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SHORT COMMUNICATION

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Synthesis of polyurethane/clay intercalated nanocomposites

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Abstract A kind of polyurethane/organophilic montmorillonite (PU/OMT) nanocomposite based on polyether, OMT, phenylmethane diisocyante and diglycol was synthesized and characterized by X-ray diffraction (XRD) and high-resolution electron microscopy (HREM). A polyether/OMT hybrid was first prepared in a nanocomposite form as confirmed by XRD. It was shown that there is a multilayered structure consisting of alternating PU chains stacked with the layers of the silicate layers in the microstructure of the PU/OMT nanocomposite as confirmed by study of the XRD patterns and the HREM images. The contents of the hard segment of PU and OMT had an effect on the basal spacing of the PU/OMT nanocomposite.

Key words Polyurethane · Montmorillonite · Nanocomposites · Intercalation

Introduction

In the last two decades, layered inorganic materials have been used to enhance the properties of polymer materials with a polymer molecular chain intercalating galleries of adjacent inorganic layers to form delamination and intercalation nanocomposites, which represents an improvement or new properties compared to the original polymer [1, 2].

Montmorillonite is a type of natural clay mineral and has a layered structure. It consists of stacked, layered silicates 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 is modified by organic cations (e.g., alkylammonium ions) and becomes organophilic montmorillonite (OMT). This method solves the incompatible problem on the interface between polymer and silicate, and it is easier to intercalate many kinds of organophilic polymers into layered silicate [4].

Because of the enhancement and novel properties of polymer/layered silicate nanocomposites compared to pure polymer, many new nanocomposites based on polymer/clay have been investigated, such as nylon 6/clay [5, 6, 7], epoxy resin/clay [8], polyimide/clay [9], polyethylene oxide/clay [10], polycaprolactone/clay [11] and poly(methylmethacrylate)/clay nanocomposites [12].

Polyurethane (PU) elastomer is a thermoplastic copolymer with unique properties, and it is one of the most useful commercial polymer materials. Hence, more attention has been given to the synthesis, morphology, chemical and mechanical properties of this family of materials [13, 14]. The linear structure of segmented PU is in the form of $(A–B)_n$. The soft-segment part B is normally a polyester or polyether (PE) macrogel of molecular weight between 1,000 and 3,000, and the hard-segment part A is composed of a low-molecular

weight diol or diamine reacted with diisocyanate. Owing to the difference in the chemical structure of the soft and the hard segment, short, hard segments form microdomains by mutual attractions involving intermolecular hydrogen bonding. In the present study, a PU/clay nanocomposite was synthesized by a two-stage route.

Experimental

Materials

The original purified sodium montmorillonite (MMT) was made in Shanghai, China. The PE used was poly(propylene oxide) glycol, whose average molecular weight is about 1,000. The other inorganic and organic reagents were available commercially. All the reactants and solvent were analytic or chemical grade and were used without purification.

Preparation of OMT

After screening MMT with a sieve of 325 mesh to remove impurities, the montmorillonite having a cationic-exchange capacity of 76.6 mEq/100 g was obtained. MMT was gradually added to a previously prepared solution of hexadecyltrimethylammonium 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 repeatedly with hot deionized water several times to remove the residue of $16Me^+Br^-$. The filtrate was titrated with 0.1 mol/l $AgNO_3$ until no precipitate of AgBr was formed to ensure the 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 sieve of 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 clear residual water. OMT was mixed with PE with rapid stirring at room temperature for 4 hto disperse OMT homogeneously in PE. Then the colloidal PE/OMT hybrid was obtained.

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 30 min at 70 °C. Then diglycol, the chain extender and several drops of glycerin, the cross-linking agent, were added to the mixture with vigorous stirring for 10 min at 80 °C. Finally the product was poured into a flat mold and placed in a vacuum oven at 100 °C for 24 h to obtain the PU/OMT nanocomposite.

