Preparation and Properties of Recycled HDPE/Clay Hybrids

Yong Lei,[1] Qinglin Wu,[1] Craig M. Clemons[2]

[1]*School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, Louisiana 70803*
[2]*Performance Engineered Composites, USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive Madison, Wisconsin 53705-2398*

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ABSTRACT: Hybrids based on recycled high density polyethylene (RHDPE) and organic clay were made by melt compounding. The influence of blending method, compatibilizers, and clay content on clay intercalation and exfoliation, RHDPE crystallization behavior, and the mechanical properties of RHDPE/clay hybrids were investigated. Both maleated polyethylene (MAPE) and titanate could improve the compatibilization of RHDPE and clay. RHDPE/clay hybrids containing completely exfoliated clay were obtained using a two-step blending method. Without compatibilizers, the clay could not be exfoliated, and it lowered the crystallization peak temperature, crystallinity level, and the long period of RHDPE. MAPE and clay layers could act as heterogeneous nucleating agents for RHDPE. The titanate had a little influence on crystallization behavior of RHDPE. Adding clay to RHDPE reduced the impact strength but had little influence on the tensile strength. Both the storage and loss moduli increased with up to 5% of clay in hybrids containing CAPS, and there was an about 44% increase in impact strength of RHDPE/clay hybrid containing 5% MAPE compared with that of the hybrid containing no MAPE. The clay presence lowered the thermal stability of RHDPE. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3056–3063, 2007

Key words: clay; composites; polyethylene; preparation; recycling

INTRODUCTION

Plastics account for an increasing fraction of municipal solid waste around the world. In 2000, the amount of plastic wastes reached 24.7 million tons in the United States, comprising 10.7% of the waste stream by weight, and an even larger percentage by volume.[1] Low density polyethylene (LDPE), high density polyethylene (HDPE), and polypropylene (PP) are the three largest components. With the price of petroleum increasing rapidly, plastic wastes are becoming of more interest as an inexpensive source of raw materials.

The impressive enhancement of material properties achieved with the inclusion of submicron-size fillers in plastics and elastomers has stimulated active research. Clay nanocomposites, especially nanoclay/polymer composites, exhibit dramatic increases in modulus, strength, barrier properties, flammability resistance, and heat resistance compared to conventional composites.[2–8] Because PE is hydrophobic and has poor miscibility with hydrophilic clay silicates, PE/clay hybrids are not easily prepared. In general, the clay is modified with alkylammonium groups to facilitate its interaction with PE, and the miscibility of PE with clay can be enhanced by introducing compatibilizers containing polar groups, such as maleated polyethylene (MAPE), and carboxylated PE.

There are three methods to prepare PE/clay hybrids: *in situ* polymerization,[9–12] solution intercalation,[13–15] and melt intercalation.[16–26] Melt intercalation is the most convenient and appropriate technique for the industrial preparation of polymer/clay nanocomposites. In this procedure, the clay is directly dispersed in the molten polymer using a conventional twin-screw extruder. Thus, it is a versatile and environmentally benign approach.[27] Wang et al.[16] reported on the exfoliation and intercalation behaviors of MAPE/clay nanocomposites prepared by simple melt compounding. They concluded that exfoliation and intercalation behaviors were dependent on the MAPE content and the chain length of organic modifier in the clay. Koo et al.[17] reported on the morphology evolution and anisotropic phase formation of MAPE/layered silicate nanocomposites, and it was concluded that the final morphology of the nanocomposite depends on the clay content. As clay content was increased, four stages of morphological development were found: (1) disordered exfoliation, (2) ordered exfoliation, (3) dual morphologies of intercalation and exfoliation, and (4) intercalation. With the aid of MAPE, Kato et al.[20] prepared PE/clay hybrids that exhibited higher tensile yield strengths and tensile

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Correspondence to: Q. Wu (wuqing@lsu.edu) or Y. Lei (yonglei168@hotmail.com).

