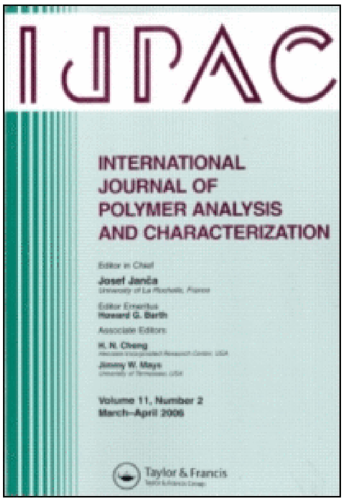

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

A Study on the Synthesis and Properties of Polyurethane/Clay Nanocomposites

Lei Song[a]; Yuan Hu[a]; Baoguang Li[a]; Shaofeng Wang[a]; Weicheng Fan[a]; Zuyao Chen[b]
[a] State Key Lab of Fire Science, University of Science and Technology of China, Anhui, China [b] Structure Research Laboratory, University of Science and Technology of China, Anhui, China

To cite this Article Song, Lei , Hu, Yuan , Li, Baoguang , Wang, Shaofeng , Fan, Weicheng and Chen, Zuyao(2003) 'A Study on the Synthesis and Properties of Polyurethane/Clay Nanocomposites', International Journal of Polymer Analysis and Characterization, 8: 5, 317 — 326

To link to this Article: DOI: 10.1080/10236660304871

URL: http://dx.doi.org/10.1080/10236660304871

International Journal of Polymer Anal. Charact., 8: 317–326, 2003
Copyright © Taylor & Francis Inc.
ISSN: 1023-666X print
DOI: 10.1080/10236660390226301

A Study on the Synthesis and Properties of Polyurethane/Clay Nanocomposites

Lei Song, Yuan Hu, Baoguang Li, Shaofeng Wang,
and Weicheng Fan
State Key Lab of Fire Science,
University of Science and Technology of China,
Anhui, China

Zuyao Chen
Structure Research Laboratory,
University of Science and Technology of China,
Anhui, China

Polyurethane/organophilic montmorillonite (PU/OMT) nanocomposites based on polyether, organophilic montmorillonite, phenylmethane diisocyante, diglycol, and glycerine were synthesized and characterized by x-ray diffraction (XRD). Delaminated or intercalated structures in polyurethane/OMT nanocomposites with different OMT content were found. The mechanical, thermal, and inflammability properties of PU/OMT nanocomposites were investigated through tensile, thermogravimetry, differential scanning calorimetry, and cone calorimetry experiments. It is shown that polyurethane/OMT nanocomposites have enhanced tensile strength, improved thermal stability, and flame retardant properties relative to bulk polyurethane. The tensile strength of PU/OMT with 4.7 wt% OMT content was double compared to that of bulk PU. The thermal and flame retardant properties of PU/OMT were enhanced compared to that of bulk PU. The thermal and flame retardant properties of PU/OMT increased with increasing OMT content.

Received 4 September 2001; accepted 2 January 2002.

Financially supported by the Natural Science Foundation of China (Grant No. 50003008), the China NKBRSF project (No. 2001CBY09600), and Anhui "the tenth five years" tackle key problems project.

Address correspondence to Yuan Hu, State Key Lab of Fire Science, University of Science and Technology of China, Hefei 230026, Anhui, China. E-mail: yuanhu@ustc.edu.cn

Keywords: Polyurethane; Nanocomposite; Clay; Tensile strength; Thermal stability; Flame retardant

In the past 20 years, layered silicate has been used to enhance the properties of polymeric materials with polymer chains intercalating galleries of adjacent silicate layers to form delaminated and intercalated nanocomposites, which represent an improvement over or new properties of the original polymer[1,2].

Montmorillonite is a natural clay mineral that contains a layered structure. It consists of stacked, layered silicate of about 1 nm thickness including two silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. There are some hydrophilic cations residing in the gallery, such as Na^+ or K^+ ions, which can be exchanged by other cations[3]. The montmorillonite can be modified with organic cations (e.g., alkylammonium ions) to become organophilic montmorillonite (OMT). This method solves the incompatibility problem on the interface between polymer and silicate and makes it easier to intercalate many kinds of organophilic polymers into layered silicate[4].

