

Polyethylene/Maleic Anhydride Grafted Polyethylene/Organic-Montmorillonite Nanocomposites. I. Preparation, Microstructure, and Mechanical Properties

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ABSTRACT: In this study, three cationic surfactants (hexadecyltrimethylammonium chloride, hexadecyldimethylbenzylammonium chloride, and octadecyltrimethylammonium chloride) were used to modify montmorillonite and polyethylene (PE)/maleic anhydride grafted polyethylene (PE-g-MAH)/organic-montmorillonite (Org-MMT) nanocomposites, prepared by two blending processes (direct-melt blending and solution blending). X-ray diffractometry and transmission electron microscopy were used to investigate the intercalation behavior and microstructure of composites. Mechanical properties were also tested. It was found that the intercalation effect of PE/PE-g-MAH/Org-MMT could be enhanced by increasing the content of PE-g-MMT, using the silicate modified by a cationic surfactant with a benzyl group or long alkyl chain, adopting the solution-blending method or using high-density polyethylene as matrix. The degree of crystallinity of composites and the crystalline thickness perpendicular to the crystalline plane [like (110) and (200)] decreased with increasing amounts of PE-g-MAH and, under certain prescription, the crystalline

thickness of the composite made by the solution method was much smaller than that made by direct-melt blending. This clearly showed that Org-MMT and PE-g-MAH had a heterogeneous nucleation effect on crystallization of PE from the melt, resulting in a decrease of crystalline thickness, and the heterogeneous nucleation effect was more evident in the nanocomposite made by the solution-blending method than in that made by the direct-melt intercalation process. The tensile strength initially increased and then decreased with increasing contents of PE-g-MAH. The maximum value in tensile strength (23.3 MPa) was achieved when the concentration of PE-g-MAH was 6 wt %. The impact strength increased concomitantly with the content of PE-g-MAH; it was 122.2 J/m when the concentration of PE-g-MAH was 9 wt %. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3974–3980, 2004

Key words: nanocomposites; crystallization; intercalation; polyethylene (PE); montmorillonite

INTRODUCTION

Hybrid organic–inorganic composites, constituting a promising class of materials, synergistically integrate the advantages of organic polymers and inorganic materials, such as excellent processing properties, generally considered to be characteristic of polymers, and high modulus and strength, which are characteristic of inorganic materials. However, the properties of hybrid organic–inorganic composites are greatly influenced by the length scale of the dispersed phase.^{1–3} Generally speaking, the smaller the inorganic filler particles and the more homogeneously they are dispersed in the polymer matrix, to some extent, the more the physical and mechanical properties can be enhanced. Polymer/clay silicate nanocomposites are a new class of polymer matrices modified by inorganic particles with dimensions in the 0.1- to 100-nm

range.^{4–7} These particles, with a very high aspect ratio, strongly modify the macroscopic properties of the polymer even though only a tiny amount of filler is used. These nanocomposites exhibit improved modulus, lower thermal expansion coefficient and gas permeability, higher swelling resistance, and enhanced ionic conductivity, compared to the characteristics of pristine polymers, presumably attributable to the nanoscale structure of the hybrids and the synergism between the polymer and the silicate.^{8,9}

Preparing nanocomposites with intercalating layered silicates has been proved to be an effective method to diminish the length scale of the component phase. A promising approach to prepare nanocomposites is by the polymer melt-direct intercalation processing, which is simple to operate and friendly to the environment, and many polymer systems (e.g., polystyrene,¹⁰ polyamide,¹¹ poly(ethylene oxide),¹² polypropylene,^{13–15} polyoxymethylene¹⁶) containing silicate have been prepared in this way.

Polyethylene (PE) is one of the most widely used polyolefin polymers and, because it does not contain any polar groups in its backbone, it was not thought

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that homogeneous dispersion of the silicate layers in PE could be achieved. In general, the clay is modified with alkylammonium groups to facilitate its interaction with a polymer, and polyethylene is modified with a polar monomer [such as polyethylene-*graft*-maleic anhydride (PE-g-MAH)] to enhance its miscibility with inorganic clay.

