

Preparation and Characterization of Polyethylene–Clay Nanocomposites by Using Chlorosilane-Modified Clay

Chungui Zhao, Meng Feng, Fangling Gong, Huaili Qin, Mingshu Yang

State Key Laboratory of Engineering Plastics, Center for Molecular Science, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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ABSTRACT: Clay was modified by trimethylchlorosilane; after modification, hydroxyl groups at the edge of layers were reacted and CEC value was drastically decreased. Polyethylene–clay composites were prepared by melt compounding. Wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) showed that intercalated nanocomposites were formed using organoclay ion-exchanged from chlorosilane-modified clay, but conventional composites formed using organoclay directly ion-exchanged from crude clay. Dynamic mechanical anal-

ysis (DMA) of PE and PE–clay composites was conducted; the results demonstrated that nanocomposites were more effective than conventional composites in reinforcement and addition of organoclay resulted in the increase of glass transition temperature (T_g), but crude clay had no effect on T_g of PE–clay composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 676–680, 2004

Key words: clay; modification; polyethylene (PE); nanocomposites

INTRODUCTION

A variety of inorganic materials, such as calcium carbonate, and silicate minerals have been successfully and widely used as fillers or additives to enhance the properties of polymers. Of particular interest are polymer–clay nanocomposites because adding a low fraction of clay to the polymer matrix would enhance a large number of physical properties, such as mechanical,^{1–4} barrier,^{5,6} and flammability resistance.^{7,8} The most commonly used clay is layered silicate such as montmorillonite.

Polyethylene (PE) is one of the most widely used classes of polymers and with relative low cost, but its mechanical properties are low. In general, there are three methods to prepare PE–clay nanocomposites, solution intercalation,^{9,10} *in situ* polymerization,^{11–14} and melt intercalation.^{15–18} Melt intercalation is the most appropriate technique for the industrial preparation of polymer–clay nanocomposites, by which the clay layers are directly dispersed in the molten polymer using a conventional two-screw extruder. In fact, PE is a nonpolar polymer. It is difficult to fabricate PE–clay nanocomposites by melt intercalation even using a dioctadecyldimethylammonium-modified clay. Introducing maleic anhydride to modulate the polarity between the hydrophilic clay surface and the

hydrophobic PE has obtained exfoliated PE–clay nanocomposites,^{15–18} and exfoliated nanocomposites improve the mechanical properties to a certain extent,¹⁷ but introduction of maleic anhydride may weaken some properties, such as environmental stability and hygroscopy.

There are a few OH groups at the edge of clay layers, which have an adverse effect on the intercalation of polyolefin.¹⁹ The modification of montmorillonite by chlorosilanes has been reported in our former studies.^{20,21} In this paper, trimethylchlorosilane was used to react with OH groups at the edge of clay layers, and PE–clay composites were prepared by melt compounding using organoclay ion-exchanged from chlorosilane-modified clay. After chlorosilane-modification, OH groups at the edge of clay layers were reacted and the wetting ability between PE and organoclay would be improved. Furthermore, the loss of hydroxyl groups resulted in the decrease of cation exchange capacity (CEC), which caused the reduction of interlayer attraction. Both of these effects would improve the intercalation of PE into interlayers. The structure of PE–clay composites was characterized by wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). Dynamic mechanical properties of PE–clay composites were measured and compared.

EXPERIMENTAL

Materials

The crude clay used was Na-montmorillonite (MMT, Zhangjiakou Qinghe Chemical Factory, People's Re-

Correspondence to: M. Yang (yms@sklep.icas.ac.cn).

public of China). WAXD showed that the interlayer spacing (d_{001}) was 0.98 nm. MMT was dried for 8 h at 100°C in vacuum before used.

Trimethylchlorosilane [(CH₃)₃SiCl; industry grade, abbreviated as TMSCl], dioctadecyldimethylammonium chloride [(C₁₈H₃₇)₂N(CH₃)₂]⁺Cl⁻; industry grade, abbreviated as DOAc) and ammonium chloride (NH₄Cl, AR grade) were purchased from Beijing Chemical Reagent Co. and used as received. Acetone (AR grade) was dried by anhydrous MgSO₄ and then distilled before use. Ethanol (AR grade) was used without further purification.

