

Preparation and Properties of a Novel Elastomeric Polyurethane/Organic Montmorillonite Nanocomposite

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ABSTRACT: A novel elastomeric polyurethane (EPU)/organic montmorillonite (OMMT) nanocomposite has been synthesized. 18 Alkane-3 methyl-amine chloride and dihydroxethyl-12 alkane-3 methyl-amine chloride were used as intercalation agents to treat Na⁺-montmorillonite and for forming two kinds of OMMTs. The better OMMT was chosen according to fourier transform infrared spectroscopy (FTIR) and wide angle X-ray diffraction (WAXD). Three types of EPU/OMMT nanocomposites were synthesized by *in situ* polymerization of EPU, with different amounts of OMMT. A combination of FTIR, WAXD, and transmission electronic microscopy (TEM) studies showed that EPU/OMMT composites were on the nanometer scale and the

segmented structure of EPU was hindered by the presence of the OMMT, due to the reaction between toluene diisocyanate (TDI) and the intercalation agents. Properties such as tensile property, differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA) were researched and compared. Results showed that the EPU/3% OMMT had the best physical and mechanical properties because of its uniform dispersion of the organic silicate layers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3578–3585, 2006

Key words: elastomeric polyurethane; montmorillonite; nanocomposites

INTRODUCTION

Elastomeric polyurethane (EPU) is a widely used polymer with unique properties and can form a variety of starting materials. Hence, such materials have received wide attention for their morphological, chemical, and mechanical properties.^{1–3}

In recent years, nanostructured hybrid organic–inorganic composites, based on organic polymer and inorganic clay minerals consisting of silicate layers whose thickness is 1 nm scale, have attracted great interest in research.^{4,5} Some researchers have prepared polyurethane nanocomposites containing intercalated silicate layers and examined their physical and mechanical properties.^{6–8}

In this study, first, 18 alkane-3 methyl-amine chloride and dihydroxethyl-12 alkane-3 methyl-amine chloride were used as intercalation agents to treat Na⁺-montmorillonite and for forming two kinds of organic montmorillonites (OMMTs). The better OMMT was chosen according to fourier transform infrared spectroscopy (FTIR) and wide angle X-ray diffraction (WAXD). Then, three types of EPU/OMMT nanocomposites were synthesized by *in situ* polymerization of EPU, with different amounts of

OMMT. A combination of FTIR, WAXD, and transmission electronic microscopy (TEM) studies showed that EPU/OMMT composites were on the nanometer scale and the segmented structure of EPU was hindered by the presence of the OMMT, due to the reaction between toluene diisocyanate (TDI) and the intercalation agents. Last, properties such as tensile properties, differential scanning calorimeter (DSC), and thermogravimetric analyses (TGA) were investigated and compared. Results showed that the EPU/3% OMMT had the best physical and mechanical properties.

EXPERIMENTAL

Materials

Na⁺-montmorillonite (MMT), industrial grade, was obtained from Zhejiang Fenghong Clay Company (China). 18 Alkane-3 methyl-amine chloride and dihydroxethyl-12 alkane-3 methyl-amine chloride, chemically pure, were received from Zhejiang Chemical Agent Company (China). Polyether glycol (GE-210, $M_n = 2000$), chemically pure, was supplied by Shanghai Gaoqiao Petrochemical Company (China). Toluene diisocyanate (TDI) and MOCA, chemically pure, were all provided by Shanghai Chemical Agent Company (China).

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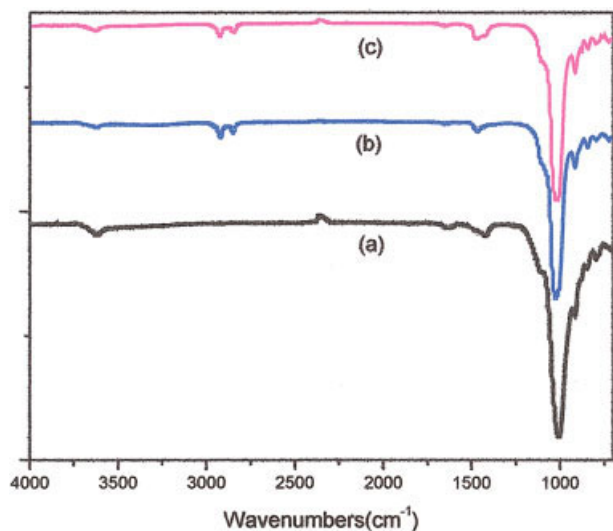


Figure 1 FTIR spectra of (a) MMT; (b) DK1; and (c) DK2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Preparation of OMMT

