Mechanical Properties and Microstructure of HDPE/Al(OH)$_3$/Silicone Oil Composite

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ABSTRACT: The effect of surface modification on the mechanical properties and microstructure of the composites of high-density polyethylene (HDPE), silicone oil, and aluminum hydroxide [Al(OH)$_3$] was investigated. The dispersion of silicone oil in the HDPE composites was studied by scanning electric microscope (SEM) and differential scanning calorimetry (DSC). In the HDPE/Al(OH)$_3$/silicone oil composites, two types of dispersion structure of silicone oil were observed resulting from different surface modifications. In the composites surface modified with titanate NDZ-130, calcium stearate, or oleic acid, silicone oil encapsulates around Al(OH)$_3$ particles, and both the notched impact strength and the elongation at break are very high. However, in the composites surface modified with silane KH-550 or silane-*g*-HDPE, silicone oil and Al(OH)$_3$ particles separately disperse in HDPE, and both the notched impact strength and the elongation at break are very low. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1896–1903, 2002

Key words: high-density polyethylene; aluminum hydroxide; silicone oil; composite; surface modification; phase structure

INTRODUCTION

It is of increasing commercial importance to produce polymers with reduced flammability for application in construction and automotive industrials, house appliances, and electrical equipments. In addition to reduced flammability, good mechanical properties and processability are the most important requirements. Some halogen-contained flame retardants have been used to make flame-retardant polymers for many years, but they give off smoke and hazardous gas during burning of the polymers, which hinders their practical applications to a great extent. The application of nonhalogen flame retardants such as magnesium hydroxide [Mg(OH)$_2$] and aluminum hydroxide [Al(OH)$_3$] is of great interest, which were shown to be effective halogen- and acid-free fire retardants.[1] However, satisfactory flame retardancy of polymers requires very high contents of these fillers, which leads to a marked deterioration in certain physical properties of the materials, in particular, their toughness.[2]

Many methods were used to improve the toughness of highly filled polymer composites. Surface modification is the most common method. Coupling agents such as silanes can increase the tensile strength of the composites with little effect on the toughness.[3,4,5] The presence of surface activators such as fatty acids and their salts leads to a decrease in tensile strength and a slight increase in impact strength.[5,6] Some polymers functionalized with compounds such as maleic anhydride and silanes can increase the tensile strength of the composites markedly, however, with little effect on the toughness.[5] Rubbers are

also used to improve the toughness of the composites. An increase in impact strength is achieved, because ethylene–propylene copolymer (EPR) is added into the polypropylene/Mg(OH)$_2$ composite.[6] The impact strength is increased further with maleic anhydride-functionalized EPR. In summary, satisfactory mechanical properties cannot be achieved by the common methods, as mentioned above.

Formation of a soft interphase between filler particles and matrix was proven to be an effective method to improve the toughness of highly filled polymer composites. The work of Galeski et al.[7,8] showed that encapsulation of chalk particles by oligomer of ethylene oxide increases the elongation and impact strength of the polyolefin composites. Fu[9] observed that surface treatment of calcium carbonate (CaCO$_3$) with phosphate can increase the impact strength of HDPE/CaCO$_3$ composites markedly. The work of Ou et al.[10] showed that the silane-coupling agent with a long soft chain can significantly increase the impact strength of polypropylene/kaolin composites. However, a decrease in tensile strength is observed in both the studies above.

The phase structures of the three phase composites are obviously affected by the interfacial interaction between filler particles and polymer. In the research of Pukanszky et al.[11,12,13] of polypropylene/elastomer filler, two phase structures can be obtained: elastomer and filler particles are dispersed separately with functionalized polypropylene; elastomer encapsulates filler particles with functionalized elastomer. The research also showed that there is a close relationship between the phase structures and the mechanical properties of the composites.

In our previous work,[14] the silicone oil and special surface modification have a great effect on the elongation at break and notched-Izod impact strength of the HDPE composites with high loading of Mg(OH)$_2$ and Al(OH)$_3$. The objective of the present study was to study the effect of surface modification on the mechanical properties of HDPE/Al(OH)$_3$/silicone oil composites. The dispersion structure of silicone oil was investigated to explain the effect of silicone oil.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) 5000 (Yangtse Petroleum Chemical Co. Ltd., China), melt–flow ratio 0.923 g/10 min (2.16 kg at 190°C), was used as the matrix polymer. Al(OH)$_3$ APYRAL 60 (Nabaltec Co. Ltd., Germany), median particle size 1.5 μm, was used as the filler. Dimethyl silicone oil (The Research Institute of Shanghai Special Resin Co., China) was used as an additive to improve the toughness of HDPE/Al(OH)$_3$ composites.

