

Structure–Property Relationships of LLDPE—Highly Filled with Aluminum Hydroxide

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ABSTRACT: The mechanical performance, rheological behavior, and phase morphology of linear low-density polyethylene (LLDPE) highly loaded with aluminum hydroxide [Al(OH)₃] were investigated. It was found that titanate surface-active agent and ethylene-vinyl acetate copolymer (EVA) improve the processing and ductile properties of the composite remarkably but are accompanied by the deterioration of the tensile strength. Addition of vinyl triethoxy silane (VTEO) and dicumyl peroxide (DCP) improves the tensile strength of the composite because of the silane crosslinking structure introduced. A synergistic effect of interface modifying and silane crosslinking method in improving mechanical performance of the composite is presented. Phase morphology of the LLDPE/Al(OH)₃ composites was studied by means of scanning electron microscopy (SEM) technique. SEM micrographs indicate that a core-shell type with Al(OH)₃ as a core and EVA as a shell is formed in the composite. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2485–2490, 2002

Key words: linear low-density polyethylene; aluminum hydroxide; interface modification; silane; crosslinking

INTRODUCTION

Much attention has been paid to the polymers filled with inorganic compounds. The original purpose of adding fillers to polymers was primarily to reduce the cost. However, in recent years, fillers are used to modify the physical properties, such as flexural modulus and heat distortion temperature of polymers, or to impart some functional roles, such as reducing the fire hazard of them.¹

Substituting the halogenated flame retardants, with their ability to produce an unacceptable level of smoke, with nonhalogen materials is an important trend in the production of linear low-density polyethylene (LLDPE) cable.² Aluminum hydrox-

ide has attracted interest because of its potential use in the flame retardancy of polyolefins. It has become one of the most popular replacements for halogen-based fire retardants with their toxic, corrosive gases generated during the combustion. To confer adequate fire retardance, aluminum hydroxide [Al(OH)₃] must be present at high loadings for LLDPE composite. However, the high loading of Al(OH)₃ in LLDPE results in significant deterioration of mechanical and processing properties.^{3,4} This is due to insufficient interactions between LLDPE with nonpolar, hydrophobic molecular chains and Al(OH)₃ with its polar and hydrophilic groups. To avoid reduction in mechanical properties of LLDPE/Al(OH)₃, interface adhesion and phase dispersion between LLDPE matrix and fillers have to be improved. Traditionally, this can be achieved by surface-active agent treatment of fillers or addition of copolymer acting as a compatibilizer. For instance, EVA was a

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good compatibilizer for LLDPE/Al(OH)₃ composite because a strong interaction via a hydrogen bond was found between the carbonyl groups present in EVA and hydroxyl groups of hydrated aluminum. However, ductile improvement is often accompanied by the deterioration of tensile strength because of the softening effect of the surface-active agent and the compatibilizer.⁵⁻⁸

Generally, the bigger the particle size of Al(OH)₃ inorganic compounds used, the lower the cost. In this article, Al(OH)₃ of an average particle size of 400 mesh is used to modify LLDPE to reduce the filler cost. The effects of titanate, ethylene-vinyl acetate copolymer (EVA), and silane crosslinking on the mechanical performance and rheological behavior of LLDPE/Al(OH)₃ composite were studied. The relationship between mechanical properties and microstructure of the composites was also discussed.

EXPERIMENTAL

Materials

Polyethylene (F280 W) used here was LLDPE with a melt index (GB 3682-83) of 2 g/10 min and a density of 0.918 g/cm³, obtained from Canada, and Al(OH)₃ powder of a mean particle size of 400 mesh was provided by Fengyang Powder Corp., China. Isopropyl triisostearoyl titanate as surface-active agent was received from Jiangnan Reagents Corp., Changzhou, China. EVA and vinyl triethoxy silane (VTEO) (A151) were received from Union Carbide. Dicumyl peroxide (DCP) having a molecular weight of 324 g/mol and a 1-min half-life time ($t_{1/2}$) at a temperature of 171°C was provided by Institute of Chemistry and Engineering, Harbin, China.

Sample Preparation

LLDPE was mixed with other materials such as EVA and Al(OH)₃ simultaneously in a Haake internal mixer at a temperature of 170°C and a rotor speed of 40 rpm until torque stabilization was reached.