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moduli than those of PE matrices and those of PE/inorganic clay composites, and the gas permeability of the PE/MAPE blend decreased 30% when clay was added. The addition of clay increased the crystallization peak temperature of PE, and lowered the crystallinity level, acting as a nucleating agent.[14,18,19,24] The thermal conductivity of the PE/clay nanocomposites decreased with an increase of the silicate volume fraction.[23]

Although some work on the reinforcement on recycled PE has been done,[28–30] little effort has been made to study recycled PE/clay systems. Since the recycling process generally consists of several stages, including waste collection, separation, cleaning, drying, grinding, and repelletizing, the properties of recycled plastics could be different from those of corresponding virgin plastics. Thus, conditions for the modification of recycled plastics with clay may also change. In this work, the objectives are to prepare hybrids containing exfoliated clay from recycled high density polyethylene (RHDPE) and organic montmorillonite by melt compounding, and to study the effect of clay and compatibilizers on the crystallization behavior, mechanical properties, and thermal stability of RHDPE.

EXPERIMENTAL

Materials

Recycled high density polyethylene (RHDPE) was obtained from Avangard Industries (Texas, USA), with a melt flow index of 0.7 g/10 min (190°C) and a density of 939.9 kg/m^3. A natural montmorillonite modified with a quaternary ammonium salt, Cloisite®15A, was obtained from Southern Clay Products (Texas, USA). Two compatibilizers were used: (1) Epolene (TM) G-2608 from Eastman Chemical Company (USA), a maleated polyethylene (MAPE), and (2) CAPS L38/L (CAPS) from Kenrich Petrochemicals (USA), a titanium-derived mixture. The initiator used was dicumyl peroxide (DCP) from Aldrich Chemical Company.

Preparation of RHDPE/clay hybrids

The hybrids of RHDPE/clay/MAPE were prepared using either a two-step or a one-step compounding method. In the two-step blending method, a masterbatch was first made by melt-blending MAPE with the clay in a weight proportion of 1 : 1 or 1 : 2 in a Haake blender (Model Rheomix 600) with a screw speed of 60 rpm at 165°C for 10 min. Both torque and temperature were measured during compounding. In the second step, the masterbatch was blended with RHDPE and more MAPE for 10 min at a screw speed of 60 rpm. The loading level was varied from 1 to 7% of clay, and from 1 to 10% of MAPE based on the RHDPE weight. In the one-step method, all of the materials were added simultaneously and compounded for 15 min at 60 rpm. The neat RHDPE for control, RHDPE/MAPE systems for control, some of the RHDPE/clay/MAPE hybrids, and RHDPE/clay/CAPS hybrids were blended using the one-step method. The loading level of CAPS was varied from 0.05% to 0.35% based on the RHDPE weight.

The plates for mechanical property testing were prepared by compression molding the compound at 175°C, using a three-piece stainless steel mold in a Wabash V200 hot press (Wabash, ID) for 5 min and then cooling to room temperature under pressure. The pressure during heating and cooling was controlled at 30 tons. For tensile testing and dynamic mechanical analysis (DMA), the nominal thickness of tensile specimens was 1 mm, while the nominal thickness for the impact test specimens was 4 mm.

Measurements

Wide angle X-ray diffraction (XRD) analysis was carried out to investigate the effectiveness of the clay intercalation and the change of crystalline thickness of RHDPE. A 2θ range from 2° to 40° in reflection mode was scanned at a 2°/min. A computer-controlled wide angle goniometer coupled to a sealed-tube source of Cu Kα radiation ($\lambda = 1.54056$ Å) was used. The Cu Kα line was filtered electronically with a usual thin Ni filter. The interlayer distance of the clay in the hybrids was calculated from the (001) plane diffraction peak using Bragg's equation, and the crystalline thickness perpendicular to the reflection plane was obtained according to Scherrer's equation with the instrument width of 0.16°.

The crystallization behavior of RHDPE in the hybrids was measured using a differential scanning calorimeter (TA DSC Q100). Samples of 4–5 mg were placed in aluminum capsules and heated from 40 to 160°C at 10°C/min to eliminate the heat history before cooling at 10°C/min. The heat flow rate corresponding to the crystallization of RHDPE in hybrids was corrected for the content of clay and MAPE. The value of crystallization heat was also corrected for the crystallization heat of MAPE.

Thermogravimetric analysis (TGA) was employed to observe the thermal character of hybrids with a TA Q50 Thermogravimetric Analyzer under nitrogen at a scan rate of 10°C/min from room temperature to 650°C. Samples of 6–8 mg were used for each run.