Because of the enhanced and novel properties of polymer/layered silicate nanocomposites compared to bulk polymer, many new nanocomposites based on polymer/clay have been investigated, such as nylon 6/clay[5–7], epoxy resin/clay[8], polyimide/clay[9], polyethylene oxide/clay[10], polycaprolactone/clay[11] and poly(methyl methacrylate)/clay nanocomposites[12]. Chen et al.[13] synthesized polyurethane (PU) mixed with organoclay, which was modified with 12-aminolauric acid or benzidine to obtain PU/clay nanocomposites.

Polyurethane elastomer is a thermoplastic copolymer with unique properties, and it is one of the most useful commercial polymeric materials. Hence, more attention has been given to the synthesis, morphology, chemical, and mechanical properties of this family of materials[14]. In our present study, a polyurethane/clay nanocomposite was synthesized by a two-stage route, and its structure and properties were investigated by thermogravimetry (TG), differential scanning calorimetry (DSC), and cone calorimetry.

EXPERIMENT

Materials

The original purified sodium montmorillonite (MMT) was made in Shanghai, China. The polyether (PE) used was poly(propylene oxide) glycol, whose average molecular weight was about 1000. The other inorganic and organic reagents were available commercially. All the reactants and solvent were analytical or chemical grade and were used without purification.

Preparation of OMT

After screening MMT with a 325-mesh sieve to remove impurities, Montmorillonite with a cationic exchange capacity of 76.6 meq/100 g was obtained. MMT was gradually added to a previously prepared solution of hexadecyl trimethyl ammonium bromide ($16Me^+Br^-$), which was dissolved in hot distilled water at 80°C, and the resultant suspension was stirred vigorously for 4 h. The treated montmorillonite, a white precipitate, was washed with hot deionized water several times to remove $16Me^+Br^-$ residue. The filtrate was titrated with 0.1 mol/L $AgNO_3$ until no precipitate of AgBr was formed to ensure complete removal of bromide ions. The product was placed in a vacuum-drying oven at 80°C for 12 h. The dried product was ground and screened with a 325 mesh to obtain the OMT.

Synthesis of PE/OMT Hybrid

OMT and PE were placed in a vacuum oven at 80°C for 12 h to remove residual water. OMT was mixed with PE with rapid stirring at room temperature for 4 h to disperse OMT homogeneously in PE, obtaining a colloidal PE/OMT hybrid.

Synthesis of the PU/OMT Nanocomposite

PU/OMT was synthesized with a two-step process. Toluene diisocyanate (TDI), colloidal PE/OMT hybrid, and sufficient *N*,*N*-dimethylformamide (DMF) were mixed with vigorous stirring for 90 min at 70°C. Afterward, diglycol, the chain extender, and glycerin, the cross-linking agent, were added to the mixture with vigorous stirring for 30 min at 80°C. Finally, the product was poured into a flat mold and placed in a vacuum oven at 110°C for 24 h to obtain the PU/OMT nanocomposite.

Characterization

X-ray diffraction (XRD) experiments were performed directly on the samples using a Japan Rigaku D/max-rA X diffractionmeter (30 kV, 10 mA) with Cu ($\lambda = 1.54$ Å) irradiation at the rate of 2°/min in the range of 1.5–10°. The tensile strength tests were carried out with a DCS-5000 instrument according to ASTM D882 specifications. Samples were cut to 100 × 10 × 0.25 mm in size, and the crosshead speed was set at 250 mm/min. For each data point, five samples were tested, and the average value was taken. The differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) of samples were carried out under N_2 atmosphere with NETZSCH STA409C thermal analyzer from 20° to 700°C at a heating rate of 15°C/min. Cone calorimeter experiments were performed at heat flux of $35\,KW/m^2$ using a cone-shaped heater. Typical results from the cone calorimetry were reproducible to within about 10%.