The melt grafting of silane onto LLDPE was in a Haake internal mixer under the same conditions as presented above. The grafted LLDPE was then transferred to a preheated compression mold and hot pressed at 180°C under pressure of 20 MPa to sheets of 1.0 mm in thickness and punched into a dumbbell shape. The dumbbell

shape samples were subsequently crosslinked in hot water before tensile test.

Titanate-treated Al(OH)₃ was prepared by mixing. Titanate dissolved in ethanol by 1 : 1 vol at 50°C was added to Al(OH)₃ and then the mixture was agitated at 110°C for 15 min.

Characterization

The gel fraction was determined by the weight difference between the samples before and after the extraction with xylene for 24 h.

Tensile and elongation at break properties were measured on an Instron 4302 Universal Tester, according to the Chinese standard GB/T 1040-92.

Titanate and Al(OH)₃ with or without titanate treatment were identified by using Fourier transform infrared (FTIR) characterization. Al(OH)₃ treated with titanate was extracted with ethanol for 24 h and then dried in an oven under vacuum at 80°C to a constant weight before FTIR test. All the samples were ground with a certain amount of KBr and were compression molded into thin films for the FTIR test.⁹

The phase morphology of the composites was examined by scanning electron microscopy (SEM; Hitachi S520). Some specimens were prepared by immersing test pieces in liquid nitrogen before breaking, and other specimens were those fractured in tensile testing. Surfaces of the test pieces were coated with gold.

RESULTS AND DISCUSSION

Interaction between Al(OH)₃ Filler and Titanate Compound

Interfacial property is one of the key factors in determining the mechanical properties of polymer filled with inorganic compound.¹⁰ First, good phase dispersion will be obtained if polymer matrix and filler have similar surface characteristics. In addition, interfacial adhesion should also be appropriate between polymer and filler. Thus, it is of importance to study the interaction between filler and polymer matrix.

It has been suggested that titanate is a good surface-active agent for polymer filled with inorganic compound,¹¹⁻¹⁴ whereby the interaction between aluminum hydroxide and titanate was investigated. FTIR spectra of Al(OH)₃, titanate, and titanate-treated Al(OH)₃ are shown in Figure 1.

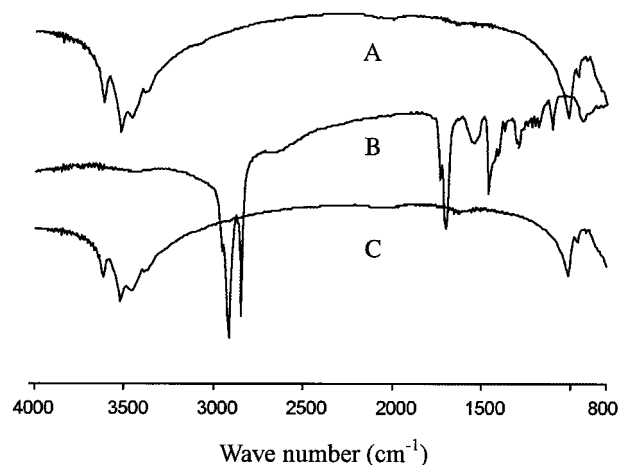


Figure 1 FTIR spectra of (A) aluminum hydroxide; (B) isopropyl triisostearoyl titanate; and (C) aluminum hydroxide, which was surface treated with titanate, was extracted with ethanol for 24 h.

The absorption band of —C=O group at 1720 cm^{-1} disappears in Figure 1(C) when the soluble portions of titanate-treated Al(OH)_3 were extracted by ethanol solvent, indicating that titanate does not react with Al(OH)_3 . However, the isopropyl group in titanate has a strong interaction with Al(OH)_3 because of their similar molecule polarity. In addition, triisostearoyl groups in titanate are thus exposed on the outside surface of Al(OH)_3 , which reduces the surface energy of the inorganic compound and makes possible finer dispersion of Al(OH)_3 particles in filled LLDPE composite. The good compatibility and strong interfacial adhesion between LLDPE matrix and Al(OH)_3 can thus possibly be obtained.

