Synthesis and characterization of PMMA/montmorillonite nanocomposites by emulsion polymerization

J. P. ZHENG, J. X. WANG, S. GAO, K. D. YAO
College of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China
E-mail: jpzheng@tju.edu.cn

Recently, polymer/montmorillonite (MMT) nanocomposites have been studied extensively for their excellent performance compared with virgin polymers and traditional organic-inorganic composites. More and more novel organic-inorganic nanocomposites have been prepared based on many polymers and MMT, such as nylon [1], PS [2], PVC [3] and so on.

Poly(methyl methacrylate) (PMMA) is an important member in the family of polyacrylic and methacrylic esters. It has several desirable properties, including exceptional optical clarity, good weatherability, high strength, and excellent dimensional stability. So it is used in many areas. PMMA/MMT nanocomposites have been reported to be synthesized by melt intercalation [4], *in situ* [5, 6], suspension [7] and emulsion [8] polymerization. However, MMT was used directly or modified by long chain alkyl ammonium ions in all the previous works. When the MMT was used directly, the intercalated structure was formed [9] generally, while the exfoliated nanocomposite could be obtained using modified MMT [8]. In this paper, MMT was modified by cetyltrimethylammonium bromide(CTAB), lauryl alcohol, γ-methacryl oxyporpyl trimethoxysilane (KH-570) and acrylic acid. And the corresponding modified MMT were named MMT1, MMT2, MMT3 and MMT4, respectively. Then, the modified MMT was used to synthesize nanocomposites with MMA by emulsion polymerization. The results indicated that the exfoliated nanocomposites could be obtained by all four kinds of MMT. The type of the modifier has the influence on the number- and weight-average molecular weights (Mn, Mw) and polydispersity indices (PDI) of PMMA.

Na-MMT (Zhe Jiang, China) was modified respectively by above four modifiers at 80 °C for 1 h, stirred in an aqueous solution. The product was washed with distilled water and dried at 100 °C. Methyl methacrylate (MMA) (Tian Jin, China) was washed by NaOH, distilled at air condition to remove inhibitor and stored at 0 °C before polymerization. Other organic and inorganic materials were commercially available and used as received. Modified MMT and surfactant (SDS) were added into reactor filled with distilled water and bubbled with nitrogen for 30 min, followed by initiator ($K_2S_2O_8$) and MMA monomer. The polymerization was carried out at 75 °C for 12 h with stirring. After being coagulated by the addition of HCl, the product was filtered, washed with distilled water and dried under vacuum condition. The molecular weights of the PMMA extracted from the nanocomposites were examined by gel permeation chromatography (GPC). The average interlayer spacing of MMT before and after intercalation were investigated by X-ray diffraction (XRD), using Rigaku D/MAX-2500 diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 KV and a generator current of 100 mA, scanning over the 2θ range from 1° to 30° at a scanning rate of 2°/min. The nanostructure features were characterized by Transmission electron micrographs (TEM), using HITACHI H-800 TEM with 200 KV accelerating voltage. Thermogravimetric analyses (TGA) were performed on a NETZSCH TG 209 instrument in nitrogen atmosphere at a heating rate of 10 °C/min.

Fig. 1 shows the XRD patterns of original MMT and four modified MMT. The sharp peak corresponding to the (001) plane of the original MMT appears at 7.08°. According to the Bragg's equation: $\lambda = 2d \sin\theta$, the d_{001} is 1.25 nm. After modification, all diffraction peaks shift towards lower angles, indicating that all four modifiers can intercalate into the sheets of MMT.

The XRD patterns of composites prepared by MMA and the four modified MMT are shown in Fig. 2. No peak corresponding to the (001) plane of MMT can be observed, which means the delamination or the basal spacing of silicates in PMMA/MMT nanocomposites may be above 8.3 nm. In addition, the absence of the d_{001} peaks implies that the layered ordered structure of modified MMT was destroyed when the PMMA molecular chains grew in the layers of modified MMT and the exfoliated nanocomposites were formed during the polymerization.

TEM is used to confirm the morphology of nanocomposite. Fig. 3 shows the TEM images of the nanocomposite, in which the bright field represents the PMMA matrix and the dark lines stand for the MMT layers. Fig. 3a reveals that the MMT particles have been dispersed in PMMA matrix irregularly with the particle size from 40 to 100 nm. It can be seen that the MMT layers are well distributed and the well order between MMT layers has disappeared in Fig. 3b. These results indicate that an exfoliated PMMA/MMT nanocomposite has been successfully prepared.

