

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

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ABSTRACT: A novel polyether polyurethane/clay nanocomposite was synthesized using polytetramethyleneglycol (PTMEG), 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylenediamine, and modified Na⁺-montmorillonite. Here, organic-modified montmorillonite (O-MMT) was formed by applying 1,6-hexamethylenediamine as a swelling agent to treat Na⁺-montmorillonite. The X-ray analysis showed that exfoliation occurred for the higher O-MMT content (40 wt %) in the polymer matrix. Mechanical analysis indicated that when the O-MMT was used as chain extender to replace a part of 1,2-diaminopropane to form

PU/clay nanocomposites, the strength and strain-at-break of the polymer were enhanced with increased content of O-MMT in the matrix. When the O-MMT content attained about 5%, the tensile strength and elongation at break were over two times that of the pure PU. The thermal stability and the glass-transition of O-MMT/PU nanocomposites also increased with increasing the O-MMT content. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 534–541, 2004

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

INTRODUCTION

A nanocomposite is a composite material having more than one solid phase with a dimension in the 1 ~ 20nm 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 or layered silicates have been developed. Because of the much stronger interfacial forces between the nanometer-sized domains, such nanocomposites exhibit many better physical properties, such as thermal, mechanical, and barrier properties, than those of conventional composites.

PU/clay nanocomposites were first reported by Pinnaia and colleagues.^{20–27} The authors focused on the compatibility between organic-clay and polyols, and found that montmorillonite 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 and nanolayer exfoliation was achieved, and the me-

chanical properties and thermal stability of PU/clay nanocomposites were increased.

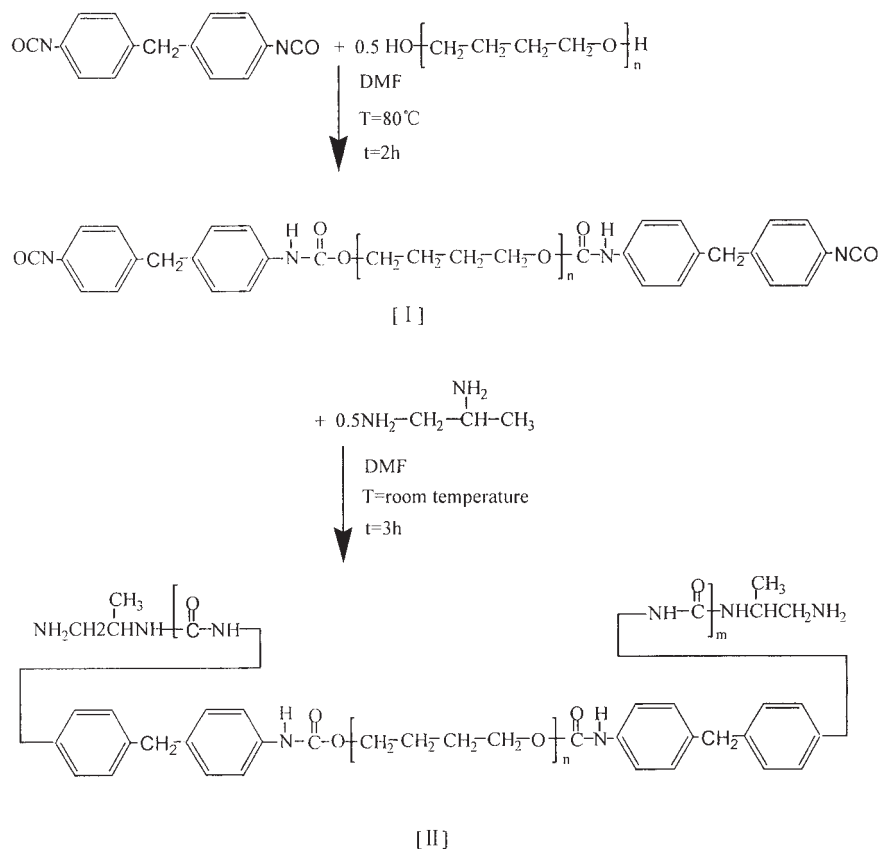
The aim of this work was to design a new polyether polyurethane nanocomposite based on organic-modified montmorillonite (O-MMT) employed as chain extender in the synthetic process. In our procedure, 1,6-hexamethylenediamine (carbon number < 12, with two -NH₂ groups) was used as a swelling agent to treat Na⁺-montmorillonite and was intercalated into clay nanolayers to form the O-MMT. Then, the O-MMT was used as a part of the chain extender replacing a part of 1,2-diaminopropane to form PU/clay nanocomposites. Our research interest focused on the effect of the O-MMT content upon the mechanical properties of the nanocomposites. Tensile stress, elongation at break, thermal stability, glass-transition, and water absorption of the O-MMT/PU nanocomposites were all investigated.

