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Study on the solvothermal preparation of polyethylene/organophilic montmorillonite nanocomposites

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Exfoliated polyethylene/organophilic montmorillonite (PE/OMT) nanocomposites were prepared based on polyethylene and organophilic montmorillonite using solvothermal methods and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The effects of the alkyl ammonium cationic exchange fraction, ion exchange capacity of the OMT and OMT content in the nanocomposites on the formation of exfoliated nanocomposites were investigated. The organophilic montmorillonite with a low ion exchange capacity and high alkyl ammonium cationic exchange fraction could easily form an exfoliated structure in the PE/OMT nanocomposite. The intercalated nanocomposites, prepared by a solution method at atmospheric pressure, could transform into exfoliated nanocomposite after treatment by solvothermal methods.

Introduction

In the past few years, polymer/layered inorganic materials exfoliated and intercalated nanocomposites have interested my research team since they represent an improvement or new properties as compared to the original polymer such as higher heat distortion temperatures, enhanced flame resistance, increased mechanical modulus, better barrier properties and improved thermal properties.[1–6] These improved properties may be due to the synergistic effects of nanostructure and the interaction of layered inorganic materials with organic polymers. One of the most studied composite systems are hybrids based on an organic polymer and layered clay minerals consisting of silicate layers such as montmorillonite.[4–10]

Polyethylene (PE) is one of the most widely used polyolefin polymers. Because polyethylene is a non-polar and flexible polymer, it is thought that montmorillonite (MMT) is not easily dispersed homogeneously in polyethylene. In general, montmorillonite is modified with alkyl ammonium to facilitate its interaction with a polymer because the alkyl ammonium makes the hydrophilic MMT surface organophilic to form organophilic montmorillonite (OMT). However, OMT does not disperse well in the non-polar polypropylene or polyethylene since such a non-polar polymer is still too hydrophobic.[10–12] Jeon and co-workers reported the intercalated morphology of HDPE nanocomposites prepared by blending HDPE with sodium montmorillonite cation-exchanged with protonated dodecylamine in solution.[10] However, the presence of fairly large stacks indicated poor dispersion. When *in situ* polymerization was performed on a polyethylene/clay nanocomposite it showed an exfoliated morphology.[12–14] The non-polar polymer/clay nanocomposites were prepared by melt mixing based on the introduction of a modified oligomer to mediate the polarity between the clay surface and the polymer, such as maleated polypropylene/clay and maleated polyethylene/clay.[15–20] Polyethylene/clay intercalated nanocomposites require modification of the clay without modification of the polyethylene[17] but stable PE/clay exfoliated nanocomposites with pure PE are difficult to obtain. The solvothermal method is a powerful technique for preparing materials under a pressure–temperature domain condition. In this paper, we report on the preparation of exfoliated polyethylene/organophilic montmorillonite nanocomposites by solvothermal methods and the verification of their microstructure by XRD and HREM.

Experimental

Materials

Sodium MMT and hexadecyltrimethylammonium bromide ($16Me^+Br^-$) were purchased from Shanghai of China. The high-density polyethylene ($M_w = 3.5 \times 10^5$) used to intercalate into galleries of organophilic montmorillonite and other inorganic and organic reagents were commercially available and used without further purification.

Preparation of organophilic montmorillonite (OMT)

Varying mass ratios of sodium MMT and hexadecyltrimethylammonium bromide ($16Me^+Br^-$) were gradually added to hot distilled water at 80 °C, and the resultant suspension was stirred vigorously for 2 h. The treated montmorillonite, a white precipitate, was washed repeatedly with hot deionized water several times to remove residual $16Me^+Br^-$. The filtrate was titrated with 0.1 mol L^{-1} $AgNO_3$ until no precipitate of AgBr was formed so as to ensure the complete removal of bromide ions. The product was placed in a vacuum drying oven at 80 °C for 12 h. The dried product was ground and screened (400 mesh) to obtain the OMT. Different types of OMT containing different amounts of alkyl ammonium reagent could be prepared by varying the mass ratios of MMT and $16Me^+Br^-$. The mass ratios of MMT to $16Me^+Br^-$ used were 1.5 : 1, 2.5 : 1 and 3 : 1.

