

Synthesis and Characterization of Elastomeric Polyurethane/Clay Nanocomposites

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Received 12 September 2000; accepted 12 October 2000

ABSTRACT: An elastomeric polyurethane/clay (PU/clay) nanocomposite based on poly(propylene glycol) (PPG), glycerol propoxylate, and toluene-diisocyanate (TDI) was synthesized by intercalative polymerization technology. The results of wide angle X-ray diffraction (WAXD) studies showed that the gallery distance of the clay in the hybrid was enlarged from 1.9 to 4.5nm or more. Introducing clay in the PU matrix resulted in an increase in both the tensile strength and elongation at break. When the clay content reached about 8%, the tensile strength and elongation at break were two times and five times respectively to that of the pure PU. In addition, the clay intercalative route to the nanocomposite synthesis also effected the thermal properties of the nanocomposites. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1444–1448, 2001

Key words: nanocomposite; polyurethane; montmorillonite; intercalative polymerization

INTRODUCTION

Polyurethane (PU) is a versatile polymeric material, which can be tailored to meet the diversified demands of modern technologies such as coatings, adhesives, reaction injection molding plastics, fibers, foams, rubbers, thermoplastic elastomers, and composite. Increasing the strength of PU elastomers without sacrificing its high elongation at break is an important object for elastomeric polyurethane development. The mechanical properties of PU can be modified either by varying PU chemical structure, resulting from step-growth polymerization of isocyanate resins with polyols, or by dispersing inorganic or organic fillers into the pure PU. A wide variety of fillers, including

tale, mica, and wollastonite, have been applied in PU formulation to reduce cost and to increase the rigidity.¹ However, filler additions frequently result in a reduction in the elongation at break. Elastomeric PU/clay nanocomposites was first reported by Pinnavaia et al.² They focused on compatibility between organo-clay and polyols. They found that the montmorillonite clay exchanged with long chain onium ions (carbon number ≥ 12) and had a good compatibility with several polyols commonly used for synthesizing polyurethane. Zilg et al.³ reported that PU nanocomposites containing synthetic fluoromica could simultaneously increase their tensile strength and elongation at break. Chen et al.^{4,5} synthesized a novel segmental PU/clay nanocomposite via poly(ϵ -caprolactone)/clay (PCL/clay) route. They reported that the mechanical properties increased by introducing a small amount of PCL/clay in the composite. However, the composite was transformed from an elastomer to a plastic as the amount of PCL/clay in the composite increased.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 59833130.

Journal of Applied Polymer Science, Vol. 82, 1444–1448 (2001)
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In the present paper, an alkylammonium modifying montmorillonite, a natural clay, was intercalated into the polyols to prepare the elastomeric PU/clay nanocomposite. Our interesting research focused on effects of the clay content and route of clay compounding with polyols on the mechanical properties of the nanocomposites. Three types of polyol with different molecular weights and functionalities were used for preparing PU and PU/clay nanocomposites. The ratio of the polyols was kept constant to ensure the same chemical structure of the PU and PU/MMT nanocomposites. It was found that the mechanical properties had maximum values with the clay content when it reached 8 wt %. The maximum tensile stress and the maximum elongation at break were increased by two times and five times, respectively. The WAXD patterns showed that the glycerol propoxylate had better compatibility with the organo-clay than poly(propylene glycol). This corresponded to the formation of a nanocomposite from the clay compounding with glycerol propoxylate that, in turn, resulted in the best mechanical properties. The molecular weight of poly(propylene glycol) seemed to have no obvious effect on the intercalative behavior as explained by WAXD results. However, the nanocomposites from the clay compounding with the low molecular weight polyol route showed better mechanical properties than that from the clay compounding with the high molecular weight polyol route.

EXPERIMENTAL

Materials

Poly(propylene glycol) (PPG1, $\overline{M}_n = 1000$, and PPG2, $\overline{M}_n = 2000$, made by Beijing Chemical Reagent Co.), glycerol propoxylate (GPO3, $\overline{M}_n = 3000$, Made by Dow Chemical Co.), toluenediisocyanate (TDI; made by Beijing Chemical Reagent Co.), Na-montmorillonite clay (the cation exchange capacity, CEC = 90–100 mmol/100 g, with a particle size of about 40–70 μm , made by Zhangjiakou Qinghe Chemical Factory.) were used.