The storage modulus, E', of the hybrids was measured with a TA Q800 DMA system (New Castle, DW). For each group, five replications with the size of $60 \times 12 \times 1$ mm^3 were tested. Before testing, all of the DMA specimens were conditioned for 72 h at a temperature of 23°C and a relative humidity of 50%. The storage modulus of each DMA specimen was measured in dual cantilever mode at a frequency of 1 Hz at room temperature. After the DMA test, the tensile strength was measured for according to the ASTM D638 using an INSTRON machine (Model 1125, Boston, MA). For each treatment level, six replications were tested. A TINIUS 92T impact tester (Testing Machine Company, Horsham, PA) was used for the Izod impact test. All the samples were notched on the center of one longitudinal side according to the ASTM D256. For each treatment level, five replications were tested. Statistical analysis (i.e., Duncan's multiple range test) was done to test difference of various properties at different treatment levels.

RESULTS AND DISCUSSION

Compounding

Figure 1 shows mixing torque data for the blends. The peak and equilibrium torque for RHDPE were about 786.5 N m/kg and 386 N m/kg, respectively. They were greatly lowered to about 375 N m/kg and 182 N m/kg, respectively, with the addition of 5% clay. When compatibilizers were added, they increased significantly. The blend compatibilized with MAPE had a peak torque of 700 N m/kg and its equilibrium torque of 386 N m/kg, which was the same as that of RHDPE. An incompatible blend, characterized by no interaction between phases, frequently exhibits interlayer slip that promotes a reduction of the torque of the blend.[31] Thus, this suggests that the compatibility of RHDPE with the clay was very poor since the equilibrium torque of RHDPE/clay was about half of that of neat RHDPE. The fact that the torque of the compatibilized blends was obviously increased suggests that there was much less slippage at the interface, and the compatibilization between RHDPE and clay was improved with the addition of MAPE and CAPS compatibilizers.

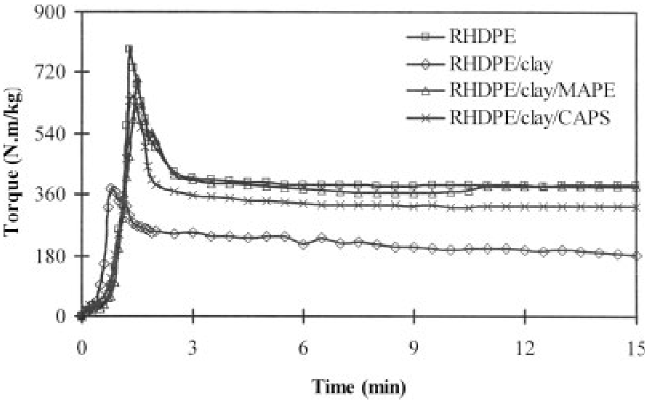

Figure 1 Mixing torque for blends. Compounding performed at 165°C and 60 rpm for 15 min. The concentrations of clay, MAPE, and CAPS are 5, 5, and 0.25%, respectively.

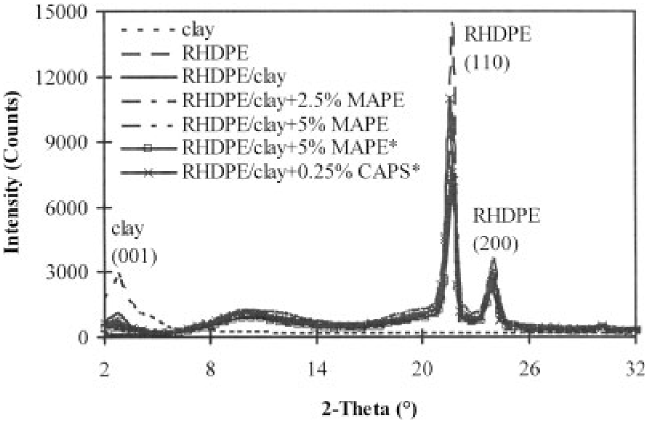

Figure 2 XRD patterns of the clay, RHDPE, and RHDPE/clay (100/5 w/w) hybrids at 2°/min for 2θ angles of 2° to 32°. *: This hybrid was prepared using the one-step method.