Rheological Behavior

The rheological behavior of LLDPE/ Al(OH)_3 composites prepared under predetermined conditions with a Haake rotational mixer was investigated. Figure 2 shows the relationship between the compounding torque and the compounding time of the LLDPE/ Al(OH)_3 composites. The experimental results indicate that the balance torque in the compounding of either EVA or titanate surface-active agent with LLDPE/ Al(OH)_3 is lower than that in the blending of LLDPE and Al(OH)_3 . As the balance torque is in direct proportion to the viscosity of the material, it is obvious that the viscosity and processing property of LLDPE/ Al(OH)_3 composite improves by addition of either EVA or the titanate surface-active agent to it.^{15,16}

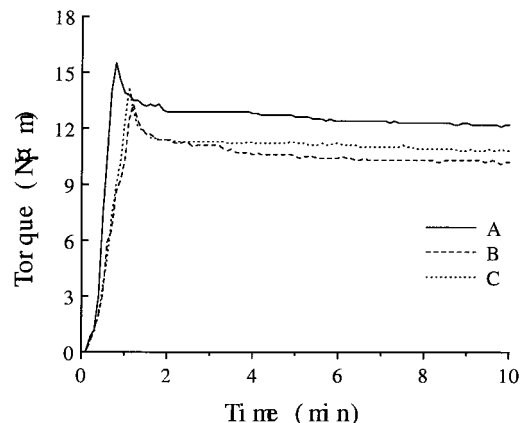


Figure 2 The rheological behavior of LLDPE/ Al(OH)_3 composites: (A) LLDPE/ Al(OH)_3 (100/140); (B) LLDPE/ Al(OH)_3 /EVA (100/140/40); (C) LLDPE/ Al(OH)_3 / Al(OH)_3 was treated with 1.5 wt % titanate.

Figure 3 presents the influence of DCP content on the torque of the composites. The possibility of homopolymerization of vinyl triethoxy silane and crosslinking reaction was excluded because of a low concentration of silane and DCP used.^{17,18} It is found that the more DCP used, the higher the balance torque, indicating that the extent of silane grafting onto LLDPE increases with DCP concentration. To achieve good processing behavior of the composite, the degree of silane grafting and DCP concentration should be controlled within a proper level.

Mechanical Properties

Figure 4(A) represents the effects of titanate surface-active agent content on mechanical perfor-

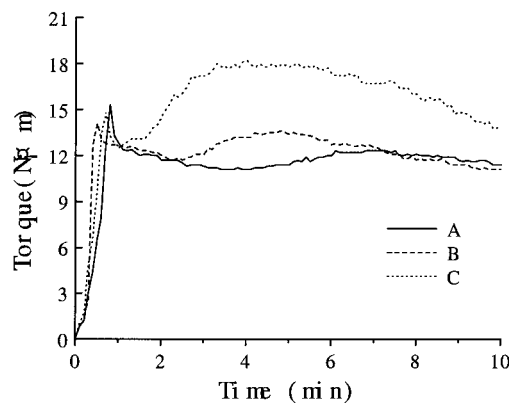


Figure 3 The rheological behavior of LLDPE/ Al(OH)_3 /EVA/silane (100/140/40/2) composites containing DCP; Al(OH)_3 was treated with 1.5 wt % titanate before mixing. (A) DCP 0 phr; (B) DCP 0.05 phr; (C) DCP 0.15 phr.

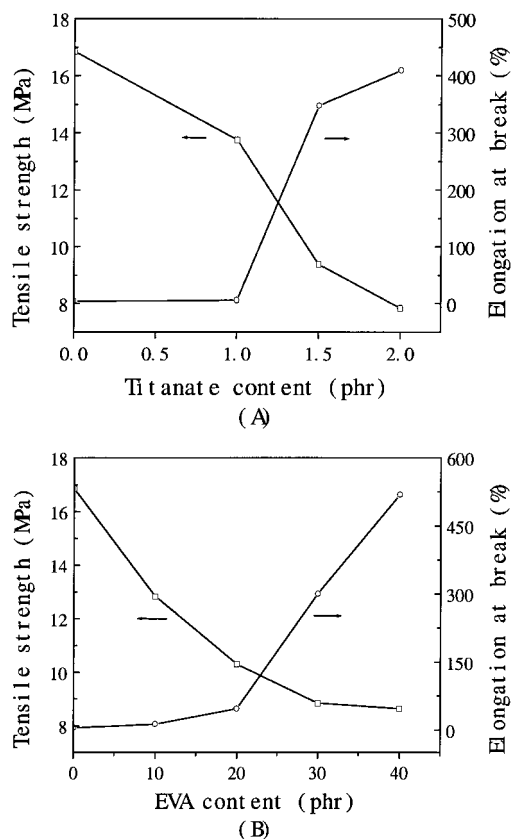


Figure 4 Influence of titanate and EVA content on mechanical properties of LLDPE/Al(OH)₃ (100/140) composites: (A) titanate; (B) EVA.

