Chinese Journal of Polymer Science Vol. 28, No. 4, (2010), 615–624

Chinese Journal of Polymer Science
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Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2010

EFFECT OF SURFACE MODIFICATION OF MONTMORILLONITE ON THE PROPERTIES OF RIGID POLYURETHANE FOAM COMPOSITES*

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Abstract This study investigated the influence of various organically modified montmorillonites (organoclays) on the structure and properties of rigid polyurethane foam (RPUF) nanocomposites. The organoclays were modified with cetyltrimethyl ammonium bromide (CTAB), methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride (MT2ETOH) and tris(hydroxymethyl)aminomethane (THMA) and denoted as CMMT, Cloisite 30B and OMMT, respectively. MT2ETOH and THMA contain hydroxyl groups, while THMA does not have long aliphatic tail in its molecule. X-ray diffraction and transmission electron microscopy show that OMMT and Cloisite 30B can be partially exfoliated in the RPUF nanocomposites because their intercalating agents MT2ETOH and THMA can react with isocyanate. However, CMMT modified with nonreactive CTAB is mainly intercalated in the RPUF matrices. At a relatively low filler content, the RPUF/CMMT composite foam has a higher specific compressive strength (the ratio of compressive strength against the apparent density of the foams), while at relatively high filler contents, RPUF/Cloisite 30B and RPUF/OMMT composites have higher specific compressive strengths, higher modulus and more uniform pore size than the RPUF/CMMT composite.

Keywords: Organoclay; Rigid polyurethane foam; Nanocomposite; Mechanical properties.

INTRODUCTION

Rigid polyurethane foam (RPUF) is an important polymeric foam material because of its unique properties, such as high abrasion resistance and tear strength, excellent shock absorption and low density, and the flexibility in properties that can be obtained by varying the synthesis and processing conditions. RPUF has been widely used in applications such as building insulation appliances, transportation, packaging, furniture and food and drink containers. However, RPUF has some disadvantages, such as low cellular stability, low mechanical properties and so on. Therefore, great interests have been paid on improving the properties of RPUF[1–6].

On the other hand, since the development of nylon 6/montmorillonite (MMT) nanocomposites in early 1990's[7, 8], organically modified MMT (organoclay) has been widely used in many polymers such as polyethylene[9], polypropylene[10], polystyrene[11, 12], poly(methyl methacrylate)[13], polyimide[14], polyvinylidene-fluoride[15], ethylene propylene diene monomer rubber[16], bismaleimide[17], poly(acrylonitrile-butadiene-styrene)[18], epoxy resin[19, 20], polyurethane (PU)[21–26] and so on. The organoclay may act as a reinforcement agent to improve the mechanical properties of the polymers, or as a flame retardant additive to improve the thermal stability and flame retardancy of the polymers.

Since pristine MMT are intrinsically hydrophilic while most polymers are hydrophobic, to disperse MMTs in the polymer matrics, it is necessary to replace the hydrophilic inorganic cations (Na^+, Ca^+, or K^+) residing in the gallery space of MMTs with more organophillic cations[27–30]. The most commonly used intercalating agent

* This work was financially supported by the National Natural Science Foundation of China (Nos. 20574060 and 50773066).
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Received September 10, 2009; Revised November 27, 2009; Accepted December 4, 2009
doi: 10.1007/s10118-010-9111-0

or surface-modifier for Na-MMTs is cetyltrimethyl ammonium bromide (CTAB). On the other hand, previous studies[11, 31, 32] have shown that intercalating agents with functional groups that are reactive with the polymer matrices are more effective than CTAB and other nonreactive intercalating agents in dispersing organoclays uniformly in the polymer matrices.

As is well known, hydroxyl groups (—OH) can react with the isocyanate groups (—NCO) of diphenylmethylate-4,4′-diisocyanate (MDI), one of the raw materials of RPUF, so it is usually expected that the intercalating agents with —OH groups can improve the interface interaction between organoclay fillers and PU matrix. However, the influence of different types of intercalating agents on the properties of organoclay filled RPUF has not been investigated in detail. In this study, two surface-modifiers, namely CTAB without —OH groups in its molecule and tris(hydroxymethyl)aminomethane (THMA) containing three —OH groups in its molecule were used to treat Na-MMT. A commercially available organoclay (Cloisite 30B) using methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride (MT2ETOH) as the intercalating agent, which contains two —OH groups in its molecule, was used as the third sample. The purpose of this study is to investigate the influence of different types of intercalating agents on the dispersion of organoclays in RPUF, the foam structure and the final mechanical properties of RPUF.