Effect of compatibilizers on intercalation behavior

The XRD patterns of the clay and RHDPE/clay (100/5 w/w) hybrids in the 2θ range of 2° to 32° spectra are shown in Figure 2. The peaks appearing at the angle lower than 6° correspond to clay, and those at the angle higher than 6° are for RHDPE. As seen from Figure 3(a), a strong peak (001) was present at the position of 2.75° for clay, which corresponds to a d-spacing of 3.22 nm according to the Bragg equation:

$$2d \sin \theta = n\lambda \tag{1}$$

where d is the distance between crystallographic planes, and θ is half of the angle of diffraction, n is an integer, and λ is the wavelength of the X-ray. After compounding RHDPE with 5% clay only, the peak was blunted, indicating that most of the clay is still in the original stacking condition.[24] When 2.5% MAPE or 0.25% CAPS was added, the (001) peak still appeared, but its intensity was obviously lowered, especially for the system containing 2.5% MAPE. Thus, RHDPE molecular chains entered the planar galleries with the help of MAPE or CAPS and exfoliation of the clay layers took place, but some clay still kept the original stacking condition. The (001) peak disappeared when 5% MAPE was added, indicating that the clay was totally exfoliated. However, for the hybrid of RHDPE/clay containing 5% MAPE prepared by the one-step method, the (001) peak still existed although it was weak, appearing at 2.86° even higher than that of the hybrid of RHDPE/clay containing 2.5% MAPE prepared by the two-step method. Thus, the two-step method was more effective in exfoliating clay layers than the one-step method.[14,15]

Effect of clay and compatibilizers on RHDPE crystallization

The diffractograms of RHDPE and its hybrids with clay at values of 2θ greater than 6° had the same

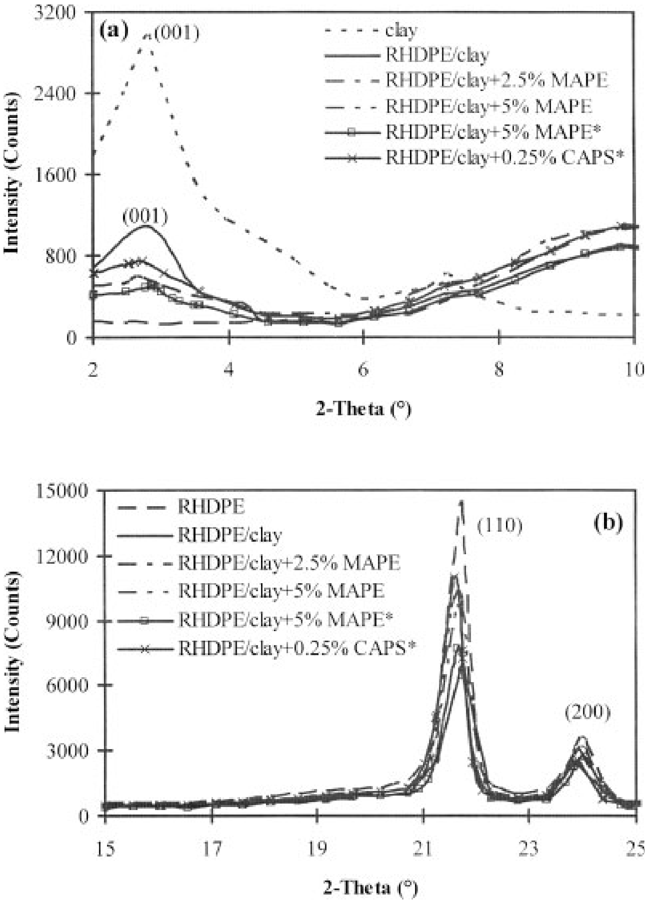

Figure 3 XRD patterns of the clay, RHDPE, and RHDPE/clay (100/5 w/w) hybrids at 2°/min for 2θ angles of (a) 2° to 10°; (b) 15° to 25°. ∗: These hybrids were prepared using the one-step method.

shape [Fig. 3(b)]. The diffraction peaks for the (110) and (200) planes of HDPE shifted little when clay and compatibilizers were added (Table I), suggesting that the dimensions of the polyethylene cell did not change. However, the intensity of the peaks did change, suggesting differences in crystallinity. This was further explored by DSC, and the DSC cooling curves of RHDPE and RHDPE/clay hybrids are shown in Figure 4.

