Novel Preparation and Mechanical Properties of Rigid Polyurethane Foam/Organoclay Nanocomposites

Zhongbin Xu,[1,2] Xiling Tang,[1,2] Aijuan Gu,[1] Zhengping Fang[1]

[1]*Institute of Polymer Composites, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China*
[2]*State Key Laboratory of Polymer Reaction Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China*

ABSTRACT: A novel method for preparing rigid polyurethane (PU) foam/organoclay nanocomposites was developed through the direct incorporation of an organoclay into PU foam matrices without the addition of any physical or chemical blowing agent. The resultant foams with an appropriate content of the organoclay had a finer cell structure than the pristine PU foams because the organoclay not only acted as a nucleating agent as expected but also acted as a blowing agent of the PU foams; this could be attributed to the bound water between the interlayers of the organoclay. In addition, the incorporation of the organoclay up to 4 phr resulted in improvements in the tensile and compressive strengths, with the maximum values appearing at 2 phr (110 and 152%, respectively). The significant improvement in the mechanical properties could be attributed to the finer cell structure and the increased internal strength of the materials due to the higher degree of hydrogen bonding. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 439–447, 2007

Key words: blowing agents; mechanical properties; organoclay; polyurethanes; structure-property relations

INTRODUCTION

Polyurethane (PU) foams, at the fifth position in the production volume of plastics,[1] account for the largest market among polymeric foams in the world. PU foams can be categorized as flexible foams, semirigid foams, and rigid foams according to their mechanical properties, such as their rigidity, stiffness, tensile, and compressive properties. With desirable properties such as high abrasion resistance and tear strength, excellent shock absorption, and low density, rigid PU foams have a remarkably broad range of applications in structural and semistructural applications. However, for such structural and semistructural applications, rigid PU foams still present some disadvantages, such as low cellular stability and low mechanical strength. The compressive strength and tensile strength are key physical properties of materials for withstanding strain in applications. Therefore, there is great interest in developing rigid PU foams of high performance.

Since the development of nylon 6/clay nanocomposite by Toyota researchers,[2,3] clays have been successfully incorporated into many polymers either as reinforcement agents to improve the physical and mechanical properties of the polymers or as fillers to reduce the amount of the polymer and thus decrease the cost of the resultant products.[4–7] Montmorillonite (MMT), a kind of clay, consists of two external silica tetrahedral sheets and a central octahedral sheet of alumina. This clay structure plays important roles in improving mechanical, thermal, and diffuse-barrier properties of polymer-layered silicate nanocomposites.[8–11] Recently, a great deal of effort has been devoted to the development of nanostructured PU/clay composites.[12–20] These reported works mainly focused on the dispersion status of clay in the matrices of PU elastomers, adhesives, or films and the thermal stability and/or modulus of such PU nanocomposites. The results showed that the PU/clay nanocomposites exhibited improvements in the elongation, insulation, and aging[21] behavior as well as the modulus and tensile strength, but a reported decrease or no enhancement was reported for the compressive strength in comparison with that of the matrix of rigid PU foams.[12,17–20] To the best of our knowledge, up to date, little work has been done on developing rigid PU foam/clay composites with simultaneously improved compressive and tensile strengths, which are key mechanical properties in structural applications. Moreover, no work has been focused on investigating the dispersion status of clay in PU matrices of rigid foams.

TABLE I
Formulations for Preparing the PU Foams and Rigid PU Foam/Organoclay Nanocomposites and Hydrogen-Bonding Indices of the Rigid PU Foam/Organoclay Nanocomposites

Sample	Clay (phr)	Water (phr)	Polyether polyols (phr)	Catalyst A-33 (phr)	Dibutyltin dilaurate (phr)	DMP-30 (phr)	Silicone oil (phr)	MDI 5005 (molar ratio)	Hydrogen-bonding index
PU/clay 0	0	1	100	1.0	0.05	1.5	2.0	150	0.84
PU/clay 1	1	0	100	1.0	0.05	1.5	2.0	150	2.15
PU/clay 2	2	0	100	1.0	0.05	1.5	2.0	150	2.17
PU/clay 4	4	0	100	1.0	0.05	1.5	2.0	150	0.96
PU/clay 8	8	0	100	1.0	0.05	1.5	2.0	150	1.13

To overcome the disadvantages of the poor compressive and tensile strengths of PU foams in structural applications, this work focuses on developing a novel method to prepare PU foam/organoclay nanocomposites with greatly and simultaneously improved compressive and tensile strengths, investigating the dispersion status of clay in PU matrices of rigid foams and discussing the relationship between the cell structure and mechanical properties of the nanocomposites.

