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SHORT COMMUNICATION

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Study of elastomeric polyurethane nanocomposites prepared from grafted organic–montmorillonite

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Abstract 4,4′-Diphenylmethane diisocyanate (MDI) was grafted on to organic–montmorillonite (OMMT) by reaction between hydroxyl groups (−OH) on surface of the montmorillonite and the isocyanate groups (−NCO) of MDI, thus forming grafted organic–montmorillonite (MOMMT). Intercalated nanocomposites based on polyurethane (PU) and MOMMT were prepared by solution intercalation technology. The interface interaction of PU/MOMMT nanocomposites was better than that of PU/MMT composites. The tensile strength, elongation at break, and tear strength of the PU/MOMMT nanocomposites increased for MOMMT content up to 5% *w*/*w*, and then decreased with further increase in MOMMT content. At the same filler content, the tensile strength and tear strength of PU/MOMMT nanocomposites were higher than those of PU/OMMT nanocomposites, whereas the elongations at break of PU/MOMMT nanocomposites were smaller than those of PU/OMMT nanocomposites. The initial temperatures of weight loss of PU/MOMMT nanocomposites were lower than for PU/MMT composites in the first step of thermal degradation, whereas in the second step initial temperatures of weight loss were higher for PU/MOMMT nanocomposites.

Keywords Montmorillonite · 4,4′-Diphenylmethane diisocyanate · Grafted · Polyurethane nanocomposites

Introduction

Polymer/layered silicate nanocomposites (PLSN) have attracted much interest because they have unexpected hybrid properties synergistically derived from the two components. Compared with conventional filled microcomposites, PLSN typically have higher modulus and strength, because of the effect of the nanoscale structure [1–4]. Polyurethane (PU) is a versatile polymeric material with desirable properties, for example high abrasion resistance, tear strength, excellent shock absorption, flexibility, and elasticity. By blending with inorganic fillers its performance has been improved further. In 1998, PU/clay nanocomposites were introduced. The nanocomposites were formed by adding methylene diphenyl prepolymer to a mixture of organoclay and polyol. The nanocomposites had improved strength, toughness and modulus [5]. PU/clay nanocomposites based on poly(caprolactone) (PCL), diphenylmethane diisocyanate, butanediol, and PCL/clay prepolymer were synthesized. PCL/clay prepolymer was first prepared in a nanocomposite form. Addition of 1.4% PCL/clay prepolymer resulted in PU/clay nanocomposites with much improved mechanical properties [6]. The hydrogen bonding and mechanical properties of PU/clay nanocomposites have been studied. Hydrogen bonding decreased with increasing amount of clay but reached a plateau at 5% *w*/*w* concentration. Increased tensile strength, elongation at break, and thermal stability and reduced water absorption were observed for PU/clay nanocomposites compared with pure PU [7–10, 14, 15]. PU/layered silicates nanocomposites with high tensile strength and high elongation at break were synthesized by using reactive swelling agent-modified silicates. Dispersion of layered silicates in PU was transformed from an

intercalated to an exfoliated structure when the number of hydroxyl groups of the swelling agent was increased. The improved morphology of the nanocomposites resulted in ultrahigh efficiency in enhancing the mechanical properties of PU [11]. A polyether/organoclay hybrid was first prepared. The polyether/organoclay was then reacted with toluene-2,4-diisocyanate (TDI) and diglycol to obtain PU nanocomposites. The basal spacing of the nanocomposites was effected both by the content of the hard segment of PU and by the layered silicate [12]. A type of PU/clay nanocomposite was synthesized by using modified 4,4′-diphenylmethane diisocyanate, modified polyether polyol (MPP), and MPP-treated clay. When the amount of clay was increased the strength and strain-at-break of the nanocomposites increased but thermal conductivity decreased slightly [13]. A PU/clay nanocomposite was synthesized using poly(tetramethylene glycol), 4,4′-diphenylmethane diisocyanate, 1,6-hexamethylenediamine-modified clay, and 1,2-diaminopropane. When the modified clay was used as a chain extender to replace part of 1,2-diaminopropane in the formation of PU/clay nanocomposites, the strength, strain-at-break and thermal properties of the nanocomposites were better than those of pure PU [16, 17]. PU/clay nanocomposites were synthesized using poly (ethylene adipate)diol, 1,4-butanediol, 4,4-diphenylmethane diisocyanate, and organified with hydroxyl end-group-treated clay. The barrier properties, thermal stability, and tensile properties of the PU nanocomposites increased substantially with increasing dispersibility of the treated clay [18]. Exfoliation of clay layers was achieved in a trihydroxyl branched polyether polyol by direct mixing and the corresponding exfoliated PU/clay nanocomposite was prepared. The interaction between the polyol and clay and the mixing temperature had important effects on the occurrence of exfoliation and intercalation [19]. The TDI-modified organoclay was prepared. Its interlayer distance was much greater. The modified organoclay was used to obtain intercalated polystyrene nanocomposites [20].

