

Surface-Modifiers of Clay on Mechanical Properties of Rigid Polyurethane Foams/Organoclay Nanocomposites

Zhongbin Xu,^{1,2} Xiling Tang,^{1,2} Aijuan Gu,³ Zhengping Fang,¹ Lifang Tong¹

¹Institute of Polymer Composites, Zhejiang University, Hangzhou, Zhejiang, People's Republic of China

²State Key Laboratory of Polymer Reaction Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou, Zhejiang, People's Republic of China

³Department of Materials Science & Engineering, Materials Engineering Institute, Soochow University, Suzhou, Jiangsu, People's Republic of China

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ABSTRACT: Three different surface modifiers, octadecyl trimethyl ammonium (ODTMA), octadecyl primary ammonium (ODPA), and decanediamine (DDA) were used to modify Na⁺-montmorillonite (MMT), and the resultant organoclays were coded as ODTMA-MMT, ODPA-MMT, DDA-MMT, respectively. Rigid PU foams/organoclay composites were prepared by directly using organoclay as the blowing agent without the addition of water. Investigation shows that the morphology of the nanocomposites is greatly dependent on the surface modifiers of clay used in the composites. In detail, DDA-MMT is partially exfoliated in the PU matrix with the smallest cell size, while two others are intercalated in the PU matrices with smaller cell sizes. The sequence of their cell sizes is pristine PU foams > rigid PU foams/ODTMA-MMT > rigid PU foams/ODPA-MMT > rigid PU foams/DDA-MMT, and the aver-

age cell size of rigid PU foams/DDA-MMT composites decreases evidently from 0.30 to 0.07 mm. Moreover, all rigid PU foams/organoclay composites show remarkable enhanced compressive and tensile strengths as well as dynamic properties than those of PU foams, and the enhancement degree coincides well with the relative extent of internal hydrogen bonding of materials and gallery spacing of organoclay. For example, in the case of rigid PU foams/DDA-MMT composite, 214% increase in compressive strength and 148% increase in tensile strength compared with those of pure PU foams were observed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2988–2995, 2007

Key words: dispersion; rigid polyurethane foams; organoclay; surface-modifier

INTRODUCTION

The biggest disadvantage of polyurethane (PU) foams when used as structural or semistructural materials is their low mechanical strengths, such as compressive strength and tensile strength, which are key physical properties of materials to stand strain when being used. Recently, clay, or montmorillonite, has been successfully introduced to a polymer system^{1–5} and extensively used in the polymer industry either as a reinforcement to improve the physical, mechanical properties of the final polymer or as a filler to reduce the amount of polymer used in the shaped structures, thereby lowering the high cost of the polymer systems. The special structure of clay plays important roles in improving mechanical, thermal, and diffuse barrier properties of polymer-layered silicate nanocomposites.^{6–9} To date, a great deal of effort has been devoted to the development of nanostructured PU/clay composites.^{10–19} These

investigations show that PU/clay composites exhibit an improvement in elongation, insulation, aging,¹⁹ tensile modulus, and strength, but a decrease or no enhancement in compressive strength.^{10,15–18}

To overcome the aforementioned problems, we have devised a novel method to prepare rigid PU foams/clay nanocomposites, in which organoclay not only acts as the reinforcement, but also as a blowing agent for the PU foams.²⁰ Moreover, the most interesting result is that rigid PU foams/organoclay nanocomposites with appropriate organoclay loading have significant higher values of both compressive and tensile strengths than those of pure PU foams with maximum values appearing at 2 phr clay.²⁰

It is well known that the dispersion of organoclay in the polymer matrix offers a significant influence on the mechanical properties of polymer/organoclay nanocomposites, and it is mainly dependent on the modification agent used to prepare the organoclay.^{21–27} Our previous work mainly focused on investigating the effects of cell structure and hydrogen bonding on the mechanical properties of rigid PU foams/organoclay nanocomposites fabricated via the novel method developed by ourselves, and the

Correspondence to: A. Gu (ajgu@suda.edu.cn).

dispersion mode of clay in the PU matrix is intercalation accompanied by less exfoliation. Therefore, there is an interest to investigate the effect of dispersion mode of clay in the PU matrix on mechanical properties of rigid PU foams/organoclay nanocomposites and to evaluate the possibility of further improvement in both compressive and tensile strengths by changing the dispersion mode of clay in the PU matrix.

Herein, to prepare rigid PU foams/organoclay nanocomposites with various dispersion modes of organoclay in the PU matrix, three different surface-modifiers of clay were selected to modify organoclays, and their effects on mechanical properties of the nanocomposites resulting from the different dispersion modes of organoclay in the PU matrix were investigated in detail.

EXPERIMENTAL

Materials

Polyether polyols 4110 (OH value, 430 ± 30 KOH mg/g); viscosity, 2000–3000 mPa/s at 25°C) were obtained from Jiangsu Chemical Research Institute, China. Diphenylmethane-4,4'-diisocyanate (MDI), 5005, made by Huntsman, USA (NCO wt % 31; viscosity: 170–270 mPa s at 25°C) was used as received. A-33 (33 wt %, triethylene diamine in dipropylene glycol), dibutyltin dilaurate, silicone oil, and 2,4,6-Tri(dimethylaminomethyl) phenol (coded as DMP-30) purchased from Jiangsu Chemical Research Institute, China. Water was used as the blowing agent of pure PU foams but not PU foams/organoclay nanocomposites.