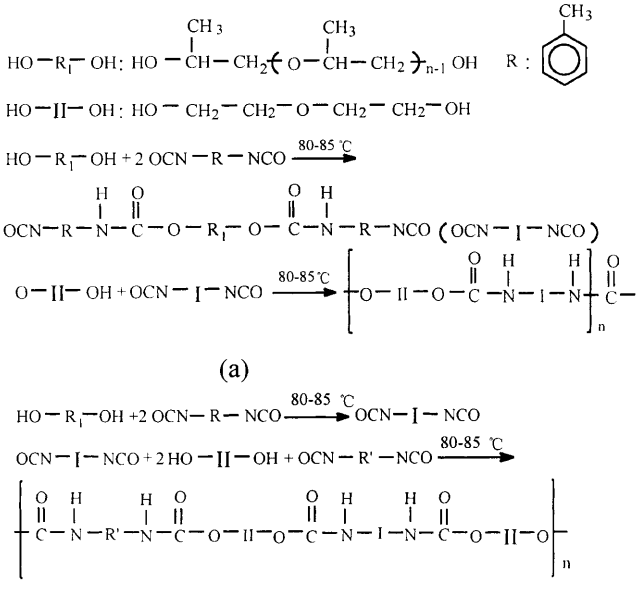
Characterization

X-ray diffraction (XRD) experiments were performed directly on the samples using a Japan Rigaku D/max-rA X diffraction meter (30 kV, 10 mA) with Cu ($\lambda = 1.54$Å) irradiation at a rate of 20/min in the range of 1.5–10°. The samples for high-resolution electron microscopy (HREM) study were prepared by ultramicrotomy. The PU/OMT sample was added to DMF with stirring for 2 h at 50 °C and most of the PU in PU/OMT dissolved in DMF. After centrifugation, the deposit was placed in a vacuum oven at 100 °C for 24 h and was then ground to a powder and placed into epoxy capsules. The epoxy was cured at 70 °C for 12 h in a vacuum oven. Then, the cured epoxies containing PU/OMT were microtomed into 80–100-nm thick slices at room temperature. HREM images were obtained using a Jeol 2010 instrument with an acceleration voltage of 200 kV.

Results and discussion

The main probable synthesizing processes of PU/OMT nanocomposites based on different molar ratios of reactants are shown in Scheme 1a and b, respectively. Firstly, PE reacted with TDI and the prepolymer was obtained. Secondly, diglycol, which extended the molecular chain of the prepolymer, reacted with the prepolymer to obtain PU. The molecular weight of diglycol was less than that of PE, so the density of the hard segment in sample b was more than that in sample a and the molecular chain of sample b was harder than that of sample a. The –NCO content of PU was analyszed via titration [14]; the conversions of TDI were 99.2 and 99.3 wt% in Scheme 1a and b, respectively.

The XRD patterns of MMT and OMT are shown in Fig. 1. The basal spacing of MMT increased from 12.6 to 19.6 Å. When MMT was modified by $16Me^+Br^-$, the gallery of MMT was intercalated and was expanded by the molecular chain of $16Me^+Br^-$. The contents of OMT



Scheme 1 Synthesis of polyurethane (*PU*)/organophilic montmorillonite (*OMT*) nanocomposite: **a** sample a: molar ratio of reactants polyether/toluene diisocyanate (*TDI*)/diglycol = 1:2:1. **b** sample b: molar ratio of reactants polyether/TDI/diglycol = 1:3:2

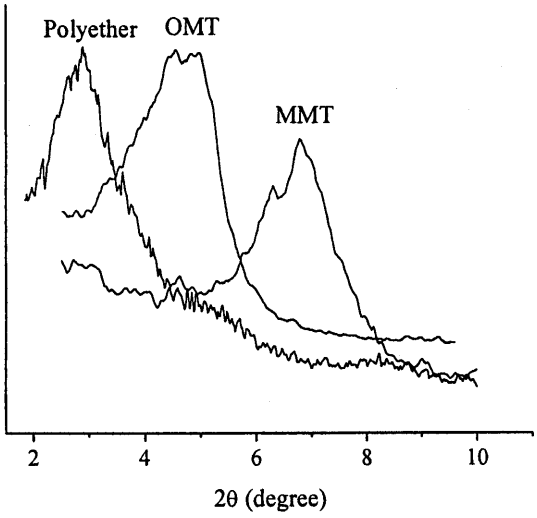


Fig. 1 X-ray diffraction (*XRD*) patterns of sodium montmorillonite (*MMT*) and organophilic montmorillonite (*OMT*)