EXPERIMENTAL

Materials

Montmorillonite (Zhangjiako Qinghe Chemical Factory, China) with a cationic exchange capacity of 78.6meq/100g and 1,6-hexamethylenediamine (Tianjing Chemical Reagent Co., China) were used as received. 4,4'-Diphenylmethane diisocyanate (MDI, Yantai Wanhua Chemical Reagent Co., China) and polytetramethylene glycol (PTMEG, Mn = 2000, Du-

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Scheme 1 Reaction pattern followed to obtain the PU segments.

pont) were dehydrated under vacuum at 60°C for 24 h. Dimethylformamide (DMF, 99%, Tianjing Chemical Reagent Co.) and 1,2-diaminopropane (Shanghai Chemical Reagent Co., China) were dried over calcium hydride for two days and then were distilled under vacuum.

Preparation of organophilic clay (O-Mont)

Montmorillonite was first screened with a 300-mesh sieve to remove impurities. 20g of the screened montmorillonite was gradually added to a previously prepared solution of 10.6g Na_2CO_3 dissolved in $200 \times 10^{-3} \text{ m}^3 \text{ H}_2\text{O}$ at 70°C, and the resultant suspension was vigorously stirred for 24 h. Then the treated montmorillonite was filtered and washed by de-ionized water until complete removal of CO_3^{2-} ions, ensured by titrating with 0.1N CaCl_2 . The filter cake was then dried at 70°C for 24 h in vacuum, ground, and screened with a 300-mesh sieve to obtain the Na-montmorillonite.²⁸ 10g of the screened Na-montmorillonite was gradually added to a previously prepared solution of 1,6-hexamethylenediamine 12.5g dissolved in $1000 \times 10^{-3} \text{ m}^3$ of 0.01N HCl at 70°C, and the resultant suspension was vigorously stirred for 6 h. Then, the white precipitate formed was isolated by

filtration, suspended in $400 \times 10^{-3} \text{ m}^3$ of hot water, and stirred for 2 h. To ensure complete removal of chloride ions, the precipitate was washed repeatedly until no further formation of AgCl was detected after addition of 0.1N AgNO_3 to the washing water. The product was finally filtered and dried in vacuum 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 polyurethane (Scheme 1)

5g of 4,4'-Diphenylmethane diisocyanate (MDI) and 19.5g of polytetramethylene glycol (PTMEG) at a molar ratio of 2 : 1 were dissolved in DMF solvent, then the whole solution was mixed under nitrogen atmosphere for 2 h at 90°C to form a prepolymer. Then, 0.74g of 1,2-diaminopropane was gradually added to the prepolymer with vigorous stirring at room temperature for 4 h to complete the reaction. The PU films were formed by casting the solution onto glass plates and then removing the solvent in vacuum at 70°C for 36 h.³⁰

Preparation of PU/clay nanocomposites (Scheme 2)

Following the procedure of synthesizing PU prepolymer as described in the previous section, different

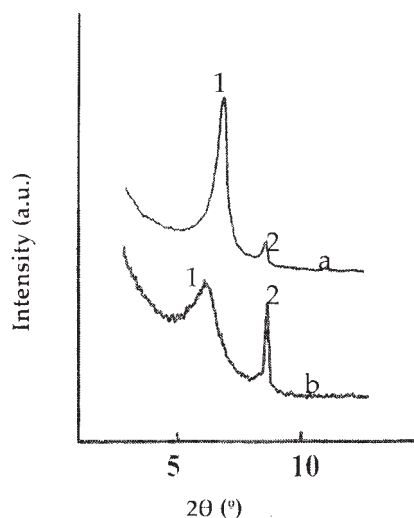


Figure 1 XRD patterns of (a) montmorillonite, and (b) organomodified montmorillonite.

tography (GPC) system with DMF as the solvent. The calibration curves for GPC were obtained by using polystyrene as standards.