Three organoclays were used. One was a montmorillonite ion-exchanged with octadecyl trimethyl ammonium, coded as ODTMA-MMT, which was supplied by Zhejiang Huate Clay Products of China. The second one was Na⁺-montmorillonite modified by octadecyl primary ammonium, coded as ODPA-MMT, which was provided by Zhejiang Fenghong Clay Chemicals. The third one was Na⁺-montmorillonite (cation-exchange capacity = 90 meq/100 g) partially protonated by decanediamine (DDA), coded as DDA-MMT, which was synthesized by ion exchange reaction between Na⁺-montmorillonite and DDA following the procedure described in litera-

tures.^{25,27–29} The DDA has been partially protonated by adding insufficient hydrochloric acid to the reaction medium during the process. DDA was previously mixed with HCl in water and heated at 60°C for a few minutes. The CEC DDA/clay ratio was 1 : 5 and the molar DDA/HCl ratio was 1 : 1. As DDA has two NH₂— group, the molar DDA/HCl ratio with 1 : 1 was to make DDA excessive and then partially protonated. DDA was obtained from Huadong Medicine, Equipment Chemical Reagent Branch, China.

Preparation of pure PU foams and rigid PU foams/organoclay nanocomposites

Pure PU foams and rigid PU foams/clay nanocomposites were prepared by one-shot process. For preparing rigid PU foams/organoclay composites, water was not added into the formulations, and organoclay was used as both reinforcement and blowing agent.²⁰ In addition, all rigid PU foams/organoclay nanocomposites contain 2 phr (parts per hundreds of resin) organoclay, because it was found to be the optimum clay loading in our previous work according to its integrate mechanical properties.²⁰

The detailed formulations for pure PU foams and PU foams/organoclay nanocomposites are shown in Table I. For preparing pure PU foams, according to the formulation listed in Table I, appropriate content of catalysts (A-33 and dibutyltin dilaurate), surfactant (silicone oil), crosslinking agent (DMP-30), and blowing agent (water) were added into 100 g polyether polyols in a plastic beaker with a high shear stirrer at 3000 rpm for 2 min at ambient temperature to form component A. Then, MDI was added with a molar ratio of 1.5 : 1 (relative to polyols 4110, NCO/OH = 1 : 2) into component A to assure the complete reaction of polyols, with the high shear stirrer at 3000 rpm for another 2 min at ambient temperature. After that, the mixture was immediately poured into a glass mold (300 × 300 × 100 mm) to produce free-rise rigid PU foams followed by postcuring at 70°C for 6 h in an oven.

For preparing rigid PU foams/clay nanocomposites, organoclays were dehydrated in an oven at 70°C overnight before use. According to the formulation listed in Table I, appropriate content of dried organoclay powder was first mixed with 100 g polyether

TABLE I
The Formulations for Preparing of Rigid PU Foams/Organoclay Nanocomposites

Sample code	Clay content (phr)	Water content (phr)	Polyether polyols (phr)	Catalyst A-33 (phr)	Dibutyltin dilaurate (phr)	DMP-30 (phr)	Silicone oil (phr)	MDI 5005 (molar ratio)
Pure PU foams	0	1	100	1.0	0.05	1.5	2.0	150
PU foams/ODTMA-MMT	2	0	100	1.0	0.05	1.5	2.0	150
PU foams/ODPA-MMT	2	0	100	1.0	0.05	1.5	2.0	150
PU foams/DDA-MMT	2	0	100	1.0	0.05	1.5	2.0	150

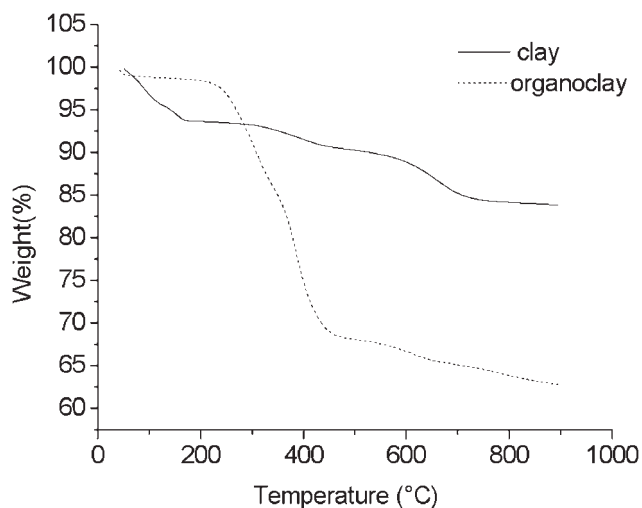


Figure 1 TGA curves of pristine clay and organoclay.

polyols in a plastic beaker by a high shear stirrer for 2 min at ambient temperature, and subsequently an oil bath sonication was applied to the suspension of organoclay in polyether polyols at 50°C for 2 h, using a KQ-100DE ultrasonicator (100 W, nominal frequency of 50 kHz). Catalysts (A-33 and dibutyltin dilaurate), surfactant (silicone oil), and crosslinking agent (DMP-30) were always added into the polyols/clay mixture to form component A. Then, the residual process is identical with the corresponding part of the preparation of pure PU foams. In this procedure for preparing rigid PU foams/clay nanocomposites, water was not added into the formulations as the blowing agent. All ingredients were mixed by an impeller at 3000 rpm.