EXPERIMENTAL

Materials

Trifunctional polyether polyol 4110 (OH value = 430 ± 30 mg/g of KOH, viscosity = 2500–3500 MPa s at 25°C) was obtained from the Jiangsu Chemical Research Institute Co., Ltd. (Nanjing, China). Diphenylmethylate-4,4′-diisocyanate (MDI) 5005 (Huntsman Corp., Salt Lake City, UT; 31 wt % NCO, viscosity = 170–270 MPa s at 25°C) was used as received. The commercial organoclay, ion-exchanged with one-tail octadecyl primary ammonium, and the pristine clay (an MMT with a cation-exchange capacity of 90 mequiv/100 g) were supplied by Zhejiang Huate Clay Products (Hangzhou, China). A-33 and dibutyltin dilaurate were purchased from the Jiangsu Chemical Research Institute, and both were used as catalysts. Silicone oil and DMP-30, also from the Jiangsu Chemical Research Institute, were used as the surfactant and crosslinking agent to prepare PU foams, respectively. Water was used as the blowing agent of the pure PU foams.

Preparation of the pure PU foams and rigid PU foam/clay nanocomposites

The pure PU foams and rigid PU foam/clay nanocomposites were prepared by a one-shot process. For the preparation of the pure PU foams, water was added, and it acted as a blowing agent. According to the formulation listed in Table I, the appropriate contents of the catalysts (A-33 and dibutyltin dilaurate), surfactant (silicone oil), crosslinking agent

(DMP-30), and water (blowing agent) were added to 100 g of polyether polyols in a plastic beaker equipped with a high-shear stirrer; a speed of 3000 rpm for 2 min was applied at the ambient temperature to form component A. Then, MDI was added with a molar ratio of 1.5 : 1 (with respect to polyol 4110; NCO/OH = 1.2) into component A to ensure the complete reaction of the polyols, with the stirrer at 3000 rpm for 2 min more at the ambient temperature. After that, the mixture was immediately poured into a glass mold (300 × 300 × 100 mm) to produce free-rise rigid PU foams, and this was followed by postcuring at 70°C for 6 h in an oven.

For preparing the rigid PU foam/clay nanocomposites, the organoclays were dehydrated in an oven at 70°C overnight before use. According to the formulation listed in Table I, the appropriate content of the dried organoclay powder was first mixed with 100 g of polyether polyols in a plastic beaker by a high-shear stirrer for 2 min at the ambient temperature, and subsequently, oil-bath sonication was applied to the suspension of the organoclay in the polyether polyols at 50°C for 2 h with a KQ-100DE ultrasonicator (100 W, nominal frequency = 50 kHz) (Kunshan Instruments Ltd., Kunshan, China). The catalysts (A-33 and dibutyltin dilaurate), surfactant (silicone oil), and crosslinking agent (DMP-30) were always added to the polyol/clay mixture to form component A. Then, MDI was added in a molar ratio of 1.5 : 1 (with respect to polyol 4110; NCO/OH = 1.2) into component A to ensure the complete reaction of the polyols by a high-shear stirrer for 2 min more at room temperature; after that, the protocol was exactly the same as that followed for the PU foams. In this foam processing, water was not added to the formulations. The mixture of all the ingredients was mixed by an impeller at 3000 rpm.

Measurements

Fourier transform infrared (FTIR) spectra of rigid PU foam/organoclay composites were recorded to characterize the hydrogen bonding between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} on a Vector-22 FTIR spectrometer (Bruller Optics, Billerica,
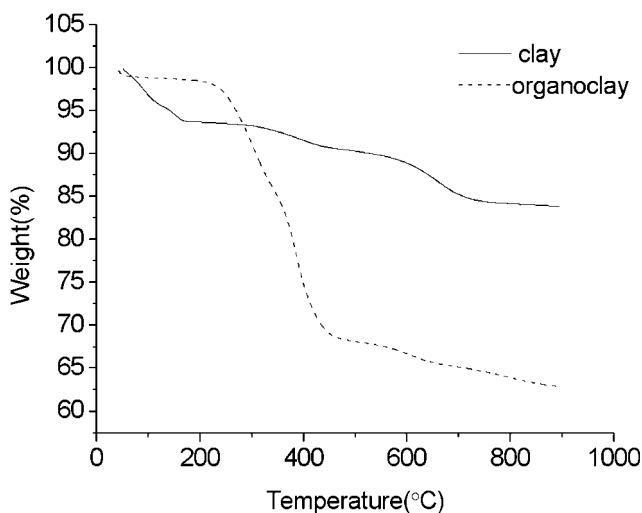
Figure 1 TG curves of the pristine clay and organoclay.

MA). Samples were prepared with KBr powder to obtain membranes whose thickness was about 40–60 μm.

The contents of bound water intercalated between interlayers of the organoclay were determined by thermogravimetry (TG) analysis in a TA SDT Q600 thermal analyzer (TA Instruments, New Castle, DE) under a nitrogen atmosphere. Each sample was heated from 50 to 900°C at a heating rate of 10°C/min.