Differential scanning calorimetry (DSC) data were obtained with a DSC822E under N_2 atmosphere with a heating rate of $10^\circ C \text{ min}^{-1}$. The thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer 7 Series thermal analysis system at a scan rate of $10^\circ C \text{ min}^{-1}$ in a nitrogen atmosphere. Tensile properties of the sample were tested with an Instron mechanical tester (model DY-35) at a crosshead speed of 0.5 m min^{-1} . The I-shaped specimens were prepared with $4 \times 10^{-3} \text{ m}$ in width, $16 \times 10^{-3} \text{ m}$ in length, and $2 \times 10^{-4} \text{ m}$ in thickness. For each datum point, five samples were tested, and the average value was taken.

The water absorption methods of pure PU and PU/clay nanocomposites was carried out according to the specifications of ASTM D570, and the test specimens were cut in the shape of $76.2 \times 25.4 \times 1 \times 10^{-3} \text{ m}$. The specimens were dried in vacuum at $80^\circ C$ for 24 h, cooled in a desiccator, and then immediately weighed with 0.001g precision to get the initial weight (W_0). Subsequently, the conditioned specimens were entirely immersed into a container of deionized water maintained at $25 \pm 0.2^\circ C$ for 24 h, taken out of the water, and the surface water on specimens was removed with a dry cloth. Then, the specimens were weighed immediately to get 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 simplified chemical structure of PU and O-MMT/PU are

shown. As shown in Scheme 1, in the first step, PTMEG reacts with MDI at a 2M ratio of PTMEG/MDI to form an isocyanate-terminated prepolyurethane. In the second step, 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 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, leading to formation of the O-MMT/PU nanocomposites with the O-MMT content varying regularly from 0 to 50 wt %.

Structural characterization

The X-ray diffraction patterns of the montmorillonite and the O-MMT are shown in Figure 1. The first diffraction peaks at $2\theta = 7.04^\circ$ and 6.30° , corresponding to a spacing of montmorillonite and O-MMT platelets of 1.255 and 1.403 nm, respectively, indicate that the silicate layer galleries in the montmorillonite were intercalated by 1,6-hexamethylenediamine. The second diffraction peaks at $2\theta = 8.38^\circ$, the peak of montmorillonite weaker than that of O-MMT, could be explained by the fact that the silicate layer galleries in the montmorillonite were also intercalated by 1,6-hexamethylenediamine at $2\theta = 8.38^\circ$ and the silicate layer galleries in the montmorillonite were increased.

The X-ray patterns of PU, PU5, PU10, PU20, PU30, and PU40 are shown in Figure 2. It is clear that in the XRD patterns of PU/clay nanocomposites, peaks at $2\theta = 6.30$ and 8.38° were all totally absent. The situ-polymerization of 1,6-hexamethylenediamine and prepolymer form PU/clay nanocomposites in the silicate layers, and the silicate layers were larger. Such results

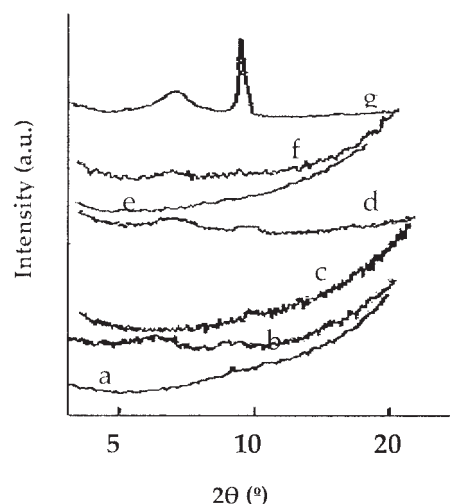


Figure 2 XRD patterns of PU and O-MMT/PU nanocomposites: (a) PU; (b) 5% O-MMT/PU; (c) 10% O-MMT/PU; (d) 20% O-MMT/PU; (e) 30% O-MMT/PU; (f) 40% O-MMT/PU; and (g) 50% O-MMT/PU.