The strong interface interaction between silicate layers and PU matrix was important for preparation of PU/layered silicates nanocomposites with high mechanical properties. In this study, a modified organoclay was first synthesized by grafting 4,4′-diphenylmethane (MDI) on organoclay. PU nanocomposites were then prepared from PU and the modified organoclay. The tensile strength, tear strength, and thermal stability of PU/modified organoclay nanocomposites were higher than those of PU/organoclay, because of the presence of chemical bonding between the silicate layers of modified organoclay and the PU matrix.

Experimental

Materials

Poly(propylene glycol) (PPG, $\overline{M}_n$ =2000) was produced by Arch Chemicals (USA). 4,4′-Diphenylmethane diisocyanate (MDI) was produced by Huntsman (USA). 1,4-Butanediol (BDO) was purchased from Shanghai Chemical Reagent Company (China). Ca-montmorillonite (MMT) was obtained from Nanjing Clay Mineral Factory (China) and had a cation-exchange capacity (CEC) of 110 mequiv/100 g and a mean size of 40 μm. Cetryltrimethyl ammonium bromide (CTAB) was manufactured by Shanghai Lingfeng Chemical Reagent Company (Chian). Toluene was supplied by Nanjing Chemical Reagent Factory (China). *N*,*N*-Dimethylformamide (DMF) was manufactured by Shanghai Chemical Reagent Factory (China).

Preparation of organic–montmorillonite

A mixture of MMT and water was heated at 80 °C with stirring. An aqueous solution of CTAB was poured into the mixture and stirred vigorously for 6–8 h. The product, organic–montmorillonite (OMMT), was isolated by filtration, washed with water to remove CTAB residues, thoroughly dried in a vacuum oven, then ground to an average particle size of 40 μm.

Preparation of grafted organic–montmorillonite

MDI was added to a toluene/OMMT (95/5) suspension and reacted for 4–6 h at 80–90 °C with stirring. The product, grafted organic–montmorillonite (MOMMT), was isolated by filtration, extracted with toluene for 4 h under reflux in a Soxhlet extractor, then thoroughly dried and ground to an average particle size of 40 μm.

Synthesis of PU

The PU was synthesized by use of an MDI/PPG/BDO mole ratio of 3/1/2. Under nitrogen, MDI was put in a vessel and melted completely by heating to 70 °C. PPG was added and the mixture was heated to 85 °C for 2.5 h with stirring. BDO was added when the temperature had dropped to 40 °C and the mixture was stirred vigorously for 1–2 min.

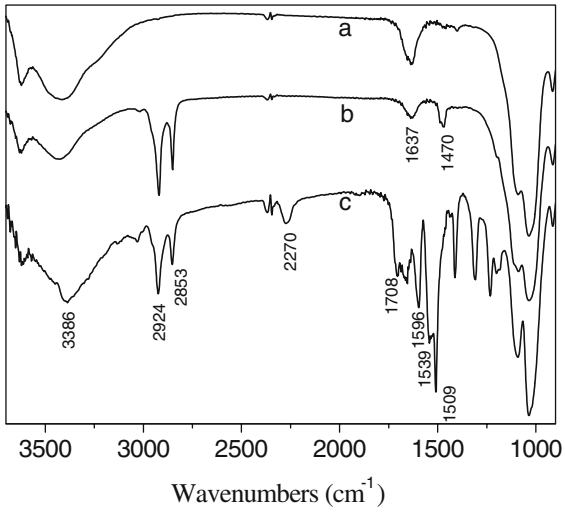

Fig. 1 FTIR spectra of MMT(*a*), OMMT(*b*) and MOMMT(*c*)