EXPERIMENTAL

Materials

Polyether polyol 4110 (OH value = 430 ± 20 of KOH, viscosity = 4500–5500 mPa·s at 25°C) and polyether polyol 635 (OH value = 500 ± 20 of KOH, viscosity = 4000–6000 mPa·s at 25°C) were purchased from Jiangsu Zhongshan Chemical Co., Ltd. (Nanjing, China). Diphenylmethylate-4,4′-diisocyanate (MDI) MR-100 with 30.5 wt%–32 wt% NCO and viscosity of 170–270 mPa·s at 25°C was purchased from Nippon Polyurethane Industry Co., Ltd. (Tokyo, Japan). The catalysts A-33 and dibutyltin dilaurate (DBDL) and the crosslinking agent 2,4,6-tri(dimethylaminomethyl)phenol (DMP-30) were purchased from Youth Advanced Material Co., Ltd. (Shanghai, China). The foam stabilizer AK8818 was provided by Dymatic Shichuang Chemical Co., Ltd. (Nanjing, China). Distilled water was used as the blowing agent. The Na-MMT with a cation-exchange capacity (CEC) of 110 mmol/100g was provided by Zhejiang Fenghong Clay Chemicals Co., Ltd. (Huzhou, China). The commercial organoclay (Cloisite 30B) treated with methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride (MT2ETOH) was provided by Southern Clay Products, Inc. (USA). CTAB and THMA purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were used as received.

Modification of Na-MMT

15 g of the Na-MMT was dispersed in water to form a uniform dispersion and then gradually added to an aqueous solution of THMA (2.18 g dissolved in 500 mL of 0.0375 mol/L HCl) or CTAB (6.02 g dissolved in 500 mL distilled water) and vigorously stirred for 6 h at 60°C in an oil bath. After the treatment, the MMT suspension was repeatedly washed with distilled water and filtrated until no precipitates appeared when the filtrate was titrated with a 0.1 mol/L $AgNO_3$ solution. Then the filter cakes were dried in a vacuum oven at 80°C for 12 h. The products were ground for the next use. The MMTs treated with THMA and CTAB were denoted as OMMT and CMMT, respectively.

Preparation of Pure RPUF and RPUF/Organoclay Nanocomposites

The pure RPUF and RPUF/organoclay nanocomposites were both prepared by a one-step method. For preparing the pure RPUF, the catalysts (2 g of A-33 and 0.04 g of DBDL), surfactant 1 g of AK8818, 1 g of crosslinking agent DMP-30 and 0.25 g of distilled water which acted as foaming agent were added to a mixture of polyether polyols (96 g of polyol 4110 and 4 g of polyol 635) in a plastic beaker equipped with a high-shear stirrer, and stirred at a speed of 2500 r/min for 2 min at the ambient temperature to obtain a uniform mixture. 130 g of MDI was added to the mixture and stirred at 2500 r/min for about 20 s at the ambient temperature. The NCO/OH ratio was 1.05–1.2 (with respect to polyol 4110). After that, the mixture was immediately poured into a glass mold (300 mm × 300 mm × 300 mm) to produce the free-rise RPUF, then the RPUF was post-cured at 80°C for 12 h

in an oven.

For preparing the RPUF/organoclay nanocomposites, the organoclays were dehydrated in an oven at 70°C overnight before use. Appropriate amount of the dried organoclay powder was first added to the mixture of polyether polyols (96 g of polyol 4110 and 4 g of polyol 635) and stirred by a high-shear stirrer at a speed of 2500 r/min for 2 min at the ambient temperature. Then the mixture was sealed and sonicated at 50°C for 2 h using a KQ-100DE ultrasonicator (100 W, nominal frequency = 50 kHz) (Kunshan Instruments Ltd., Kunshan, China) to further improve the dispersion of the organoclays in the polyether polyols. The following steps for preparing RPUF/organoclay nanocomposites were the same with those for preparing RPUF as above mentioned.

Measurements

Fourier transform infrared (FTIR) spectra of the original MMT and organoclays were recorded by a Vector-22 FTIR spectrometer (Bruller Optics, Billerica, MA) with a resolution of 2 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1} using KBr pellets. The actual contents of intercalating agents in the organoclays were determined by thermogravimetric (TG) analysis with a TA SDT Q600 thermal analyzer (TA Instruments, American) under a nitrogen atmosphere from 25°C to 800°C at a heating rate of 10 K/min. The samples were maintained at 100°C for 15 min to remove absorbed water in the samples.

X-ray diffraction (XRD) was carried out at the ambient temperature on a Rigaku D/MAX-2550PC diffractometer (Tokyo, Japan) at a voltage of 40 kV, a current of 30 mA using Cu Kα radiation at a wavelength of λ = 0.154 nm, to determine the basal spacing of the clays. All samples were scanned in the 2θ range of 0.5°–30° at a scanning rate of 6 (°)/min.

The morphologies of the organoclays in the polymer matrices were observed by transmission electron microscopy (TEM) (JEM-1200EX, JEOL Ltd, Tokyo, Japan). The specimens were embedded in epoxy resin, and cut into thin films with a thickness of about 70–90 nm by ultramicrotomy at room temperature.

The cellular structures of the samples were observed by a JEOL JSM-35C (JEOL Ltd, Tokyo, Japan) scanning electron microscope (SEM) using an acceleration voltage of 25 kV. Samples were cut at ambient temperature and the fracture surface was sputter-coated with gold before observation. Image analysis was performed on the SEM micrographs using Image-Pro Plus software (Media Cybernetics, Inc.) to obtain the average cell diameter.

The compressive strength of the composites was measured on an RGT-X010 universal testing machine (Shenzhen Reger Instrument Co., Ltd., Shenzhen, China) according to GB 8813-88. The samples were cubes with dimensions of 50 mm × 50 mm × 50 mm (width × length × thickness). The crosshead speed of the compression tests was set as 2 mm/min, and the values of the compressive strength were recorded when the deformation of the samples reached 10%.