X-ray diffraction (XRD) was carried out at the ambient temperature on a Rigaku (Tokyo, Japan) D/MAX-2550PC diffractometer (40 kV, 30 mA, Cu Kα radiation with $\lambda = 1.54$ Å) to measure the basal spacing of the organoclays. Each sample was scanned in the 2θ range of 0.5–30° at a scanning rate of 6°/min.

Transmission electron microscopy (TEM) micrographs were obtained with a JEM-1200EX electron microscope (JEOL Ltd., Tokyo, Japan) to examine the intercalation and exfoliation states of the clay in the composites. The TEM specimens were cut about 70–90 nm thick with a diatome diamond knife at room temperature.

The cellular structure of the samples in the thickness direction was investigated with a polarizing microscope on an XP-J203E polarizer (Shanghai Changfang Optical Instrument Co., Ltd., Shanghai, China).

The compressive strength of the samples, with dimensions of $50 \times 50 \times 50$ mm^3 (width $\times$ length $\times$ thickness), were measured with an RGT-X010 universal testing machine (Shenzhen Reger Instrument

Co., Ltd., Shenzhen, China) according to GB/T8813. The crosshead speed of compression was set to 2 mm/min. The value of the compressive strength was recorded when the samples reached 10% deformation.

The tensile strength tests were carried out with an RGT-X010 universal testing machine (Shenzhen Reger Instrument) according to the specifications of GB/T9641-88. Samples were cut to dimensions of $25 \times 100 \times 10$ mm^3 (width $\times$ length $\times$ thickness). The gauge length was 55 mm, and the crosshead speed was set at 5 mm/min. For each data point, five samples were tested, and the average value was taken.

RESULTS AND DISCUSSION

TG analysis of the pristine clay and organoclay

Previous investigations by other researchers have proved that the desorbed water molecules that absorb to the cations between interlayers of clay evaporate in the temperature range of 50–170°C, and the dehydroxylation of bound water molecules from the crystal lattice of pristine clay occurs in the temperature range of 450–900°C.[22,23] Figure 1 presents the TG curves for the pristine clay and organoclay. In the temperature range of 50–170°C, the pristine clay had a 6.67 wt % loss of the desorbed water, whereas the organoclay had only a 1.66 wt % loss of the desorbed water. However, in the temperature range of 450–900°C, the two samples had almost equal weight losses (5.98%) of bound water molecules from the crystal lattice of the organoclay. In addition, the great difference between the two TG curves is that the organoclay sample had a large weight loss (ca. 29.8%) in the temperature range of 230–450°C, which was attributed to the thermal decomposition of the organosurfactant.

Design of the formulations and foaming process for preparing the rigid PU foam/organoclay nanocomposites