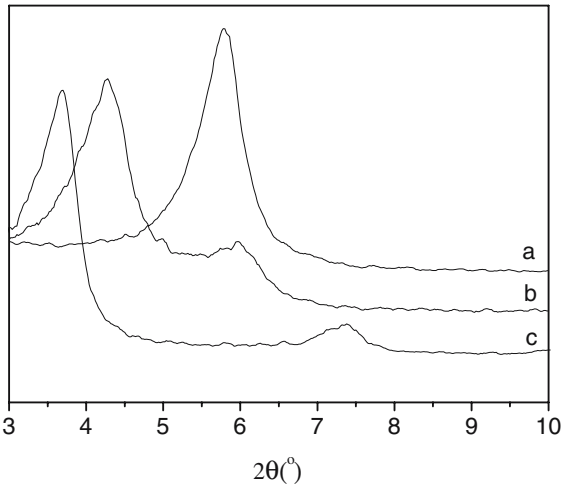

Fig. 2 XRD patterns of MMT(*a*), OMMT(*b*) and MOMMT(*c*)

After degassing, the product, PU, was placed in a mold at 140–160 °C for 12–16 h.

Preparation of PU/OMMT or PU/MOMMT composites

The OMMT or MOMMT was added to a solution of PU in DMF. The mixture was stirred vigorously for 6 h and treated by ultrasonic dispersion for 30–60 min. The products were poured into molds and the PU/OMMT or PU/MOMMT composites were obtained after complete removal of DMF.

Characterization

Fourier-transform infrared spectroscopy (FT-IR) analysis was performed with a Vector22 spectrometer. X-ray diffraction (XRD) was performed with a D/Max instrument. In the Molau test the samples and DMF were put in a test tube and agitated to form a uniform suspension which was then left undisturbed for 7 days, then the solution state was observed. The sample was embedded in epoxy resin and ultrathin sections were obtained by use of an ultramicrotome. Transmission electron microscopy (TEM) photographs were taken with a JEM-200CX microscope. Tensile tests were performed with an Instron 4466 tensile tester. Thermogravimetric (TG) analysis was performed with a TA 2100-SDT2960. The initial temperatures of weight loss in the first and second steps were denoted $T_{\mathrm{I}}^{\mathrm{i}}$ and T_{II}^{i} and