Dynamic mechanical analysis (DMA) was conducted on a DMA Q800 (TA Instruments, American) in a dual cantilever mode at a frequency of 1 Hz. The temperature ranged from 30°C to 250°C with a heating rate of 5 K/min. The sample size was approximately 60 mm × 13 mm × 3 mm.

RESULTS AND DISCUSSION

Structure of the Na-MMT and Organically Modified MMTs

The FTIR spectra (Fig. 1) show the chemical structures of the Na-MMT and the organoclays. The absorption bands at 3624 cm^{-1} and 3426 cm^{-1} are ascribed to the free —OH stretching and the hydrogen-bonded —OH stretching respectively. Compared with that of CMMT, the bands area of OMMT and Cloisite 30B increases, demonstrating the increase in the —OH content caused by the introduction of THMA and MT2ETOH. The 1734 cm^{-1} band for Cloisite 30B is caused by the free-of-hydrogen-bonding carbonyl, and the bands at 1468 and 1379 cm^{-1} are associated with the $-CH_3$ group in CTAB and MT2ETOH. At the same time, the band at 1468cm^{-1} is also associated with the $RN(CH_3)_3^+$ ion in CTAB. Besides, the bands at 2920 cm^{-1} and 2850 cm^{-1} are caused by the stretching of $-CH_2$ group, which comes from CTAB and MT2ETOH with long aliphatic tail in their molecules.

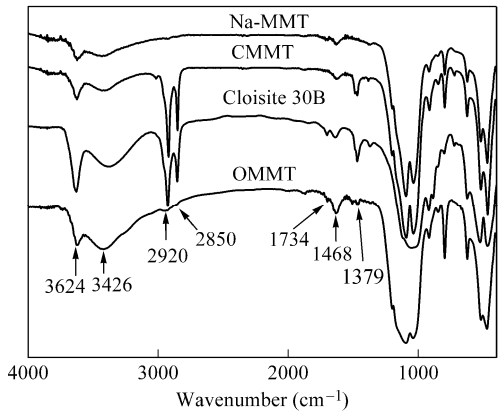

Fig. 1 FTIR spectra of Na-MMT and organoclays

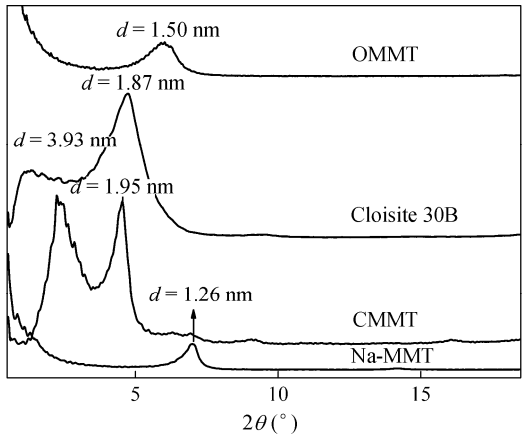

Fig. 2 XRD images of Na-MMT and organoclays

The XRD patterns of Na-MMT and the organoclays are presented in Fig. 2. The basal spacing of Na-MMT is 1.26 nm calculated from the Bragg's Equation $2d \cdot \sin\theta = \lambda$, in which d is the basal spacing, θ is the Bragg peak angle, λ = 0.154 nm, the X-ray wavelength. The basal spacing of Cloisite 30B and OMMT is 1.87 nm and 1.50 nm, respectively, which are larger than that of Na-MMT. There are two peaks in the CMMT pattern, in which the peak at d = 3.93 nm is the second order peak to that at d = 1.95 nm. These all prove that the surface-modifiers are intercalated into the MMT galleries.

The TG curves for Na-MMT, OMMT, Cloisite 30B and CMMT are shown in Fig. 3. According to previous studies, the mass loss between 50–170°C in the TG curve of Na-MMT is due to the absorbed water in the interlayer galleries, and the mass loss between 450–900°C is due to the crystal water[33, 34]. The organic contents of the various organoclays were determined from Fig. 3, which were 5.28 wt% for OMMT, 30.5 wt% for CMMT and 26.5 wt% for Cloisite 30B, respectively. The reason for the relatively low organic content for OMMT should be related to the high water solubility of THMA which can be detached during the purification procedure.

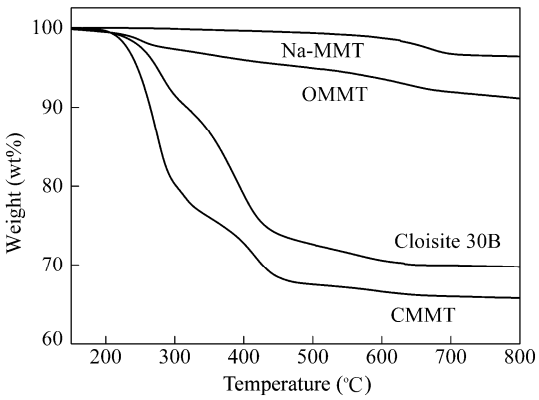

Fig. 3 TG curves of Na-MMT and organoclays

The Morphological Characterization of the Organoclays in RPUF Nanocomposites

The morphologies of the three organoclays in RPUF nanocomposites were analyzed by both XRD and TEM[35]. Figure 4 shows the XRD patterns of the three RPUF nanocomposites at different organoclay contents. It is shown that at filler content less than 5 wt%, CMMT are mainly intercalated and when the CMMT content is 5 wt%, the basal spacing of a part of the CMMT platelets increases to around 12.63 nm, suggesting that a part of CMMT platelets are exfoliated to a certain degree. For Cloisite 30B, at the filler content of 1 wt%, no intensity