Table 1 Organophilic montmorillonite (*OMT*) contents and X-ray diffraction data of sodium montmorillonite (*MMT*), OMT, polyether/OMT and polyurethane (*PU*)/OMT nanocomposites

		OMT (wt%)	2θ (°)	D (Å)
MMT			7.01	12.6
OMT		100	4.50	19.6
Polyether/OMT		20	2.80	31.5
PU/OMT sample a	a1	10	1.93	45.5
	a2	15	2.04	43.7
	a3	20	2.10	42.1
	a4	25	2.15	41.1
PU/OMT sample b	b1	10	1.82	48.5
	b2	15	1.94	45.5
	b3	20	2.12	41.7
	b4	25	2.21	39.9

in the hybrids and the basal spacing (001) are given in Table 1. The characteristic peak of the PE/OMT hybrid shifted from 19.6 to 31.5 Å; this confirmed that PE molecular chain intercalated into the gallery of OMT. PE did not react with the silicate sheet but the hydroxyl of PE formed a hydrogen bond with the hydroxyl on the silicate sheet. XRD curves of two series of PU/OMT samples that were prepared with different molar ratio of reactants (sample a: PE/TDI/diglycol = 1:2:1; sample b: PE/TDI/diglycol = 1:3:2) are shown in Figs. 2 and 3. Numbers 1, 2, 3 and 4 correspondi to 10, 15, 20 and 25 wt% contents of OMT in the hybrids. In the XRD curves of samples a and b, as well as the PE/OMT hybrid, the PU molecular chain intercalated into the gallery of OMT. The unique difference was the peak of OMT shifted to a lower angle compared to that of PE/OMT. The basal spacings of samples a1, a2, a3, a4, b1, b2, b3 and b4 were 45.5, 43.7, 42.1, 41.1, 48.5, 45.5, 41.7

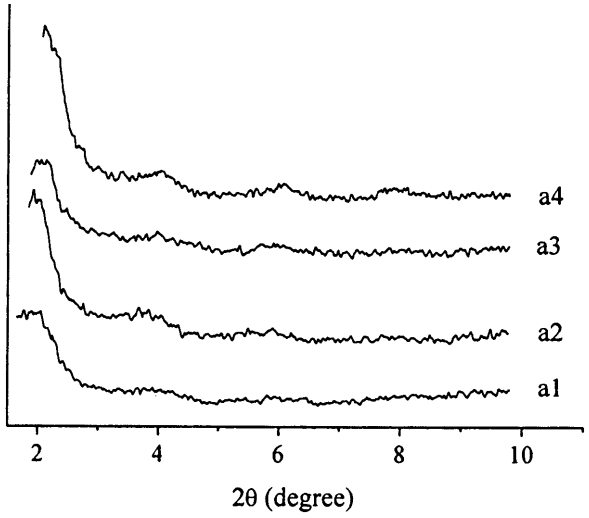


Fig. 2 XRD patterns of polyurethane (*PU*)/OMT nanocomposites (sample a) (molar ratio of reactants: polyether/toluene diisocyanate (*TDI*)/diglycol = 1:2:1; the OMT contents of samples a1, a2, a3 and a4 were 10, 15, 20 and 25 wt%, respectively)