Wang and coworker¹⁷s reported the exfoliation and intercalation behaviors of maleated polyethylene/clay nanocomposites prepared by simple melt compounding and they concluded that exfoliation and intercalation behaviors were dependent on the maleated polyethylene and the chain length of organic modifier in the clay. Jeon and coworkers¹⁸ reported the intercalated morphology of high-density polyethylene (HDPE) nanocomposites prepared by blending HDPE with sodium montmorillonite cation-exchanged with protonated dodecylamine in solution. Koo and coworkers¹⁹ reported morphology evolution and anisotropic phase formation of maleated polyethylene/layered silicate nanocomposites. They concluded that the final morphology of the nanocomposite evolves by four stages: (1) disordered exfoliation, (2) ordered exfoliation, (3) dual morphologies of intercalation and exfoliation, and (4) intercalation. Some authors also reported the preparation of polyethylene/clay nanocomposite.^{20,21} To the best of our knowledge, however, there are few studies that report the effects of silicate and modified oligomer on the microstructure of the composites. In this investigation, three cationic surfactants and two processing methods were used to prepare PE/PE-g-MAH/Org-MMT nanocomposite and X-ray diffraction (XRD) was used to measure the microstructure of the nanocomposites.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) and low-density polyethylene (LDPE) were purchased from Yanshan Petrochemical Co. (China) and used without any treatment (the brands were 5000s and 1F7B, respectively). Montmorillonite was available from Lin'an Chemistry Agent Factory (China). Surfactants used were purchased from Shanghai Cleansing Agent Factory (China). PE-g-MAH (with 1.09 wt % maleic anhydride grafted level) and organic-montmorillonite (300 mol) were synthesized by our laboratory.

Preparation of PE/PE-g-MAH/Org-MMT

Direct-melt blending process

PE-g-MAH and Org-MMT were melt mixed in a roller mill at 145–150°C for 15 min at a certain prescription to make a master batch, after which the master batch and conventional PE were melt mixed at a certain

prescription in a roller mill at 150–155°C for 15 min. The resulting sheet was compression molded at 160°C for 30 min into a plate with thickness of 4 mm.

Solution-blending method

PE-g-MAH and Org-MMT were mixed in dimethylbenzene at 130°C for 30 min at a certain prescription to make a master batch, after which the master batch and conventional PE were melt mixed at a certain prescription in a roller mill at 150–155°C for 15 min. The resulting sheet was compression molded at 160°C for 30 min into a plate with thickness of 4 mm.

Measurements

XRD studies was carried out to investigate the intercalation effect of nanocomposites. A D/max- γ B diffractometer was used with Cu-K α radiation at room temperature by use of a graphite filter. The diffractograms were scanned in 2θ ranges from 1.2 to 10° at a rate of 1°/min. The interlayer distance of Org-MMT in composites was calculated from the (001) plane diffraction peak by using Bragg's equation. The D/max- γ B diffractometer was also used to confirm the crystalline type of PE in the mentioned composites and to investigate the change of crystalline thickness of PE in the composites. The diffractograms were scanned in 2θ ranges from 2.2 to 30° at a rate of 2°/min.

Transmission electron microscopy (TEM) was obtained with a TEM 100sx using an acceleration voltage of 200 kV.

The tensile test was carried out with a Model LJ-1000 testing machine at a crosshead speed of 50 mm/min at room temperature. The Izod impact strength was examined with a Model IZODUJ-4 impact-testing machine at room temperature according to GB1040-1996 and GB1843-1986, respectively. The specimens used were prepared with a vulcanization machine (QLB 400 × 400 × 2) by compression molding.

RESULTS AND DISCUSSION

Effect of the amount of PE-g-MAH on intercalation behavior

The XRD patterns of HDPE/PE-g-MAH/Org-MMT composites are shown in Figure 1 and X-ray parameters calculated from the (001) plane peaks are summarized in Table I. As can be seen from Figure 1 and Table I, when the content of PE-g-MAH was 15 wt % in the HDPE/PE-g-MAH/Org-MMT composites, the (001) plane peaks of Org-MMT around $2\theta = 4.6^\circ$ in the XRD curves, as expected, were shifted to lower angles about $2\theta = 2.3^\circ$, showing that the interlayer distance was enlarged from 1.9 to 3.9 nm. This clearly indicates