A 500-mL round-bottomed, three-necked flask with a mechanical stirrer, thermometer, and condenser with drying tube was used as a reactor. Ten grams of MMT was gradually added to a prior prepared solution of 18 alkane-3 methyl-amine chloride (3.48 g) or dihydroxyethyl-12 alkane-3 methyl-amine chloride (3.52 g), which were dissolved in a 120 mL ethanol and water mixture (weight ratio, 1 : 1), and the resultant suspension was vigorously stirred for 2 h. The treated MMT was repeatedly washed by deionized water. The filtrate was titrated with 0.1N AgNO₃ until no precipitate of AgCl was formed to ensure the complete removal of chloride ions. The filter cake was then placed in a vacuum oven at 80°C for 12 h for drying. The dried cake was ground to obtain the OMMTs.

Synthesis of EPU/OMMT nanocomposites

Preparation of pure EPU

TDI (0.3 mol) and polyether glycol (0.1 mol) at a molar ratio of 3 : 1 were dissolved in dimethylformamide solvent, and then the whole solution was heated to 80°C for 2 h to form a prepolymer. Lastly, 0.2 mol of MOCA was added to the prepolymer, with rapid stirring at 80–100°C, and the final concentration was cast into a mold and then sulfurated at 150°C for 3 h.

Preparation of EPU/OMMT nanocomposites

Different amounts of OMMT (1, 3, 5 wt %) were prepared. Following the procedure of synthesizing EPU prepolymer as described in the previous section, the whole EPU solution was cooled to room temperature.

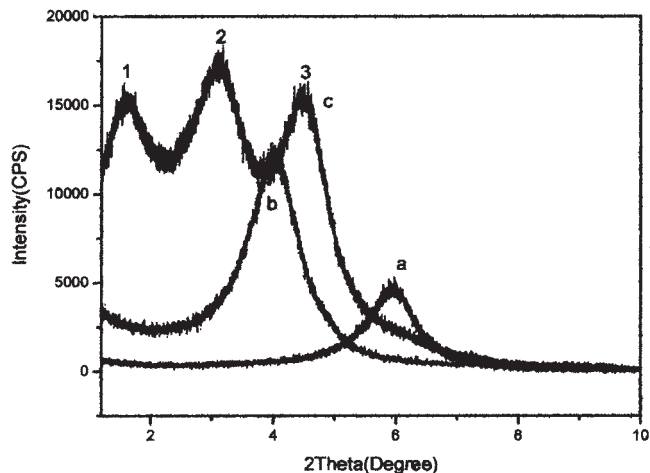


Figure 2 WAXD spectra of (a) MMT; (b) DK1; and (c) DK2.

At room temperature, the OMMT was added to the EPU, with stirring for 2 h. After degassing of the mixture, and removal of the solvent at 150°C, the EPU film was obtained.

Characterization

To measure the change of gallery distance of OMMT and OMMT/EPU before and after intercalation, WAXD was performed at room temperature with a Rigaku D-Max/400 (Japan) X-ray diffractometer. The X-ray beam was nickel-filtered Cu α ($\lambda = 0.154$ nm) radiation operated at 50 kV and 150 mA. X-ray diffraction data were obtained from 1° to 10° (2θ), at a rate of 2°/min. Infrared transmission spectra of MMT, OMMT, and OMMT/EPU nanocomposites were obtained using a FTIR spectrometer, model Dos X from Nicolet corp. The scan range was from 4000 to 400 cm^{-1} , with a resolution of 2 cm^{-1} . The samples for TEM were first prepared by microtoming the OMMT/EPU nanocomposites into 80- to 100-nm thick slices at -30°C. The graphs were obtained with a Hitach H-800 instrument, using an acceleration voltage of 100 kV accelerating voltage. The tensile tests were carried out with an Instron Model 4204 instrument at room temperature, with a crosshead speed of 500 mm/min. The samples were manufactured in a standard dumbbell-

TABLE I
WAXD Data of MMT and OMMT

Serial number	λ (Å)	2θ (°)	d (nm)
a	1.54056	6.036	1.46303
b	1.54056	4.030	2.19070
c-1	1.54056	1.680	5.25419
c-2	1.54056	3.172	2.78303
c-3	1.54056	4.540	1.94473