Measurements

The contents of boundwater intercalated between interlayers of organoclay were determined by thermogravimetry analysis (TGA) in a TA SDT Q600 thermal analyzer under a nitrogen atmosphere. The sample was heated from 50 to 900°C with a heating rate of 10°C/min.

X-ray diffraction (XRD) was conducted at ambient temperature on Rigaku (Japan) D/MAX-2550PC diffractometer (40 kV, 30 mA, Cu K α radiation with $\lambda = 1.54 \text{ \AA}$) to measure the *d*-spacing of organoclays. Each sample was scanned from $2\theta = 0.5$ to 30° at a scanning rate of 5° min^{-1} .

Transmission electron micrographs (TEM) were obtained by using a JEM-1200EX electron microscope to examine the intercalation and exfoliation states of clay in composites. The TEM specimens were cut into thin film with a thickness of 70–90 nm by using a Diatome diamond knife at room temperature.

The cellular structure of a sample in the thickness direction was investigated by a polarizing micro-

scope on a XP-J203E polarizer (Shanghai Changfang Optical Instrument, China). The cell size was measured by measuring a minimum of 30 cell diameters.¹⁵

The Fourier transformed infrared spectroscopy (FTIR) spectra of PU foams/organoclay composites were recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} on a Vector-22 FTIR spectrometer.

Dynamic mechanical analysis (DMA) for rigid PU foams/organoclay composites from 25 to 250°C were performed on a NETZSCH DMA 242 C (NETZSCH, Selb, Germany) operated at a driving frequency of 1.0 Hz and a scanning rate of 5°C/min in nitrogen atmosphere. The specimen geometry was $20 \times 5 \times 3 \text{ mm}$ (length \times width \times thickness).

The compressive strength of a sample was measured by an RGT-X010 universal testing machine (Shenzhen Reger Instrument, China) with a crosshead speed of 2 mm/min according to GB/T8813. The specimen had a dimension of $50 \times 50 \times 50 \text{ mm}$ (width \times length \times thickness). The value of the compressive strength was recorded when the samples reached 10% deformation.

The tensile strength was tested using a RGT-X010 universal testing machine (Shenzhen Reger Instrument, China) with a crosshead speed of 5 mm/min according to GB/T9641-88. The size of each sample was $25 \times 100 \times 10 \text{ mm}$ (width \times length \times thickness). For each data point, five samples were tested, and the average value was taken.

RESULTS AND DISCUSSION

Thermogravimetry analysis of pristine clay and organoclay

Previous investigations by other researchers have proved that the desorbed water molecules adsorbed to the cations between interlayers of clay

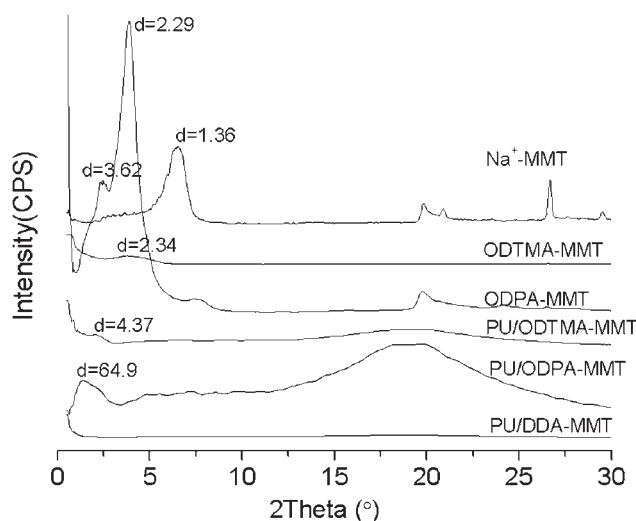


Figure 2 XRD images of organoclay and rigid PU foams/organoclay nanocomposites.