Preparation of Organo-clay

Five grams Na-montmorillonite was dissolved in 95 g distilled water under a vigorous stirring condition to form a uniformly dispersed solution, and then 3 g hexadecyl-octadecyl trimethylammo-

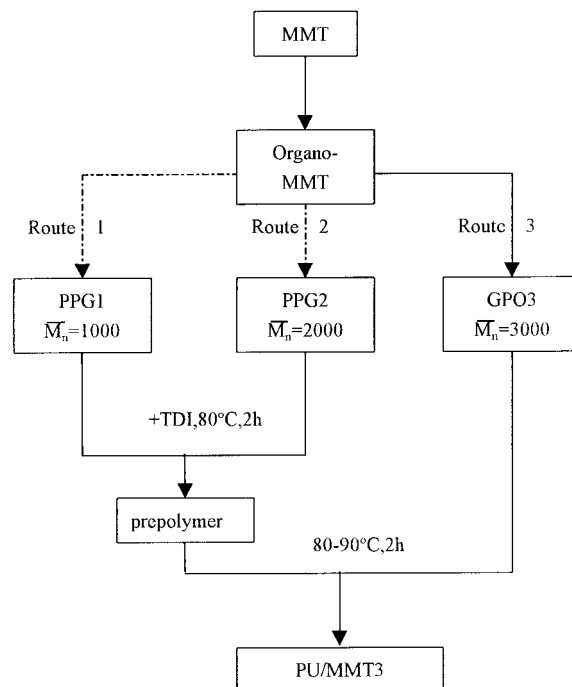


Figure 1 A schematic diagram of clay compounding route for synthesis of PU/MMT nanocomposites.

nium chloride (intercalative reagent) was added to the solution and then stirred for 1 h at 80°C. The dispersion solution was filtered and repeatedly washed with distilled water to remove the excess intercalative reagent—i.e., until there was no white precipitate observed in the wash water testing by a 0.1 mol/L AgNO_3 solution. The product was then vacuum-dried to a constant weight and ground into powder (diameter about 40–60 μm) to get the organo-montmorillonite (organo-MMT).

Synthesis of Pure PU

The elastomeric pure PU was synthesized by a two-stage route (Fig. 1). In the first stage, PPG1 and PPG2 were degassed under vacuum (<2 mmHg) at 110°C for 1 h. A mixture of PPG1 and PPG2 polyols was then reacted with an excess TDI at 80°C for 2 h to form an isocyanate-terminated PU prepolymer. In the second stage, GPO3 was degassed for 2 h. The prepolymer was then poured into GPO3 at room temperature. The mixture was blended uniformly and poured into the glass molds (100 × 70 × 1 mm and 70 × 50 × 5 mm) and cured at 85°C for 10 h under N_2 atmosphere to get the PU sample.

Synthesis of PU/Clay Nanocomposites

The synthesis of PU/MMT3 is shown in Figure 1. A designed amount of the organo-MMT was intercalated with GPO3 by stirring for 2 h in a sealed container to obtain a stable polyol organo-MMT dispersion. The degassed organo-MMT dispersion was mixed with the PU prepolymer, then cured under the same conditions as mentioned before to obtain the PU/MMT3 nanocomposite. In order to investigate the effect of the intercalative route between organo-MMT and the three polyols on the nanocomposites, the organo-MMT was also intercalated with the PPG1 and PPG2 respectively. The synthesis procedures shown in Figure 1 were used to synthesize the PU/MMT1 and PU/MMT2 nanocomposites. The polyols of PPG1, PPG2, and GPO3 were used in the constant ratio to ensure all the nanocomposites samples had the same chemical structure.