Table I is the Mn, Mw and PDI of the pure PMMA and the extracted PMMA from the four nanocomposites. The data show the modified MMT has some effect on the average molecular weights of the PMMA. The Mn and Mw of the PMMA1, PMMA2 and PMMA4 are higher than the pure PMMA. But the Mn and Mw
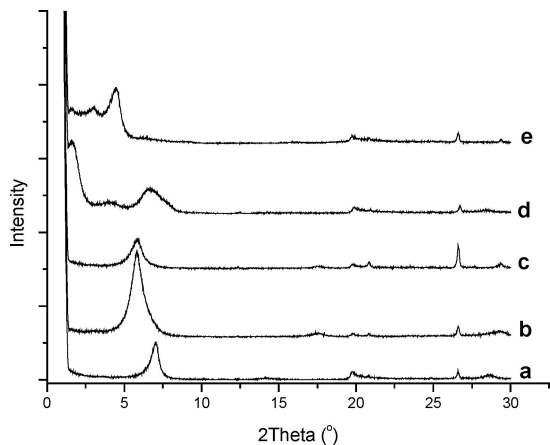
Figure 1 XRD patterns of original MMT and four modified MMT: (a) original MMT, (b) MMT4, (c) MMT3, (d) MMT2, (e) MMT1.
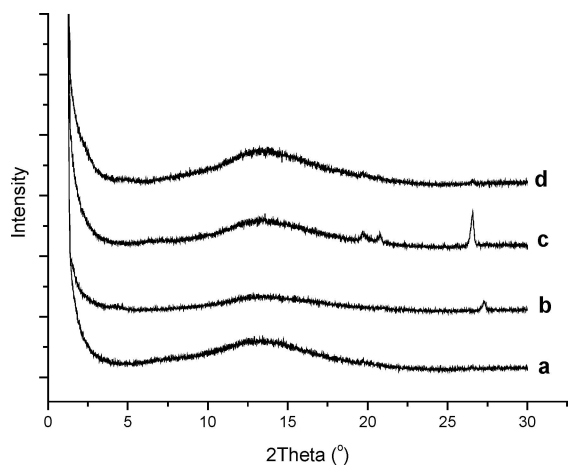

Figure 2 XRD patterns of nanocomposites prepared by MMA and the four modified MMT: (a) MMT4, (b) MMT3, (c) MMT2, (d) MMT1.

of the PMMA3 are visible low. In addition, PDI of all four PMMA are smaller than pure PMMA. Note that PMMA4 achieves the highest average molecular weights and the smallest PDI. So, acrylic acid is a suitable modifier for MMT compounding with MMA by emulsion polymerization.

TABLE I *Mn, Mw* and PDI of the pure PMMA and the extracted PMMA from the four nanocomposites[a]

Samples	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PDI (M_w/M_n)
Pure PMMA	6.9	31.1	4.5
PMMA1	11.4	34.1	3.0
PMMA2	11.6	47.0	4.1
PMMA3	4.2	16.1	3.9
PMMA4	27.9	52.9	1.9

[a]The extracted PMMA from the four nanocomposites are named PMMA1, PMMA2, PMMA3 and PMMA4, respectively.
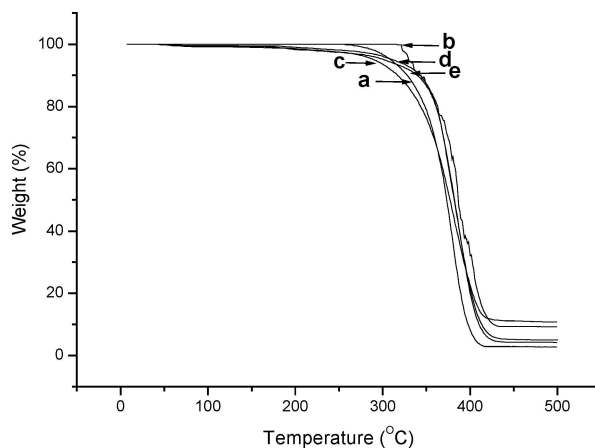

Figure 4 TGA curves of the pure PMMA and nanocomposites with 5 wt% four modified MMT: (a) pure PMMA, (b) MMT4, (c) MMT3, (d) MMT2, (e) MMT1.