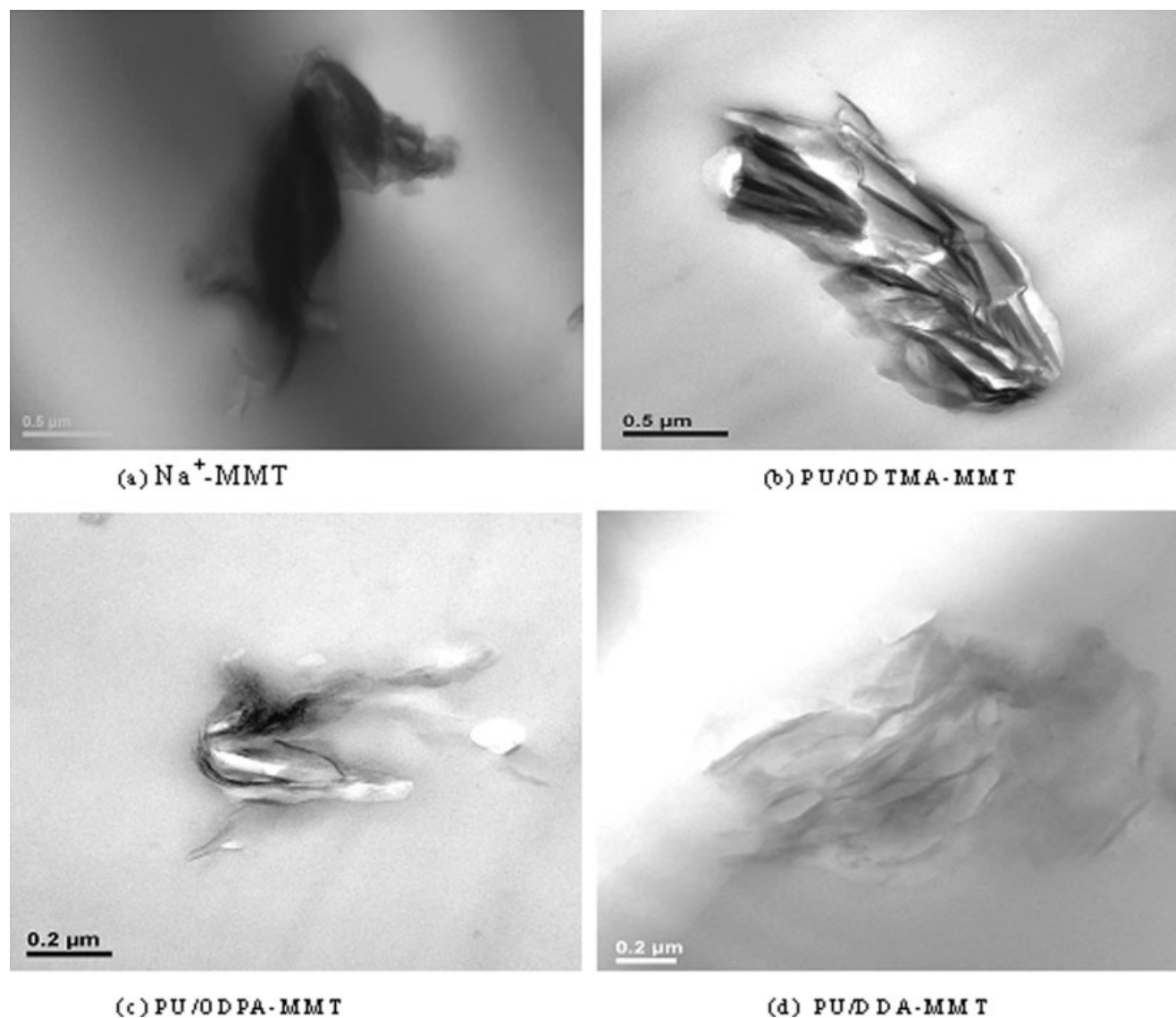


Figure 3 TEM images of Na^+ -MMT and rigid PU foams/organoclay composites.

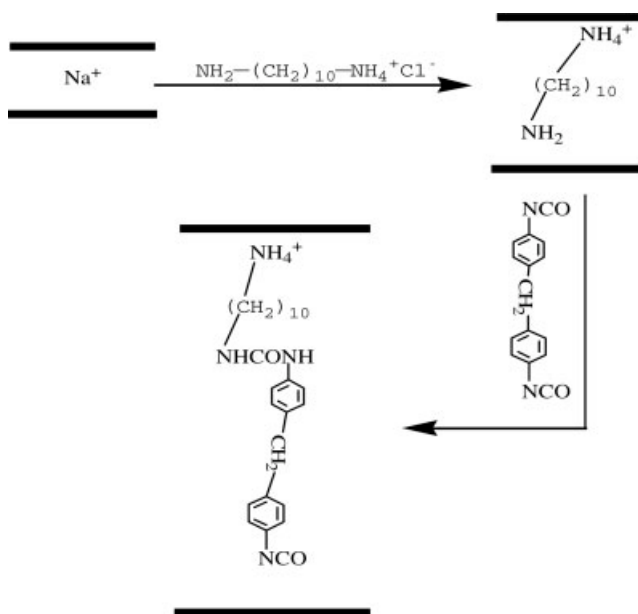
evaporates at the temperature range of 50–170°C, and the dehydration of the boundwater molecules from the crystal lattice of pristine clay evaporates at the temperature range of 450–900°C.^{29,30} Figure 1 presents the TGA curves for pristine clay and organoclay. It can be seen that at the temperature range of 50–170°C, the pristine clay has 6.67 wt % loss of the desorbed water, while organoclay only has 1.66 wt % loss of the desorbed water. However, at the temperature range of 450–900°C both samples have almost the equal weight loss (5.98 wt %) of boundwater molecules from the crystal lattice of organoclay. In addition, the great difference between the two TGA curves is that the organoclay sample has large amount (about 29.8%) of weight-loss at the temperature range of 230–450°C, which was contributed by the thermal decomposition of the surface modifier.

The morphology of rigid PU foams/organoclay nanocomposites

The X-ray diffraction patterns of various clays and PU/organoclay nanocomposites are presented in Figure 2. The gallery spacing of the Na^+ -montmorillonite is 1.36 nm at $2\theta = 6.5^\circ$, and the gallery spacing of ODTMA-MMT platelets or ODPA-MMT platelets is 2.34 nm or 3.62 nm, respectively. The diffraction peak of rigid PU foams/ODTMA-MMT composite is at $2\theta = 2.03^\circ$, corresponding to a spacing of 4.37 nm, indicating that the silicate layer galleries of the ODTMA-MMT were intercalated when introduced



Scheme 1 Reaction between NH_2- and isocyanate groups.