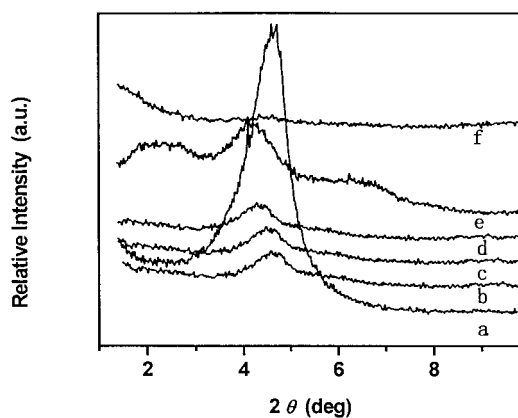


Figure 1 XRD patterns of Org-MMT (modified by hexadecyltrimethylammonium chloride) (a) and HDPE/PE-g-MAH/Org-MMT nanocomposites with the following proportions: (b) 97 : 0 : 3, (c) 91 : 6 : 3, (d) 88 : 9 : 3, (e) 82 : 15 : 3, (f) 76 : 21 : 3.

that macromolecular links had intercalated into the interlayers of Org-MMT. However, the result is quite different from that when the content of PE-g-MAH was less than 15 wt %, where the (001) peak of Org-MMT does not shift. This indicates that the nonpolar macromolecular segments of HDPE can hardly directly intercalate into the interlayers of Org-MMT and that adding a sufficient quantity of PE-g-MAH to HDPE/Org-MMT composite was the key to preparing a nanocomposite based on HDPE and Org-MMT. Moreover, the (001) plane peak of Org-MMT in the composite disappeared in the scope of measurement when the content of PE-g-MAH was more than 21 wt %, which indicated that the interlayer distance of Org-MMT was sufficiently large; in other words, the silicate interlayer in the composite had been exfoliated, and accordingly silicate interlayers were dispersed evenly in the PE matrix at nanoscale. A possible reason for this phenomenon is that when a small amount of PE-g-MAH is included in PE/PE-g-MAH/Org-MMT, instead of intercalating into interlayers of Org-MMT, the macromolecular links of PE-g-MAH wrap

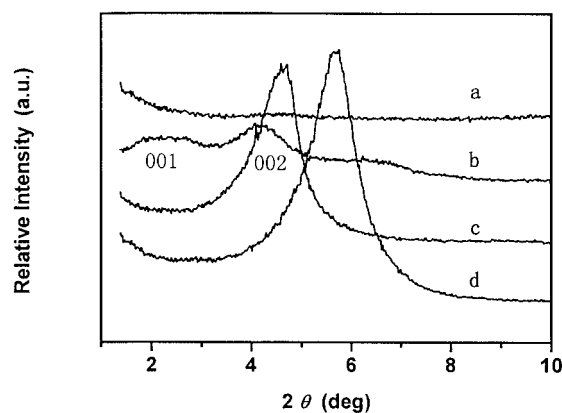


Figure 2 XRD patterns of Org-MMT (c), Ca-MMT (d), HDPE/PE-g-MAH/Org-MMT nanocomposites processed by solution method (a) and by direct-melt blending process (b). HDPE/PE-g-MAH/Org-MMT = 82 : 15 : 3.

around particles of Org-MMT. Only when adequate PE-g-MAH is present in PE/PP-g-MAH/Org-MMT does Org-MMT begin to be intercalated. By further increasing the amount of PE-g-MAH, the interlayer of Org-MMT in the composite is exfoliated.