RESULTS AND DISCUSSION

The XRD patterns of MMT and OMT are shown in Figure 1. The basal spacing of MMT increased from 1.26 to 1.96 nm. When MMT was modified by $16Me^+Br^-$, the gallery of MMT was intercalated and expanded by molecular chains of $16Me^+Br^-$. The OMT content in the hybrids and the basal spacing (001) are given in Table I. The characteristic peak of PE/OMT hybrid shifted from 1.96 to 3.15 nm; this result confirmed that PE molecules intercalated into the galleries of OMT.

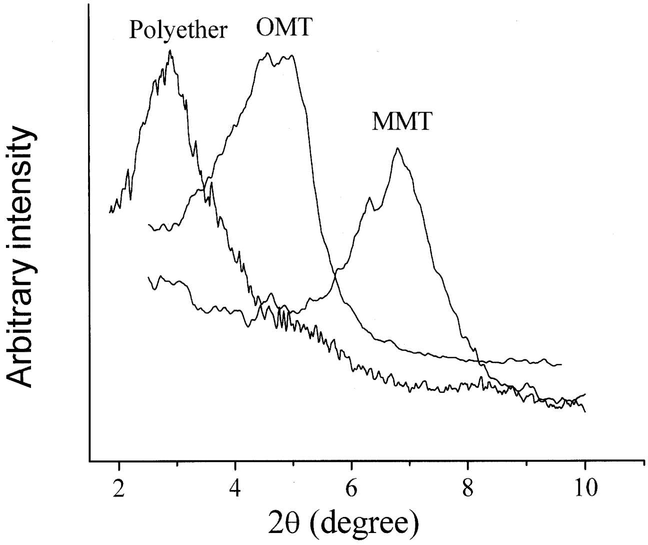

FIGURE 1 XRD patterns of MMT and OMT.

TABLE I OMT (wt%) content and XRD data of MMT, OMT, polyether/OMT, and PU/OMT nanocomposites

	OMT	2θ (°)	(nm)[a]
MMT[b]		7.01	1.26
OMT[c]	100	4.50	1.96
Polyether/OMT	20	2.80	3.15
Sample			
1	1.2	—	—
2	2.3	—	—
3	3.5	—	—
4	4.7		4.35
5	6		4.29

[a] Basal spacing (001).

[b] M: montmorillonite.

[c] O: organophilic montmorillonite.

Although PE molecules did not react with the silicate sheet, the hydroxyl of PE formed a hydrogen bond with the hydroxyl on the silicate sheet. XRD curves of a series of PU/OMT samples that were prepared with different OMT content are shown in Figure 2. Designations 1–5 correspond to 1.2, 2.3, 3.5, 4.6, and 6 wt% content OMT in the hybrids, respectively. In Figure 2, the disappearance of the XRD peaks ($2\theta = 1.5$–$10°$) in samples 1, 2, and 3 indicates that these silicate layers are completely exfoliated and dispersed in the PU matrix to form a delaminated nanocomposite. Meanwhile, for samples 4 and 5, the formation of nanocomposite was in the form of an intercalated structure with the basal spacing of 4.35 and 4.29 nm. When the content of layered silicate increased, the basal spacing decreased. When the content of layered silicate increased, the intercalated layered silicate swelled a lesser extent.

The mechanical properties of PU/OMT nanocomposites and bulk PU are given in Table II and Figure 3. In Table II, the tensile strength of samples 1–4 was higher than that of bulk PU, and the elongation of those samples was also higher than that of bulk PU. More than a twofold increase in strength was realized by the addition of only 4.7 wt% of OMT. The layered silicate, which functions as fibers in a fiber-reinforced plastic, enhanced tensile strength of the polymeric material. However, the tensile strength of sample 5 was much lower than that of sample 4, probably because of the high content of OMT resulting in phase separation between OMT and bulk PU.

The TGA analysis of bulk PU and PU/OMT nanocomposites is shown in Table III and Figure 4. The TGA curves clearly show that the PU/OMT exhibited enhanced thermal stability compared to bulk PU.