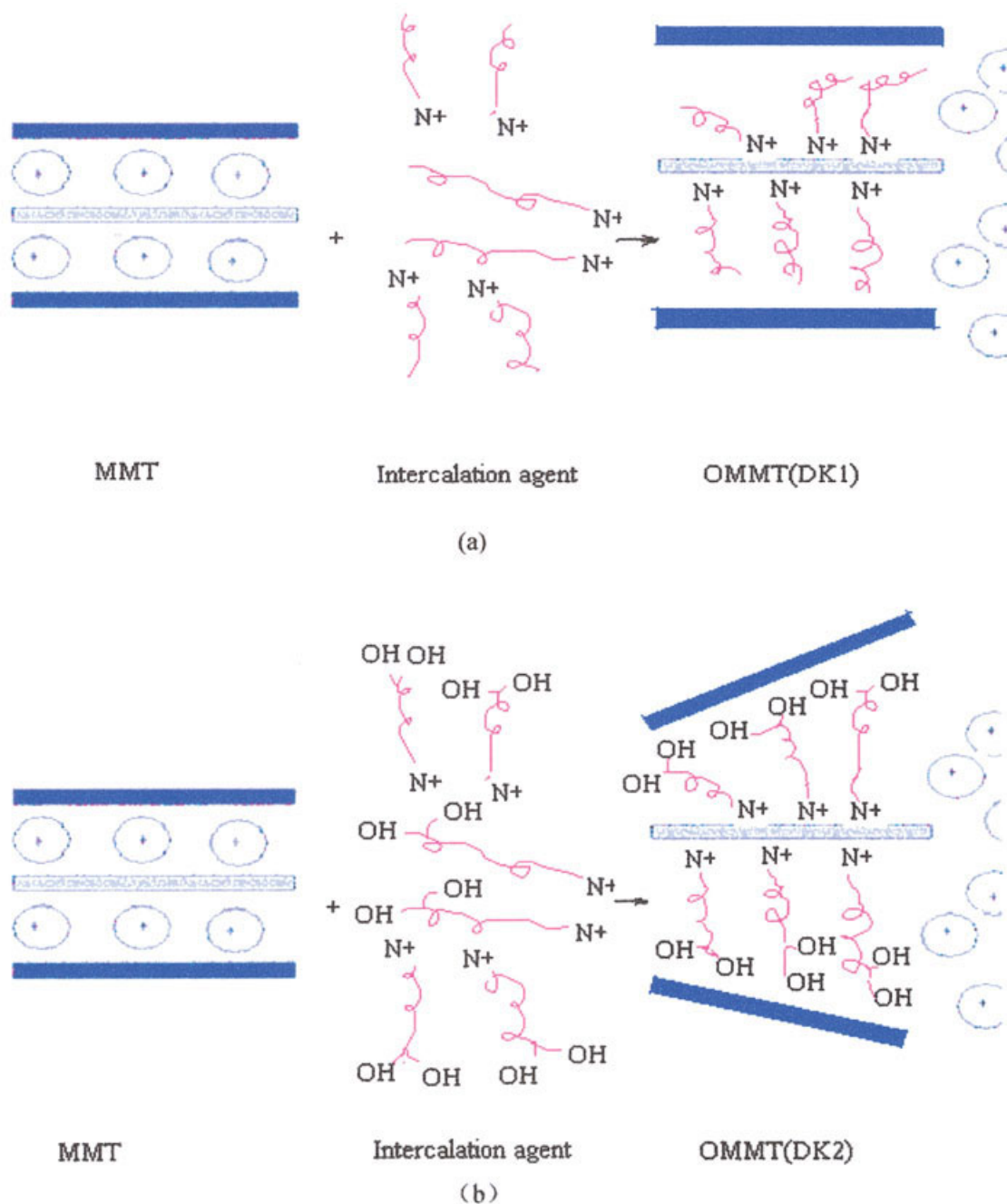


Figure 3 Scheme of modification process of (a) DK1; and (b) DK2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shape, and all measurements were repeated five times and averaged. The heat of fusion and melting temperature of OMMT/EPU nanocomposites were obtained with a DSC 5SC/580 from Seiko Instrument and Electronics Ltd. TGA of OMMT/EPU nanocomposites was carried out at $10^{\circ}\text{C}/\text{min}$ under air (flow rate $5 \times 10^{-7} \text{ m}^3/\text{s}$, air liquid grade), using a Universal V3.8B TA microbalance. In each case, the mass of the sample used was fixed at 10 mg, and the samples (powder mixtures) were positioned in open vitreous silica pans.

The precision of the temperature measurements was 1°C over the whole range of temperatures.

RESULTS AND DISCUSSION

Analysis of OMMT

The MMT samples modified with 18 alkane-3 methylamine chloride and dihydroxyethyl-12 alkane-3 methylamine chloride are termed DK1 and DK2.