Effect of blending process on intercalation behavior

The solution-blending method was adopted to prepare a PE-g-MAH/Org-MMT master batch to compare with the direct-melt blending process. As shown in Figure 2 and Table II, the (001) plane peak of Org-MMT in the composite made by the direct-melt blending process shifted from its original location of 4.6 to 2.3°, showing the formation of intercalation nanocomposite. However, the (001) plane peak of Org-MMT in the composite processed by the solution-blending method disappeared in the scope of measurement, indicating the formation of an exfoliated nanocomposite. That is, better intercalation effects can be obtained by adopting the solution-blending method, rather than the direct-melt intercalation process, to make a

TABLE I
Values of 2θ and d for HDPE/PE-g-MAH/Org-MMT Nanocomposites^a

HDPE/PE-g-MAH/ Org-MMT	2θ (°)		d (nm)	
	001	002	001	002
0/0/100	4.64	—	1.90	—
97/0/3	4.60	—	1.92	—
91/6/3	4.52	—	1.95	—
88/9/3	4.31	—	2.05	—
82/15/3	2.27	4.19	3.89	2.11
76/21/3	—	—	—	—

^a Org-MMT was modified by hexadecyltrimethylammonium chloride.

TABLE II
Values of 2θ and d for HDPE/PE-g-MAH/Org-MMT Nanocomposites^a

HDPE/PE-g-MAH/Org-MMT	2θ (°)		d (nm)	
	001	002	001	002
Ca-MMT	5.68	—	1.56	—
Org-MMT	4.64	—	1.90	—
by direct-melt/blending process	2.27	4.19	3.89	2.11
by solution-blending method	—	—	—	—

^a Org-MMT was modified by hexadecyltrimethylammonium chloride.

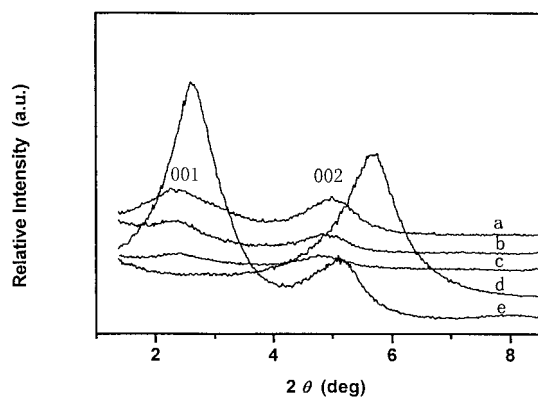


Figure 3 XRD patterns of Ca-MMT (d), Org-MMT (modified by hexadecyldimethylbenzylammonium chloride) (e) and HDPE/PE-g-MAH/Org-MMT nanocomposites with the following proportions: (a) 97 : 0 : 3, (b) 91 : 6 : 3, (c) 88 : 9 : 3.

master batch. The reason is that the high mobility and fewer entanglements in the solution-blending process may facilitate the diffusion of the molecules into the interlayers of silicate. Moreover, the presence of solvent accelerates the intercalation behavior of PE-g-MAH into the interlayer of Org-MMT. It is thought that the diminished entropy attributed to the confinement of polymer is compensated by an increase resulting from the desorption of a multitude of intercalated solvent molecules.^{22,23}

Effect of surfactant on the intercalation behavior

Besides hexadecyltrimethylammonium chloride, two other kinds of cationic surfactant (hexadecyldimethylbenzylammonium chloride and octadecyltrimethylammonium chloride) were also used to modify montmorillonite. Accordingly, HDPE/PE-g-MAH/Org-MMT nanocomposites were prepared by the obtained Org-MMT through the direct-melt blending process. As shown in Figure 3, Table III, Figure 4, and Table IV, the intercalation effect of macromolecules into the interlayer of Org-MMT (modified by hexadecyldimethyl-

TABLE III
Values of 2θ and d for HDPE/PE-g-MAH/Org-MMT Nanocomposites^a

HDPE/PE-g-MAH/ Org-MMT	2θ (°)		d (nm)	
	001	002	001	002
Ca-MMT	5.68	—	1.56	—
Org-MMT	2.63	5.13	3.36	1.72
97/0/3	2.46	5.00	3.59	1.77
91/6/3	2.39	4.93	3.70	1.79
88/9/3	2.32	4.80	3.80	1.84

^a Org-MMT was modified by hexadecyldimethylbenzylammonium chloride.