The following surface modifiers were investigated: (1) silane coupling agent KH-550 (Nanjing Shuguang Chemical General Co., China); (2) titanate coupling agent NDZ-130 (Nanjing Shuguang Chemical General Co.); (3) silane-grafted HDPE (a commercial product); and (4) calcium stearate and oleic oil.

Compounding

Al(OH)$_3$ filler was treated with surface modifiers (2 wt %). The components were mixed in a mixing chamber of HAAKE RC90 rheometer at 160°C and rotor speed of 64 rpm for 15 min.

Specimen Preparation

Test specimens for morphology observation and mechanical properties testing were prepared by compression molding at 165°C under a pressure of 15 MPa in the form of sheets 1.0 and 3.0 mm in thickness.

Mechanical Properties

Tensile dumbbell specimens were cut from 1-mm-thick sheets and tested by using an Instron 4465 electron tensile tester according to Chinese Standard GB-1040-79 with crosshead speed of 50 mm/min. Notched specimens in a thickness of 3 mm were tested in a Ray-Ran impact tester according to Chinese Standard GB-1043-79 at hammer speed of 3.5 m/s and pendulum weight of 0.818 kg.

DSC Analysis

The crystallization behavior of the HDPE matrix, under nitrogen, was studied using a Perkin–Elmer DSC-7 programmed with a heat–hold–cool–heat cycle. The sample was heated from 50 to 180°C at 10°C/min, held at 180°C for 5 min, cooled back to 50°C at 10°C/min, and finally heated to 180°C at 10°C/min.

SEM Observation

Fracture surfaces for morphology observation were prepared by fracturing the notched impact

Table I   Effect of Surface Modifications on the Mechanical Properties of HDPE/Al(OH)$_3$ Composites[a]

Surface Modifier	Yield Strength (MPa)	Elongation at Break (%)	Notched Impact Strength (kJ/m^2)
HDPE[b]	24.0	>1000	38.4
None	20.6	1.0	2.0
NDZ-130	15.1	1.5	4.7
Calcium stearate	14.3	1.3	2.3
Oleic oil	14.3	1.7	3.8
KH-550	23.3	1.1	3.2
Silane-g-PE[c]	31.0	1.5	3.5

[a] Composition content: HDPE/Al(OH)$_3$ 100 : 140 (phr).
[b] Sample content: virgin HDPE.
[c] Sample content: HDPE/Al(OH)$_3$/silane-g-HDPE 100 : 140 : 6 (phr).
[d] Crosshead rate: 5 mm/min.

samples in the impact tester at 23°C. The fracture surfaces were then golden-coated and observed by using a Hitachi-S-2150 scanning electric microscope (SEM).

RESULTS AND DISCUSSION

Mechanical Properties of HDPE/Al(OH)$_3$ Composites

The effect of surface modification on the mechanical properties of the HDPE composite is shown in Table I. Incorporation of 140 phr Al(OH)$_3$ to HDPE leads to a great decrease in both notched Izod impact strength and elongation at break. The presence of surface modifiers has little effect on both the notched Izod impact strength and the elongation at break. However, surface modifiers have different effects on the yield strength of the composites. Surface modification using titanate NDZ-130, calcium stearate, or oleic oil leads to a

decrease in yield strength. Surface modification using silane KH-550 or silane-g-HDPE leads to an increase in yield strength.