Scheme 2 Intercalation of MMT with DDA.

into the PU matrix. The spacing of organoclay in the rigid PU foams/ODPA-MMT composite increases to 6.4 nm, which is much larger than that in rigid PU

foams/ODTMA-MMT composite. For the XRD patterns of rigid PU foams/DDA-MMT composite, peaks were all totally absent, suggesting the clay platelets may be partially exfoliated in the PU matrix. These changes of gallery spacing of organoclay indicate that both rigid PU foams/ODTMA-MMT and rigid PU foams/ODPA-MMT composites are intercalated, while rigid PU foams/DDA-MMT is mainly intercalated or partially exfoliated. This conclusion is corroborated with TEM photos as shown in Figure 3. The morphology of rigid PU foams/ODTMA-MMT composite is intercalation [Fig. 3(b)] compared with that of Na⁺-montmorillonite [Fig. 3(a)]. Figure 3(c) shows that the clay platelets are more largely intercalated in the PU/ODPA-MMT nanocomposite, whereas DDA-MMT platelets are mainly intercalated or partially exfoliated in the PU matrix [Fig. 3(d)].

The reason leading to the different morphology can be found from the interaction between organoclays and the PU matrix. It is well known that NH₂- can easily react with isocyanate group (NCO-),³¹ as shown in Scheme 1.

So free NH₂-groups in the molecule of partly protonized DDA (NH₂-(CH₂)₁₀-NH₄⁺Cl⁻) can

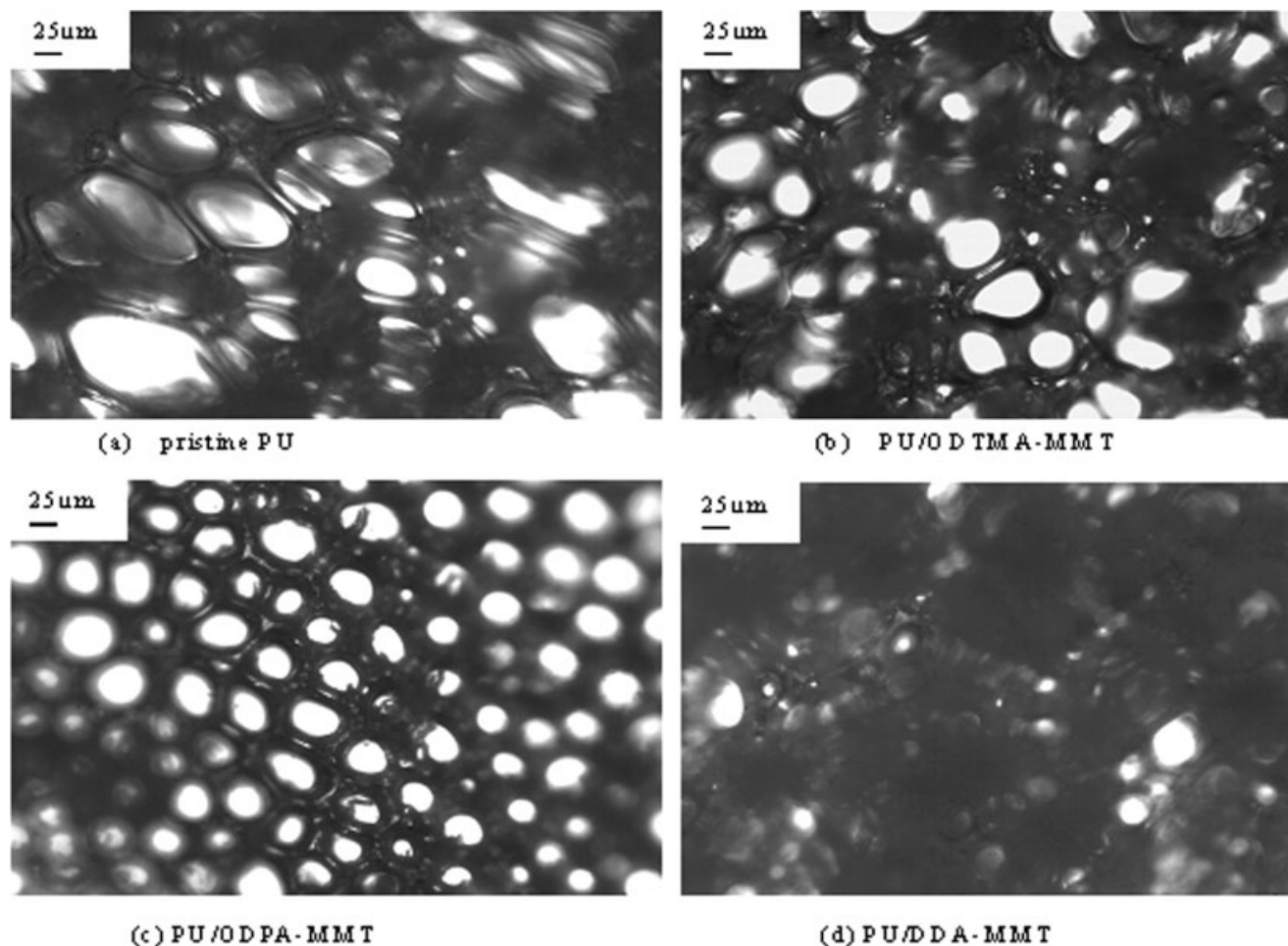


Figure 4 Polarizing microscope images of pristine PU foams and rigid PU foams/organoclay nanocomposites.