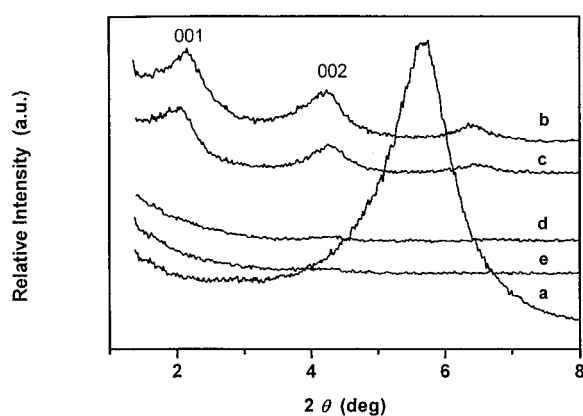


Figure 4 XRD patterns of Ca-MMT (a), Org-MMT (modified by octadecyltrimethylammonium chloride) (b) and HDPE/PE-g-MAH/Org-MMT nanocomposites with the following proportions: (c) 97 : 0 : 3, (d) 91 : 6 : 3, (e) 88 : 9 : 3.

ylbenzylammonium chloride and octadecyltrimethylammonium chloride, respectively) was enhanced by increasing the amount of PE-g-MAH, which was similar to that by using hexadecyltrimethylammonium chloride as a cationic surfactant. However, it was noticed that macromolecules could intercalate into the interlayers of Org-MMT (modified by hexadecyldimethylbenzylammonium chloride) at a lower content of PE-g-MAH than the Org-MMT modified by hexadecyltrimethylammonium chloride. For example, when the concentration of PE-g-MAH was 9 wt %, the (001) plane peak of Org-MMT modified by hexadecyldimethylbenzylammonium chloride in PE/PE-g-MAH/Org-MMT shifted to 2.3° and its intensity was weak. This implied that macromolecules had intercalated into the interlayer of silicate and most of the silicate particles had been exfoliated. By contrast, macromolecules did not intercalate into the interlayers of Org-MMT modified by hexadecyltrimethylammonium chloride at a PE-g-MAH content of 9 wt %. As a result, a better intercalation effect can be obtained by adopting the Org-MMT modified by hexadecyldimethyl-

TABLE IV
Values of 2θ and d for HDPE/PE-g-MAH/Org-MMT Nanocomposites^a

HDPE/PE-g-MAH/ Org-MMT	2θ (°)		d (nm)	
	001	002	001	002
Ca-MMT	5.68	—	1.56	—
Org-MMT	2.16	4.24	4.09	2.08
97/0/3	2.04	4.24	4.33	2.08
91/6/3	—	—	—	—
88/9/3	—	—	—	—

^a Org-MMT was modified by octadecyltrimethylammonium chloride.

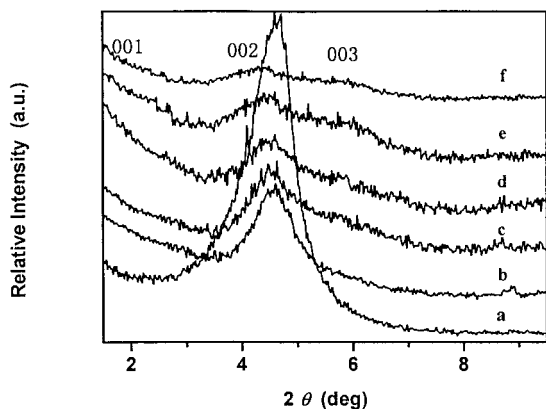


Figure 5 XRD patterns of Org-MMT (a) and LDPE/PE-g-MAH/Org-MMT nanocomposites with the following proportions: (b) 97 : 0 : 3, (c) 91 : 6 : 3, (d) 88 : 9 : 3, (e) 82 : 15 : 3, (f) 76 : 21 : 3 (Org-MMT was modified by hexadecyltrimethylammonium chloride).

benzylammonium chloride. A possible reason for this phenomenon is that the benzyl group in the surfactant has a larger volume than that of the methyl group, thus enlarging the distance of interlayers of Org-MMT more efficiently when entering the galleries of Org-MMT. It was observed that the (001) plane diffraction peak of silicate modified by octadecyltrimethylammonium chloride in PE/PE-g-MAH/Org-MMT disappeared in the scope of measurement when the content of PE-g-MAH was 6 wt %. Therefore, better intercalation behavior can also be obtained by adopting a surfactant containing a larger alkyl.