Characterization

A Japan made X-ray diffractometer D/max-RB was used to characterize the intercalative behavior. The operation parameters were $\text{CuK}\alpha$ radiation at the generator voltage of 40 kV and current of 100 mA. The scanning rate was $8^\circ/\text{min}$ with intervals at 0.02° . The diffraction intensity was recorded automatically. The tensile tests were carried on an Instron-1122 testing machine according to the specifications of ASTM D882. Samples were cut to $100 \times 10 \times 1 \text{ mm}^3$ in size, and test at crosshead speed of 500 mm/min. The thermogravimetric analysis (TGA) was carried on a Perkin-Elmer 7 Series thermal analysis system at a scan rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

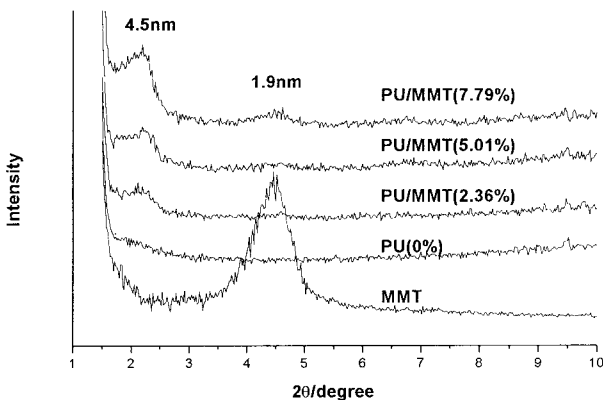


Figure 2 Effect of clay content on WAXD of organo-MMT, PU, and PU/MMT3 nanocomposites.

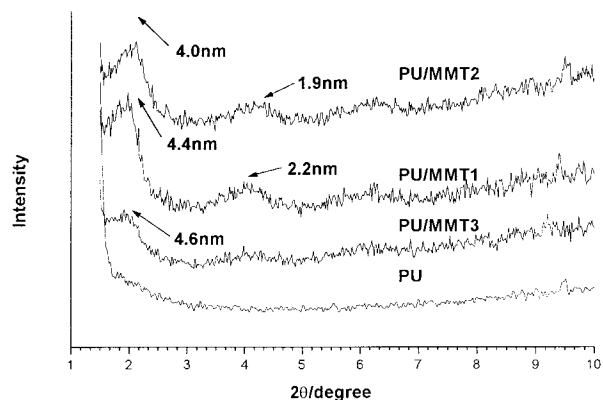


Figure 3 Effect of polyol molecular weight and functionality on WAXD of PU/MMT nanocomposite with a constant clay content of 5 wt %.

RESULTS AND DISCUSSION

Effect of Clay Content on X-ray Diffraction Behavior

The wide angle X-ray diffraction (WAXD) analysis of organo-MMT, pure PU, and the PU/MMT3 with different clay content are shown in Figure 2. The organo-MMT has a characteristic diffraction peak at $2\theta = 4.58^\circ$. Based on the Bragg equation, the interlayer distance of the clay is 1.9 nm. However, the characteristic peak of the clay in the PU/MMT nanocomposites shifts to the low angle of $2\theta = 1.95^\circ$ with an increase in the interlayer distance to 4.5 nm. These results showed that the PU molecules intercalate into the layers of the clay. Correspondingly, the peak relative intensity increased with increasing clay content in the range of 0–8 wt %. When the clay content higher than 8 wt %, the curve of PU/MMT (7.8%) in Figure 1 shows an additional broad peak at 1.9 nm, which implies that some of the clay is in the nanocomposite aggregate.

Effect of Polyol Molecular Weight and Functionality on Intercalative Behavior

In order to study the effect of molecular weight and functionality of the polyol on the intercalative behavior of the nanocomposites, a constant amount of the organo-MMT was intercalated with PPG1, PPG2, and GPO3 respectively to obtain PU/MMT1, PU/MMT2 and PU/MMT3 nanocomposites. Figure 3 shows that the WAXD patterns of the PU/MMT1 and PU/MMT2 nanocomposites are more complex than that of the PU/MMT3.