Mechanical Properties of HDPE/Al(OH)$_3$/Silicone Oil Composites

The effect of silicone oil on the mechanical properties of HDPE/Al(OH)$_3$ composites is shown in Table II. The effects of silicone oil on the mechanical properties of the composites can be summarized as three types. In the composite without surface modification, the incorporation of silicone oil leads to a great increase in notched Izod impact strength, but has no effect on the elongation at break. In the composites surface modified by titanate NDZ-130, calcium stearate, or oleic oil, the incorporation of silicone oil leads to a great increase in both notched Izod impact strength and elongation at break. In the composites surface modified by silane KH-550 or silane-g-HDPE, the

Table II   Effect of Silicone Oil on Mechanical Properties of HDPE/Al(OH)$_3$ Composites[a]

Surface Modifier	Yield Strength (MPa)	Elongation at Break (%)	Notched Izod Impact Strength (kJ/m^2)
None	14.0	1.0	18.4
NDZ-130	10.0	275	35.5
Oleic oil	11.4	282	32.3
Calcium stearate	12.0	267	32.5
KH-550	14.9	3.0	5.6
Silane-g-HDPE[b]	19.7	7.0	3.9

[a] Composite content: HDPE/Al(OH)$_3$/Silicone Oil 100 : 140 : 8 (phr).
[b] Sample content: HDPE/Al(OH)$_3$/silane-g-HDPE/Silicone oil 100 : 140 : 6 : 8 (phr).

incorporation of silicone oil has little effect on both the notched Izod impact strength and the elongation at break.

On the basis of the analysis above, surface modification markedly influences the mechanical properties of the HDPE/Al(OH)$_3$/silicone oil composites. It is in the composites treated with special surface modifiers that the incorporation of silicone oil can markedly increase the notched Izod impact strength and elongation at break.

Dispersion of Silicone Oil in the HDPE Composites

There are two possible explanations for silicone oil to improve the toughness of the HDPE/Al(OH)$_3$ composites treated with special surface modifiers. First, silicone oil probably disperses homogeneously in HDPE matrix to improve the plastic deformation ability of the matrix and then to improve the toughness of the composites. Second, silicone oil probably encapsulates around filler particles to increase the deformation ability of the matrix around filler particles and then to improve toughness of the composites. Therefore, it is important to find out the dispersion type of silicone oil in the composites to reveal the toughening mechanism for silicone oil in the composites.

SEM Analysis

Dispersion of Silicone Oil in HDPE/Silicone Oil Blend

Figure 1(a) shows the microstructure of HDPE, where there are no dark holes in the surface. A contrasting morphology is shown in Figure 1(b) for HDPE/silicone oil blend, where there are many dark holes in the surface. The silicone oil used in the study, with a weight loss of 2 wt % after thermal treating at 160, 200°C for 12 h, should be stable enough not to evaporate at the processing temperature so that the dark holes should be imprints of silicone oil drops. It must be noted that even though no etching process is performed, silicone oil drops can be observed clearly by SEM.

On the basis of the analysis above, silicone oil is not compatible with HDPE, and it disperses in HDPE as dispersed drops. Therefore, the first explanation for silicone oil to increase the toughness of the HDPE composites can be excluded.

Dispersion of Silicone Oil in HDPE/Al(OH)$_3$ Composites

Figure 2(a) shows the microstructure of the HDPE composite containing 140 phr Al(OH)$_3$
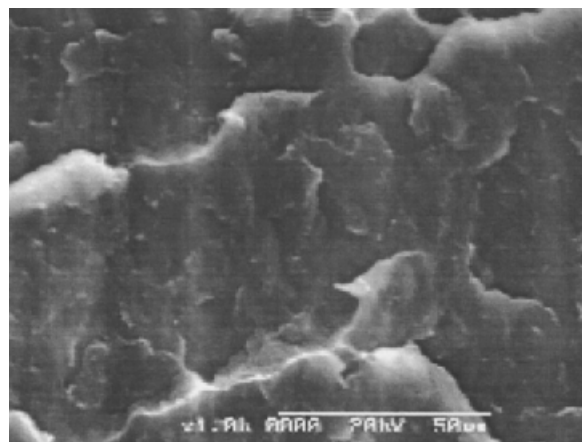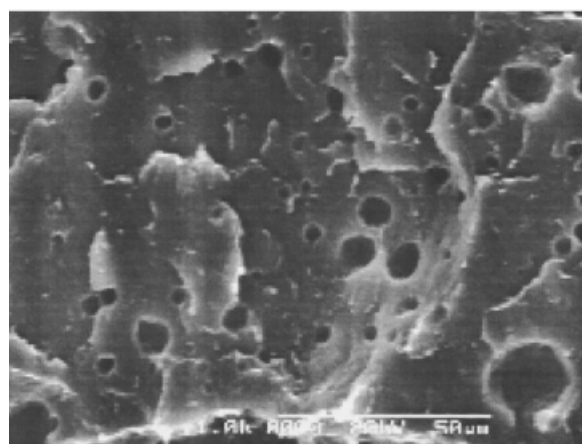
Figure 1 SEM micrographs of cryogenic impact fracture surfaces. (a) HDPE; (b) HDPE/silicone oil 100 : 8.
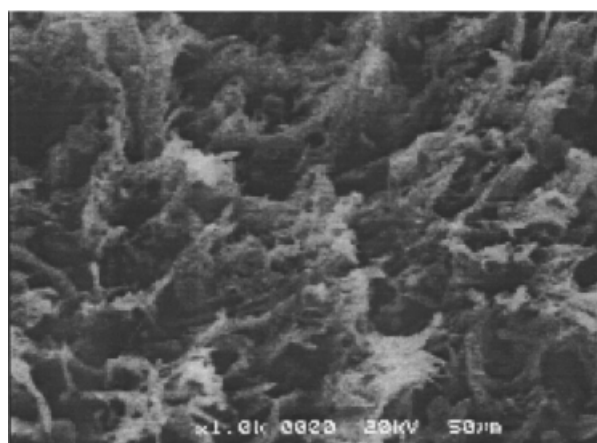
modified with titanate NDZ-130, where Al(OH)$_3$ particles can be identified with some plastic deformation around them. The incorporation of silicone oil markedly promotes the plastic deformation of HDPE [Fig. 2(b)]. However, the dispersion of silicone oil cannot be observed, which probably is concealed by the large amount of plastic deformation.