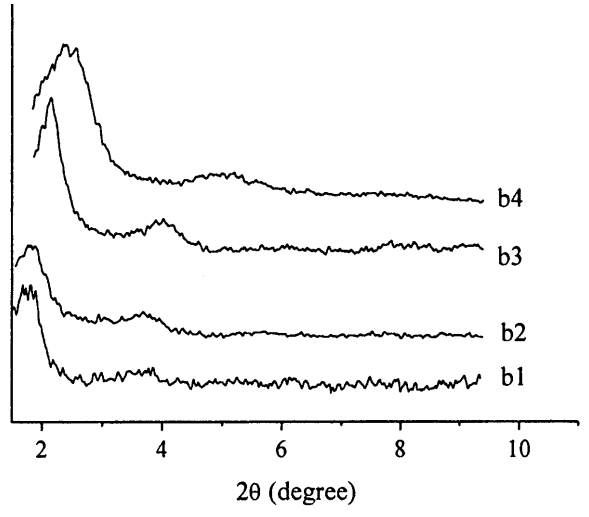


Fig. 3 XRD patterns of PU/OMT nanocomposites (sample b) (molar ratio of reactants: polyether/TDI/diglycol = 1:3:2; the OMT contents of samples b1, b2, b3 and b4 were 10, 15, 20 and 25 wt%, respectively)

and 39.9 Å, respectively. The microstructure of the PU/OMT hybrid contained the linear PU molecular chain intercalated in the gallery of silicate layers to form a multilayer structure consisting of alternating linear PU molecular chains stacked with the layers of the silicate layers. When the content of the layered silicate was increased, the basal spacing was decreased. When the content of the layered silicate was increased, the layered silicate was difficult to intercalate and swell. The molar ratios of the reactants of samples a and b were PE/TDI/diglycol = 1:2:1 and PE/TDI/diglycol = 1:3:2,

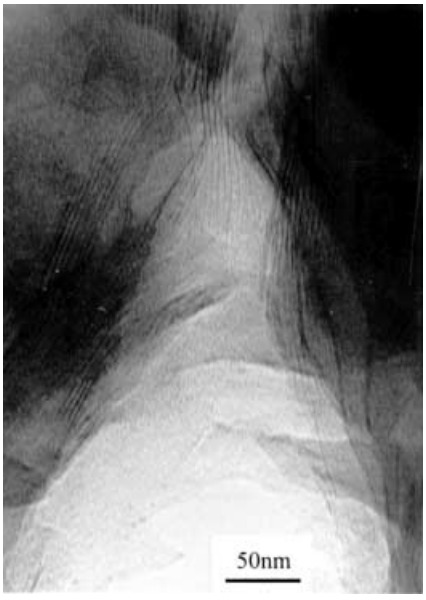


Fig. 4 High-resolution electron microscopy images of PU/OMT nanocomposites (sample a2)

respectively. PU in sample b had a higher hard segment content compared to that in sample a. It is well known that short, hard segments form microdomains by mutual attractions involving intermolecular hydrogen bonding. When the contents of the layered silicate were 10 and 15%, the basal spacing of sample a was narrower than that of sample b. It is implied that intercalation of PU and expansion of the gallery of layered silicate in sample a is difficult in comparison with that in sample b. Probably the molecular chain of PU in sample a was more flexible than that in sample b. When the contents of the layered silicate were 20 and 25%, the basal spacing of sample a was larger than that of sample b. The movement of the molecular chain of PU was probably restricted owing to the forming intermolecular hydrogen bond and the loading layered silicate in sample b in the course of the reaction. So the intercalation of PU was affected by the content of the hard segment of PU and the content of layered silicate. The XRD curves had second peaks corresponding to the (002) reflections of the intercalated phase in Figs. 2 and 3.

The microstructure of the nanocomposite was confirmed further using HREM. An HREM image of sample a2 is shown in Fig. 4: the dark lines correspond to the intersection sheet layers of about 1 nm thickness; the distance of two adjacent layers is about 4–5 nm. Individual layers of the silicate are clearly visible as regions of alternating narrow, dark and light bands within the particle (fringes).

Conclusion

A kind of PU/organophilic layered silicate nanocomposite was synthesized. Firstly, a kind of PE/OMT hybrid was prepared; PE was dispersed and intercalated into the gallery of the layered silicate. Then, PE/OMT reacted with TDI and diglycol to obtain PU/OMT intercalated nanocomposites as verified by XRD and HREM analysis. The basal spacing of the intercalated PU/OMT was coeffected by the content of the hard segment of PU and the layered silicate.

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