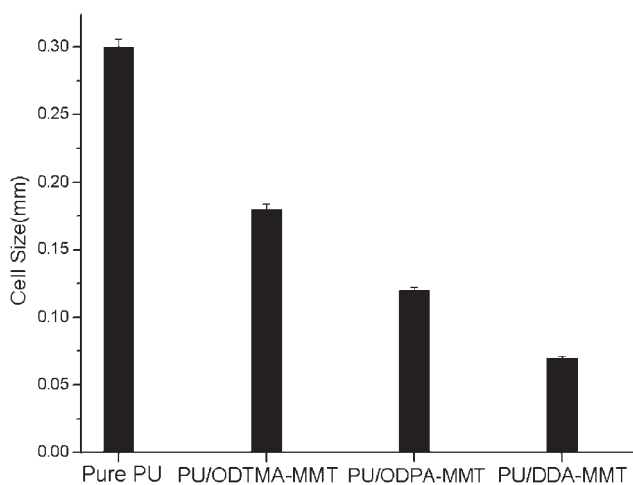


Figure 5 Cell sizes of rigid PU foams/organoclay nanocomposites.

react with the isocyanate group in the molecule of PU, and thus leading to the partial exfoliation of the clay platelets (Scheme 2). However, the other two organoclays do not have reactive groups which can react with the PU matrix, and so they appear in interacted states in the PU matrix.

The morphologies of rigid PU foams/organoclay composites demonstrate that surface modifiers of clay has a great effect on the dispersion of clay platelets in the PU matrix, which would in turn affect the mechanical properties of PU foams/organoclay composites.

Figure 4 gives the polarizing microscope images magnified by 500 times, and the cell sizes of rigid PU foams/organoclay composites are shown in Figure 5. It can be seen that three PU foams/organoclay composites have smaller cell sizes than those of pristine PU foams; the detail sequence of their cell sizes is pristine PU foams > PU foams/ODTMA-MMT > PU foams/ODPA-MMT > PU foams/DDA-MMT. In detail, the average cell size of rigid PU/DDA-MMT composites decreases evidently from 0.30 to 0.07 mm, indicating that surface-modifiers of clay have a great effect on the cell structure of rigid PU foams/organoclay composites, which directly in turn determines the mechanical properties of the composites as discussed later in this article.

The chemical structure of PU foams/organoclay composites

The FTIR spectra (Fig. 6) show the structure of rigid PU foams/organoclay composites. The positions of bands for distinctive functional groups of pure PU foams and nanocomposites are identical, indicating that the chemical structures of PU foams are not altered by the presence of organoclay. However, the degrees of hydrogen bonding of three PU/organo-

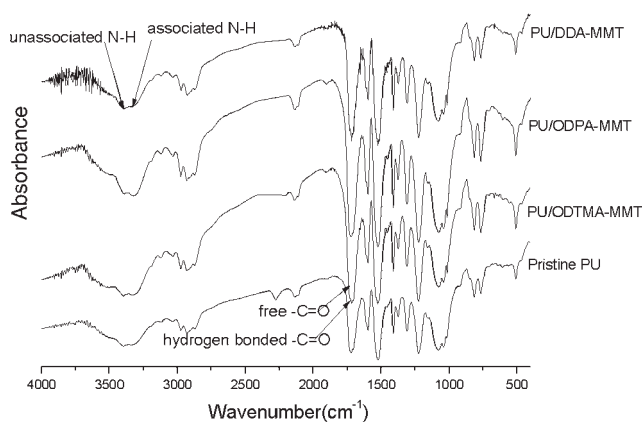


Figure 6 FTIR spectra of pristine PU and rigid PU foams/organoclay nanocomposites.

clay composites are different. In Figure 6, the infrared bands at 3402 and 3328 cm^{-1} are due to the unassociated $N-H$ stretching and the associated $N-H$ stretching in the PU molecular, respectively. The 1741 cm^{-1} band is caused by the free carbonyl, and the band at 1719 cm^{-1} is associated with the hydrogen-bonded carbonyls.^{26,32} The possible functional groups acting as the acceptors in the hydrogen bonding with $N-H$ are the urethane carbonyl ($-C=O$), the ether ($-C-O-C-$) and the oxygen of the boundwater between the interlayers of organoclays. The degree of the carbonyl groups participating in hydrogen bonding can be described by the hydrogen bonding index (R) of carbonyl groups, as given in the following equation:

$$R = \frac{C_{\text{bonded}}\epsilon_{\text{bonded}}}{C_{\text{free}}\epsilon_{\text{free}}} = \frac{A_{1707}}{A_{1734}} \quad (1)$$

where C is the concentration, ϵ_{bonded} or ϵ_{free} is the extinction of the hydrogen bonded carbonyl groups or the free carbonyl groups, respectively, and A is the intensity of the characteristic absorbance. Generally speaking, the value of $\epsilon_{\text{bonded}}/\epsilon_{\text{free}}$ is between 1.0 and 1.2,^{33,34} and which is assumed to be 1.0 in this study.

Table II reveals that the hydrogen bonding indexes of three rigid PU foams/organoclay composites are higher than pristine PU foams, and the detail sequence of their hydrogen bonding indexes is pris-

TABLE II
Hydrogen Bonding Index (R) of Rigid PU Foams/
Organoclay Nanocomposites

	R
Pure PU foams	0.84
PU foams/ODTMA-MMT	1.79
PU foams/ODPA-MMT	2.17
PU foams/DDA-MMT	2.43

tine PU foams < PU foams/ODTMA-MMT < PU foams/ODPA-MMT < PU foams/DDA-MMT, suggesting that rigid PU foams/organoclay composites have higher internal strength than pristine PU foams, and the PU foams/DDA-MMT composite has the highest internal strength among the four kinds of samples.