As shown in Figure 3, the dispersion of silicone oil cannot be observed on the cryogenic fracture surfaces of the composites either. On both the fracture surfaces, there is no evident plastic deformation. However, the dispersion of silicone oil cannot be observed yet. It seems that 140 phr filler loading is too high to observe the dispersion of silicone oil by SEM.

Figure 4(a) shows the microstructure of the HDPE composite containing 20 phr Al(OH)$_3$ mod-
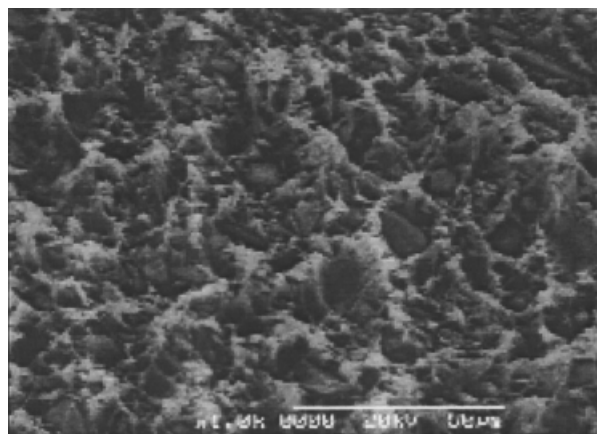
(a)

(b)

Figure 2 SEM micrographs of impact fracture surfaces. (a) HDPE/Al(OH)$_3$-Ti 100 : 140; (b) HDPE/Al(OH)$_3$-Ti/silicone oil 100 : 140 : 8.

ified with titanate NDZ-130, in which filler particles are well dispersed. The HDPE matrix adheres strongly around the filler particles and there are no gaps between filler particles and matrix. However, there are circular gaps around filler particles [Fig. 4(b)], when 8 phr silicone oil is presented in the composite. At the same time, the dark holes shown in HDPE/silicone oil blend [Fig. 1(b)] cannot be observed. Because both HDPE and Al(OH)$_3$ filler cannot absorb silicone oil, it should be silicone oil that disperses in the circular gaps around filler particles.

Effects of Surface Modifications on the Dispersion of Silicone Oil in the HDPE Composites

As has been shown, it is appropriate to observe the dispersion of silicone oil in the HDPE compos-

ites with 20 phr filler loading, so the composites containing 20 phr filler and 8 phr silicone oil were chosen to observe the dispersion of silicone oil.

Figure 5(a) shows the microstructure of the composite containing 20 phr untreated Al(OH)$_3$ and 8 phr silicone oil. As shown in Figure 4(b), there are also some gaps around filler particles; however, some dark holes similar to those shown in Figure 1(b) can be observed at the same time. The morphology observation reveals that in this composite silicone oil encapsulates filler particles to some extent, but not as perfectly as in the composites containing Al(OH)$_3$ surface modified with titanate NDZ-130.