A low-density polyethylene (PE-M-18D022, density: 0.919 g/cm³, melting flow index: 2.0 g/10min) was bought from Yanshan Petrochemical Co. and used as composite matrix resin.

Preparation of organoclays

MMT (10 g) and TMSCl (12 g) were mixed in acetone (100 mL) and refluxed for 36 h under stirring conditions. The product was filtered and washed with acetone for two times and then washed with 95% ethanol for several times to make sure that the product contained no Cl⁻ (no white precipitate was detected by 0.1M aqueous AgNO₃ solution in the filtrate). The product was dried for 8 h at 100°C in vacuum and then ground to get chlorosilane-modified clay (re-marked as TMA).

Clay (MMT or TMA, 10 g) was ion-exchanged with DOAc (6.0 g) in the ethanol : H₂O (1 : 1 weight) mixed solvent (200 mL) at 75°C for 2 h under agitation. The products were filtered and washed with ethanol : H₂O (1 : 1 weight) mixed solvent several times to make sure that the products contained no Cl⁻ (no precipitate was detected by 0.1M aqueous AgNO₃ solution in the filtrate). The products were dried for 8 h at 100°C in vacuum and then ground to get organoclays (sample of MMT and TMA ion-exchanged with DOAc was remarked as DOM and TMD, respectively).

Melt compounding

PE and clays were melting compounded in a twin-screw extruder (Haake RC90). The temperature profiles of the barrel were 120–150–160–160°C from the hopper to the die, and the screw speed was 100 rpm.

The extruded pellets were injection-molded into plates of 2-mm thickness by a Mini-Max 183 molder (CSI Co.). The plates were cut and ground into test pieces (15 × 2 × 2 mm) for the dynamic mechanical analysis. The plates were also used for the measurements of WAXD and TEM. The characteristics and names of the six materials are illustrated in Table I.

Characterization

Infrared spectra of KBr disks were recorded on a Perkin-Elmer System 2000 Fourier-transformed infra-

TABLE I
The Composites and Their Abbreviations

Abbreviation	PE (wt %)	Clay type	Clay content (wt %) ^a
PE	100	—	0
PE/MMT5	100	MMT	5
PE/DOM5	100	DOM	5
PE/TMD5	100	TMD	5
PE/TMD10	100	TMD	10
PE/TMD15	100	TMD	15

^a Except for MMT, values represent the weight percent of organoclay.

red spectrometer. Cation exchange capacity (CEC) of MMT and TMA was measured using NH₄Cl as intercalating agent by the method described by Peech.²²

Wide-angle X-ray diffraction and TEM were used to investigate the structure of clay in the composites. WAXD was carried out by using a Rigaku D/max 2400 diffractometer and Cu K α radiation ($\lambda = 0.154$ nm) at a generated voltage of 40 kV and current of 120 mA at room temperature. The composites were analyzed in plate while organoclays in powder. The diffractograms were scanned from 1.5° to 30° in the 2 θ range in 0.02° steps; scanning rate was 8 °/min. TEM was performed by a Hitachi (Japan) H-800 with an acceleration voltage of 100 kV. The ultrathin slices were prepared by sectioning the injection-molded samples along the direction perpendicular to the injection under cryogenic condition.

Dynamic mechanical analysis (DMA) was carried out under a nitrogen atmosphere by a Perkin-Elmer DMA-7 at a heating rate of 5.0°C/min; the dynamic temperature spectra were obtained in three-point bending mode at a vibration frequency of 1 Hz with temperatures from -150 to 100°C.

RESULTS AND DISCUSSION

Modification of MMT by chlorosilane

Fourier-transformed infrared spectra for chlorosilane-modified and crude clay were compared, and the results are shown in Figure 1. The sharp band at 3,620 cm⁻¹ is the stretching vibration of isolated OH groups (not formed hydrogen bond), and the band at 3,440 cm⁻¹ is the stretching vibration of OH groups formed hydrogen bond.²³ After modification by TMSCl, the adsorption at 3,620 and 3,440 cm⁻¹ weakens, and the new bands belonging to the characteristic adsorption of methyl group at 2,920 and 2,855 cm⁻¹ appear. The results indicated that TMSCl had successfully reacted with the OH groups at the edge of clay layers.