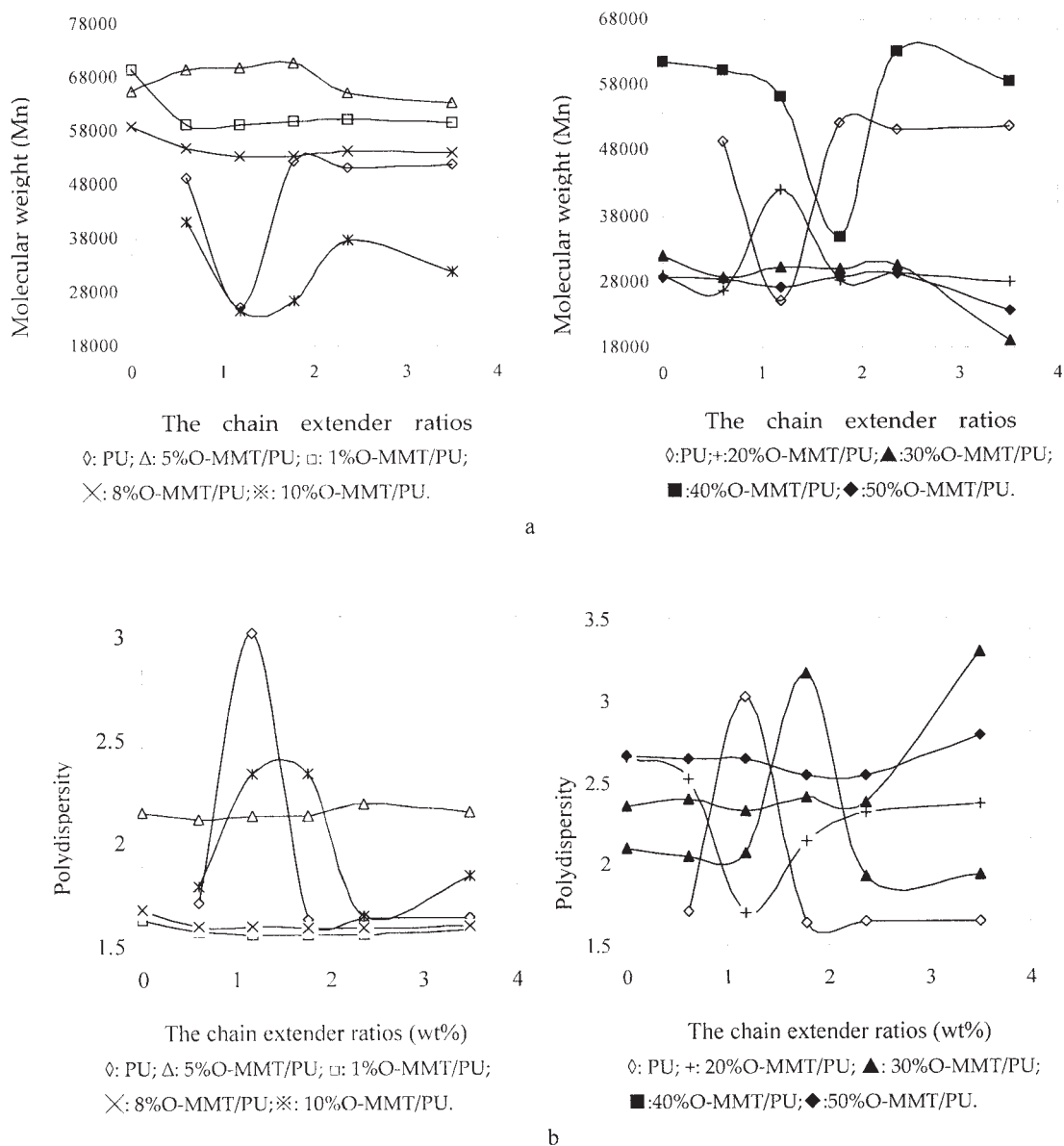


Figure 3 The molecular weight (Mn) and the polydispersity of PU and O-MMT/PU at different chain extender ratios: (a) the molecular weight (Mn); (b) the polydispersity.