It is well known that water easily reacts with isocyanate groups to generate polyurea and carbon dioxide with the release of exothermic reaction heat,[1] as shown in Scheme 1. Therefore, water has been the typical and sensitive blowing agent of PU foams, and the content of water in formulations for PU foams directly determines their cell structure[24] and
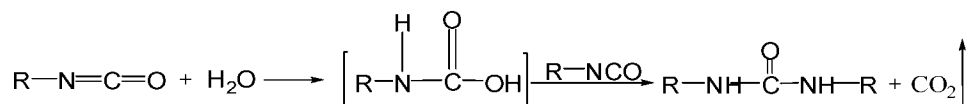
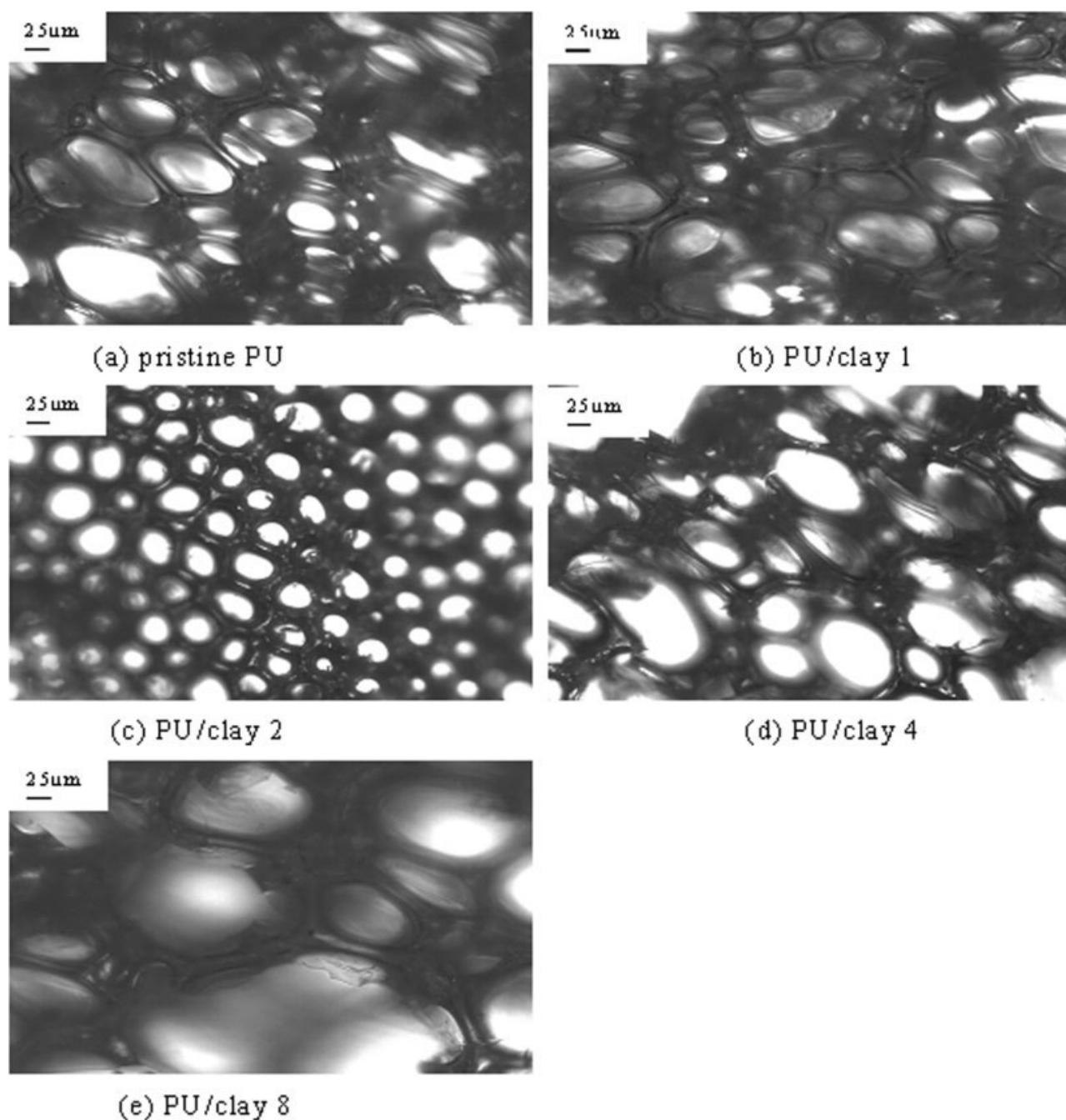**Scheme 1** Reaction between water and isocyanate group.

Figure 2 Polarized optical microscopy images of the pristine PU foams and rigid PU foam/organoclay nanocomposites.

thereby determines the mechanical properties of the resultant PU foams.

As discussed previously in the TG analysis, bound water that is intercalated between interlayers of organoclays cannot evaporate in an oven below 200°C, so when we design formulations for PU foam/organoclay nanocomposites, the intercalated bound water between interlayers of organoclays should be considered.

Sonication can be performed in a water bath [25] and an oil bath. To prevent water molecules existing in the

atmosphere[18] from getting into the system, oil-bath sonication was used to observe the function of the organoclay in the foaming process. Water was extracted from the formulations for the PU foam/organoclay nanocomposites, and no physical or chemical blowing agent was used. In addition to the role of the clay as a nucleating agent, the organoclay could also act as a blowing agent of PU foams. This could be attributed to the bound water intercalated between the interlayers of the organoclays, which could be deduced from the hydrogen bonding that formed
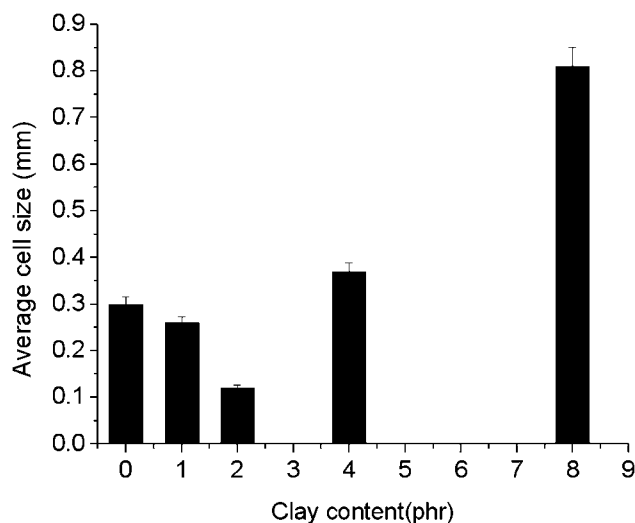
Figure 3 Average cell sizes of the rigid PU foam/organo-clay nanocomposites.

between the organoclay and PU matrix because a blowing agent was necessary for forming the PU foams.