Table II lists the CEC values of MMT and TMA. Compared with MMT, the CEC value of TMA has drastically decreased. Protonation or loss of OH

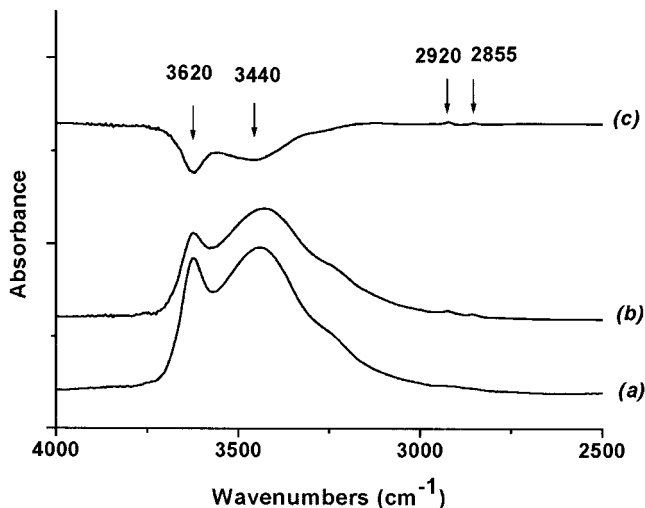


Figure 1 FT-IR and differential spectra of clays. (a) MMT, (b) TMA, and (c) TMA-MMT.

groups decreases the anionic charge of smectites.²⁴ After modification by TMSCl, OH groups at the edge of layers had been reacted and corresponding CEC value decreased.

Structure of PE-clay composites

The clay-based composites are structurally characterized as conventional, intercalated, and exfoliated, which typically are elucidated using X-ray diffraction (XRD) and TEM. In an intercalated system, the polymer chains intercalate into the interlayers but preserve the stacking of layers, while in an exfoliated system the clay is dispersed in the continuous polymer matrix as individual layers. Both these two types of composites are called nanocomposites, but in a conventional system the polymer chains don't intercalate into the interlayers and keep phase separated with clay.

Figure 2 shows WAXD patterns for organoclays and PE-clay composites. The characteristic peak toward low angle corresponds to the (001) plane diffraction of clay layers, and corresponding values of interlayer spacing are marked in the figure. The (001) plane diffraction peak of DOM appears at 2.58° , and interlayer spacing is 3.4 nm. The diffraction peak of PE/DOM5 is also at 2.58° , but the peak became narrower than that of DOM, demonstrating that PE chains didn't intercalate into the interlayers of DOM. For PE/DOM5, the peak at 4.93° (interlayer spacing of 1.8

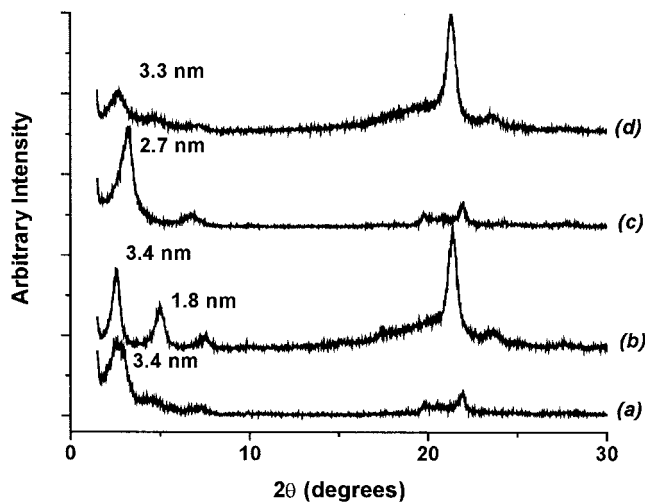


Figure 2 WAXD patterns of DOM (a), PE/DOM5 (b), TMD (c), and PE/TMD5 (d).