On the other hand, the rigid organoclay blocks form closely packed structures in the matrix of the elastic PU blocks. These rigid blocks, called the domains of organoclays, substantially strengthen the entire system, playing the role of an effective filler.

The mechanical properties of rigid PU foams/organoclay nanocomposites

Figure 7 shows the DMA plots of rigid PU foams/organoclay nanocomposites. The elastic modulus of rigid PU/organoclay composites is much greater than that of pure PU foams. It is noteworthy that the intercalated clay can bring in a significant improvement in elastic modulus, while the exfoliated clay is obviously much more effective. The incorporation of DDA-MMT, ODPA-MMT, or ODTMA-MMT, respectively, in PU foams leads to an enhancement of the elastic modulus of 4.8, 4, or 1.5 times over that of pure rigid PU foams, respectively. The enhancement degree coincides well with both sequences of the internal strength of materials and the gallery spacing of organoclay. In detail, the higher the internal strength of materials and/or the gallery spacing of organoclay, the higher the enhancement degree of mechanical properties of rigid PU/organoclay composites, when compared with pristine PU foams.

Figures 8 and 9 present the compressive strength and tensile strength of the PU/organoclay nanocomposites, respectively. It is found that both compressive

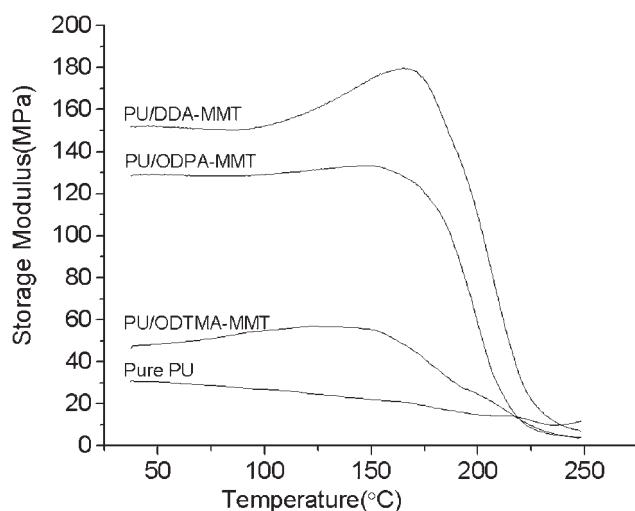


Figure 7 DMA curves of pure PU foams and rigid PU foams/organoclay nanocomposites.

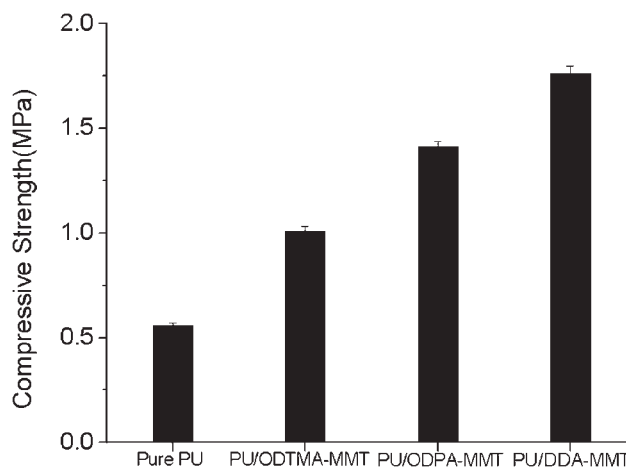


Figure 8 Compressive strength of pure PU foams and rigid PU foams/organoclay nanocomposites.

sive strength and tensile strength increase dramatically with the addition of organoclay in the PU matrix. Comparing the compressive strength and tensile strength of pure PU foams (0.56 MPa in compression and 0.86 MPa in tension), with the addition of ODTMA-MMT, ODPA-MMT, or DDA-MMT in PU foams, respectively, there are about 80%, 152%, or 214% increase in the compressive strength, respectively, while there is a 44%, 110%, or 148% increase in the tensile strength. Two factors can be used to interpret the enhancement in both compressive strength and tensile strength, that is, the increased internal strength of materials resulting from higher hydrogen bonding and the enlarged gallery spacing of organoclay in the PU matrix.

CONCLUSIONS

The morphology (including the dispersion state of organoclay in the PU matrix and the cell structure of

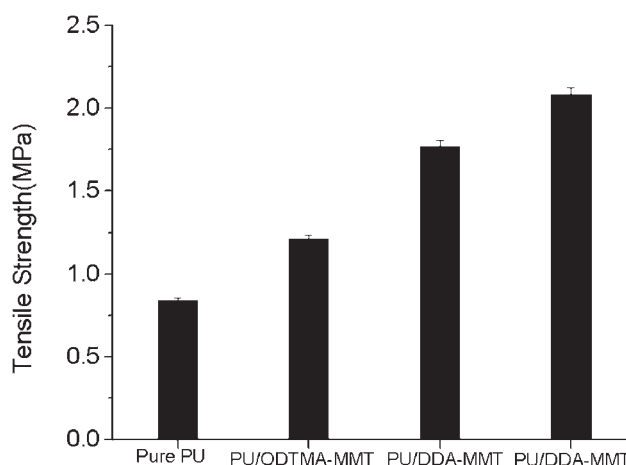


Figure 9 Tensile strength of pure PU foams and PU foams/organoclay nanocomposites.