Effect of polyethylene structure on intercalation behavior

LDPE was used to prepare LDPE/PE-g-MAH/Org-MMT nanocomposites to investigate the effect of the structure of polyethylene on intercalation behavior. As shown in Figure 5, the (001) plane peaks of Org-MMT in composites shifted to a lower angle with increasing content of PE-g-MAH, which is similar to the intercalation behavior of HDPE/PE-g-MAH/Org-MMT nanocomposites. Nevertheless, under a certain prescription, the (001) plane peak of Org-MMT in LDPE/PE-g-MAH/Org-MMT nanocomposites appeared at a higher angle than that in HDPE/PE-g-MAH/Org-MMT nanocomposites, which indicated that a better intercalation effect could be obtained by using HDPE as the matrix in PE/PE-g-MAH/Org-MMT nanocomposites. This may be attributable to a higher level of branched segments in LDPE that need to rearrange when the macromolecules intercalate into the galleries of silicate, thus making it harder for LDPE, than for HDPE, macromolecules to insert interlayers of silicate.

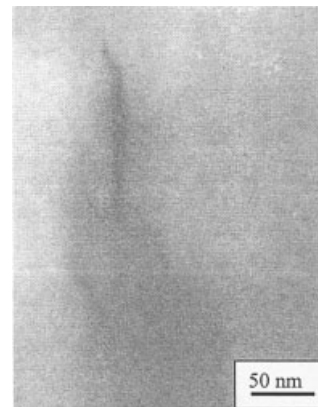


Figure 6 Transmission electron micrograph (TEM) of HDPE/PE-g-MAH/Org-MMT nanocomposite. Montmorillonite was treated by octadecyltrimethylammonium chloride.

Microstructure of PE/PE-g-MAH/Org-MMT nanocomposites

Transmission electron microscopy (TEM) was used to measure the morphology of PE/PE-g-MAH/Org-MMT nanocomposites. Slides with a thickness around 70–80 nm had been prepared by ultramicrotomy at 16°C and observed by TEM. Figure 6 shows that multilayered Org-MMT (thickness \sim 10 nm) was obtained in PE/PE-g-MAH/Org-MMT, which confirmed that polymer molecules had intercalated into the interlayers of silicate and that most interlayers of silicate were exfoliated in the PE matrix. An observation at a larger scope showed that layers of Org-MMT were dispersed evenly in the PE matrix.

To investigate the effect of organo-montmorillonite on the crystallization of HDPE, diffractograms were scanned with the range from 2.2 to 30° at the rate of 2°/min. The diffractogram for HDPE/PE-g-MAH/Org-MMT (82 : 15 : 3, by solution method) is presented in Figure 7. A multipeak separation program

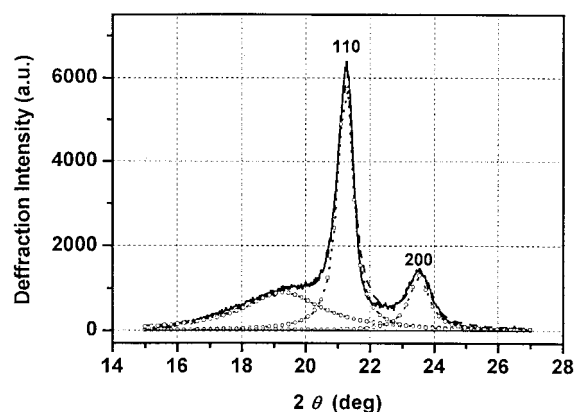


Figure 7 XRD patterns of HDPE/PE-g-MAH/Org-MMT nanocomposite. HDPE/PE-g-MAH/Org-MMT = 82 : 15 : 3, processed by solution blending method.