Based on Scherrer's equation, the crystalline thickness perpendicular to the reflection plane (L_{hkl}), the long period, can be calculated as[14,32]

$$L_{hkl} = \frac{K\lambda}{\beta_0 \cos\theta} \tag{2}$$

$$\beta_0^2 = \beta_M^2 - \beta_I^2 \tag{3}$$

where β_0 is the width of the diffraction beam (rad); β_M is the measured width of the diffraction beam (rad); β_I is the instrument width (rad); K is the shape factor of crystalline thickness, related to β_0 and L_{hkl}. When β_0 is defined as the half-height width of diffraction peaks, $K = 0.9$. The crystallization peaks were treated using a multipeak separation program MDI Jade 5.0 to separate the amorphous peaks as Liang et al. reported.[14] The calculated results are summarized in Table I. The crystallinity level of the RHDPE matrix was obtained by dividing the value of crystallization heat by 293 J/g, the assumed heat of crystallization for 100% crystalline PE.[33] The corresponding results are listed in Table II.

The values of L_{hkl} of RHDPE were 18.9 nm for the (110) plane and 15.9 nm for the (200) plane. As shown, the introduction of clay reduced both values of L_{hkl} a little, and lowered crystallinity level from 56.9% to 54.1%. The crystallization peak temperature (T_c) of RHDPE was 118.3°C, and the addition of 5% clay decreased the T_c to 111.2°C. It was reported that clay increased the crystallization temperature acting as a nucleating agent, and reduced the degree of crystallinity of virgin HDPE.[14,19,24] The nucleation of clay was also observed in Figure 5 with the data listed in

TABLE I
Crystalline Peaks and Thickness of RHDPE and RHDPE/Clay (100/5 w/w) Hybrids

System	Peak position θ (°)		Crystalline thickness (nm)	
	(110)	(200)	L_{110}	L_{200}
RHDPE	10.87	12.02	18.9	15.9
RHDPE/clay	10.82	12.00	18.5	16.2
RHDPE/clay +2.5% MAPE	10.83	11.97	20.1	17.2
RHDPE/clay +5% MAPE	10.85	12.01	16.0	15.5
RHDPE/clay +5% MAPE[a]	10.83	12.03	18.4	16.0
RHDPE/clay +0.35% CAPS[a]	10.80	11.96	18.9	16.9

[a] These hybrids prepared using the one-step blending method.

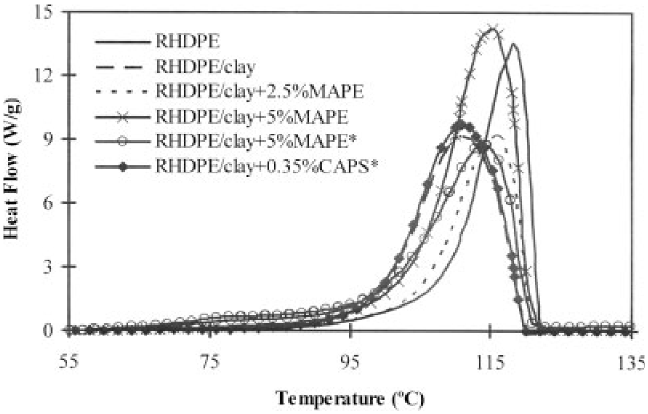

Figure 4 DSC curves of RHDPE and RHDPE/clay (100/5 w/w) hybrids for a cooling rate of 10°C/min in N_2. ∗: These hybrids were prepared using the one-step method.

TABLE II
Crystallization Temperatures and Levels of RHDPE and RHDPE/Clay Hybrids by DSC

Systems	Crystallization temperature (°C)	Crystallization enthalpy (J/g)	Crystallinity level (%)
RHDPE	118.3	166.8	56.9
RHDPE/clay (100/5 w/w)	111.2	158.7	54.1
RHDPE/clay+2.5%MAPE	115.2	161.7	55.2
RHDPE/clay+5%MAPE	115.1	153.1	52.3
RHDPE/clay+5%MAPE[a]	114.0	149.4	51.0
RHDPE/clay+0.35%CAPS[a]	111.0	165.2	56.4
MAPE	102.1	69.2	23.6
RHDPE+2.5%MAPE	112.5	169.0	57.7
RHDPE+5%MAPE	114.2	154.9	52.9

[a] These hybrids prepared using the one-step blending method.