rigid PU foams/organoclay composites) of rigid PU foams/organoclay composites is greatly depended on the nature of organoclays, and the nature of organoclays lies on their surface modifiers. DDA-MMT can be partially exfoliated in the PU matrix because of the reaction between free NH_2 — functional groups in DDA-MMT and the isocyanate groups of the PU matrix, and the corresponding nanocomposite has the smallest cell size. However, ODTMA-MMT and ODPA-MMT are intercalated in the PU matrix, and the corresponding composites show some what smaller cell sizes of the foam matrix than that of pristine PU foams. In addition, hydrogen bonding indexes of three rigid PU foams/organoclay composites are higher than pristine PU foams. Rigid PU/organoclay composites show remarkable enhanced compressive and tensile strengths as well as dynamic properties than PU foams, simultaneously, and the enhancement degree coincides well with the sequences of the internal strength of materials and gallery spacing of organoclay.

References

1. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T. *J Mater Res* 1993, 8, 1179.
2. Uhi, F. M.; Davuluri, S. P.; Wong, S. C.; Webster, D. C. *Chem Mater* 2004, 16, 1135.
3. Krikorian, V.; Pochan, D. *J Macromol* 2004, 37, 6480.
4. Chaiko, D. J.; Leyva, A. A. *Chem Mater* 2005, 17, 13.
5. Alexandre, M.; Dubois, P. *Mater Sci Eng R: Rep* 2000, R28, 1.
6. Asim, P.; Sadhan, C. *J Polym* 2005, 46, 3394.
7. Woo, J. C.; Se, H. K.; Young, J. K. *Polymer* 2004, 45, 6045.
8. Mariarosaria, T.; Giuliana, G.; Vittoria, V. *Polymer* 2002, 43, 6147.
9. Yao, K. J.; Song, M.; Hourston, D. *J Polym* 2002, 43, 1017.
10. Cao, X.; Lee, L. J.; Widya, T. *Polymer* 2005, 46, 775.
11. Wang, Z.; Pinnavaia, T. *J Chem Mater* 1998, 10, 3769.
12. Chang, J. H.; Yu, A. N. *J Polym Sci Part B: Polym Phys* 2002, 40, 670.
13. Tien, Y. I.; Wei, K. H. *Macromolecules* 2001, 34, 9045.
14. Chen, T. K.; Tien, Y. I.; Wei, K. H. *Polymer* 2000, 41, 1345.
15. Widya, T.; Macosko, C. W. *J Macro Sci Part B: Phys* 2005, 44, 897.
16. Krishnamurthi, B.; Bharadwaj-Somaskandan, S.; Shutov, F. In *Proceedings of the Polyurethanes Expo*, Columbus, OH, September 30 to October 3, 2001. p 239.
17. Javni, I.; Zhang, W.; Karajkov, V. *J Cell Plast* 2002, 38, 229.
18. Mondal, P. Ph.D. Thesis, Indian Institute of Technology, Bombay, 2004.
19. Kresta, J. E.; Wu, J.; Crooker, R. M. U.S. Pat. 6,518, 324, (2003).
20. Xu, Z. B.; Tang, X. L.; Gu, A. J. China Pat. 200610052995.1 (2006).
21. Chiu, H. T.; Wu, J. H. *J Appl Polym Sci* 2005, 98, 1206.
22. Nam, P. H.; Fujimori, A.; Masuko, T. *J Appl Polym Sci* 2004, 93, 2711.
23. Wang, H. S.; Zhao, T.; Yu, Y. Z. *J Appl Polym Sci* 2005, 96, 466.
24. López-Quintanilla, M. L.; Sánchez-Valdés, S.; Ramos de Valle, L. F.; Medellín-Rodríguez, F. J. *J Appl Polym Sci* 2006, 100, 4748.
25. Chen, H. W.; Chiu, C. Y.; Chang, F.C. *J Polym Sci Part B: Polym Phys* 2002, 40, 1342.
26. Kuan, C. H.; Ma, C. M.; Chung, W. P.; Su, H. Y. *J Polym Sci Part B: Polym Phys* 2005, 43, 1.
27. Zhang, W. A.; Liang, Y.; Luo, W. *J Polym Sci Part A: Polym Chem* 2003, 41, 3218.
28. Park, J. H.; Jana, S. C. *Macromolecules* 2003, 36, 2578.
29. García-López, D.; Gobernado-Mitre, I.; Fernández, J. F. *Polymer* 2005, 46, 2758.
30. Lee, J. Y.; Lee, H. K. *Mater Chem Phys* 2004, 85, 410.
31. Wirpsza, Z. *Polyurethanes: Chemistry, Technology, and Applications*; Ellis Horwood: New York, 1993.
32. Ke, Y.; Luo, C. F.; Qi, Z. N. *J Appl Polym Sci* 1999, 71, 1139.
33. Seymour, R. W.; Estes, G. M.; Cooper, S. L. *Macromolecules* 1970, 3, 579.
34. Tien, Y. I.; Wei, K. H. *Polymer* 2001, 42, 3213.