nm) became very sharp. This may be caused by the deintercalation of partial intercalating agents in some interlayers during the compounding process. PE/DOM5 is a conventional composite. The interlayer spacing of TMD (the diffraction peak at 3.28° , $d_{001} = 2.7$ nm) is smaller than that of DOM (the peak at 2.58° , $d_{001} = 3.4$ nm) due to the decrease of CEC value after modification by TMSCl. In the case of PE/TMD5, the peak shifts to a lower angle of 2.65° , interlayer spacing is increased to 3.3 nm, and the peak became broader and intensity became weaker, indicating that PE chains intercalated into the interlayers and the intercalated nanocomposites were obtained. TEM can be used to directly study the dispersion of clay in the polymer matrix. Figure 3 shows the TEM image of PE/TMD5, which contained 5 wt % of organoclay. The dark lines represent the clay layers, whereas the bright



Figure 3 TEM image of PE-clay nanocomposite for containing 5wt% of TMD.

TABLE II
CEC value of MMT and TMA

Sample	MMT	TMA
CEC (mmol/100 g)	89	42

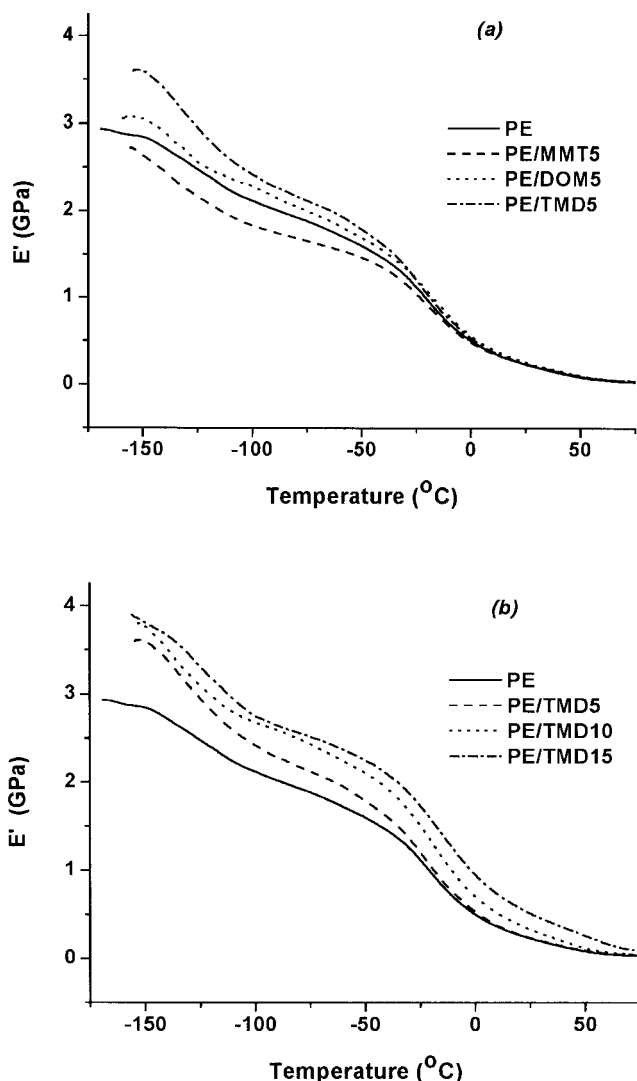


Figure 4 Storage moduli and temperature spectra for PE and PE-clay composites.

areas represent the PE matrix. It is clear that stacks of clay containing several to decades of layers were dispersed within the PE matrix.

From the above results, one can see that the interaction between PE and DOM was so weak that PE chains couldn't intercalate into interlayers, and conventional composites were formed using organoclay directly ion-exchanged from crude clay. After modification by TMSCl, the wetting ability between PE and TMD was improved because OH groups at the edges of layers had lost, and this availed to the intercalation process. What's more, interlayer attraction was reduced due to the decrease of CEC value. PE chains could intercalate into the interlayers to form intercalated nanocomposites. Both the improvement of wetting ability and the decrease of interlayer attraction promote the intercalation of PE into interlayers.