The microstructure of the composite containing silane-*g*-HDPE is shown in Figure 5(b). It is apparent that there are many dark holes similar to
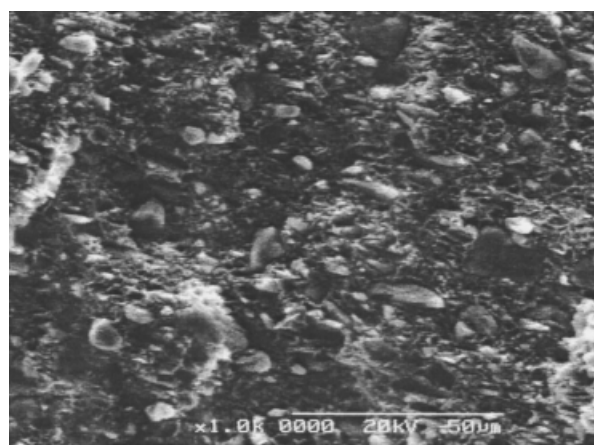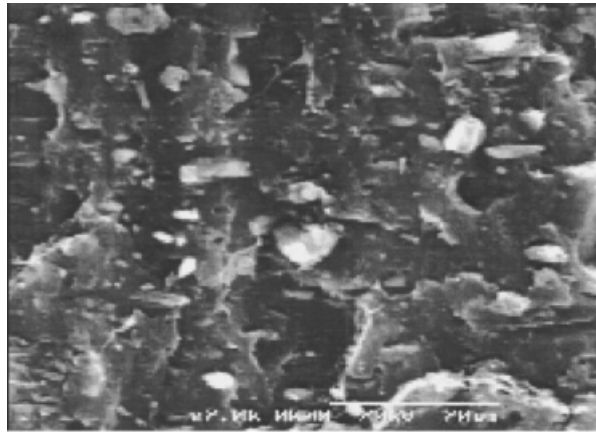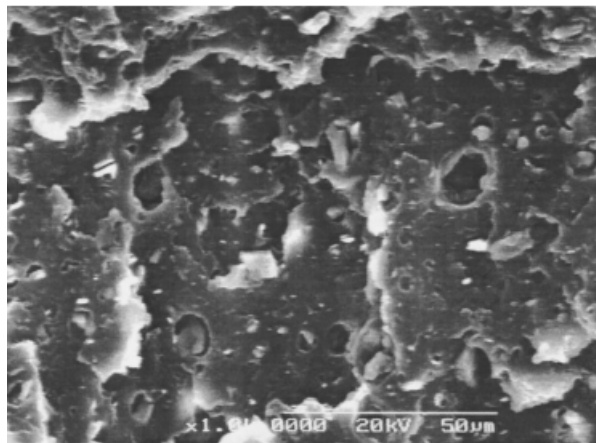

(a)
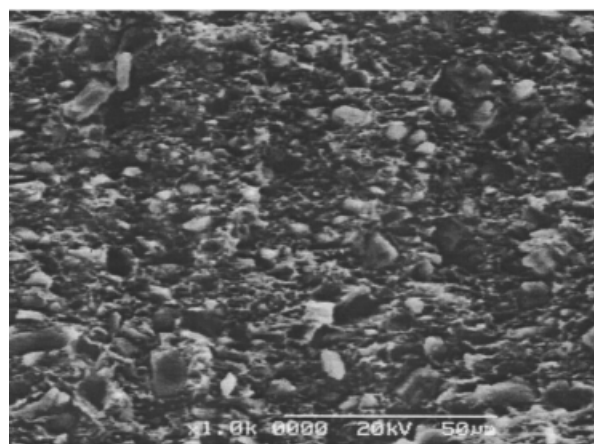
(b)

Figure 3 SEM micrographs of cryogenic impact fracture surfaces. (a) HDPE/Al(OH)$_3$-Ti 100 : 140; (b) HDPE/Al(OH)$_3$-Ti/silicone oil 100 : 140 : 8.

(a)

(b)

Figure 4 SEM micrographs of impact fracture surfaces. (a) HDPE/Al(OH)$_3$-Ti 100 : 20; (b) HDPE/Al(OH)$_3$-Ti/silicone oil 100 : 20 : 8.

those shown in Figure 1(b) on the surface, and there are no gaps around the filler particles. The morphology observation shows that filler particles and silicone oil are separately dispersed in the composite.