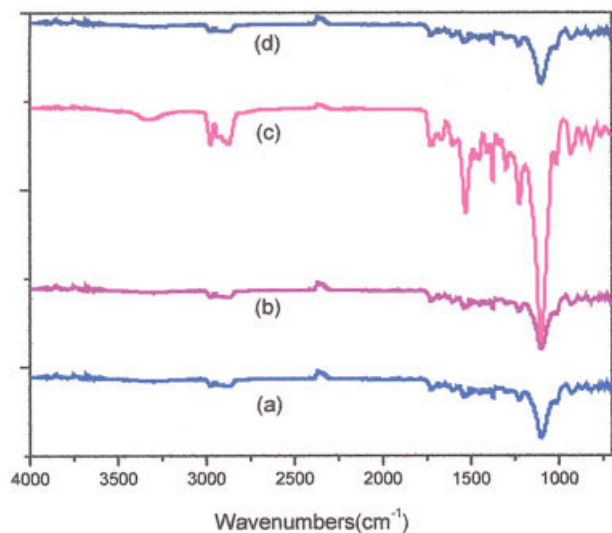


Figure 4 FTIR spectra of (a) EPU; (b) 1% DK2/EPU; (c) 3% DK2/EPU; and (d) 5% DK2/EPU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FTIR analysis

The FTIR spectra of original MMT, DK1, and DK2 are shown in Figure 1. The 3620–3650 cm^{-1} peak was caused by the stretching of —OH, which was due to the physical and chemical water existing in the Na^+ -MMT. The peaks at 1030–600 cm^{-1} resulted from the stretching vibration of Si—O and Al—O bonds in the MMT structure.^{9–12} In the spectra of DK1 and DK2, except for the peaks existing in the MMT, there are new peaks at 2800–3000 cm^{-1} and 1469 cm^{-1} , which were caused by C—H stretching and bending absorptions in the organic intercalation agents. The disappearing peak at 1640 cm^{-1} illustrated the exchanging of Na^+ cations in the MMT and N^+ cations in the intercalation agents.

WAXD analysis

The WAXD patterns of original MMT, DK1, and DK2 are shown in Figure 2. Curve (a), WAXD of pure MMT, shows a characteristic peak at 6° of 2θ , which was assigned to the 001 basal reflection. In curve (b), WAXD of DK1, the shifting of peaks from $2\theta = 6^\circ$ to 4° resulted from expansion of basal spacing of silicate layers by intercalation of 18 alkane-3 methyl-amine chloride. As far as the d -spacing of DK2 was concerned, there were three peaks in the WAXD spectrum. This indicated the different expansion degree of silicate layers in DK2, which was due to the different structure of the intercalation agents.^{13–16} The data of MMT, DK1, and DK2, calculated by Bragg formula: $2d \sin \theta = n\lambda$, are summarized in Table I. It can be concluded that the intercalation effect of DK2 is better

than that of DK1, which is due to its larger basal spacing.

Discussion of modification mechanism of MMT with different intercalation agents

The MMT clay is a phyllosilicate mineral. Cations such as Na^+ , K^+ , and Ca^{2+} , compensate the negative charge that exists in the crystal lattice of the each silicate layer in MMT. Polar molecules, such as 18 alkane-3 methyl-amine chloride and dihydroxyethyl-12 alkane-3 methyl-amine chloride that can make MMT more organophilic, can penetrate between the layers and swell.¹⁷ The schematic depicting of the intercalation process between the original MMT and the two kinds of intercalation agents is illustrated in Figure 3. The interlayer spacing of DK2 is so large that it is greater than the extended chain length of dihydroxyethyl-12 alkane-3 methyl-amine chloride, the intercalation agent of DK2. The underlying mechanism may be related to the strong polarity of —OH groups, branching chains of dihydroxyethyl, and space distributing morphology of molecular chains of the intercalation agent.

Analysis of OMMT/EPU nanocomposites

FTIR analysis

The microdomain structure of the EPU and the different DK2 content EPU nanocomposites were analyzed by FTIR as shown in Figure 4. It was found that the positions of peaks for distinctive functional groups were similar both in pure EPU and in 1 and 5% DK2/EPU composites. Compared with pure EPU, detect-