Table II. When 5% clay was added to RHDPE/MAPE systems, both the T_c and the crystallization rate increased. However, the crystallization behavior can be affected by the dispersion state and contents of fillers, the surface chemistry of the fillers, and the viscosity of composites.[18] For the RHDPE/clay system, clay could play a nucleating role and increase the crystallization temperature; on the other hand, it could also impede the crystallization because of a decrease in the diffusion rate of PE chain caused by an increase of viscosity, and shift T_c to a lower temperature. Without compatibilizers, the nucleating role of clay was weakened because of the poor compatibility. On the other hand, the melt flow index of the RHDPE was only 0.7 g/10 min (190°C), and the addition of solid clay increased the bulk viscosity and significantly lowered the crystallization rate (Fig. 4). It was believed that the influence of the viscosity increase on T_c overwhelmed that of the nucleation, resulting in the lowered T_c. The same phenomenon was noticed by Wang et al.[18] Although the addition of clay broadened the crystallization temperature range (Fig. 4), the lowered crystallization rate resulted in the lowered crystallization degree.

With the addition of 2.5% MAPE, the L_{hkl} of RHDPE/clay hybrid increased. The crystallization rate and crystallinity level both increased, and the T_c of the RHDPE/clay hybrid increased to 115.2°C, suggesting that MAPE and intercalated clay could act as heterogeneous nucleating agents for RHDPE, just as some researchers have reported.[14,18,19,24] As shown in Figure 5, the T_c shifted to a higher temperature when more MAPE was added to RHDPE, indicating the nucleation of MAPE in RHDPE. The lowered crystallinity level suggested that MAPE reduced the perfection of RHDPE crystals. The nucleating role of MAPE and exfoliated clay was confirmed by the fact that the L_{hkl} of RHDPE/clay hybrids obviously decreased and the crystallization rate significantly increased while the crystallinity stayed at the same level with increasing concentration of MAPE from 2.5% to 5%. The crystallization rate of RHDPE in RHDPE/clay hybrid containing 5% MAPE, the hybrid in which the clay was totally exfoliated [Fig. 3(a)], was even higher than that of pure RHDPE. The addition of 0.35% CAPS did not influence the T_c of the RHDPE/clay system, but increased the crystallization rate a little, resulting in the increased L_{hkl} and crystallinity level.

For the RHDPE/clay hybrid containing 5% MAPE, the L_{hkl} of the (110) plane was only 16.0 nm when the hybrid was prepared by the two-step method, but it was 18.4 nm when prepared by the one-step method. The hybrid prepared by the one-step method had a slightly smaller T_c and crystallinity level, and an obviously lower crystallization rate than that prepared using the two-step method, suggesting that the exfoliated clay layers were better nucleating agents than the congregated clay particles. Thus, the method for introducing clay and MAPE into RHDPE affected the RHDPE crystallization behavior.

Mechanical properties of the hybrids

The effect of the clay content on the mechanical properties of the selected hybrids is shown in Table III. The RHDPE/clay/MAPE hybrids were produced by

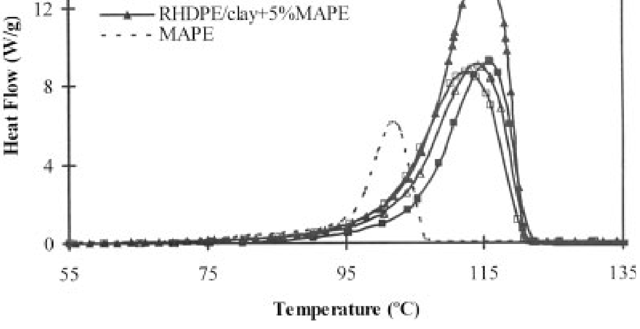

Figure 5 DSC curves of MAPE, RHDPE/MAPE, and RHDPE/clay (100/5 w/w)/MAPE hybrids for a cooling rate of 10°C/min in N_2.

TABLE III
Effect of Clay Content on Mechanical Properties of RHDPE/Clay Hybrids

Compatibilizer	Clay content (wt %)	Storage modulus (GPa)	Loss modulus (GPa)	Tensile strength (MPa)	Impact strength (kJ/m^2)
MAPE	0	1.48 (b)	0.147 (b)	32.6 (a)	12.3 (a)
	1	1.58 (a)	0.159 (a)	33.6 (a)	12.0 (a)
	3	1.56 (a)	0.156 (a)	32.6 (a)	10.7 (b)
	5	1.43 (b)	0.154 (a)	32.6 (a)	8.0 (c)
	7	1.47 (b)	0.163 (a)	30.7 (b)	7.3 (d)
CAPS	0	1.48 (c)	0.147 (b)	32.6 (a)	12.3 (a)
	1	1.50 (c)	0.152 (b)	31.9 (ab)	8.0 (b)
	3	1.76 (a)	0.171 (a)	30.9 (b)	6.0 (c)
	5	1.86 (a)	0.180 (a)	31.6 (ab)	5.9 (c)
	7	1.65 (b)	0.180 (a)	33.0 (a)	4.1 (d)