mance of the composite. Elongation at break and tensile strength of neat LLDPE are 534.8% and 27.6 MPa, respectively. Elongation at break of LLDPE filled with 140 phr Al(OH)₃ is very poor compared with that of the LLDPE, as seen from Figure 4(A). When titanate is used as a surface-active agent for Al(OH)₃, elongation at break of the composite changes little with titanate content

below 1.5 phr, and a further increase of titanate results in a sharp increase of elongation at break, whereas the yield tensile strength decreases consistently. Monolayer coverage may be reached with titanate compound at around 1.5 phr, which accounts for the sharp change of elongation, whereas a softening effect of titanate is probably ascribed to the slow decrease in tensile strength of the composite.⁵⁻⁷

Figure 4(B) shows the effects of EVA concentration on mechanical properties of LLDPE/Al(OH)₃ composites. It is found that EVA has the same effects as titanate on the mechanical performance of the composites. In LLDPE/Al(OH)₃ composite, EVA has physical interaction with both Al(OH)₃ filler and LLDPE matrix. EVA encapsulates Al(OH)₃ owing to its excellent processing property. The polyethylene segments in EVA is compatible with the LLDPE matrix. Thus, a strong interface interaction is obtained in the LLDPE/Al(OH)₃ composites.

The results indicate that interface properties have been changed between LLDPE matrix and Al(OH)₃ when surface-active agent or EVA is used, leading to the change of mechanical properties.

The effect of DCP concentration on mechanical properties of LLDPE/Al(OH)₃ composites was also studied. Silane was first grafted onto LLDPE, mixed with Al(OH)₃ and EVA, and then crosslinked in hot water. The tensile strength and elongation at break and gel fraction of the composite reach an ideal value when DCP concentration is about 0.15 phr, as seen in Table I. The addition of excessive DCP would result in deterioration of ductile properties owing to the formation of overmuch silane crosslinking structure, which restrains the movement and elongation of the polymer chains. Silane crosslinking and interface modification can improve mechanical proper-

Table I Influence of DCP Content on Mechanical Properties of LLDPE/Al(OH)₃/EVA/silane (100/140/40/2) [Al(OH)₃ was treated with 1.5 wt % titanate before mixing]

DCP (phr) ^a	Gel Fraction (%)	Tensile Strength (MPa)	Elongation at Break (%)
0	11.4	8.7	272.9
0.05	19.8	9.8	198.6
0.1	36.7	10.8	130.4
0.15	60.1	11.9	96.2
0.2	71.1	12.3	68.7

^a phr, part of reagent per hundred parts of LLDPE.

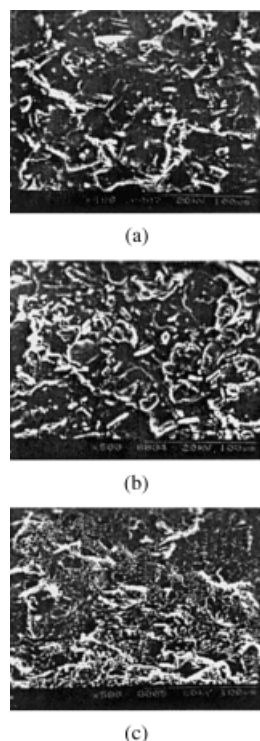


Figure 5 Scanning electronic micrographs of fractured surfaces of LLDPE/Al(OH)₃ composites in liquid nitrogen: (a) LLDPE/Al(OH)₃ (100/140); (b) LLDPE/Al(OH)₃/(100/140), Al(OH)₃ was treated with 1.5% titanate before mixing; (c) LLDPE/Al(OH)₃/EVA (100/140/40).

ties of LLDPE/Al(OH)₃ composites synergistically.