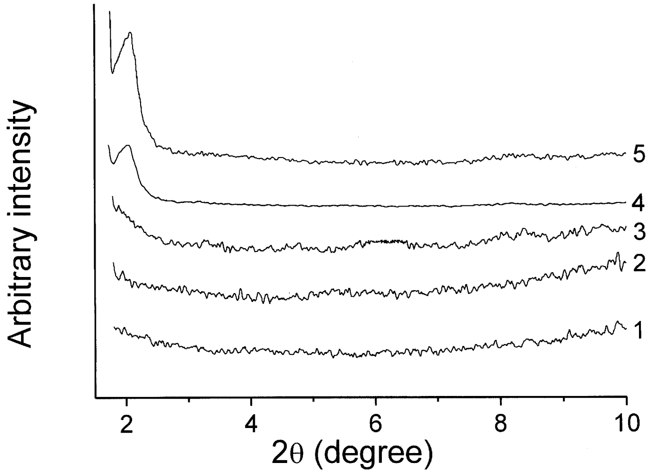

FIGURE 2 XRD patterns of PU/OMT nanocomposites. (OMT contents of samples 1–5 were 1.2, 2.3, 3.6, 4.7, and 6 wt%, respectively.)

Table III shows the temperature at which 20 and 80% degradation occurred (T_1, T_2) and the amount of residue at 630°C. The data in Table III shows that thermal stability of the nanocomposites corresponds to the OMT content in the nanocomposite. When the OMT content was increased, thermal stability enhancement increased. Moreover, when the temperature was increased, thermal stability enhancement increased. The amount of residue, which is not volatile at 630°C, was increased when the OMT content was increased. This result implies that OMT in the nanocomposites enhanced carbonaceous char formation.

High temperature DSC analysis of bulk PU and PU/OMT nanocomposites is shown in Figure 5. The DSC curves show pyrolysis of bulk PU and PU/OMT. There is a clear endothermic peak in the DSC

TABLE II The mechanical properties of bulk PU and PU/OMT nanocomposites

Samples	OMT (wt%)	Tensile strength (MPa)	Elongation (%)
Bulk PU	—	1.53	436
1	1.2	1.73	483
2	2.3	1.86	513
3	3.5	2.52	582
4	4.7	2.96	577
5	6	1.67	402

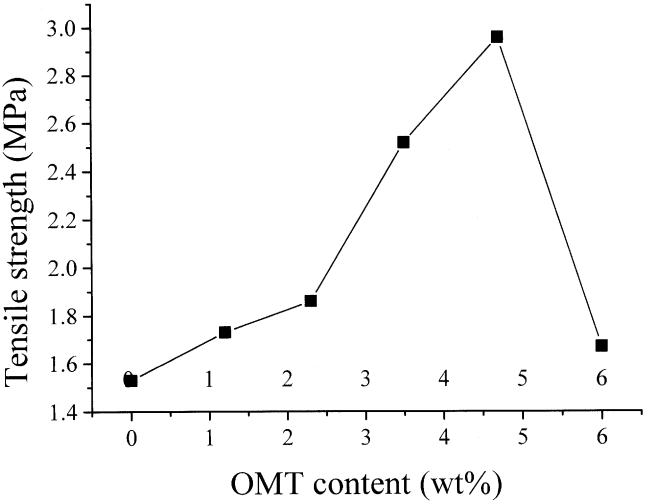

FIGURE 3 Tensile strength of bulk PU and PU/OMT nanocomposites.

curve. The peak at about 400°C corresponds to solid-phase pyrolysis. Figure 5 shows that the maximum endothermic peak temperature of bulk PU was 385°C, while Figure 3 shows that the maximum endothermic peak temperatures of PU/OMT with 3.5, 4.7, and 6 wt% OMT were 390, 394, and 400°C, respectively. Figure 5 demonstrates that the pyrolysis temperature increased as OMT content in the nanocomposites increased. The peak area of the PU/OMT nanocomposites was larger than that of bulk PU, meaning more heat of absorption. The pyrolysis heat of absorption of PU/OMT was larger than that of bulk PU.

TABLE III TGA results on bulk PU and the PU/OMT nanocomposites

Sample	OMT Content (wt%)	T_1[a] (°C)	T_2[b] (°C)	Residue at 630°C (wt%) Total (C_0)	Residue at 630°C (wt%) Real (C_0-C_{omt})
Bulk PU	0	290	360	0	0
3	3.5	302	370	6.39	2.89
4	4.7	310	385	9.80	5.10
5	6	315	405	13.67	7.67

[a] Temperature at 20% degradation of PU/OMT nanocomposite.