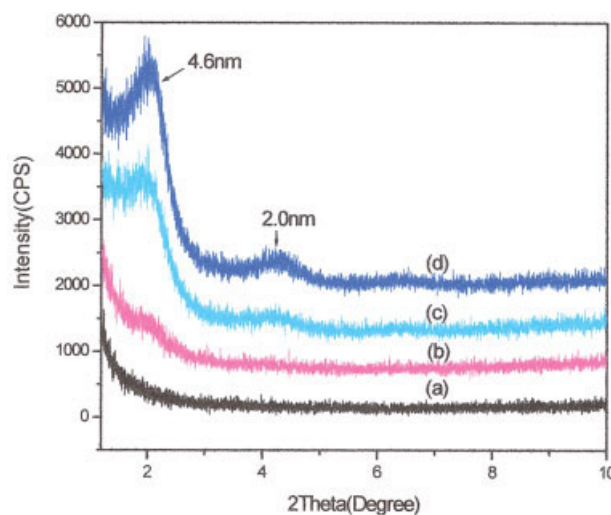


Figure 5 WAXD spectra of (a) EPU; (b) 1% DK2/EPU; (c) 3% DK2/EPU; and (d) 5% DK2/EPU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

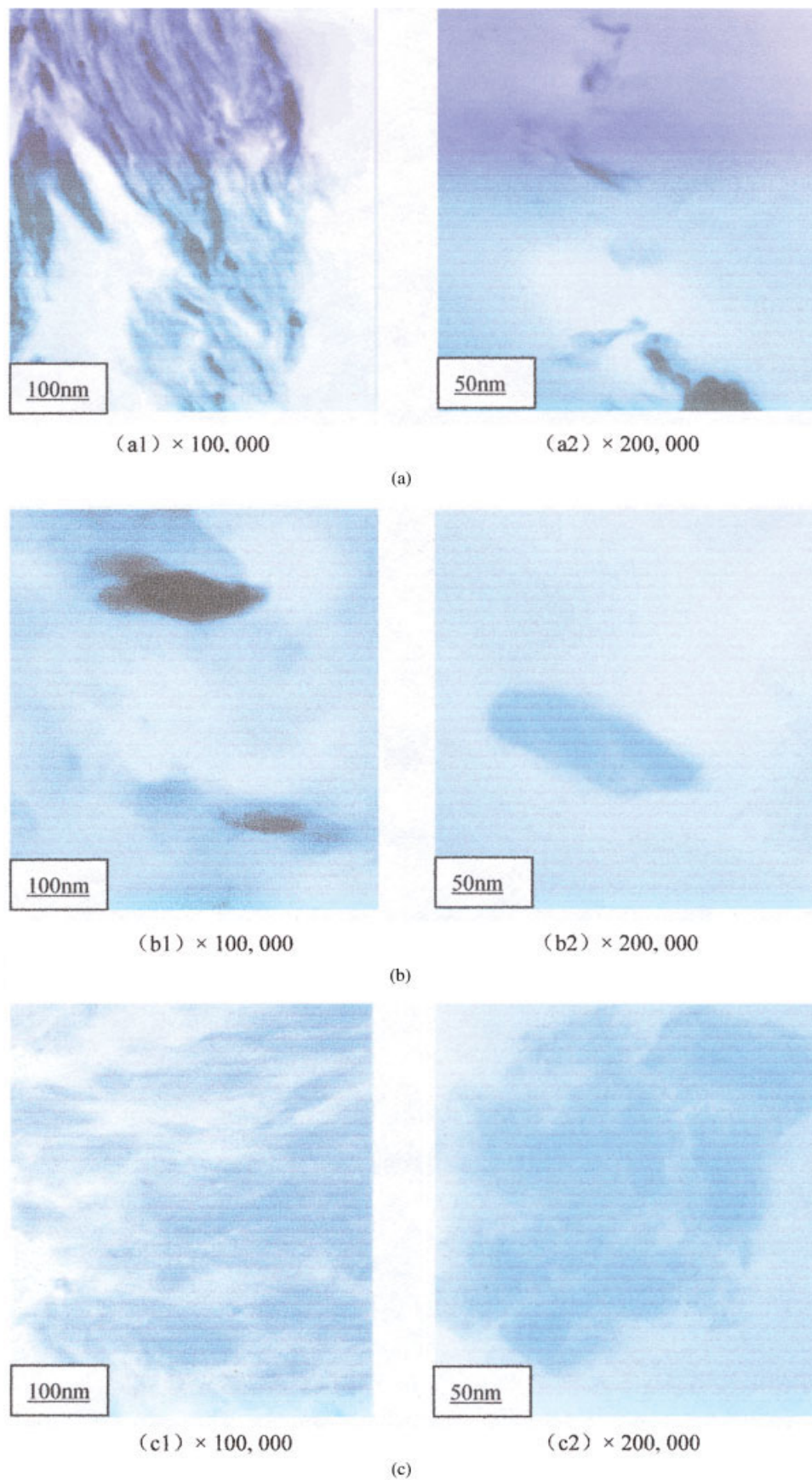


Figure 6 TEM images of (a) 1% DK2/EPU; (b) 3% DK2/EPU; and (c) 5% DK2/EPU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