DSC Analysis

Table III lists the DSC data obtained from the cooling step of the heat–hold–cool–heat cycle. The incorporation of 140 phr Al(OH)$_3$ leads to an increase in the onset temperature of crystallization ($T_{c\text{onset}}$) and the peak temperature of crystallization (T_c) values by 4.0 and 3.5°C separately for HDPE, which indicates the marked nucleating effect of Al(OH)$_3$ filler. Silicone oil has no effect on the $T_{c\text{onset}}$ and T_c values for HDPE, which is in

agreement with the SEM result (as shown in Fig. 1). The incorporation of silicone oil to the HDPE composite containing untreated Al(OH)$_3$ eliminates the nucleating effect of Al(OH)$_3$. Because silicone oil has no effect on crystallinity of HDPE, it is a reasonable deduction that silicone oil encapsulates around filler particles to eliminate the nucleating effect of Al(OH)$_3$. The DSC result is in agreement with the SEM result too (as shown in Fig. 5).

Surface modification of Al(OH)$_3$ with titanate NDZ-130 eliminates the nucleating effect of the Al(OH)$_3$ filler. In this circumstance, the incorporation of silicone oil has no effect on the $T_{c\text{onset}}$ and T_c values for HDPE. This DSC result does not support the encapsulation of silicone oil around Al(OH)$_3$ particles.
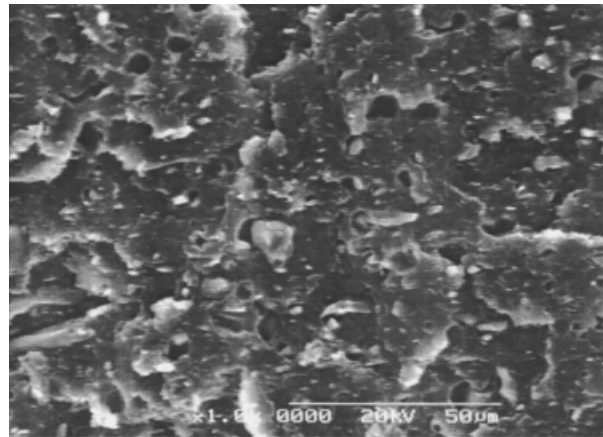
(a)
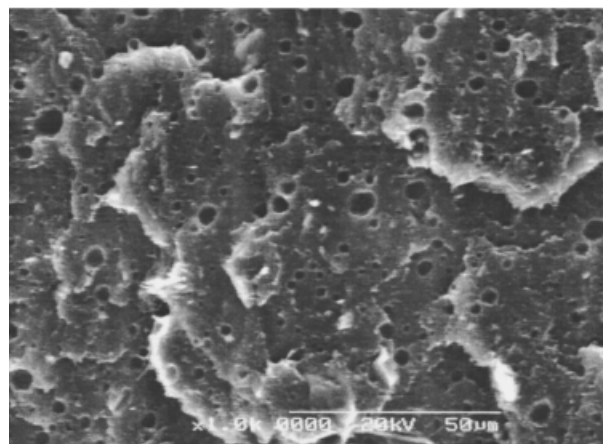
(b)

Figure 5 SEM micrographs of cryogenic impact fracture surfaces. (a) HDPE/Al(OH)$_3$/silicone oil 100 : 20 : 8; (b) HDPE/silane-g-HDPE/Al(OH)$_3$/silicone oil 100 : 6 : 20 : 8.

Table III   DSC Data

Sample	Ratio (by phr)	T_{conset}	T_c
HDPE		118.9	117.1
HDPE/silicone oil	100/8	118.6	116.9
HDPE/Al(OH)$_3$	100/140	122.9	120.6
HDPE/Al(OH)$_3$-Ti[a]	100/140	118.8	116.6
HDPE/Silane-g-HDPE/Al(OH)$_3$	100/6/140	122.9	120.4
HDPE/Al(OH)$_3$/silicone oil	100/140/8	118.9	116.9
HDPE/Al(OH)$_3$-Ti[a]/silicone oil	100/140/8	119.1	117.1
HDPE/Silane-g-HDPE/Al(OH)$_3$/silicone oil	100/6/140/8	122.0	119.4

[a] Al(OH)$_3$-Ti: Al(OH)$_3$ modified with titanate NDZ-130 by 2 wt %.

