T (°C)	Endo 2 peak T (°C)	Water absorption (%)
0 (pure PU)	−61.5	2.61	42.18	4.92
1	−61.0	9.77	—	3.37
5	−58.0	10.40	—	3.38
10	−60.0	13.59	—	3.76
20	−60.0	12.08	—	2.12
30	−61.0	9.46	—	2.04
40	−60.0	8.92	—	2.83
50	−60.5	9.77	—	3.15

^{a} Glass-transition temperatures.

began to aggregate (as suggested by the XRD in Fig. 2), leading to a further reduction of the tensile strength and the elongation at break of the nanocomposites.

Water absorption properties

The water absorption results of PU and the O-MMT/PU nanocomposites are given in Table I. They show that the water absorption of O-MMT/PU nanocomposites were all slight lower than that of pure PU. This phenomenon could be explained by the fact that the process of water absorption on O-MMT/PU was controlled by two competing factors. The first one is the MMT itself is water rich (about 8–10% water content); hence, the water absorption ratio of the O-MMT/PU nanocomposites will increase. The second factor is that, compared to pure PU, the O-MMT dispersed in the PU matrix at nanometer scale can in-
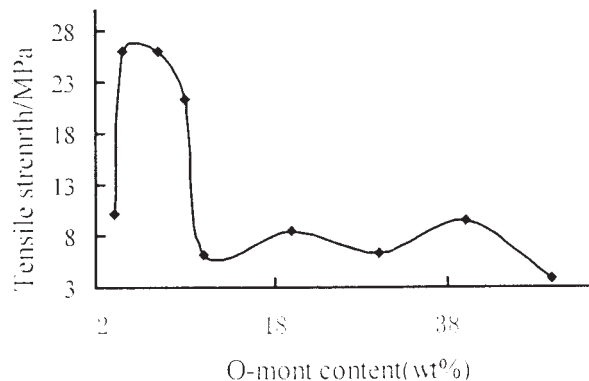
(a)
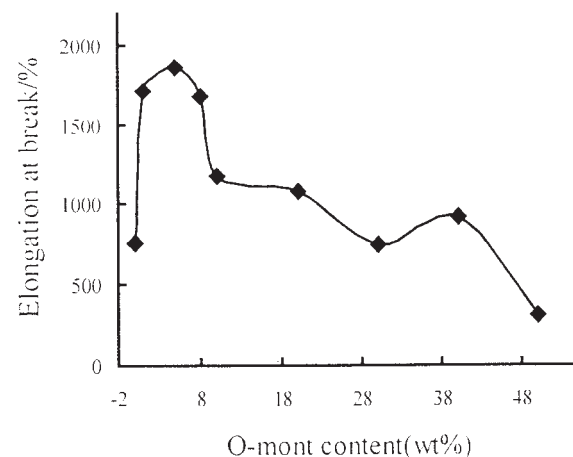
(b)

Figure 5 The effect of the O-MMT content on the tensile mechanical properties of O-MMT/PU nanocomposites.
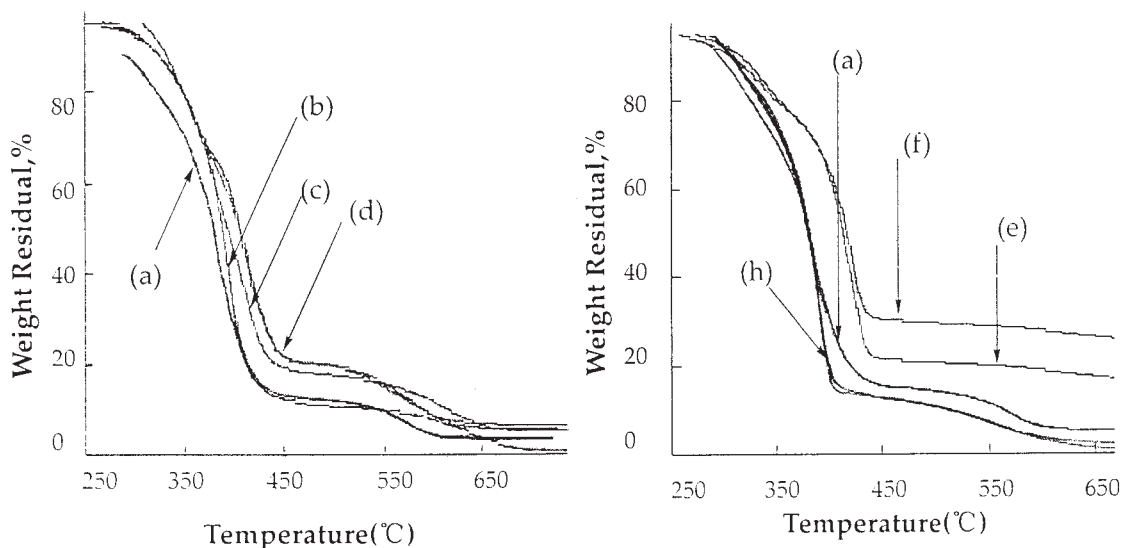

Figure 4 Dynamic TGA thermograms of PU and O-MMT/PU nanocomposites in a nitrogen environment (a) PU, (b) 1% O-MMT/PU, (c) 5% O-MMT/PU, (d) 8 and 10% O-MMT/PU, (e) 20% O-MMT/PU, (f) 30% O-MMT/PU, and (h) 40 and 50% O-MMT/PU.

crease the mean free path of water molecules to pass through the network of O-MMT/PU,[24] and result in the decrease of the water adsorption of the composites. Because of the lower water absorption for all O-MMT/PU nanocomposites than that of pure PU, it seems that the second factor would play the dominant role in the water adsorption of O-MMT/PU nanocomposites.

CONCLUSION

Novel polyether PU/clay nanocomposites were synthesized successfully with organicly modified MMT as chain extenders, and it was observed that the O-MMT was completely exfoliated in the PU matrix even at very high content (40 wt %). The structures of PU were affected by the presence of the silicate layers in these nanocomposites, as evidenced by their molecular weight and glass transition. The mechanical properties of these O-MMT/PU nanocomposites were strongly influenced by the content of O-MMT, and the tensile strength and the elongation achieved maximums when the O-MMT content was 5%. In addition, the water absorption of O-MMT/PU nanocomposites in the range of the 1–40 wt % O-MMT content were all slightly lower than that of pure PU. The thermal properties of O-MMT/PU nanocomposites were also higher than the pure PU.

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