Preparation of PE/OMT nanocomposites

OMT was dispersed homogeneously in toluene at room temperature. Meanwhile polyethylene (PE) and toluene were added into a Teflon-lined autoclave of 100 mL capacity. The autoclave was sealed into a stainless steel tank and maintained at 170 °C for 1 h, so that the PE was swelled in toluene on

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cooling to room temperature. Then the above OMT/toluene solution was added into the autoclave. The autoclave was sealed in the tank and maintained at 170 °C for 2 h. After cooling to room temperature naturally, most of the toluene was distilled from the solution. The product was poured into a flat mold, and set overnight in a vacuum drying oven at 80 °C, finally yielding the PE/OMT nanocomposite.

Characterization

X-Ray diffraction (XRD) experiments were performed directly on the samples using a Japan Rigaku D/max-rAX diffractometer (30 kV, 10 mA) with Cu (λ = 1.54 Å) irradiation at the rate of 2° min^{-1} in the range of 1.5–10°. Transmission electron microscope (TEM) images were obtained on a JEOL 2010 high-resolution electron microscope with an acceleration voltage of 200 kV. The samples for TEM were prepared by ultramicrotomy. The PE/OMT sample was placed into epoxy capsules and the epoxy was cured at 50 °C for 48 h in a vacuum oven. Then the cured epoxies containing PE/OMT were microtomed into 70 nm thick slices at room temperature. Thermogravimetric analysis (TGA) was used to observe the exchanged amount of alkyl ammonium in OMT; analyses were carried out under a N_2 atmosphere with a NETZSCH STA409C thermal analyzer from 50–700 °C at a heating rate of 10 °C min^{-1}.

Results and discussion

The sodium montmorillonite (MMT) was modified by treatment with hexadecyltrimethylammonium bromide ($16\text{Me}^+\text{Br}^-$) to form organophilic montmorillonite (OMT). MMTA is a type of montmorillonite with a cationic exchange capacity of 122 mmol/100 g. OMTA1 and OMTA2 represent two types of OMT prepared from different mass ratios of $16\text{Me}^+\text{Br}^-$ and MMT1. MMTB is a type of montmorillonite with a cationic exchange capacity of 96.5 mmol/100 g. OMTB1 and OMTB2 represent two types of OMT prepared from different amounts of $16\text{Me}^+\text{Br}^-$ and MMTB. The mass ratios of MMT and $16\text{Me}^+\text{Br}^-$ used in the preparations of OMTA1, OMTA2, OMTB1 and OMTB2 are 1.5 : 1, 2.5 : 1, 2.5 : 1 and 3 : 1 respectively. When MMT was modified with $16\text{Me}^+\text{Br}^-$, the galleries of MMT were intercalated and expanded by molecular chains of $16\text{Me}^+\text{Br}^-$. The alkyl ammonium almost completely degraded, and the weight loss above 500 °C was due to MMT degradation at 500 °C.[21] Fig. 1 shows the thermogravimetric analysis (TGA) of MMT and OMT. The curves of MMTA and MMTB overlap. At 500 °C, the weight losses for MMTA, MMTB, OMTA1, OMTA2, OMTB1, and OMTB2 are 1.4, 1.4, 23.6, 22.1, 18.3, and 16.7 wt%, respectively. If other factors are not considered, the weight loss of OMT subtracting the weight loss of MMT at 500 °C would be regarded as the amount of alkyl ammonium intercalated in the galleries of OMT. According to the cationic exchange capacity of MMT, the alkyl ammonium cationic exchange fractions of OMTA1, OMTA2, OMTB1 and OMTB2 are 81, 75, 73, and 66%. The XRD patterns of MMT and OMT are shown in Fig. 2. The basal spacing of MMTA, MMTB, OMTA1, OMTA2, OMTB1, and OMTB2 are 1.32, 1.45, 3.02, 2.08, 3.74 and 3.39 nm, respectively. The XRD patterns show that the basal spacing of OMT increases with the alkyl ammonium ion content for the same kind of MMT. It is suggested that the MMT with a lower cationic exchange capacity can be modified by relatively fewer alkyl ammonium groups and OMT obtained has a larger basal spacing and lower alkyl ammonium cationic exchange fraction.