The weight ratios of MAPE and CAPS to clay were 100:100 and 100:5, respectively. Means with the same letter for each property are not significantly different at the 5% significance level.

the two-step method to aid in exfoliation of the clay. However, the RHDPE/clay/CAPS hybrids were made using the one-step method since the recommended content of CAPS by the manufacturer was too low to make a two-step process. As shown in Table III, the impact strength decreased as clay content increased, especially for the RHDPE/clay/CAPS system. Tensile strengths changed little over the range of clay contents investigated. Loss modulus increased with the addition of clay, especially for the RHDPE/clay/CAPS system. Storage modulus had a maximum at 1–3% clay for the RHDPE/clay/MAPE, and 3–5% clay for the RHDPE/clay/CAPS system. The small increase in modulus is somewhat surprising given the large increases found by others.[18,20] Though the clay was well exfoliated, the possible existence of other fillers and additives in the RHDPE may lessen the clay enforcement.

Table IV shows the influence of MAPE content on mechanical properties of the hybrids prepared by the two-step method. The tensile strength was improved slightly by the MAPE content but large increases in impact strength were found when up to 5% MAPE was added. When the concentration of MAPE was 5%, there was about a 44% increase in impact strength compared with that of the hybrid containing no MAPE, owning to the exfoliated clay. When 10% MAPE was added, the impact strength was reduced relative to the maximum at 5% MAPE, and the tensile strength was lowered. MAPE has a much lower molecular weight than RHDPE since the melt flow index of the studied RHDPE is 0.7 g/10 min and that of MAPE is about 8 g/10 min (190°C). Thus, adding MAPE with low molecular weight to some extent must result in a decrease in mechanical properties.

TABLE IV
Effect of MAPE Content on Mechanical Properties of RHDPE/Clay Hybrids

MAPE content (wt %)	Storage modulus (GPa)	Loss modulus (GPa)	Tensile strength (MPa)	Impact strength (kJ/m^2)
0	1.81 (a)	0.181 (a)	31.6 (ab)	5.57 (b)
2.5	1.80 (a)	0.163 (b)	32.6 (a)	6.46 (b)
5	1.43 (b)	0.154 (b)	32.6 (a)	8.00 (a)
10	1.72 (a)	0.166 (b)	30.7 (b)	6.52 (b)

The loading level of clay was 5%. Means with the same letter for each property are not significantly different at the 5% significance level.

The effect of preparation method for RHDPE/clay hybrids containing 5% MAPE is shown in Table V. The impact strength of the hybrid prepared using the two-step blending method was higher, but there was no significant difference in other properties at the 5% significance level.

Thermogravimetric behavior of the hybrids

The thermogravimetric curves are plotted in Figure 6. The decomposition of RHDPE began at about 380°C, and ended at 485°C with a peak at about 470°C. The clay began to degrade at about 200°C, resulting from the low-molecular-weight compounds with which the clay was treated to become organic. The remaining weight percentage was 60%, which was almost in

TABLE V
Effect of Compounding Method on Mechanical Properties of RHDPE/Clay Hybrids

Preparation method	Storage modulus (MPa)	Loss modulus (MPa)	Tensile strength (MPa)	Impact strength (kJ/m^2)
One step	1.50 (a)	0.166 (a)	31.8 (a)	6.67 (a)
Two step	1.43 (a)	0.154 (a)	32.6 (a)	8.00 (b)

The loading levels of clay and MAPE were both 5%. Means with the same letter for each property are not significantly different at the 5% significance level.