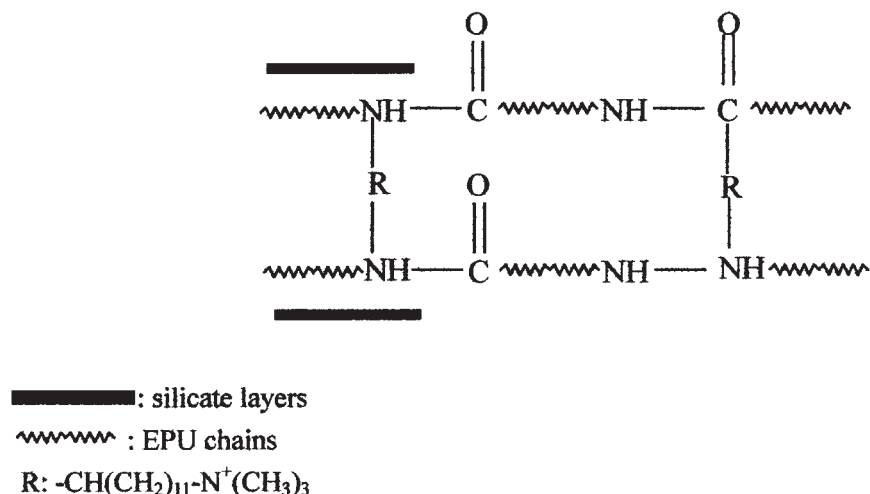


Figure 7 The schematic drawing of possible intermolecular interaction between PU molecules and DK2.

able changes took place in 3% DK2/EPU composites. The $2800\text{--}3000\text{ cm}^{-1}$ peak of C—H bond, the 1580 cm^{-1} peak of $-\text{C}=\text{O}$ bond, and the 1080 cm^{-1} peak of $\text{O}=\text{C}-\text{O}-\text{C}$ in $\text{C}-\text{O}-\text{C}$ chain were attributed to the chemical reaction of TDI between $-\text{OH}$ in polyether glycol and dihydroxyethyl-12 alkane-3 methyl-amine chloride.^{18–20} The reason for the similarity between 1% DK2/EPU and EPU composites is probably that the content of DK2 is relatively lower. In the 5% DK2/EPU, the lower intensity, compared with 3% DK2/EPU, was due to the different dispersion degree of DK2 in EPU caused by the increasing amount of DK2. This different dispersion leads to the different reaction rate of TDI with DK2, which also leads to the decreasing amount of $\text{O}=\text{C}-\text{O}-\text{C}$ chain and decreasing intensity of absorption peaks.

WAXD analysis

An important measure of the degree of silicate dispersion and exfoliation can be obtained by WAXD measurements. A series of WAXD patterns of nanocomposites containing different amounts of DK2 are shown in Figure 5. No peaks were observed in Figure 5(a), which was due to the amorphous nature of EPU. When a small amount of DK2 was incorporated in EPU (1% DK2/EPU), a slight peak appeared at $2\theta = 2^\circ$ (d -spacing = 4.6 nm), which corresponded to the expansion of the gallery space by the insertion of EPU polymer chains. As the amount of DK2 in EPU increased, the intensity of peak at $2\theta = 2^\circ$ also increased. This was attributed to the increasing amount of silicate layers having 001 basal reflection. The appearance of peaks at $2\theta = 4.5^\circ$ (d -spacing = 2.0 nm), which had something to do with the original silicate layer space of DK2 [shown in Fig. 2(c3)], illustrated the existence

of stacked DK2 of crystallographic order in the nanocomposites.^{21–23}

TEM analysis

Further evidence of nanometer-scale dispersion of silicate layers, for different amounts of DK2/EPU nanocomposites, was supported by TEM photomicrographs, as shown in Figure 6. From Figures 6(a1), 6(b1), and 6(c1), it can be observed that the nanocomposites are mainly intercalated structures; also, it can be seen that DK2 was becoming agglomerated in the composites as the amount increased.^{24,25} Meanwhile, the exfoliating silicate layer can be seen from Figures 6(a2), 6(b2), and 6(c2).