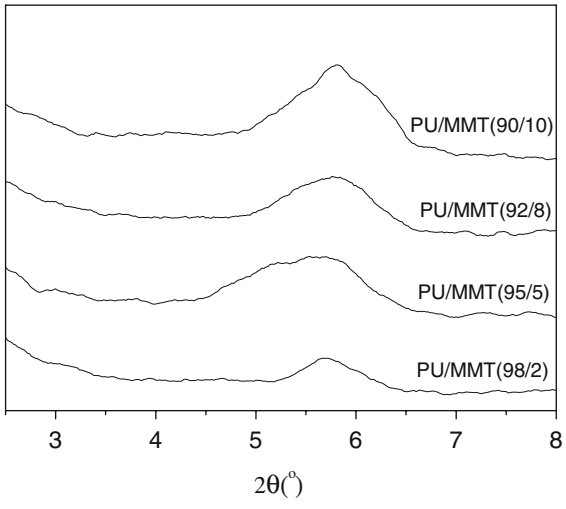

Fig. 3 XRD patterns of PU/MMT composites

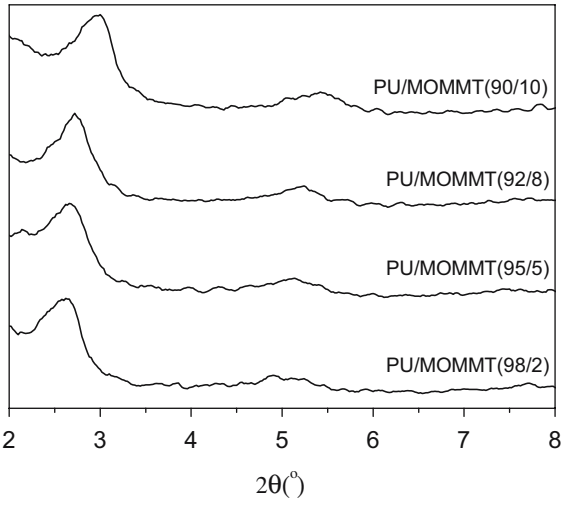

Fig. 4 XRD patterns of PU/MOMMT nanocomposites

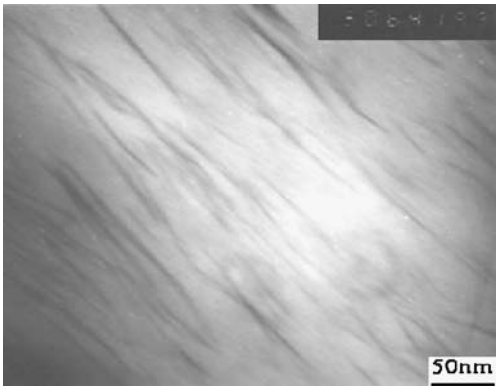

Fig. 5 TEM photograph of PU/MOMMT(95/5) nanocomposites

the corresponding temperatures to the maximum rate of weight loss were denoted $T_{\mathrm{I}}^{\max}$ and $T_{\mathrm{II}}^{\max}$.

Results and discussion

As shown in Fig. 1, a few new absorption peaks were found at approximately 2924 cm^{-1}, 2853 cm^{-1}, and 1470 cm^{-1} in the FT-IR spectrum of the OMMT. The absorption at 2924 cm^{-1} and 2853 cm^{-1} was attributed to asymmetric and symmetric stretching vibrations of C–H bonds whereas the absorption at 1470 cm^{-1} was attributed to methylene bending vibrations [3], indicating that the CTAB had been exchanged into the galleries of the silicate layers.

In the FT-IR spectrum of the MOMMT, absorption at approximately 3386 cm^{-1}, 2270 cm^{-1}, and 1708 cm^{-1} was attributed to stretching vibrations of the N–H, N=C=O and C=O bonds, respectively, and absorption at approximately 1596 cm^{-1}, 1539 cm^{-1}, and 1509 cm^{-1} was attributed to phenyl stretching vibrations, indicating that MDI was grafted on to the silicate layers by reaction between the hydroxyl groups (−OH) on surface of the silicates layers and the isocyanate groups (−NCO) of MDI [20].

As shown in Fig. 2, the diffraction peaks of the MMT, OMMT, and MOMMT appeared at approximately 5.78 °, 4.27 °, and 3.70 °, respectively, corresponding to interlayer spacing of 1.53 nm, 2.07 nm, and 2.39 nm, respectively. The interlayer spacing of OMMT was greater than that of pure MMT, because of intercalation of the swelling agent [8, 11]. Interlayer spacing of MOMMT was greater than that of OMMT, also indicating grafting of MDI on to the surface of the silicate layers [20].

The XRD patterns of PU/MMT and PU/MOMMT composites are shown in Figs. 3 and 4. The location of the diffraction peak of PU/MMT composites was no different from that of MMT, indicating that PU chains did not penetrate the galleries between the silicate layers, and PU/MMT composites were conventional particle-filled microcomposites. The diffraction peaks of the PU/MOMMT(98/2), PU/MOMMT(95/5), PU/MOMMT (92/8), and PU/MOMMT(90/10) composites occurred at approximately 2.65 °, 2.65 °, 2.72 ° and 3.02 °, respectively, corresponding to interlayer spacing of 3.33 nm, 3.33 nm, 3.24 nm, and 2.92 nm. The interlayer spacing of MOMMT in the composites was larger than that of MOMMT, indicating that PU chains had intercalated into the galleries between the silicate layers [21]. The interlayer spacing of MOMMT in the PU/MOMMT composites also decreased with increasing MOMMT content [12].