peak is observed, suggesting that Cloisite 30B clays are highly exfoliated in the RPUF matrix. However, when the filler content increases to 3 wt%, diffraction peak corresponding to a basal spacing of 4.85 nm appears, suggesting that Cloisite 30B clays are mainly intercalated in the RPUF matrix. When the filler content increases to 5 wt%, the basal spacing further increases to 5.25 nm. As to OMMT at filler contents of 1 wt% and 3 wt%, the RPUF/OMMT nanocomposite does not exhibit any discernible intensity peaks, suggesting that OMMT is highly exfoliated in the RPUF matrix. However, at the filler content of 5 wt%, a broad peak at 1.42 nm appears, which is close to that of the as-prepared OMMT. This indicates that a part of OMMT platelets remain intercalated in the RPUF matrix at high filler content. The morphologies of organoclays in the RPUF matrices are also observed by TEM at both low and high magnifications, as shown in Fig. 5. It can be found from the TEM images of low magnification that the organoclays are distributed randomly in the foam walls and agglomerates of organoclays can be observed for all organoclays with different intercalating agents, but the size and distribution uniformity of the organoclay agglomerates in the PU matrix are quite different. The OMMT agglomerates have the smallest size and are distributed more uniformly in the PU matrix. At higher magnifications, stacked platelets can be observed for RPUF/CMMT and RPUF/Cloisite 30B, indicating the existence of intercalated structure of organoclays in the RPUF matrices. However, for RPUF/OMMT composites, stacking structure of the clay platelets is not clearly observed, indicating that the OMMT platelets are highly exfoliated in the RPUF matrices, which is in good consistency with the XRD results. However, as shown in Fig. 5, the OMMT platelets still form aggregates in the RPUF matrices. The mechanism for the

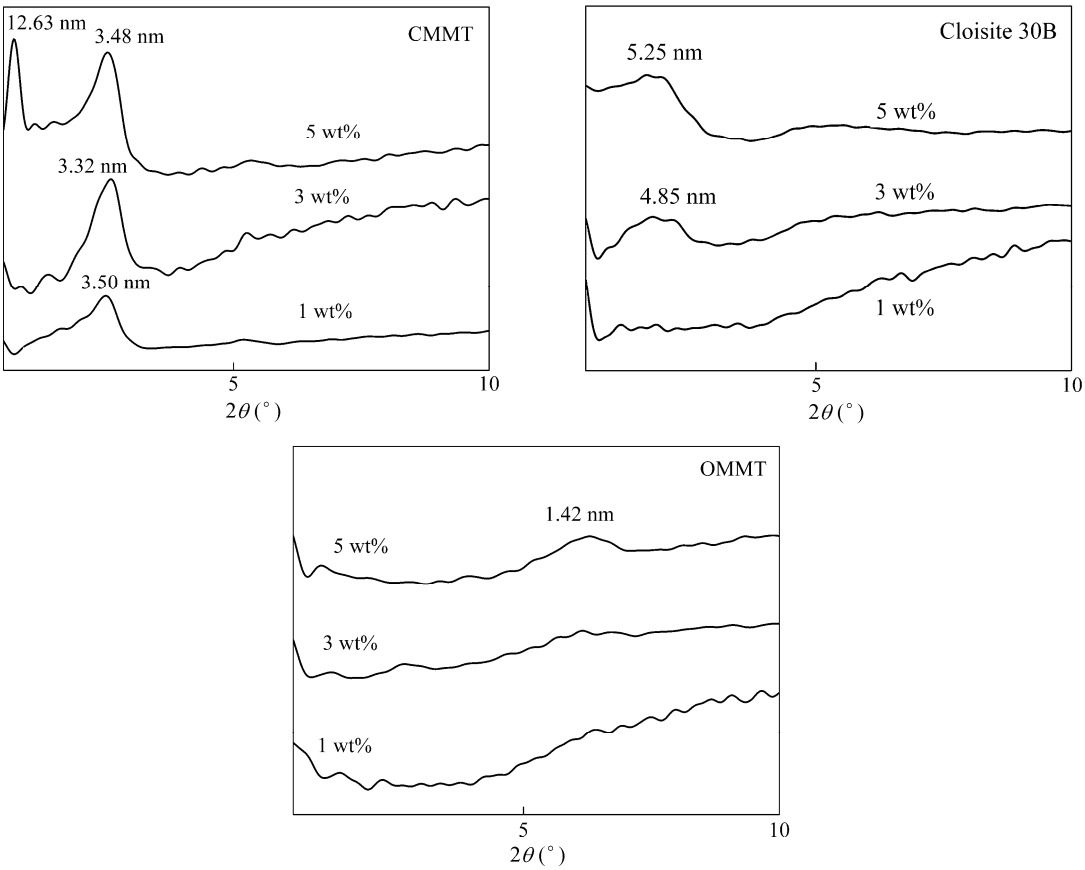

Fig. 4 XRD curves of RPUF/CMMT, RPUF/OMMT and RPUF/Cloisite 30B nanocomposites with different organoclay contents