The polarized optical microscopy images, magnified 250× (Fig. 2), obviously show that the appropriate organoclay content could lead to a finer cell structure, that is, a smaller cell size and a higher cell density, which in turn enhanced the mechanical properties of the thermoset PU foams. Figure 2(c) suggests that the composite with a low organoclay content (2 phr), in which the cell pores arrayed well, had a remarkably smaller cell size and higher cell density than the pristine PU foams. The values of the cell size of rigid PU/organoclay composites with various clay contents were obtained by the measurement of at least 30 cell diameters,[18] and their histogram curves are shown in Figure 3. Figure 3 shows that a small loading of clay greatly decreased the average cell size of the samples, whereas the rigid PU foam/organoclay composite with 2 phr organoclay had the smallest average cell size (0.12 mm), which was only about 40% of the corresponding value (0.30 mm) of the pristine PU foams. With a continuous increase in the clay loading, the average cell size of the samples increased dramatically, and a linear relationship between the cell size and clay content existed above 2 phr. For example, the rigid PU foam/organoclay composite with 8 phr organoclay had an average cell size of 0.8 mm, about 3.7 times that of the pristine PU foams. This could be attributed to the poor cell structure. The greater the amount was of the organoclay incorporated into the PU matrix, the larger the average cell size was of the PU foam/organoclay composite. As shown in Figure 2(e), the cell sizes of the composite with 8 phr organoclay were not uniform and were much bigger

than those of the pure PU foams because of the rearranged clay in the composites. When the aggregation of the organoclay occurred, more carbon dioxide was generated because, as discussed previously, the organoclay had bound water between its interlayers, so where the organoclay aggregated, there was more bound water between the interlayers of the organoclay, but where no or less organoclay existed, there was less or no carbon dioxide generated. Therefore, the organoclay content had an effect on the formation of the fine cell structure, which directly determined the mechanical properties, as discussed later.

Chemical structure of the rigid PU foam/organoclay nanocomposites

The FTIR spectra (Fig. 4) show the chemical structure of the rigid PU foam/organoclay nanocomposites. The positions of the bands for distinctive functional groups of the pure PU foams and nanocomposites are identical, and this indicates that the chemical structures of the PU foams are not altered by the presence of the organoclay. However, the degrees of hydrogen bonding of the rigid PU foam/organoclay composites are different. In Figure 4, the infrared bands at 3408 and 3328 cm^{-1} are due to the free N—H stretching and the hydrogen-bonded N—H stretching in the PU, respectively. The 1734-cm^{-1} band is caused by the free-of-hydrogen-bonding carbonyl, and the band at 1707 cm^{-1} is associated with the hydrogen-bonded carbonyls. The possible functional groups acting as acceptors in the hydrogen bonding with N—H are the urethane carbonyl (—C=O), the ether (—C—O—C—), and the oxygen
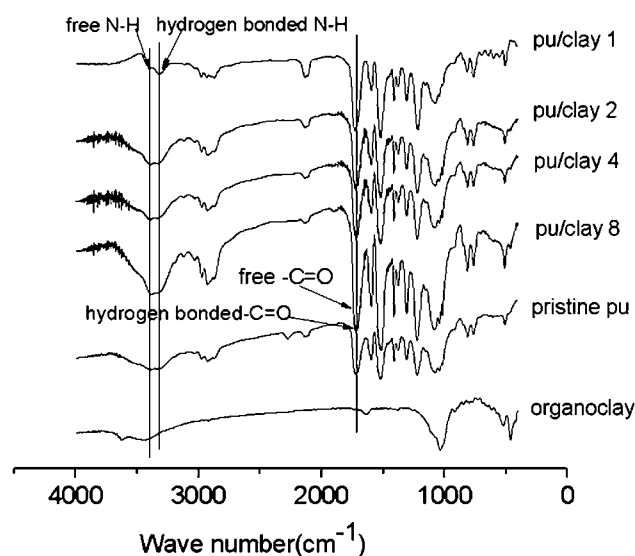

Figure 4 FTIR spectra of the pristine PU foams, organoclay, and rigid PU foam/organoclay nanocomposites.

of the bound water between the interlayers of the organoclays. A detailed description of the FTIR bands in PU can be found elsewhere.[26,27]

The degree of the carbonyl groups participating in hydrogen bonding can be described by the carbonyl hydrogen-bonding index (R), as given in the following equation:

$$R = \frac{C_{bonded}\varepsilon_{bonded}}{C_{free}\varepsilon_{free}} \qquad (1)$$

where C_{bonded} and C_{free} are the concentrations of the bonded and free carbonyl groups, respectively, and ε_{bonded} and ε_{free} are the extinction values of the bonded and free carbonyl groups, respectively. Generally, the value of $\varepsilon_{bonded}/\varepsilon_{free}$ is between 1.0 and 1.2,[28,29] and it was assumed to be 1.0 in this study. Then, the equation could be simplified as follows:

$$R = \frac{A_{1707}}{A_{1734}} \qquad (2)$$

where A is the intensity of the characteristic absorbance.