Dynamic mechanical properties

The storage moduli (E') and temperature spectra for PE and PE-clay composites are shown in Figure 4. From Figure 4(a), one could see the effect of different clay treatments on E' of PE-clay composites. Adding the same content of clay (5 wt %), E' of PE/MMT5 is lower than that of pure PE, but values of both PE/TMD5 and PE/DOM5 are higher than those of PE. MMT is incompatible with PE and dispersed worse in PE matrix due to its high polarity; introducing MMT into PE decreases the storage modulus. The polarity is decreased and its compatibility with PE enhanced after ion-exchange with DOAc; addition of DOM increases the storage modulus of PE and E' of PE/DOM5 is higher than that of PE. PE/TMD5 is a

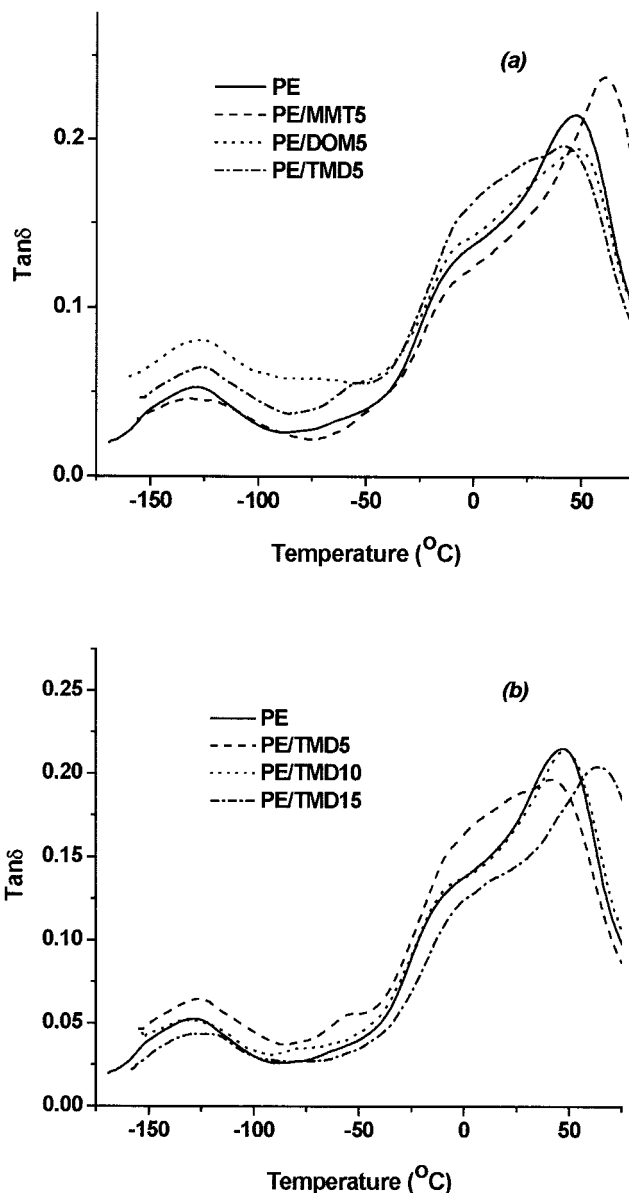


Figure 5 Loss factor and temperature spectra for PE and PE-clay composites.

TABLE III
 T_g for PE and PE–clay composites determined by DMA

Sample	PE	PE/MMT5	PE/DOM5	PE/TMD5	PE/TMD10	PE/TMD15
T_g (°C)	–129.3	–129.6	–126.1	–125.3	–126.7	–126.2

nanocomposite, and its E' is the highest. Nanocomposites are more effective than conventional composites in reinforcement. Figure 4(b) shows E' of nanocomposites for different organoclay contents. The nanocomposites have higher E' values than that of pure PE over the whole temperature range and E' of nanocomposites increase with increase in organoclay content.