Discussion of the intercalation mechanism of EPU with DK2

EPU is an important polar polymer and the OMMT environment is compatible with them. During the polymerization process, TDI not only can react with polyether glycol but also can react with $-\text{OH}$ in the intercalation agent in DK2 to form urethane esters, which have an important effect on the exfoliation of DK2. The schematic drawing of possible intermolecular interaction between PU molecules and DK2 is shown in Figure 7. The schematic intercalation process of EPU with DK2 is shown in Figure 8.

Mechanical and physical properties of OMMT/EPU nanocomposites

The mechanical properties of DK2/EPU nanocomposites and pure EPU can be seen from Table II. In Table II, the tensile strength and elongation at break of the 1,

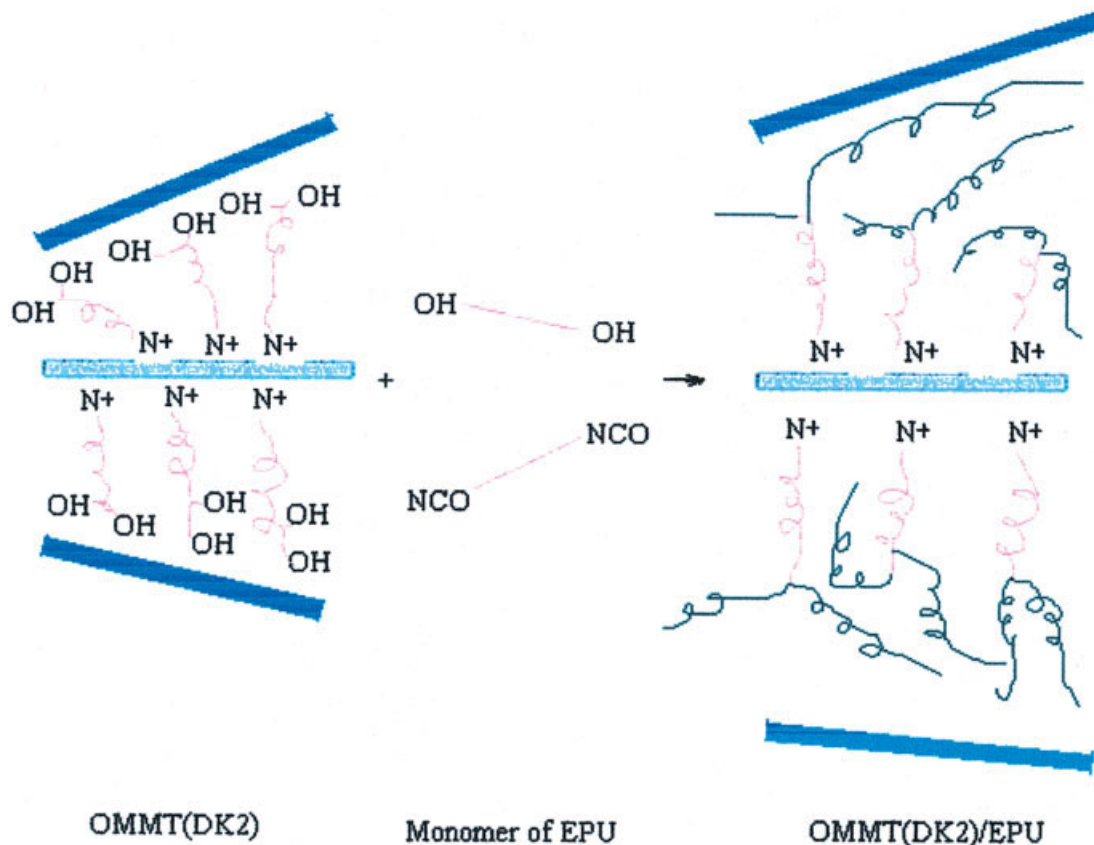


Figure 8 Scheme of intercalation process between OMMT (DK2) and monomer of EPU. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3, 5% DK2/EPU were all higher than that of pure EPU. The tensile strength of 3% DK2/EPU was about 350% higher than that of pure EPU and the elongation at break also showed a remarkable enhancement compared with that of pure EPU. When DK2 amount increased higher than 3%, the tensile strength decreased, which was due to the aggregates of DK2 in the composites.²⁶ The thermal properties of pure EPU and 1, 3, 5% DK2/EPU nanocomposites were studied by DSC, and their results are shown in Figure 9. In Figure 9, pure EPU showed the highest melting point and the other nanocomposites showed lower, which was due to defects of the crystalline phase in the composites. 3% DK2/EPU showed the lowest melting

point and this indicates the most irregular crystallinity in this composite and also indicated the best intercalation effect in this system.^{27,28} Figure 10 shows the TGA curves of pure EPU and DK2/EPU nanocomposites. The characteristic thermal parameters are the ini-