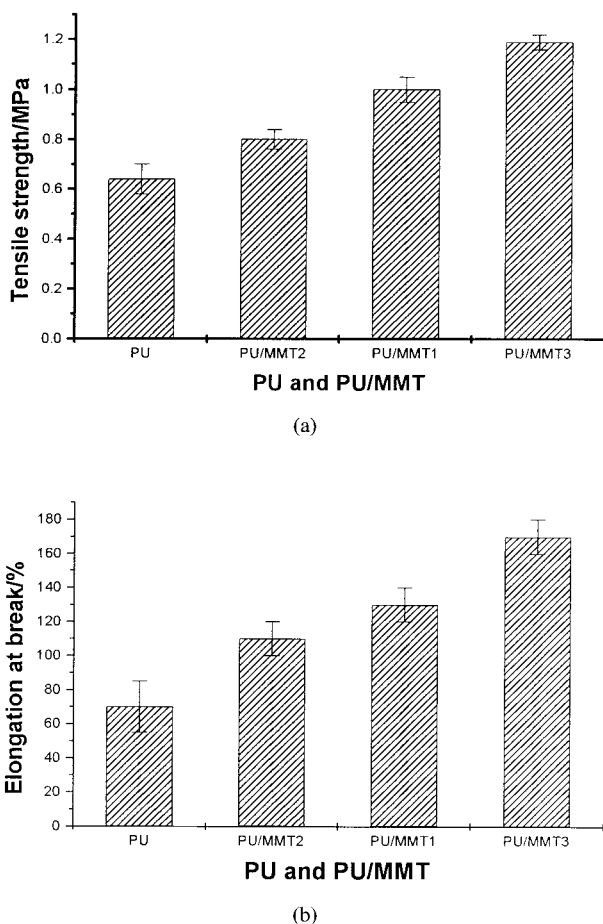


Figure 4 Effect of clay compounding route on mechanical properties of PU/MMT nanocomposites with a constant clay content of 5 wt %.

Besides the characteristic peaks at 4.6 and 4.0 nm, PU/MMT1 and PU/MMT2 have diffuse diffraction peaks at 2.2 and 1.9 nm, which is close to the diffraction peak of the organo-MMT. These results suggest that the GPO3 has superior compatibility with organo-clay and is more easily intercalated into the clay layers than PPG1 and PPG2. From this observation, we expect that the PU/MMT3 nanocomposite would have the best mechanical properties. Since the WAXD patterns of PU/MMT1 and PU/MMT2 nanocomposites show no obvious differences, it appears that the molecular weight of the polyols had no effect on the intercalative behavior.

Effect of Intercalative Way on the Mechanical Properties of the Nanocomposites

As shown in Figure 4, the route of the clay compounding obviously affects the mechanical prop-

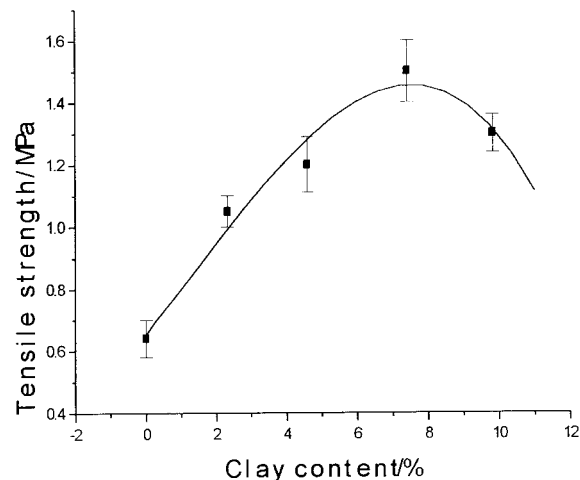
erties of the nanocomposites. Compared with the pure PU, the tensile strength of PU/MMT2 and PU/MMT1 nanocomposites increases by 25 and 55 [in Fig. 4(a)], respectively, and their elongation at break increases by 50 and 80% [in Fig. 4(b)], respectively. The maximum tensile properties were found for the PU/MMT3 nanocomposite, where its tensile strength is about twice that of pure PU and its elongation at break is about 2.5 times that of pure PU. These results can be interpreted by the intercalative behavior of the polyols as shown in Figure 3. There was a correlation between the mechanical properties (Fig. 4) and the WAXD results of the nanocomposites (Fig. 3). As the characteristic diffraction peak shifted to a smaller angle, the mechanical properties were found to increase in the nanocomposites.