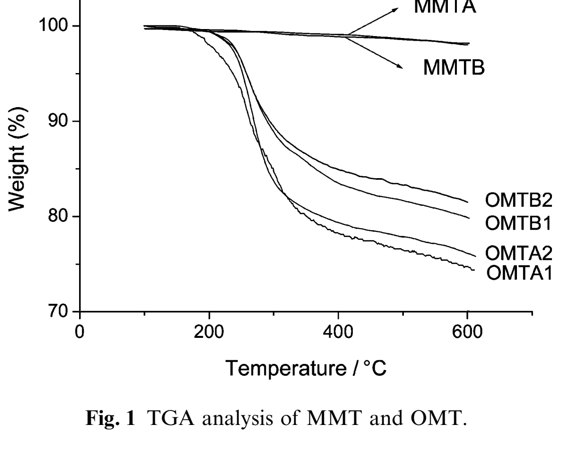

Fig. 1 TGA analysis of MMT and OMT.

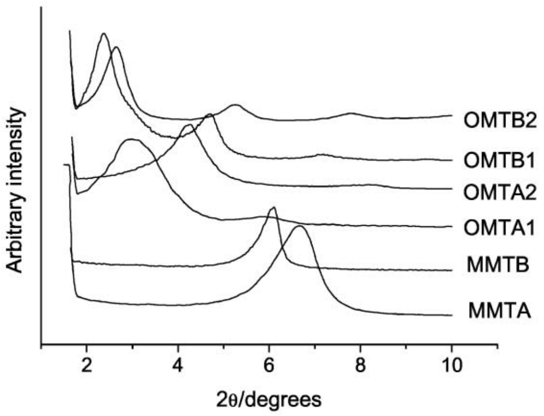

Fig. 2 XRD patterns of MMT and OMT (MMTA: MMT with an ion exchange capacity 122 mmol/100 g; MMTB: MMT with an ion exchange capacity 96.5 mmol/100 g).

The PE/OMT nanocomposites were prepared by a solvothermal method and the function of ion exchange capacity and alkyl ammonium cationic exchange fraction of OMT on the intercalation behavior of polymer was investigated. XRD curves of a series of PE/OMT samples prepared with polyethylene and different OMT content of those four types of OMT are shown in Fig. 3 and 4, respectively. In Fig. 3, the disappearance of the XRD peaks (2θ = 1.5–10°) in samples PEA11, PEA12 and PEA13 corresponding to 5, 10 and 15 wt% content OMTA1 in the hybrids respectively, indicate that these silicate layers are completely exfoliated to form exfoliated nanocomposites. Fig. 4 shows that PEB11, PEB12 and PEB13 corresponding to 5, 10, and 15 wt% content OMTB1 in the hybrids respectively are exfoliated nanocomposites.

The microstructure of the hybrids was further confirmed using TEM. Fig. 5 shows a TEM image of the sample PEA11. The dark lines correspond to intersecting layers; it shows a section of exfoliated hybrid wherein individual silicate layers are dispersed in the PE matrix. The separation of adjacent layers over 10 nm is verified by XRD and TEM analysis. But in the Fig. 4, the peak of original OMTA2 or OMTB2 is still present, so the polyethylene does not intercalate the galleries of OMTA2 or OMTB2. OMTA2 and OMTB2 have relatively low alkyl ammonium cationic exchange fractions and narrow basal spacings, so they can't be intercalated by polyethylene. The alkyl ammonium cationic exchange fraction of OMTA2 is larger than that of OMTB1, and its ion-exchange capacity is also higher than that of OMTB1. But the basal spacing of OMTB1 is larger than that of OMTA2. OMTB1 can form an exfoliated structure in PE/OMT but OMTA2 cannot. Although the basal spacing of OMTB2 is larger than OMTA1, it can't form exfoliated PE/OMT. These facts reveal that the formation of the exfoliated structure is due to the synergistic effects of the cationic exchange capacity of MMT, the alkyl ammonium cationic exchange fraction and the basal spacing of OMT. The MMT with a lower ion exchange capacity can be modified by relatively fewer alkyl ammonium cations to obtain OMT with a larger basal spacing and higher alkyl ammonium cationic