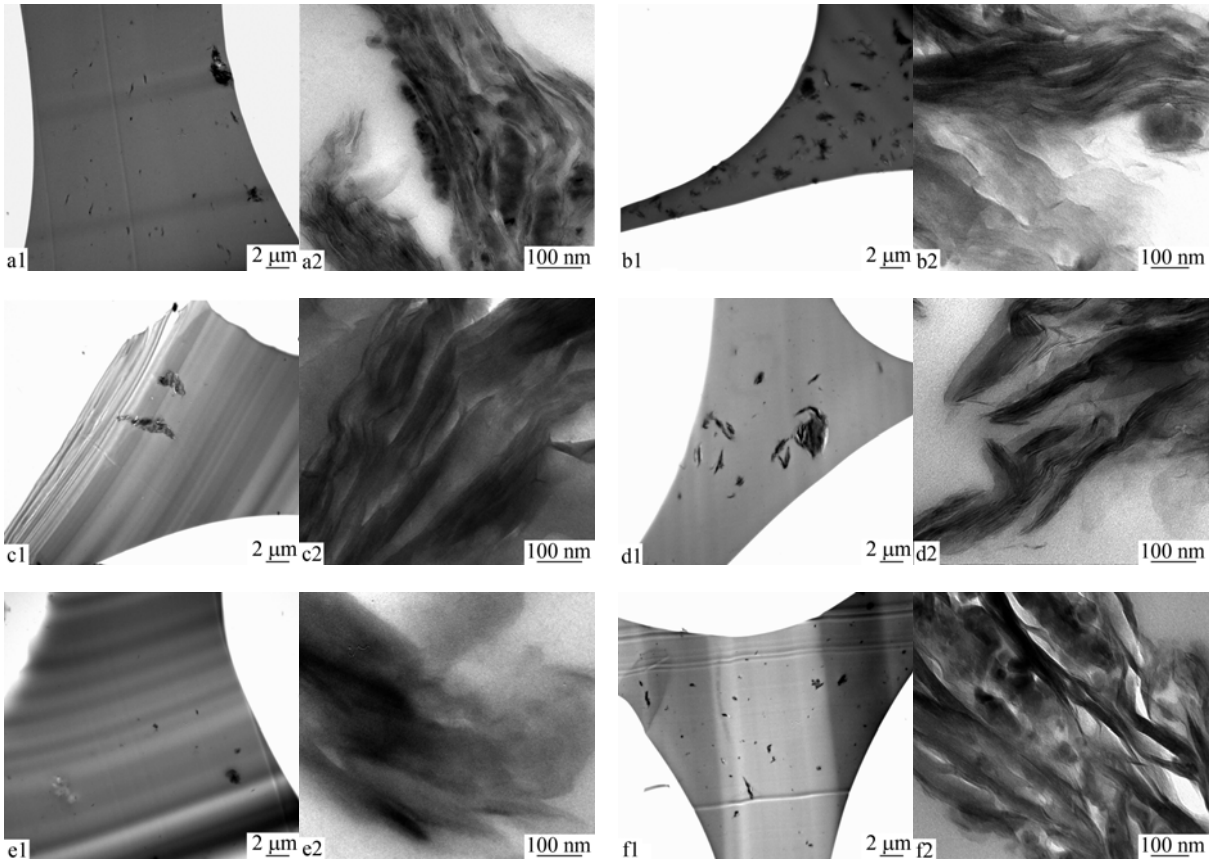

Fig. 5 TEM images of the RPUF/organoclay nanocomposites filled with 1 wt% (a1, a2) and 5 wt% (b1, b2) of CMMT, 1 wt% (c1, c2) and 5 wt% (d1, d2) of Cloisite 30B, 1 wt% (e1, e2) and 5 wt% (f1, f2) of OMMT, at low and high magnifications

formation of the OMMT aggregates with exfoliated structure can be explained as follows. According to previous studies[22, 32], the hydroxyl groups on the edge and surfaces of MMT platelets are reactive with isocyanate. And the hydroxyl groups of the intercalating agent THMA used for preparing OMMT are also reactive with isocyanate. During the preparation of RPUF, MDI was added to the polyols mixture and stirred at 2500 r/min for only 20 s before the foaming process started. At the same time, the reaction between OMMT and isocyanate occurred very rapidly, therefore, it is possible that the OMMT aggregates are crosslinked by polyurethane molecules before they are uniformly dispersed in the RPUF matrix by mechanical stirring. As a result, the XRD result indicates that OMMT is highly exfoliated, while TEM shows that OMMT remains aggregated in the RPUF matrices. Further studies need to be conducted to optimize the mixing conditions so that OMMT can be completely exfoliated and distributed uniformly in the RPUF matrix.

Figure 6 shows the SEM images of the cell structures and the distribution of cell sizes of RPUF and RPUF nanocomposites with an organoclay content of 5 wt%. There exists large cells with diameters above 300 nm in pure RPUF and the average cell diameter of pure RPUF is 110 nm, which is larger than that of organoclay filled RPUF composites. At the filler content of 1 wt%, the average pore size and size distribution of organoclay filled RPUF are similar to those of pure RPUF. But at the filler content of 5 wt%, the size distribution of RPUF/OMMT nanocomposite is narrower and the average cell size is smaller than that of pure RPUF, RPUF/CMMT and RPUF/ Cloisite 30B nanocomposites. This is related to the chemical structure of the intercalating agent of OMMT, which is more compatible with polyols and more reactive with MDI.