The incorporation of silane-g-HDPE into the HDPE/Al(OH)$_3$ has no effect on the nucleating effect of Al(OH)$_3$. The incorporation of silicone oil into the composite only leads to a slight decrease in T_{conset} and T_c values of HDPE, and Al(OH)$_3$ filler still has significant nucleating effect, which indicates the separation of filler particles and silicone oil. The DSC result is also in agreement with SEM result (as shown in Fig. 5).

On the basis of the analysis above, surface modifications markedly influence the dispersion of silicone oil in the HDPE/Al(OH)$_3$/silicone oil composites and the mechanical properties of the composites. The HDPE/Al(OH)$_3$/silicone oil composite surface modified by titanate NDZ-130, in which silicone oil encapsulates around Al(OH)$_3$ particles perfectly, has high notched impact strength and high elongation at break. The HDPE/Al(OH)$_3$/silicone oil composite without surface modification, in which silicone oil also encapsulates around Al(OH)$_3$ particles, but not as perfectly as in the composite surface modified with titanate NDZ-130, has high notched impact strength and low elongation at break. The HDPE/Al(OH)$_3$/silicone oil composite surface modified by silane-g-HDPE, in which silicone oil and Al(OH)$_3$ particles dispersed separately, has low notched impact strength and elongation at break.

It seems that good encapsulation of silicone oil around filler particles is important for silicone oil to improve the impact strength and elongation at break of the HDPE composites, and surface modifications influence the encapsulation structure and then the mechanical properties.

Processability of the HDPE/Al(OH)$_3$ Composites

The processability of the HDPE/Al(OH)$_3$ composites is evaluated by equilibrium torque of the composites in HAAKE rheometer and melt flow index (MFI) at 190°C under the load of 2.16 kg (shown in Table IV). Incorporation of silicone oil and surface modification with titanate coupling agent NDZ-130 decreases the equilibrium torque of the HDPE/Al(OH)$_3$ composites. A further decrease of the equilibrium torque is obtained by using both silicone oil and surface modification. The MFI of HDPE decreases largely from 0.927 to 0.088 with the incorporation of Al(OH)$_3$ filler, which shows that the processability of HDPE/Al(OH)$_3$ composite is very poor. Incorporation of silicone oil just increases the MFI of the HDPE/Al(OH)$_3$ composite slightly; however, surface modification with titanate coupling agent NDZ-130 increases the MFI to a great extent. It is very strange that the MFI decreases when silicone oil is incorporated into the surface-modified composite. Further investigation should explain the strange phenomena.

On the basis of the analysis above, the processability of the HDPE/Al(OH)$_3$ composites can be improved obviously through the incorporation of silicone oil and surface modification.

Table IV   Processability of HDPE and HDPE/Al(OH)$_3$ Composites

Sample	Ratio (by phr)	Equilibrium Torque (N m)	MFI
HDPE			0.927
HDPE/Al(OH)$_3$	100/140	19.6	0.088
HDPE/Al(OH)$_3$-Ti[a]	100/140	12.3	0.636
HDPE/Al(OH)$_3$/ silicone oil	100/140/8	13.8	0.164
HDPE/Al(OH)$_3$-Ti[a]/ silicone oil	100/140/8	5.0	0.440

[a] Al(OH)$_3$-Ti: Al(OH)$_3$ modified with titanate NDZ-130 by 2 wt %.

CONCLUSION

Surface modifications influence the mechanical properties of the HDPE/Al(OH)$_3$/silicone oil composites significantly. High notched Izod impact strength and elongation at break are achieved when Al(OH)$_3$ filler is surface modified by titanate NDZ-130, calcium stearate, or oleic oil, which cannot be achieved with other surface modifications. Both the notched Izod impact strength and the elongation at break are very low in the composites surface modified with silane KH-550 and silane-*g*-HDPE.

Surface modification influences the dispersion type of silicone oil in the HDPE composites. Both encapsulation structure and separate dispersion structure were observed with different surface modifications. The composites with encapsulation structure have high notched Izod impact strength and high elongation at break, and those with separate dispersion structure have low notched Izod impact strength and low elongation at break.

The processability of the HDPE/Al(OH)$_3$ composites can be obviously improved through the incorporation of silicone oil and surface modification with titanate coupling agent NDZ-130.

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