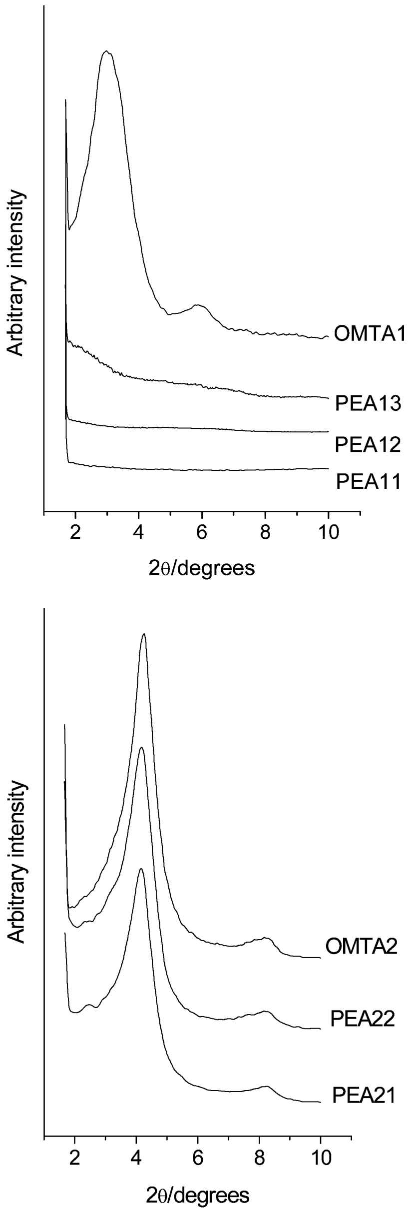

Fig. 3 XRD patterns of PE/OMTA hybrids prepared *via* a solvothermal method (OMTA1 contents of samples PEA11-PEA13 were 5, 10 and 15 wt%; OMTA2 contents of samples PEA21-PEA22 were 5 and 10 wt%).

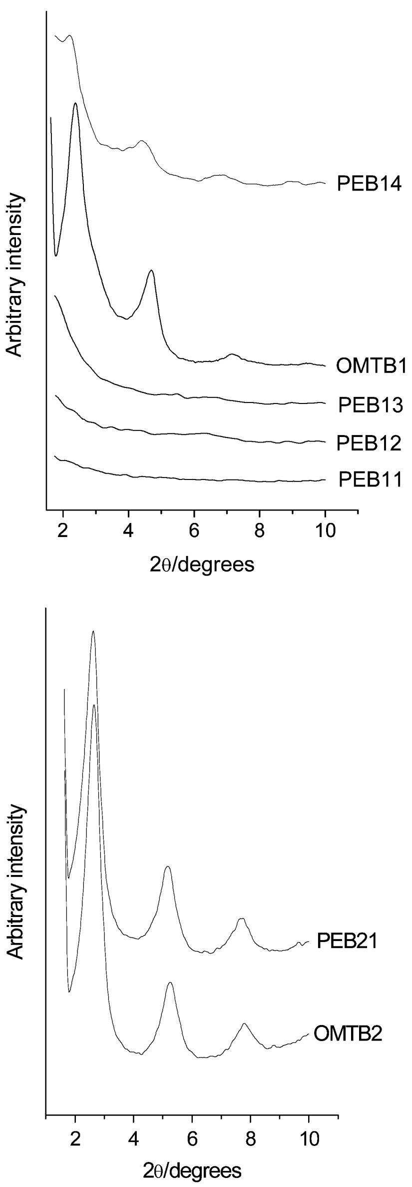

Fig. 4 XRD patterns of PE/OMTB hybrids prepared *via* a solvothermal method (OMTB1 contents of samples PEB11-PEB13 were 5, 10 and 15 wt%; OMTB1 contents of samples PEB14 was 5 wt%; OMTB2 contents of samples PEB21 was 5 wt%).

exchange fraction. The OMT with a lower ion exchange capacity, higher alkyl ammonium cationic exchange fraction and larger basal spacing more easily forms exfoliated nanocomposites.

In order to investigate the effect of the solvothermal method on formation of the exfoliated structure in PE/OMT OMTB1 was dispersed in a hot PE/toluene solution in a flask at 110 °C and atmospheric pressure and stirred for a sufficient period of time to obtain PEB14. Fig. 3 shows the XRD pattern of a sample of PEB14 with OMTB1 content of 5 wt%. The basal spacing of PEB14 is increased from 3.74 to 4.01 nm. Sample PEB14 is an intercalated nanocomposite; it could be turned into PEB11, after PEB14 was treated by the solvothermal method. That is to say, intercalated PE/OMT hybrid can be changed to exfoliated PE/OMT hybrid *via* solvothermal methods. The solvothermal method provides a pressure–temperature domain condition. The specific physicochemical properties of solvents in these conditions can, in particular, markedly improve the diffusion of polyethylene molecular chains, layers of OMT. It is effectively that the relaxing molecular chains of PE diffuse into silicate particles, intercalate into the gallery of layered silicate, swell and exfoliate layered silicate under the solvothermal conditions. It is realized that PE/OMT exfoliated nanocomposites can be obtained *via* solvothermal methods only by proper modification of MMT without modification of polyethylene.