The Mechanical Properties of Pure RPUF and RPUF Nanocomposites with Different Organoclay Contents

The organoclay contents have remarkable effect on the specific compressive strength (the ratio of compressive

strength against the apparent density of the foams) of the nanocomposites. As Fig. 7 shows, when there is 1 wt% addition of the organoclays, the specific compressive strength of RPUF/CMMT composite is slightly higher than that of pure RPUF, while that of the other two composites are somewhat lower. With the increase of organoclays, the specific compressive strength decreases. This result is consistent with the report of Lee *et al.*[22], which showed that the influence of organoclay on the mechanical properties of PU foams is rather complicated. For RPUF with a relatively low crosslinking density, organoclays can increase the compressive strength, but for RPUF with a high crosslinking density, organoclays decrease the compressive strength, because of the negative effect of organoclays on the network structure and hydrogen bond formation of PU. At the same time, there is residual water in the intergallery region of organoclays, and the hydroxyl groups on the edge and surfaces of MMT platelets are reactive with isocyanate, therefore, the stoichiometric ratio between —NCO and —OH is changed by organoclays' incorporation and the crosslinking density of the organoclay filled nanocomposite foam is decreased.

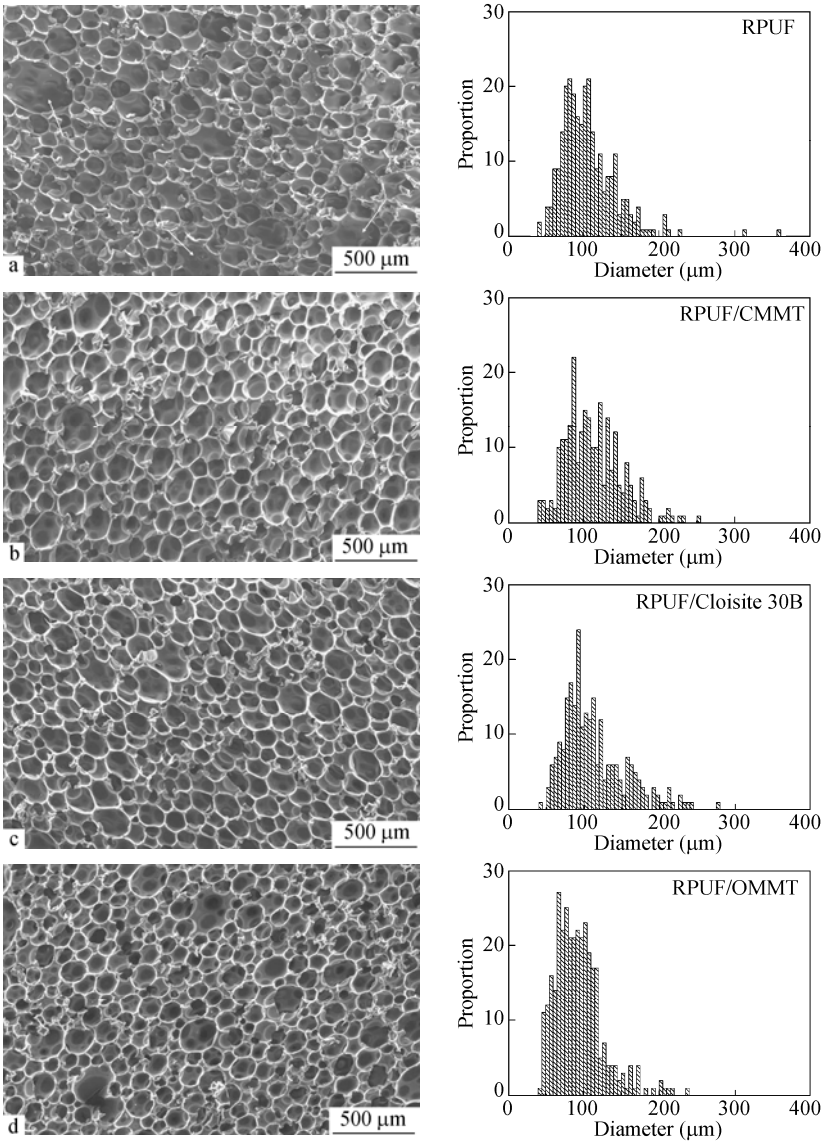

Fig. 6 SEM images and the distribution of cell sizes of RPUF and RPUF/organoclay nanocomposites with a filler content of 5 wt%: (a) RPUF, (b) RPUF/CMMT, (c) RPUF/Cloisite 30B, and (d) RPUF/OMMT

It should be noted that the specific compressive strength of RPUF/CMMT nanocompositse decreases more rapidly than that of RPUF/Cloisite 30B and RPUF/OMMT nanocomposites as the filler content increases. As mentioned above, the TEM results show that there exists organoclay agglomerates in all samples, which can act as defects and decrease the compressive strength of the nanocomposites. However, reactive intercalating agents used in OMMT and Cloisite 30B can decrease the negative effect of organoclay incorporation at relatively high filler contents because of the improvement in interface interactions between PU matrices and fillers.