Morphologies of the Composites

The phase morphology of polymer composites plays a very crucial role in determining their mechanical and rheological properties. The effects of titanate coating, addition of EVA, and silane crosslinking structure on stress dissipation and crack initiation and propagation of the composites were studied by SEM (as shown in Fig. 5).

Agglomeration of the filler is clearly observed in Figure 5(A,C). Al(OH)₃ filler is poorly dispersed and many aggregation particles can be found because of its incompatibility with LLDPE matrix. It is found that EVA has no effect on the dispersion of Al(OH)₃, but it extensively encapsulates the fillers; thus, a core-shell structure with fillers as a core and EVA as a shell is formed in the composite. From Figure 5(B), Al(OH)₃ particles are well dispersed in the polymer matrix; this can

be explained as follows. Titanate reduces the surface energy of Al(OH)₃ and weakens the interaction of Al(OH)₃ particles; thus, finer dispersion of Al(OH)₃ particles in LLDPE matrix is obtained.

Figure 6 shows the SEM micrographs of the composites' surface that is parallel to the direction of the tensile load. It is known that fillers in polymer composites act as stress concentrators leading to the initiation of failure, and hence, strongly affect the mechanical properties of the composites.

The elongation at break of LLDPE/Al(OH)₃ (100/140) composite is close to zero, suggesting a material with extremely poor mechanical performance. No visible crack propagation around the Al(OH)₃ particle was found. The concentration of stress is very high in the vicinity of the Al(OH)₃ particle where the matrix deformation is highly restricted; obviously, poor interfacial adhesion is ascribed to this observation. However, crack propagation can be clearly seen when titanate coating or EVA is introduced to the LLDPE/Al(OH)₃ composite. This demonstrates that good interfacial adhesion between the filler and the matrix is formed; then, the matrix is sensitive to stress concentration, leading to initiation of failure and crack propagation in the matrix region, as observed in Figure 6(B,C). Thus, elongation at break of the composite improves markedly. The addition of silane and DCP improve tensile

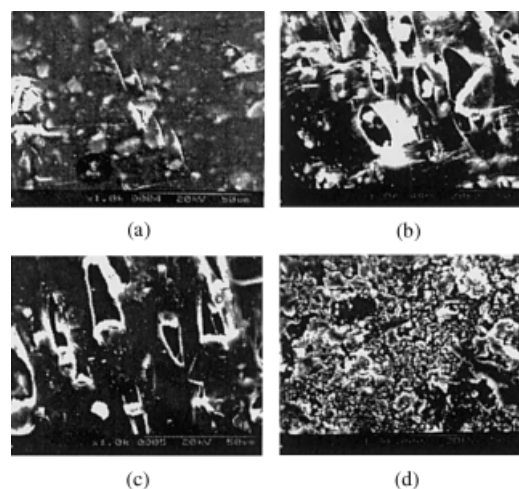


Figure 6 Effects of drawing on SEM morphology of LLDPE/Al(OH)₃ composites in tensile testing: (a) LLDPE/Al(OH)₃ (100/140); (b) LLDPE/Al(OH)₃ (100/140), Al(OH)₃ was treated with 1.5% titanate before mixing; (c) LLDPE/Al(OH)₃/EVA (100/140/40); (d) LLDPE/Al(OH)₃/EVA/silane/DCP (100/140/40/2/0.15), Al(OH)₃ was pretreated with 1.5 wt % titanate.

strength because of the crosslinking structure formed in the composite; therefore, crack propagation is somewhat restrained, as shown in Figure 6(D).

CONCLUSIONS

The tensile strength of the LLDPE/Al(OH)₃ composite decreased markedly on addition of titanate and EVA copolymer. Addition of silane and DCP improve the tensile strength of the composite because of the crosslinking structure introduced. Interface modification and silane crosslinking method have a synergistic effect in improving mechanical performance of the composite.

LLDPE highly loaded with Al(OH)₃, which is treated with titanate surface-active agent, results in superior rheological behavior and strong interfacial interaction. EVA extensively encapsulates Al(OH)₃ filler and a core-shell structure with the filler as a core and EVA as a shell in the composite is formed during mixing. This results in improving its processing ability and mechanical properties of the composite.

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