Conclusion

Exfoliated polyethylene/organophilic montmorillonite nanocomposites were prepared based on polyethylene and organophilic montmorillonite using solvothermal methods. The exfoliated structure in the PE/OMT hybrid was confirmed by studies of the XRD patterns and TEM images, and the separations of adjacent layers of 10 nm or more. The MMT with a low ion exchange capacity could be modified by low amounts of alkyl ammonium cation and OMT with a high alkyl ammonium cationic exchange fraction could be obtained easily. The alkyl ammonium cationic exchange fraction of the organophilic montmorillonite and ion exchange capacity were very important factors to achieve an exfoliated structure. The organophilic montmorillonite with low ion exchange capacity

Fig. 5 TEM image of PEA11 hybrid with solvothermal method MMT: montmorillonite; OMT: organophilic montmorillonite; PE: polyethylene; PE/OMT: polyethylene/organophilic montmorillonite.

and high alkyl ammonium cationic exchange fraction could easily form an exfoliated structure in the polyethylene matrix *via* solvothermal methods.

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References

1 R. A. Vaia, H. Ishii and E. P. Giannelis, *Chem. Mater.*, 1993, **5**, 1694.
2 H. Z.Shi, T. Lan and T. J. Pinnavia, *Chem. Mater.*, 1996, **8**, 1584.
3 F. S. Wang and Z. N. Qi, in *Proceedings of the 1997 Chinese National Symposium on Polymer*, Hefei, Oct. 1997; p. 97.
4 K. Yano, A. Usuki, T. Kurauchi and O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 2493.
5 A. Usuki, M. Kawasumi, Y. Kojima, Y. Fukushima, A. Okada, T. Kurauchi and O. Kanigaito, *J. Mater. Res.*, 1993, **6**, 422.
6 L. Biasci, M. Aglietto, G. Ruggeri and F. Ciardelli, *Polymer*, 1994, **35**, 3296.
7 T. Lan and T. J. Pinnavaia, *Chem. Mater.*, 1994, **6**, 2216.
8 P. E. Messersmith and E. P. Giannelis, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 1047.
9 D. C. Lee and L. W. Jang, *J. Appl. Polym. Sci.*, 1996, **61**, 1117.
10 H. G. Jeon, H. T. Jung, S. W. Lee and S. D. Hudson, *Polym. Bull.*, 1998, **41**, 107.
11 N. Furuichi, Y. Kurokawa, K. Fujita, A. Oya, H. Yasuda and M. Kiso, *J. Mater. Sci.*, 1996, **31**, 4307.
12 J. Heinemann, P. Reichert, R. Thomann and R. Mulhaupt, *Macromol. Rapid Commun.*, 1999, **20**, 423.
13 J. S. Bergman, H. Chen, E. P. Giannelis, M. G. Thomas and T. G. Coates, *Chem. Commun.*, 1999, **21**, 79.
14 J. Wang, Z. Y. Liu, C. Y. Guo, Y. J. Chen and D. Wang, *Macromol. Rapid Commun.*, 2001, **22**, 1422.
15 M. A. Kato, A. Usuki and A. Okada, *J. Appl. Polym. Sci.*, 1997, **66**, 1781.
16 Q. Zhang, Q. Fu, L. X. Jiang and Y. Lei, *Polym. Int.*, 2000, **49**, 1561.
17 K. H. Wang, M. H. Choi, C. M. Koo, Y. S. Choi and I. J. Chung, *Polymer*, 2001, **42**, 9819.
18 K. H. Wang, M. Xu, Y. S. Choi and I. J. Chung, *Polym. Bull.*, 2001, **46**, 499.
19 E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu and T. C. Chung, *Chem. Mater.*, 2001, **13**, 3516.
20 K. N. Kim, H. Kim and J. W. Lee, *Polym. Eng. Sci.*, 2001, **41**, 1963.
21 W. Xie, Z. G. Gao, K. L. Liu, W. P. Pan, R. Vaia, D. Hunter and A. Singh, *Thermochim. Acta*, 2001, **367–368**, 339.