Figure 5 depicts the loss factor and temperature spectra for PE and PE–clay composites. The dominant peaks around -128°C represent the glass transition of the amorphous portion of PE, and the temperature at peak point was glass transition temperature (T_g); their values are shown in Table III. T_g of PE was -129.3°C ; there was no change by adding 5 wt % of MMT into PE because the interaction between PE and MMT is very weak. However, adding DOM or TMD into PE results in an increase of T_g and the highest value appears in PE/TMD5. These are caused by the confinement of PE chains due to the addition of organoclays. T_g values of PE/TMD5, PE/TMD10, and PE/TMD15 are -125.3 , -126.7 , and 126.2°C , respectively; it appears that more TMD fraction led to a little decrease of T_g , but this influence is not obvious and needs to be studied further.

CONCLUSION

The wetting ability between PE and organoclay ion-exchanged from chlorosilane-modified clay was improved because OH groups at the edges of layers were reacted, and interlayer attraction was reduced due to the decrease of CEC. Intercalated nanocomposites were prepared by melt intercalation, but conventional composites formed using organoclay directly ion-exchanged from crude clay. Nanocomposites were more effective than conventional composites in reinforcement, and addition of organoclay resulted in the in-

crease of T_g , but crude clay had no effect on T_g of PE–clay composites.

References

- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Usuki, A.; Koiwai, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1995, 55, 119.
- Liu, L.; Qi, Z.; Zhu, X. *J Appl Polym Sci* 1999, 71, 1133.
- Wang, Z.; Pinnavaia, T. J. *Chem Mater* 1998, 10, 3769.
- Bharadwaj, R. K. *Macromolecules* 2001, 34, 9189.
- Kojima, Y.; Fukumori, K.; Usuki, A.; Okada, A.; Kurauchi, T. *J Mater Sci Lett* 1993, 12, 889.
- Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
- Vaia, R. A.; Price, G.; Ruth, P. N.; Nguyen, H. T.; Lichtenhan, J. *Appl Clay Sci* 1999, 15, 67.
- Jeon, H. G.; Jung, H. T.; Lee, S. W.; Hudson, S. D. *Polym Bull* 1998, 41, 107.
- Song, L.; Hu, Y.; Wang, S.; Chen, Z.; Fan, W. *J Mater Chem* 2002, 12, 3152.
- Heinemann, J.; Reichert, P.; Thomann, R.; Mülhaupt, R. *Macromol Rapid Commun* 1999, 20, 423.
- Rong, J.; Jing, Z.; Li, H.; Sheng, M. *Macromol Rapid Commun* 2001, 22, 329.
- Bergman, J. S.; Chen, H.; Giannelis, E. P.; Thomas, M. G.; Coates, G. M. *Chem Commun* 1999, 2179.
- Jin, Y. H.; Park, H. J.; Im, S. S.; Kwak, S. Y.; Kwak, S. *Macromol Rapid Commun* 2002, 23, 135.
- Wang, K. H.; Choi, M. H.; Koo, C. M.; Choi, Y. S.; Chung, I. J. *Polymer* 2001, 42, 9819.
- Wang, K. H.; Chung, I. J.; Jang, M. C.; Keum, J. K.; Song, H. H. *Macromolecules* 2002, 35, 5529.
- Gopakumar, T. G.; Lee, J. A.; Kontopoulou, M.; Parent, J. S. *Polymer* 2002, 43, 5483.
- Wang, K. H.; Choi, M. H.; Koo, C. M.; Xui, M.; Chung, I. J.; Jang, M. C.; Choi, S. W.; Song, H. H. *J Polym Sci Part B: Polym Phys* 2002, 40, 1454.
- Shi, H.; Lan, T.; Pinnavaia, T. J. *Chem Mater* 1996, 8, 1584.
- Zhao, C.; Yang, M.; Feng, M. *Chem J Chin Univ* 2003, 24, 928.
- Zhao, C.; Feng, M.; Gong, F.; Yang, M. *Chin J Chem* 2003, 21, 1031.
- Peech, M. *Soil Sci* 1945, 59, 25.
- Ruiz-Hitzky, E.; Rojo, J. M.; Lagaly, G. *Colloid Polym Sci* 1985, 263, 1025.
- Heller-Kallai, L. *Appl Clay Sci* 2001, 20, 27.