Table I reveals that the hydrogen-bonding index increases with the loading of the organoclays, and the maximum value of 2.15–2.17 was found at 1 and 2 phr organoclay. After that, the value of the hydrogen-bonding index dropped to a value similar to that of the pure PU foams for 4 and 8 phr, but it was still larger than that of the pure PU foams. As mentioned previously, water easily reacts with isocyanate groups to generate polyurea and carbon dioxide, so when more water is used to prepare PU foams, there are fewer carbonyl groups in the network of the resultant PU foams; this, in turn, leads to a lower hydrogen-bonding index. In the case of the rigid PU foam/organoclay nanocomposites, a higher content of the organoclay indicates that there is more bound water between its interlayers that can react with isocyanate groups to generate polyurea and carbon dioxide and thus result in a smaller hydrogen-bonding index. In other words, the values of the hydrogen-bonding index of all nanocomposites are higher than those of pure PU foams, and this suggests that nanocomposites have higher internal strength than pure PU foams.

Morphology of the rigid PU foam/organoclay nanocomposites

The XRD patterns of the organoclay and PU/organoclay nanocomposites are presented in Figure 5. The basal spacing of the organoclay was 2.5 nm at 2θ
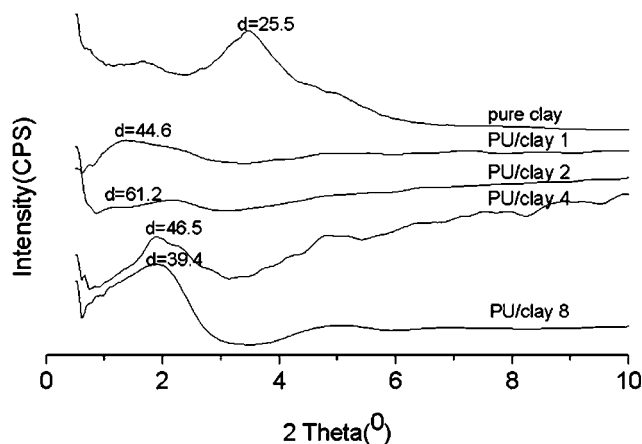
Figure 5 XRD images of the pristine PU foams and rigid PU foam/organoclay nanocomposites.

= 3.5°. The XRD spectra of the PU/organoclay composites show a characteristic broad basal reflection between 1.4 and 2.5°, which corresponds to a basal spacing of 4.4–6.1 nm, indicating that the clay was mostly intercalated. The maximum spacing of the composite with 2 phr clay increased to 6.1 nm, and a good dispersion of the clay consisting of a mixture of exfoliated and intercalated structures existed.[30] An X-ray analysis also showed that a mixture of exfoliated and intercalated structures occurred for low clay contents, whereas for higher contents, the clay tended to intercalate or aggregate. These results are corroborated with the TEM photographs shown in Figures 6 and 7. They show that the morphology of the composites was a combination of intercalation and exfoliation with low clay contents (Fig. 6), whereas an aggregation of organoclay particles existed in the matrix when the weight fraction increased (Fig. 7).