suggest the exfoliation of the clay platelets in the polymeric matrix.^{24–30} When the clay weight fraction reaches high content (O-MMT, 40.0 wt %), the montmorillonite platelets were also dispersed in the polymer matrix.

The molecular weight (Mn) and polydispersity (D) of PU, O-MMT/PU nanocomposites, and recovered PU from organoclay/PU nanocomposites at different chain extender ratios are given in Figure 3. It was found that Mn and D were strongly affected by the addition of O-MMT. Compared to the pure PU, Mn and D of 1% O-MMT/PU, 5% O-MMT/PU, and 8% O-MMT/PU showed only a slight change at different chain extender ratios. Mn of those nanocomposites was higher than that of pure PU. Such results suggest

that the mechanical properties of 1% O-MMT/PU, 5% O-MMT/PU, and 8% O-MMT/PU nanocomposites would be better than those of pure PU, and the thermal properties of those nanocomposites would be higher than those of pure PU.³¹ Results are presented and discussed in the following.

Physical properties

Differential scanning calorimetry

The thermal properties of pure PU and O-MMT/PU nanocomposites were studied by DSC, and these results are shown in Table I. In Table I, the glass transition temperatures of O-MMT/PU nanocomposites

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.

were between -58 and -61.0°C, being nearly identical to that of pure PU at -61.5°C. The effect of O-MMT, dispersed in the free volume of PU, was insignificant in influence on the glass transition temperature of pure PU. The pure PU exhibited two broad endothermic transitions at higher temperatures (Endo 1 and Endo 2) and a tiny exothermic transition at 100.0°C. O-MMT/PU nanocomposites had only one broad endothermic transition (Endo 1) at a higher temperature than that of the pure PU (Endo 1). This trend might be explained as two phases in the polymer matrix: Endo 1 in the pure PU, identified with disruption of soft segment/hard segment bonds or disruption of short-range order within the hard segment microdomains; and Endo 2, which was related to the breakup of interurethane hydrogen bonds.³² When O-MMT was used as chain extender to replace a part of the 1,2-diaminopropane, the montmorillonite was dispersed in the polymer matrix. The chain motions of polymer molecules in these silicate layers were barred and limited. The crystallizability of O-MMT/PU nanocomposites was reduced, and Endo 2 disappeared for O-MMT/PU nanocomposites.³³ These results can be in-

terpreted by the intercalative behavior of polymers as shown in Figure 2.

TGA analysis

The TGA analysis of pure PU and O-MMT/PU nanocomposites is shown in Figure 4. In Figure 4, in the temperature range from 250 to 650°C, the O-MMT/PU nanocomposites displayed higher thermal resistances than that of pure PU. This could be explained as that the chain motions of polymer molecules in these silicate layers were barred and limited, and therefore thermal properties of O-MMT/PU nanocomposites increased: the more polymer molecule chains attached in the intercalation, the higher was the thermal capability.³⁴

Stress-strain behavior

The experimental influence of the O-MMT content on the tensile mechanical properties of the nanocomposites is shown in Figure 5. It was found that the O-MMT content had a remarkable effect on the mechanical