The ability of the foam composites to recover from compression was measured. The recovery ratio is defined as $(h_r-h_{r,t})/h_r$, in which h_r is the indent depth recorded in the compression experiment, and $h_{r,t}$ is the indentation depth at various recovery time after unloading. The recovery ratios are summarized in Table 1. It can be concluded that the composite foams have good recovery properties, and the permanent deformation is small.

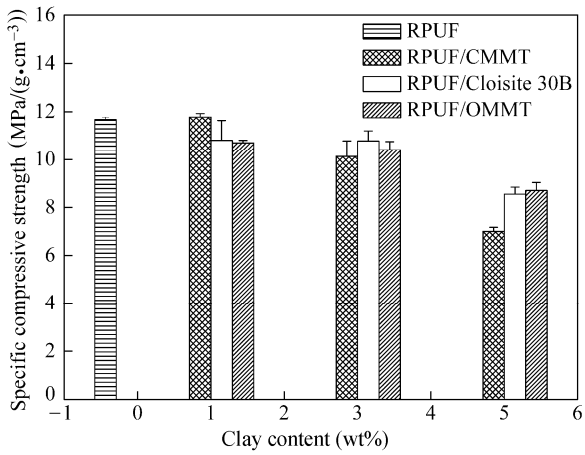

Fig. 7 Specific compressive strengths of RPUF and the nanocomposites with different organoclay contents

Table 1. The recovery ratios (%) of the samples at different times

	RPUF	CMMT			Cloisite 30B			OMMT		
		1%	3%	5%	1%	3%	5%	1%	3%	5%
After compression	75	74	76	77	77	75	73	76	73	74
2 h later	86	88	87	89	89	89	88	90	90	86
A week later	89	91	90	90	92	90	91	92	91	89

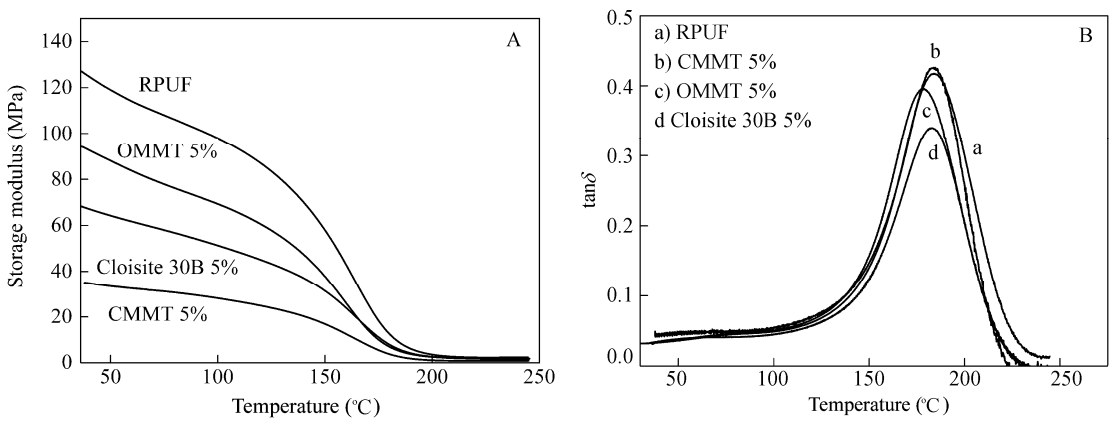

Fig. 8 Modulus (A) and (B) loss tangent curves of RPUF and RPUF/CMMT, PUF/OMMT and RPUF/Cloisite 30B with an organoclay content of 5 wt%

Figure 8 presents the storage modulus (E') and loss tangent ($\tan\delta$) curves of pure RPUF and RPUF nanocomposites with 5 wt% organoclays. It can be seen that with the addition of organoclays, the storage modulus values decrease. RPUF/OMMT and RPUF/Cloisite 30B nanocomposites have higher E' than RPUF/CMMT when the clay content is 5 wt%. The $\tan\delta$ peaks of RPUF/OMMT and RPUF/Cloisite 30B nanocomposites are smaller than those of pure RPUF and RPUF/CMMT nanocomposite, which further confirms that the reactive intercalating agents used in OMMT and Cloisite 30B can decrease the negative effect of organoclay incorporation at relatively high filler content.

CONCLUSIONS

The morphologies of the organoclays in RPUF nanocomposites greatly depend on the chemical structures of surface modifiers using for the organoclays. The XRD and TEM results show that OMMT and Cloisite 30B can be partially exfoliated in the RPUF nanocomposites because their —OH groups can react with the —NCO groups of MDI. CMMT without —OH group is mostly intercalated in the RPUF nanocomposites. At relatively low filler content, the RPUF/CMMT composite has a higher specific compressive strength than the RPUF/Cloisite 30B and RPUF/OMMT composites. On the contrary, when the filler content is high, RPUF/Cloisite 30B and RPUF/OMMT composites have higher specific compressive strength, higher modulus and more uniform pore size than the RPUF/CMMT composite. However, because the foaming reaction of RPUF is so rapid that it is difficult to disperse organoclays in the RPUF matrices uniformly. Therefore, Cloisite 30B and OMMT still form aggregates in the RPUF matrices and the improvement of the properties of RPUF is limited. Further investigations should be conducted to improve the dispersion of organoclays and the final properties of RPUF.