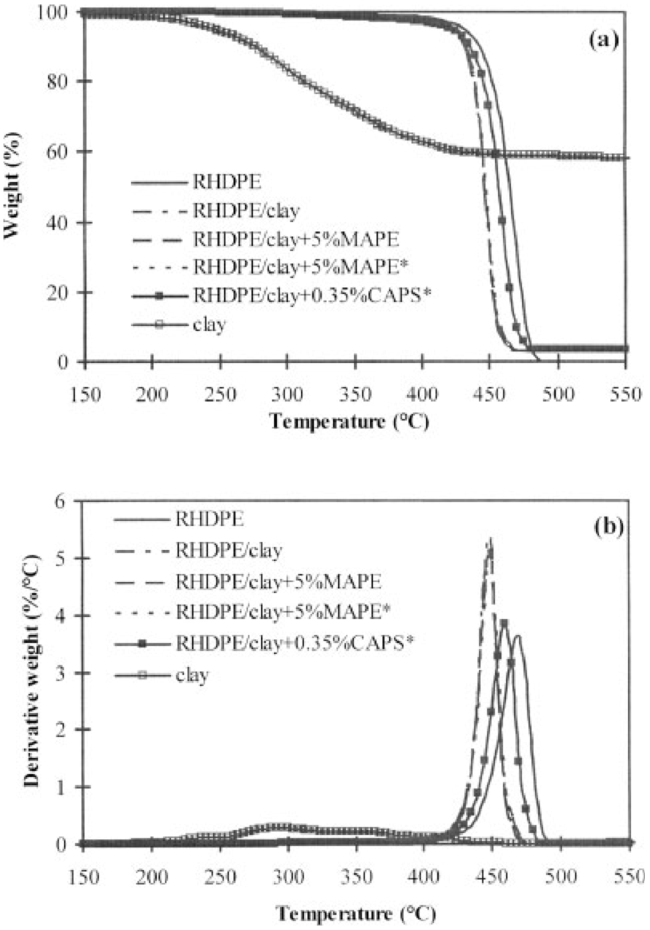

Figure 6 Temperature dependence of (a) weight loss and (b) its first derivative for RHDPE and RHDPE/clay (100/5 w/w) hybrids at 10°C/min in N_2. $*$: These hybrids were prepared using the one-step method.

accordance with the reported weight loss on ignition by the manufacturer of 39%. All of the RHDPE/clay hybrids started to lose weight at about 310°C, and the degradation ended at lower temperatures than that of neat RHDPE. The decomposition peak of RHDPE/clay hybrids shifted from about 450 to 465°C with the addition of CAPS, but the compatibilizer MAPE made little effect. Thus, the addition of clay did not improve the thermal stability of RHDPE. There appeared no difference in thermogravimetric behavior between the hybrid prepared by the one-step method and that prepared by the two-step method.

CONCLUSIONS

In this study, RHDPE and clay hybrids were made by melt compounding. The influence of preparation method, compatibilizers, and clay content on the clay intercalation and exfoliation, the RHDPE crystallization behavior, and the mechanical properties of RHDPE/clay hybrids were investigated. Both MAPE and CAPS could effectively reduce the slippage at the interface between RHDPE and clay. With the two-step blending method, the clay could be completely exfoliated using MAPE as the compatibilizer. Without compatibilizers, the addition of clay reduced the crystallization rate, L_{hkl}, T_c, and crystallinity level of RHDPE, especially the crystallization rate. With the addition of 2.5% MAPE, the crystallization rate, L_{hkl}, T_c, and crystallinity level of RHDPE/clay hybrid increased. The L_{hkl} of RHDPE/clay hybrids obviously decreased and the crystallization rate significantly increased while the crystallinity stayed at the same level with increasing concentration of MAPE from 2.5% to 5%. For the RHDPE/clay system containing 5% MAPE, the hybrid prepared by the one-step method had a slightly smaller T_c and crystallinity level, and an obviously lower crystallization rate than that prepared using the two-step method. The addition of 0.35% CAPS did not influence the T_c of the RHDPE/clay system, but increased the crystallization rate, L_{hkl}, and the crystallinity level. Adding clay to RHDPE reduced the impact strength but had little influence on the tensile strength. Both the storage and loss moduli increased with up to 5% of clay in composites containing CAPS, and a little difference was seen in composites containing 5% MAPE. The tensile strength of RHDPE/clay hybrid was improved slightly by the MAPE content but large increases in its impact strength were found when up to 5% MAPE was added. When the concentration of MAPE was 5%, there was an about 44% increase in impact strength compared with that of the hybrid containing no MAPE. Except the impact strength, there was no significant difference in mechanical properties between hybrids prepared using the one-step and two-step methods respectively, at the 5% significance level. The clay lowered the thermal stability of RHDPE.

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