TABLE V
Crystalline Thickness and Crystal Cell Parameters of HDPE and HDPE/PE-g-MAH/Org-MMT by Direct-Melt Blending Process and by Solution-Blending Method

HDPE/PE-g-MAH/Org-MMT	Crystalline thickness (nm)		X_c (%)
	L_{110}	L_{200}	
HDPE	28.900	24.303	85.4
97/0/3	25.862	22.584	75.3
88/9/3	23.087	19.791	73.4
82/15/3	21.846	18.448	71.4
76/21/3	21.268	17.643	71.2
82/15/3 (by solution-blending method)	14.961	9.772	53.2

was used to separate the amorphous peak from crystallization peaks. The diffractograms of other HDPE/PE-g-MAH/Org-MMT composites have a similar shape and are not presented here. As shown in Figure 7, the peak position of every crystal plane did not shift after the addition of Org-MMT and PE-g-MAH, which indicated that the structure of the HDPE crystal cell did not change. Based on Scherrer's equation, the crystalline thickness perpendicular to the reflection plane (L_{hkl}) can be calculated as

$$L_{hkl} = \frac{K\lambda}{\beta_0 \cos \theta} \quad (1)$$

where θ is Bragg's angle, λ is the wavelength of the X-ray (nm); β_0 is the width of the diffraction beam (rad); K is the shape factor of crystalline thickness, related to the shape of crystalline thickness and definition of β_0 , L_{hkl} . When β_0 is defined as the half-height width of diffraction peaks, $K = 0.9$. The results are summarized in Table V. The degree of crystallinity of composites, also presented in Table V, was calculated according to the following formula²⁴:

$$X_c = \frac{I_{110} + 1.46I_{200}}{I_{110} + 1.46I_{200} + 0.75I_a} \times 100\% \quad (2)$$

where I_{110} and I_{200} are the integral intensity of (110) and (200) plane crystallization diffraction peaks, respectively; I_a is the integral intensity of the amorphous diffraction peak; and X_c is the degree of crystallinity. As can be seen from Table V, the crystalline thickness perpendicular to the crystal planes, like (110) and (200), in HDPE/PE-g-MAH/Org-MMT composites decreased with increasing concentration of PE-g-MAH, verifying that introduction of Org-MMT and PE-g-MAH reduced the crystal thickness of HDPE. As a result, PE-g-MAH and Org-MMT could act as heterogeneous nucleation agents during the crystallization process of HDPE from melts. Moreover, it was found that the degree of crystallinity of composites de-

creased with increasing amount of PE-g-MAH, confirming that silicate and PE-g-MAH also reduced the perfection of PE crystals.

Mechanical properties of PE/PE-g-MAH/Org-MMT composites

The effects of the amount of PE-g-MAH on tensile strength and impact strength of PE/PE-g-MAH/Org-MMT composites are shown in Figure 8. As the content of PE-g-MAH increased, the tensile strength initially increased and then decreased. The maximum value in tensile strength (23.3 MPa) was achieved when the concentration of PE-g-MAH was 6 wt %. The impact strength increased concomitantly with the amount of PE-g-MAH. When the concentration of PE-g-MAH was 9 wt %, the impact strength of the composite was 122.2 J/m, a 60% increase compared with that of the composite containing no PE-g-MAH. By increasing the concentration of PE-g-MAH, most of the silicate interlayers were exfoliated in the composites. Because the size of the exfoliated interlayers of silicate was at the same order as that of macromolecular segments, increased free volume in the composites made it possible for the segments to move when composites were subjected to an impact force. Consequently, the impact strength of composites was enhanced by increasing the amount of PE-g-MAH.

CONCLUSIONS

The following conclusions can be drawn from the foregoing discussion. TEM and X-ray analysis indicated the formation of PE/PE-g-MAH/Org-MMT. The intercalation effect of PE/PE-g-MAH/Org-MMT could be enhanced by increasing the content of PE-g-

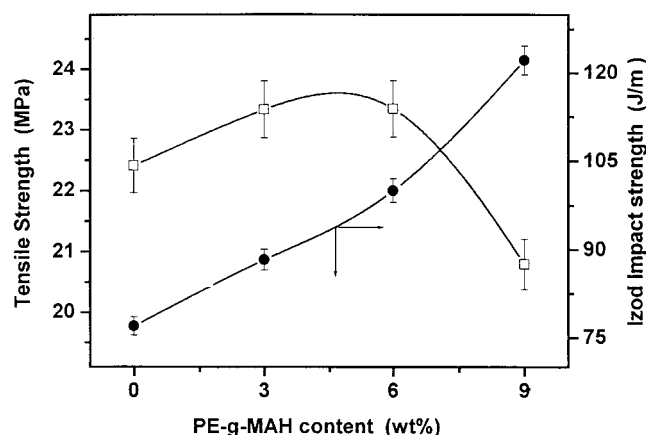


Figure 8 Plots of tensile and impact strength versus to concentration of PE-g-MAH in HDPE/PE-g-MAH/Org-MMT composites. The mass percentage of Org-MMT was 3% (Org-MMT was modified by octadecyltrimethylammonium chloride).