REFERENCES

1 Li, X.B., Cao, H.B. and Zhang, Y., Sci. China, Ser. B, 2006, 49(4): 363
2 Fabrice, S.M., Laurent, C., Jean, Y.C. and Emanuelle, C., Compos. Sci. Technol., 2006, 66: 2700
3 Fabrice, S.M., Laurent, C., Jean, Y.C. and Emanuelle, C., Compos. Sci. Technol., 2006, 66: 2709
4 Jin, H., Lu, W.Y., Scheffel, S., Hinnerichs, T.D. and Neilsen, M.K., International Journal of Solids and Structures, 2007, 44: 6930
5 Ridha, M. and Shim, V.P.W., Exp. Mech., 2008, 48: 763
6 Li, X.B., Cao, H.B. and Zhang, Y., Journal of Wuhan University of Technology-Mater. Sci. Ed., 2008, 23: 125
7 Usuki, A., Kawasumi, M., Kojima, Y., Okada, A., Kurauchi, T. and Kamigaito, O., J. Mater. Res., 1993, 8: 1174
8 Usuki, A., Kojima, Y., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T. and Kamigaito, O., J. Mater. Res., 1993, 8: 1179
9 Zhang, C.Y., Cai, H.G., Chen, B., Dong, W.M., Mu, Z.Y. and Zhang, X.Q., Chinese Journal of Catalysis, 2008, 29: 1
10 Mravcakova, M., Omastova, M., Potschke, P., Pozsgay, A., Pukanszky, B. and Piontech, J., Polym. Adv. Technol., 2006, 17: 715
11 Samakande, A., Hartmann, P.C., Cloete, V. and Sanderson, R.D., Polymer, 2007(48): 1490
12 Zhu, Y., Ma, H.Y., Tong, L.F. and Fang, Z.P., Chinese J. Polym. Sci., 2008, 26(6): 783
13 Hakan, A., Mehmet, A.T., Filip, D.P. and Yusuf, Y., Eur. Polym. J., 2008, 44: 1949
14 Huang, J.C., Zhu, Z.K., Ma, X.D., Qian, X.F. and Yin, J., J. Mater. Sci., 2001, 36: 871
15 Shah, D., Maiti, P., Gunn, E., Schmidt, D.F., Jiang, D.D., Batt, C.A. and Giannelis, E.P., Adv. Mater., 2004, 16: 1173
16 Zheng, H., Zhang, Y., Peng, Z.L. and Zhang, Y.X., Polym. Test., 2004, 23: 217
17 Meng, J.R. and Hu, X., Polymer, 2004, 45: 9011
18 Ma, H.Y., Tong, L.F., Xu, Z.B. and Fang, Z.P., Applied Clay Science, 2008, 42: 238
19 Hampton, E. and Dean, D., Chem. Mater., 2005, 17: 1990

20 Drummy, L.F., Koerner, H., Farmer, K., Tan, A., Farmer, B.L. and Vaia, R.A., J. Phys. Chem. B, 2005, 109: 17868
21 Chen-Yang, Y.W., Yang, H.C., Li, G.J. and Li, Y.K., J. Polym. Res., 2004, 11: 275
22 Cao, X., Lee, L.J., Widya, T. and Macosko, C., Polymer, 2005, 46: 775
23 Harikrishnan, G., Patro, T.U. and Khakhar, D.V., Ind. Eng. Chem. Res. 2006, 45: 7126
24 You, C.J., Xu, J.G., Xi, S., Duan, X.X., Shen, J. and Jia, D.M., Chinese J. Polym. Sci., 2005, 23(5): 471
25 Xu, Z.B., Tang, X.L., Gu, A.J. and Fang, Z.P., J. Appl. Polym. Sci., 2007, 106: 439
26 Modesti, M., Lorenzetti, A., Besco, S., Hrelja, D., Semenzato, S., Bertani, R. and Michelin, R.A., Polym. Degrad. Stab., 2008, 93: 2166
27 Yang, Y., Zhu, Z.K., Yin, J., Wang, X.Y. and Qi, Z.E., Polymer, 1999, 40: 4407
28 Zhong, Y., Zhu, Z.Y. and Wang, S.Q., Polymer, 2005, 46: 3006
29 Chua, Y.C. and Lu, X.H., Langmuir, 2007, 23:1701
30 Yang, K., Huang, Y.J. and Dong, J.Y., Polymer, 2007, 48: 6254
31 Weimer, M.W., Chen, H., Giannelis, E.P. and Gogah, D.Y., J. Am. Chem. Soc., 1999, 121: 1615
32 Tien, Y.I. and Wei, K.H., Macromolecules, 2001, 34: 9045
33 Lee, J.Y. and Lee, H.K., Mater. Chem. Phys., 2004, 85: 410
34 Garcia-Lopez, D., Gobernado-Mitre, I., Fernandez, J.F., Merino, J.C. and Pastor, J.M., Polymer, 2005, 46: 2785
35 Morgan, A.B. and Gilman, J.W., J. Appl. Polym. Sci., 2003, 87: 1329