Effect of Clay Content on the Mechanical Properties of the Nanocomposites

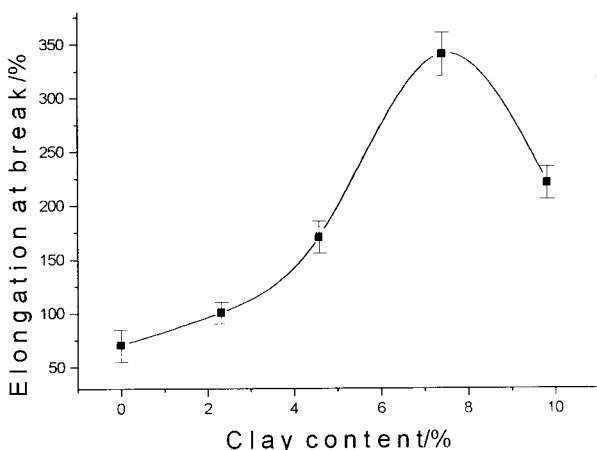
The experimental results of the clay content on the tensile mechanical properties of the nanocomposite are shown in Figure 5. It was found that the clay content had a remarkably effect on the mechanical properties. As shown in Figure 5, both the tensile strength and the elongation at break of the PU/MMT3 increased with the increasing of clay content in the range of 0–8 wt %. The maximum values of the mechanical properties were reached when the clay content was 8 wt %. When the clay content higher than 8 wt %, both the tensile strength and elongation at break of PU/MMT3 decreased. All of these results could be explained by the interaction between the pure PU and the nanometer clay layers. When the clay content was less than 8 wt %, the nanometer clay layers had a good compatibility and a strong interaction with the pure PU, when the clay content was higher than 8 wt %, the clay began to aggregate, as suggested by the WAXD in Figure 2.

TGA Analysis

The TGA results of the pure PU and the PU/MMT nanocomposites are given in Table I. The onset decomposition temperature (T_{OD}) of the PU/MMT nanocomposites and the pure PU are the same at about 315°C. However, The maximum decomposition temperature (T_{max}) of the PU/MMT3 is about 384°C, a little bit higher than that of pure PU at 377°C. Table I shows that the T_{max} of PU/MMT2 and PU/MMT1 are 379 and 380°C, respectively, which are slightly lower than that of



(a)



(b)

Figure 5 Effect of the clay content on the tensile mechanical properties of PU/MMT3 nanocomposites.

PU/MMT3. Therefore, It was found that the PU/MMT3 nanocomposites produced by route 1 not only had the best mechanical properties but also good thermal stability.

CONCLUSION

A PU/clay elastomeric nanocomposite has been successfully synthesized by an intercalative poly-

Table I The TGA Results of PU and PU/MMT (5 wt %) Nanocomposites

PU and PU/MMT	T_{OD} (°C)	T_{max} (°C)
PU	315.8	377.0
PU/MMT2	315.0	379.1
PU/MMT1	315.2	380.9
PU/MMT3	315.5	384.6

merization route. It has been found that the nanocomposites have maximum mechanical property values with the clay content. When the clay content reaches about 8 wt %, the tensile strength and the elongation at break of the PU/clay nanocomposite are increased by two and five times that of pure PU, respectively. The route of the clay compounding for synthesizing the nanocomposites also has an effect on the mechanical properties of the composites. The GPO3 has been found have a better compatibility with the clay than PPG1 and PPG2, The nanocomposites synthesized from the clay compounding with the GPO3 route had the best mechanical and thermal stability properties. Nanocomposites from the clay compounding with the low molecular weight polyol route showed better mechanical properties than that from the clay compounding with the high molecular weight polyol route.

This work was financially supported by National Natural Science Foundation of China under Contract Number 59833130.

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