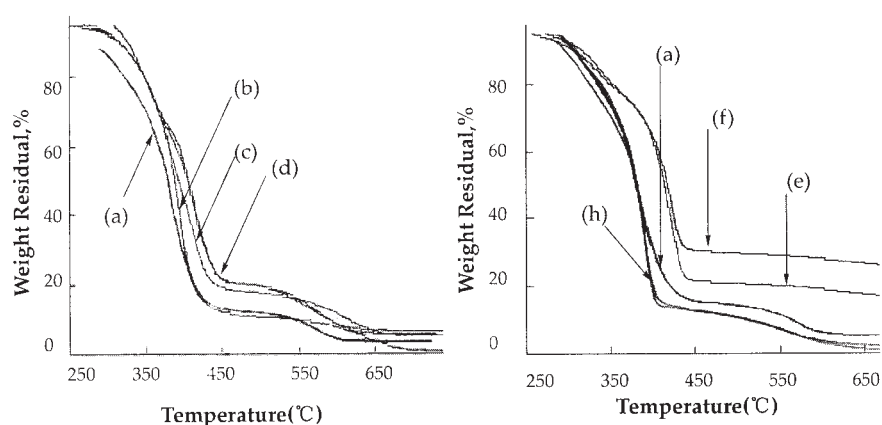


Figure 4 Dynamic TGA thermograms of PU and O-MMT/PU nanocomposites in a nitrogen environment: (a) PU; (b) 1% O-MMT/PU; (c) 5% O-MMT/PU; (d) 8 and 10% O-MMT/PU; (e) 20% O-MMT/PU; (f) 30% O-MMT/PU; (h) 40 and 50% O-MMT/PU.

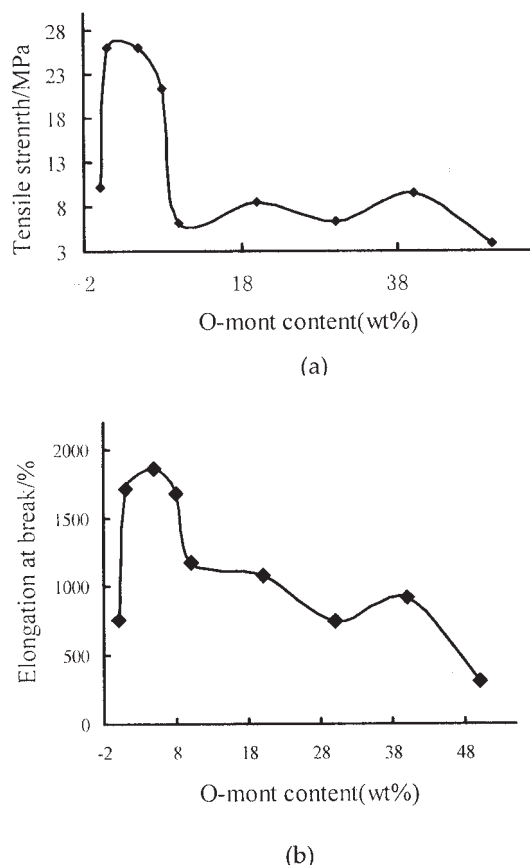


Figure 5 Effect of the O-MMT content on the tensile mechanical properties of O-mont/PU nanocomposites.

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 increased O-MMT content in the range of 1–5 wt%. When O-MMT content was in the range of 1–8%, the tensile strength and the elongation at break were higher than those 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 M_n of the pure PU and the nanometer O-MMT layers. When the O-MMT content was in the range of 1–8%, M_n of 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%, M_n of O-MMT/PU nanocomposites was lower and D of O-MMT/PU nanocomposites was higher than for pure PU; therefore, 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 began to aggregate (as suggested by the XRD in Fig. 2); such

would lead to a further reduction of the tensile strength and the elongation at break of the nanocomposites.

The water absorption results of PU and O-MMT/PU nanocomposites are given in Table I. It shows that the water absorption of O-MMT/PU nanocomposites were all slightly lower than that of pure PU.^{24,34,36} Detailed research on these phenomena is ongoing.

CONCLUSION

Novel polyether polyurethane/clay nanocomposites were synthesized successfully with organic-modified montmorillonite as chain extender, and it was observed that the O-MMT was completely exfoliated in such a 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 maxima when the O-MMT content was 5%. Additionally, the water absorptions 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 those of the pure PU.

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