Mechanical properties of the rigid PU foam/organoclay nanocomposites

Figure 8 presents the compressive and tensile strengths of the nanocomposites with different organoclay contents. The organoclay content had a remarkable effect on the compressive and tensile strengths of the nanocomposites. Both the compressive strength and tensile strength increased dramatically with a small addition of the organoclay and reached the maximum value at 2 phr organoclay; that is, the nanocomposite with 2 phr organoclay had about a 152% increase in the compressive strength and a 110% increase in the tensile strength in comparison with the pure PU foams (0.56 MPa in compression and 0.86 MPa in tension).
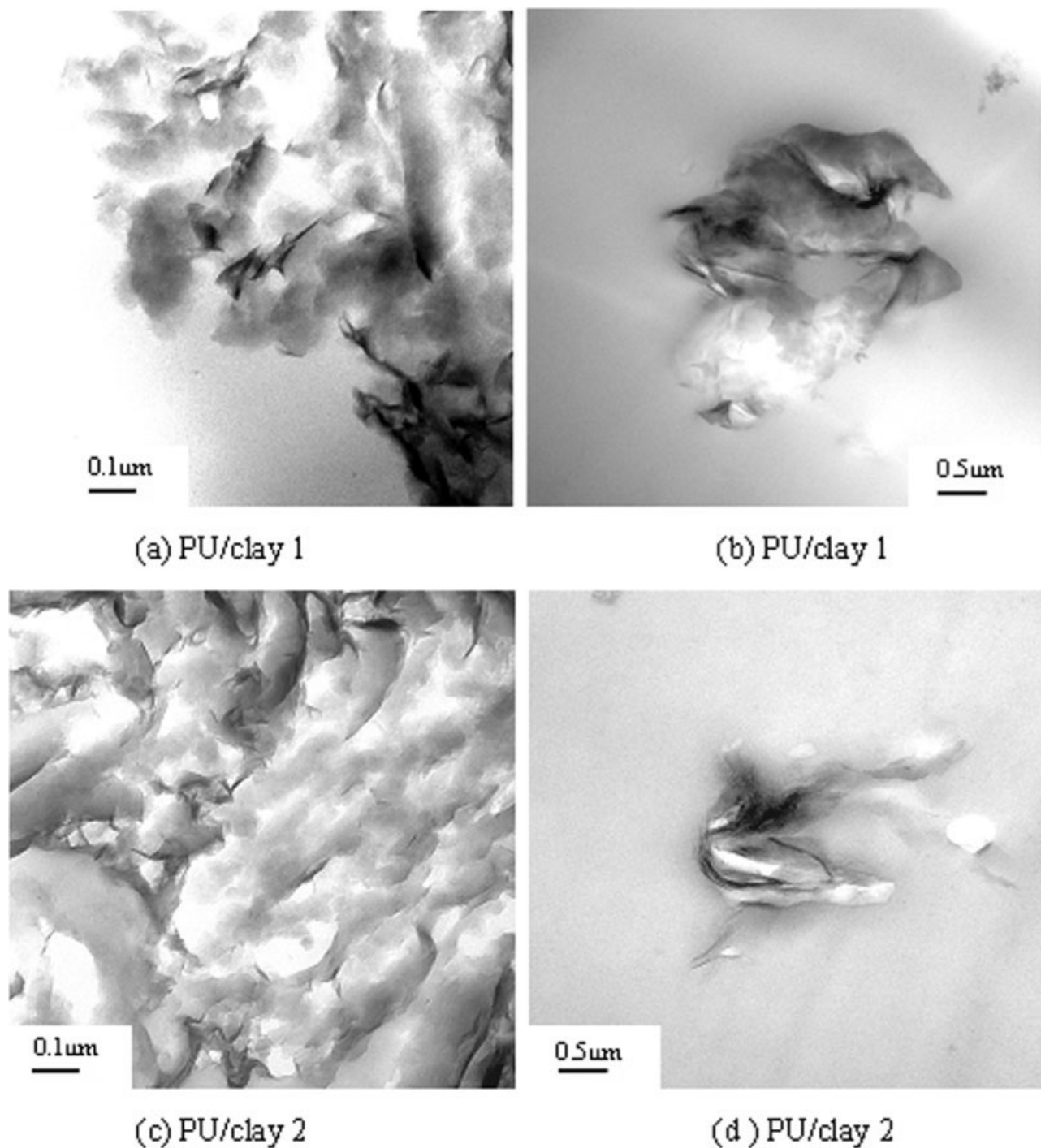
Figure 6 TEM images of the PU/clay 1 and rigid PU foam/clay 2 nanocomposites.

This result is quite different from those obtained by other researchers; their articles have suggested no enhancement or even a decrease in the compressive strength of rigid PU foam/organoclay nanocomposites.[12,17–20] Two factors can be invoked to explain this difference: (1) the increased internal strength of the PU matrix due to the higher degree of hydrogen bonding among the urethane groups and (2) the finer cell structure of the nanocomposites. With a finer and more uniform cell structure, rigid PU foam/organoclay nanocomposites can withstand more strain in applications.