[b] Temperature at 80% degradation of PU/OMT nanocomposite.

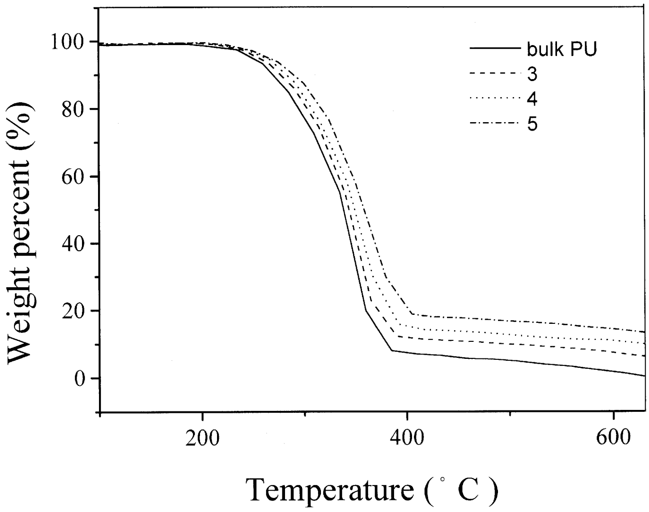

FIGURE 4 TGA analysis of bulk PU and PU/OMT nanocomposites.

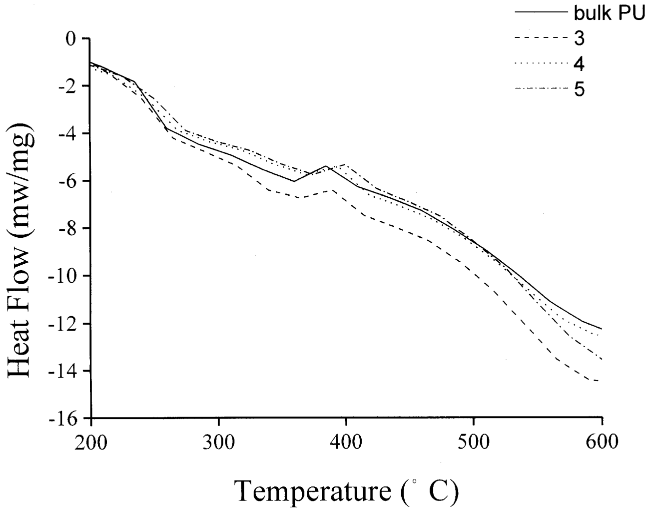

FIGURE 5 DSC analysis of bulk PU and PU/OMT nanocomposites.

Meanwhile, the pyrolysis heat of absorption of PU/OMT decreased as the OMT content increased. These results correspond to those from TGA experiments.

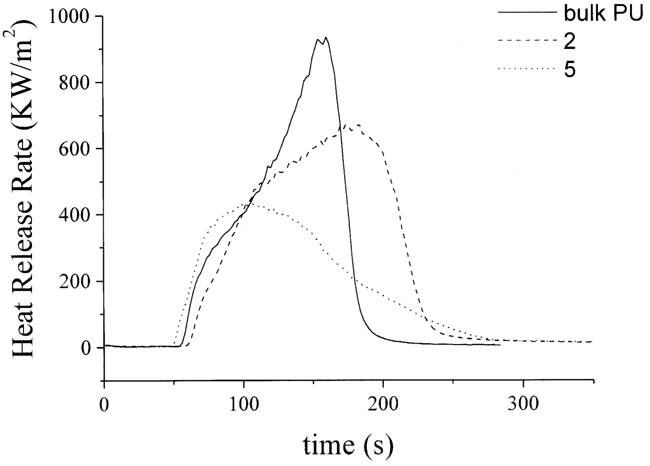

FIGURE 6 The pattern of HRR of bulk PU and PU/OMT nanocomposites.