The DMF suspension of PU/MMT composites separated into two parts—a transparent solution of PU and MMT particles deposited at the bottom of the test tube because of poor interface interaction between the MMT particles and PU matrix [3, 4, 22]. The DMF solutions of the PU/MOMMT(98/2) and PU/MOMMT(95/5) composites were pale yellow, semitransparent, homogeneous emulsions, and the MOMMT platelets remained suspended for long time

Table 1 Mechanical properties of PU, PU/MMT, and PU/MOMMT composites

Sample	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN m^{-1})
PU	10.5	1087	36.4
PU//MMT (98/2)	10.7	858	32.3
PU/MMT (95/5)	10.0	938	36.4
PU/MMT (92/8)	9.5	926	39.2
PU/MMT (90/10)	8.7	893	37.6
PU/MOMMT (98/2)	14.7	1016	45.3
PU/MOMMT (95/5)	15.5	1023	48.1
PU/MOMMT (92/8)	15.3	1018	47.2
PU/MOMMT (90/10)	14.5	1004	45.6

Table 2 TGA results for PU, PU/MMT, and PU/MOMMT composites

Sample	T_{I}^{i} (°C)	$T_{\mathrm{I}}^{\max}$ (°C)	T_{I}^{i} (°C)	$T_{\mathrm{II}}^{\max}$ (°C)
PU	277	292	347	376
PU//MMT(98/2)	301	321	382	399
PU//MMT(95/5)	300	323	382	399
PU//MMT(92/8)	302	322	383	400
PU//MMT(90/10)	302	322	383	401
PU/MOMMT(98/2)	290	314	385	401
PU/MOMMT(95/5)	289	311	385	401
PU/MOMMT(92/8)	288	309	389	403
PU/MOMMT(90/10)	288	309	389	404

because of dispersion of the silicate layers on the nanometer scale and strong interface interaction between the silicate layers and the PU matrix [3, 4, 22]. The DMF solutions of the PU/MOMMT(92/8) and PU/MOMMT (90/10) composites separated into two parts—a pale yellow emulsion and small MOMMT particles deposited at the bottom of the test tube. This was because of aggregation of some of the silicate layers of MOMMT in the PU matrix with increasing MOMMT content.

As shown in Fig. 5, the silicate layers were dispersed in the PU matrix on the 5–10 nm scale and PU chains penetrated the galleries between the silicate layers, and intercalated nanocomposites were prepared.

The mechanical properties of the PU/MMT and PU/MOMMT composites are shown in Table 1. The MMT could not reinforce PU because of poor system dispersion and compatibility [3, 23]. The tensile strength and tear strength of PU/MOMMT composites increased for MOMMT content up to 5% *w*/*w*, and then decreased with a further increase in MOMMT content, because of the aggregation of some of the silicate layers in the PU matrix [3, 18]. The tensile strength and tear strength of PU/MOMMT nanocomposites were higher than those of PU/OMMT nanocomposites, because of chemical bonding between the silicate layers of the MOMMT and PU matrix [18], whereas their elongation at break were below those of PU/OMMT nanocomposites [14].

The TGA results for PU, PU/MMT, and PU/MOMMT composites are listed in Table 2. PU underwent two thermal degradation stages—degradation of the hard segment in first stage and of the soft segment in second [24]. T_{I}^{i} and T_{II}^{i} for the PU/MOMMT composites were more than 10 °C and 37 °C higher, respectively, than that for pure PU, because of barrier effect of the silicate layers in the composites [25]. The temperature of initial weight loss of PU/MOMMT nanocomposites in the first step was lower than that for PU/MMT composites, because of the acid catalytic effect of protonated silicate layers [21, 26] and degradation of the swelling agent [7, 14]. In the second step, PU/MOMMT nanocomposites were more thermally stable, because of the increasing barrier effect of diffusion of degradation products into the gas phase which caused the "labyrinth" effect of the silicate layers dispersed on the nanometer scale in the PU matrix [25, 27], and strong interface interaction between the silicate layers and PU chains resulted in a restriction effect on PU chains [10].

Conclusion

A PU nanocomposite has been synthesized from PU and MDI-modified OMMT. The intercalated morphology of PU/MOMMT nanocomposites formed in the PU matrix was confirmed by their X-ray diffraction and TEM. The tensile strength and tear strength of PU/MOMMT (98/2) nanocomposites were 40% and 24.5% higher, respectively, than those of pure PU and the thermal stability of PU/MOMMT nanocomposites was substantially better than that of PU, because of barrier effect of the silicate layers. Reinforcement of PU by MOMMT was greater than that by OMMT, because of the presence of chemical bonding between silicate layers of MOMMT and the PU matrix. This finding is valuable information for the PU industry.

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