By careful observation, Figure 8 shows some differences for the nanocomposite with 8 phr organoclay in the compressive and tensile strengths; in detail, the nanocomposite had a lower tensile strength but a higher compressive strength than the pure PU foams. The reason is that the cell structure
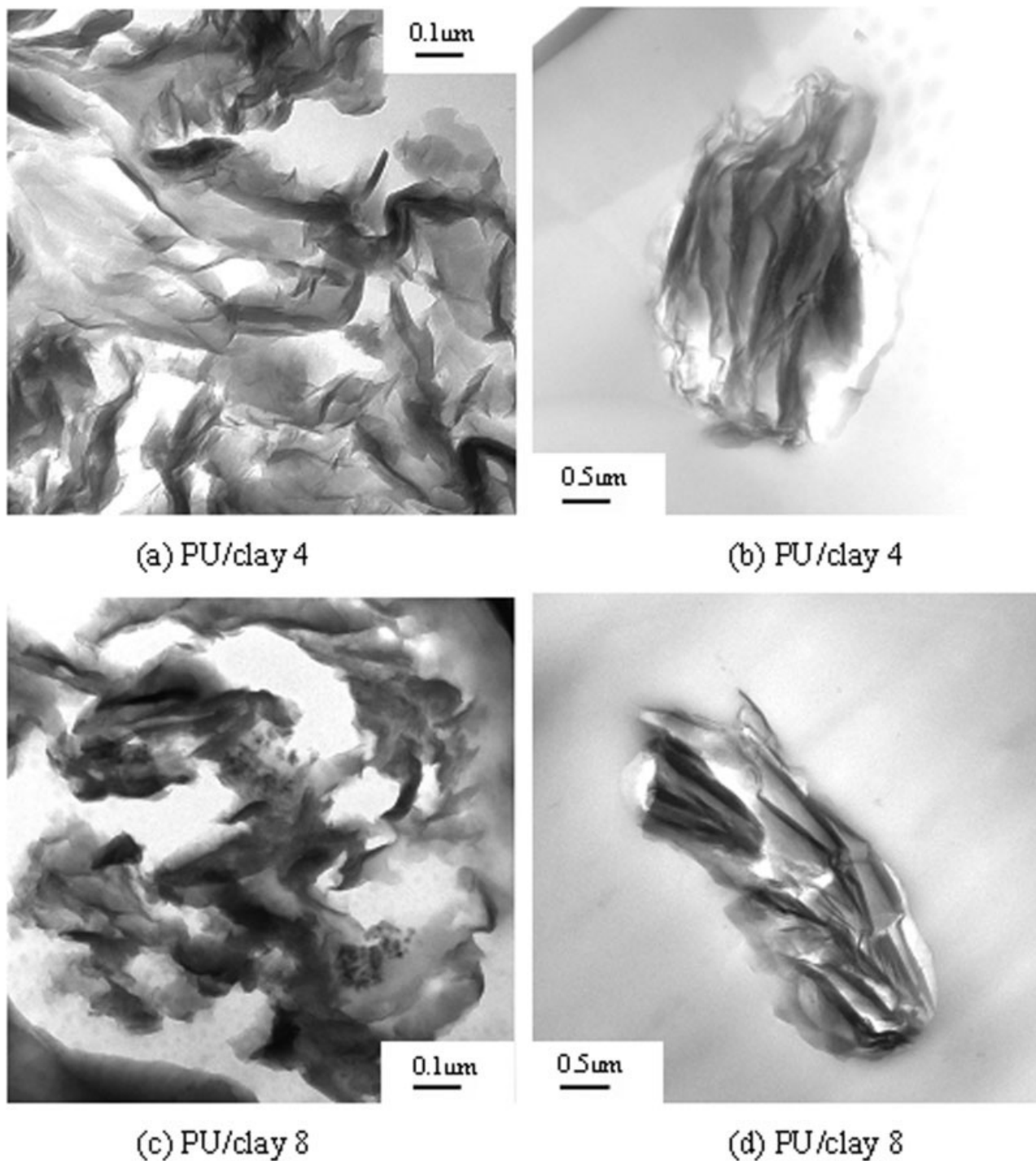
Figure 7   TEM images of the PU/clay 4 and rigid PU foam/clay 8 nanocomposites.

of the composite with 8 phr organoclay was not uniform as stated previously, and because the tensile strength of a material is generally more sensitive to a defect in the cell structure than the compressive strength, the compressive strength and tensile strength of the sample with 8 phr organoclay showed somewhat different behavior.

Conclusively, the cell structure is of great importance for the mechanical properties of PU foams: the finer the cell structure, the higher the strain level tolerated.

CONCLUSIONS

It has been found for the first time that an organoclay itself can act as a blowing agent of PU foams. In addition, an organoclay can be used as the reinforcing filler of PU foams, and an appropriate content
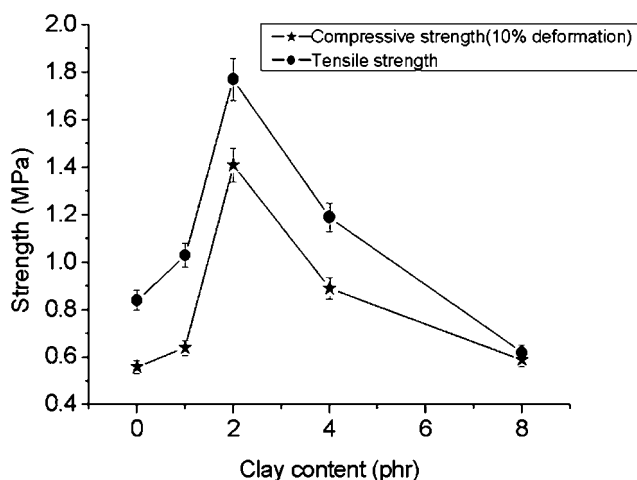
Figure 8 Compressive and tensile strengths of the pristine PU foams and rigid PU foam/organoclay nanocomposites.

(ca. 2 phr) of the organoclay can effectively improve the compressive and tensile strengths of PU foams at the same time. The results prove that the finer cell structure of nanocomposites and more hydrogen bonding between PU and organoclays are two key reasons for the significant improvement in the mechanical strength of rigid PU foam/organoclay nanocomposites.

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