Fig. 4 shows TGA curves of the pure PMMA and the nanocomposites with 5 wt% four modified MMT. The results show that the onset of thermal decomposition of the nanocomposites with 5 wt% MMT1, MMT2 and MMT4 shifted to higher temperatures. It can be suggested that the improvement of thermal stability of the nanocomposites is mainly attributed to thermal resistant of MMT and the nano-dispersion of MMT sheets in PMMA matrix. Furthermore, the nano-dispersing MMT sheets can act as physical cross-linking sites to retard the thermal decomposition of PMMA. However,
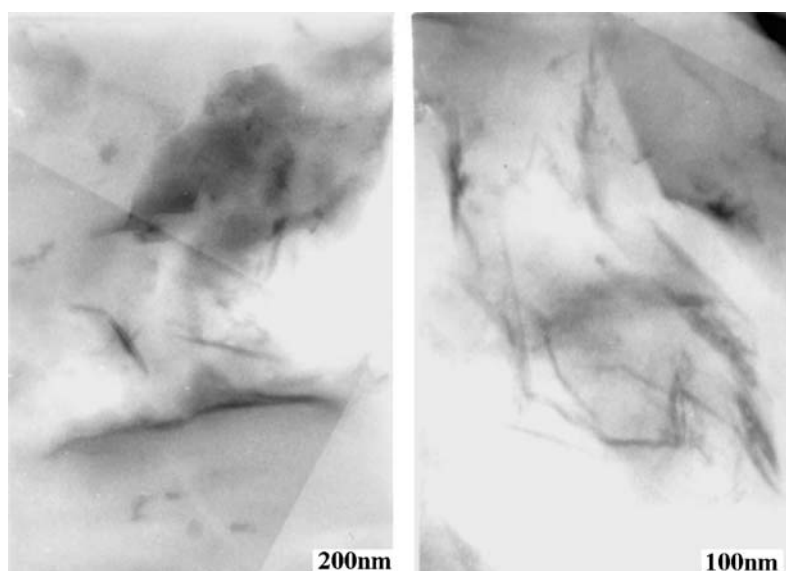

Figure 3 TEM images of the nanocomposite with 5 wt% MMT4.

the onset temperature of thermal decomposition of the nanocomposite with 5 wt% MMT3 is lower than the pure PMMA. It may be ascribed to the lower molecular weights.

In conclusion, the exfoliated nanocomposites have been prepared by MMA and four modified MMT by emulsion polymerization. The modifiers have some effect on the *Mn, Mw* and PDI of PMMA. The thermal stability of PMMA has been improved due to nano-compounding with MMT.

References

1. USUKI, Y. KOJIMA, M. KAWASUMI, A. OKADA, Y. FUKUSHIMA, T. KURAUCHI and O. KAMIGAITO, *J. Mater. Res.* **8** (1993) 1179.
2. M. W. WEIMER, H. CHEN, E. P. GIANNELIS and D. Y. SOGAH, *J. Am. Chem. Soc.* **121** (1999) 1615.
3. F. L. GONG, C. G. ZHAO, M. FENG, H. L. QIN and M. S. YANG, *J. Mater. Sci* **39** (2004) 293.
4. N. MOUSSAIF and G. GROENINCKX, *Polymer.* **44** (2003) 7899.
5. M. OKAMOTO, S. MORITA, H. TAGUCHI, Y. H. KIM, T. KOTAKA and H. TATEYAMA, *ibid.* **41** (2000) 3887.
6. G. H. CHEN, X. Q. CHEN, Z. Y. LIN, W. YE and K. D. YAO, *J. Mater. Sci lett.* **18** (1999) 1761.
7. X. Y. HUANG and J. WILLIAM, *Macromolecules.* **34** (2001) 3255.
8. Y. S. CHOI, M. H. CHOI, K. H. WANG, S. O. KIM, Y. K. KIM and I. J. CHUNG, *ibid.* **34** (2001) 8978.
9. D. C. LEE and L. E. JANG, *J. Appl. Polym. Sci.* **61** (1996) 1117.