MMT, using the silicate modified by cationic surfactant with benzyl group or long alkyl chain, either by adopting the solution-blending method or by using high-density polyethylene as the matrix. The degree of crystallinity of composites and the crystalline thickness perpendicular to the crystalline plane, like (110) and (200), decreased with increasing amount of PE-g-MAH and under certain prescription the crystalline thickness of composite made by the solution-blending method was much smaller than that made by the direct-melt blending process. This clearly indicated that Org-MMT and PE-g-MAH have a heterogeneous nucleation effect on crystallization of PE from the melt. The heterogeneous nucleation effect was more evident in the nanocomposite prepared by the solution-blending method than in that prepared by the direct-melt blending process. The tensile strength initially increased and then decreased as the concentration of PE-g-MAH increased. The maximum value in tensile strength (23.3 MPa) was achieved when the concentration of PE-g-MAH was 6 wt %. The impact strength increased concomitantly with the amount of PE-g-MAH, reaching 122.2 J/m when the concentration of PE-g-MAH was 9 wt %.

References

- Whiteside, G. M.; Mathias, T. P.; Seto, C. T. *Science* 1991, 254, 1312.
- Gleiter, H. *Adv Mater* 1992, 4, 474.
- Novak, B. *Adv Mater* 1993, 5, 422.
- Messersmith, P. B.; Giannelis, E. P. *J Polym Sci Part A: Polym Chem* 1995, 33, 1047.
- Usuki, A.; Kawasumi, T.; Kojima, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
- Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 2493.
- Giammelis, E. P. *Adv Mater* 1996, 8, 29.
- Wang, Z.; Piamavaia, T. *Chem Mater* 1998, 10, 3769.
- Cheonll, P.; Ook, P.; Gon, J.; Joon, K. H. *Polymer* 2001, 42, 7465.
- Davis, R. D.; Gilman, J. W.; Vanderhart, D. L. *Polym Degrad Stab* 2003, 79, 111.
- Sukpirom, N.; Oriakhi, C. O.; Lerner, M. M. *Mater Res Bull* 2000, 35, 325.
- Xu, W. B.; Liang, G. D.; Wang, W.; Tang, S. P.; He, P. S.; Pan, W. P. *J Appl Polym Sci* 2003, 88, 3225.
- Xu, W. B.; Liang, G. D.; Wang, W.; Tang, S. P.; He, P. S.; Pan, W. P. *J Appl Polym Sci* 2003, 88, 3093.
- Liang, G. D.; Xu, W. B. *China Plast* 2002, 16, 20.
- Xu, W. B.; Ge, M. L.; He, P. S. *J Appl Polym Sci* 2001, 82, 2281.
- Wang, K. H.; Choi, M. H.; Koo, C. M.; Choi, Y. S.; Chung, I. J. *Polymer* 2001, 42, 9819.
- Jeon, H. G.; Jung, H. T.; Lee, S. W.; Hudson, S. D. *Polym Bull* 1998, 41, 107.
- Koo, C. M.; Ham, H. T.; Kim, S. O.; Wang, K. H.; Chung, I. J. *Macromolecules* 2002, 35, 5116.
- Alexandre, M.; Dubois, P.; Sun, T.; Garces, J. M.; Robert, J. *Polymer* 2002, 43, 2123.
- Gopakumar, T. G.; Lee, J. A.; Kontopoulou, M.; Parent, J. S. *Polymer* 2002, 43, 5483.
- Arada, P.; Ruiz-Hitzky *Chem Mater* 1992, 4, 1395.
- Wu, J.; Lemer, M. *Chem Mater* 1993, 5, 835.
- Aggarwal, S. L.; Tilloy, G. P. *J Polym Sci* 1955, 18, 17.