TABLE II
Mechanical Properties of EPU and DK2/EPU
Nanocomposites

Materials	Tensile strength (MPa)	Elongation at break (%)
EPU	8.2	550.0
1% DK2/EPU	22.2	610.0
3% DK2/EPU	28.3	680.0
5% DK2/EPU	16.2	580.0

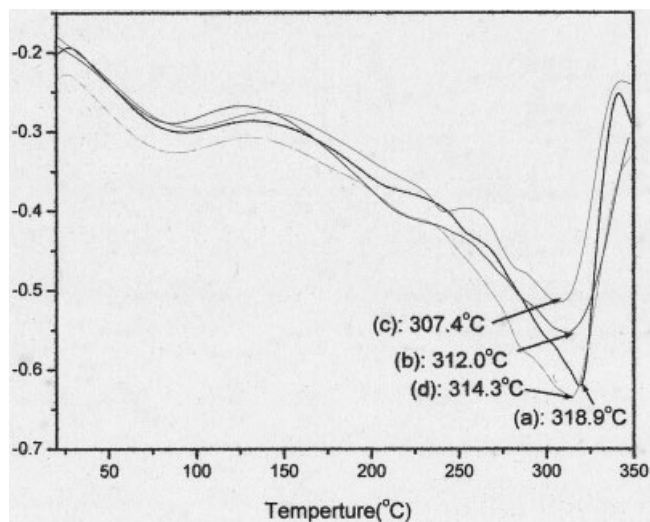


Figure 9 DSC curves of (a) EPU; (b) 1% DK2/EPU; (c) 3% DK2/EPU; and (d) 5% DK2/EPU.

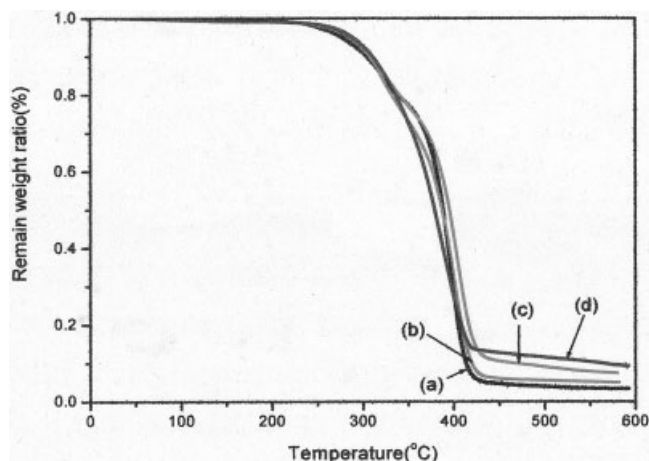


Figure 10 TGA curves of (a) EPU; (b) 1% DK2/EPU; (c) 3% DK2/EPU; and (d) 5% DK2/EPU.

tial and center temperature of thermal degradation, and the results are summarized in Table III. The first increasing and the later decreasing of the initial temperature were probably caused by the increasing amount of organic small molecules of intercalation agent. Similarly, the center temperature of thermal degradation also has this trend. The highest center temperature of 3% DK2/EPU resulted from the greatest retarding effect of EPU molecular chain. The more chains inserted between the silicate layers, the higher the center temperature. This also confirmed the best intercalation effect of the 3% DK2/EPU nanocomposites, in good agreement with the above FTIR, WAXD, and TEM analysis. On the other hand, the amount of char residue was improved with the increasing amount of DK2, which was due to improved thermal stability of the nanocomposites.^{29,30}

CONCLUSIONS

Organically modified montmorillonite was successfully prepared by ion-exchange reaction, using two kinds of intercalation agents. FTIR and WAXD methods were used and a better intercalation agent was selected. FTIR, WAXD, and TEM results verified the

TABLE III
TGA Data Analysis of EPU and DK2/EPU Nanocomposites

Materials	Char (%)	Initial temperature of thermal degradation (μ)	Center temperature of thermal degradation (μ)
EPU	3.5	185	396
1% DK2/EPU	5.0	200	400
3% DK2/EPU	8.7	210	406
5% DK2/EPU	9.9	196	389

incorporation of the better OMMT into EPU matrix and revealed that the degree of basal-spacing expansion was largely increased. The enhanced mechanical and physical properties demonstrated efficient reinforcing and better thermal stability properties of the OMMT. Results showed that 3% OMMT/EPU nanocomposite had the best properties compared with that of other nanocomposites.

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