The flame retardant properties of these nanocomposites were measured by a cone calorimeter. Heat release rate (HRR), in particular peak HRR, is one of the most important parameters for evaluating fire safety. Figure 6 shows that both the peak and average HRR were reduced significantly for the nanocomposites with low silicate content (2.3 to 6 wt%). The PU/OMT nanocomposite with OMT content of about 6 wt% had a 63% lower HRR than the bulk PU. The HRR of the nanocomposites decreased as the OMT content increased. The reason for this trend probably was because the OMT in the nanocomposites enhanced carbonaceous char formation. These results correspond with the TGA and DSC results.

CONCLUSION

Polyurethane/organophilic-layered silicate nanocomposites were synthesized by reacting a polyether/OMT hybrid with TDI, diglycol, and glycerine to obtain the PU/OMT intercalated and delaminated nanocomposites, which were verified by XRD. When OMT content was below 4.7 wt%, a delaminated nanocomposite was prepared; when OMT content was increased to 4.7 wt%, an intercalated nanocomposite was obtained. The mechanical, thermal, and flame retardant properties of PU/OMT were studied. The tensile strength of PU/OMT with 4.7 wt% OMT content was double that of bulk PU. The thermal and flame retardant properties of PU/OMT were enhanced compared to that of bulk PU and increased with increasing OMT content.

REFERENCES

[1] Giannelis, E. P., V. Mehrota, O. K. Tse, R. A. Vaia, and T. C. Sung. (1992). In *Synthesis and Processing of Ceramics—Scientific Issues,* ed. W. E. Rhine, M. T. Shaw, R. J. Gottshall, Y. Chen. Pittsburgh, PA; Materials Research Society, pp. 249–547.

[2] Vaia, R. A., H. Ishii, and E. P. Giannelis. (1993). Synthesis and properties of 2-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. *Chem. Mater.* **5(12)**, 1694–1696.

[3] Akelah, A., P. Kelly, S. Qutubuddin, and A. Moet. (1994). Synthesis and characterization of epoxyphilic montmorillonites. *Clay Miner.* **29(2)**, 169–178.

[4] LeBaron, P. C., Z. Wang, and T. J. Pinnavaia. (1999). Polymer-layered silicate nanocomposites: An overview. *Appl. Clay Sci.* **15(1–2)**, 11–29.

[5] Usuki, A., T. Mizutani, Y. Fukushima, M. Fujimoto, K. Fukumori, K. Kenzo, Y. Kojima, N. Sato, T. Kurauchi, and O. Kamigaito. (1989). Composite material containing a layered silicate. U.S. Patent 4889885.

[6] Okada, A., A. Usuki, T. Kurauchi, and O. Kamigaito. (1995). In *Hybrid Organic-Inorganic Composites*. Washington, DC: American Chemical Society, pp. 55–68.

[7] Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, and O. Kamigaito. (1993). One-pot synthesis of nylon-6 clay hybrid. *J. Polym. Sci. Part A: Polym. Chem.* **31(7)**, 1755–1758.

[8] Lan, T. and T. J. Pinnavaia. (1994). On the nature of polyimide clay hybrid composites. *Chem. Mater.* **6(5)**, 573–575.

[9] Yano, K., A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito. (1993). Synthesis and properties of polyimide clay hybrid. *J. Polym. Sci. Part A: Polym. Chem.* **31(10)**, 2493–2498.

[10] Giannelis, E. P. (1996). Polymer layered silicate nanocomposites. *Adv. Mater.* **8(1)**, 29–30.

[11] Messersmith, P. B. and E. P. Giannelis. (1995). Synthesis and barrier properties of poly(epsilon-caprolactone)-layered silicate nanocomposites. *J. Polym. Sci. Part A: Polym. Chem.* **33(7)**, 1047–1057.

[12] Lee, D. C. and L. W. Jang. (1996). Preparation and characterization of PMMA-clay hybrid composite by emulsion polymerization. *J. Appl. Polym. Sci.* **61(7)**, 1117–1122.

[13] Chen, T. K., Y. I. Tien, and K. H. Wei. (2000). Synthesis and characterization of novel segmented polyurethane/clay nanocomposites. *Polymer*. **41(4)**, 1345–1353.

[14] Penczek, P., K. C. Frisch, B. Szczepaniak, and E. Rudnik. (1993). Synthesis and properties of liquid-crystalline polyurethanes. *J. Polym. Sci. Part A: Polym. Chem.* **31(5)**, 1211–1220.