

MORPHOLOGY AND PROPERTIES OF LINEAR LOW-DENSITY POLYETHYLENE HIGHLY LOADED WITH ALUMINUM HYDROXIDE

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Abstract An experimental study was carried out to investigate the effects of isopropoxy tri(dioctyl pyrophosphoryl) titanate coupling agent on the mechanical performance, rheological property and microstructures of polyethylene highly loaded with aluminum hydroxide ($\text{Al}(\text{OH})_3$) composite. It was found that the addition of coupling agent results in reduced tensile strength and increased percentage elongation of the filled systems. Silane crosslinkable polyethylene substituting for polyethylene as matrix improves the tensile strength of the composite, while the percentage elongation of the composite still remains at a desired level. Melt viscosity of the composite will be improved by addition of titanate coupling agent. Microstructures of the composites were also studied by means of the scanning electron microscopy (SEM) technique. SEM micrographs reveal that finer dispersion of $\text{Al}(\text{OH})_3$ will be obtained upon treatment of titanate and a transition from brittle to tough fracture takes place before and after silane crosslinking structure is introduced into polyethylene highly filled with $\text{Al}(\text{OH})_3$ composite.

Key words Polyethylene, Aluminum hydroxide, Organic titanate, Silane, Crosslink

INTRODUCTION

Polyethylene (PE) has long been known as an excellent dielectric for use as an insulation material in the electric wire and cable industry. It has the advantages of excellent electric properties, easy processing and adequate mechanical properties. However, it is a combustible material and its limiting oxygen index is about 17.4, which limits its application to some extent. Halogen-based flame retardants have been used to produce flame retardant PE for many years, but they emit heavy smoke and hazardous gases during combustion. $\text{Al}(\text{OH})_3$ is one of the non-halogen fillers, which improves the fire resistance of polymers and diminishes the smoke evolved from burning. In recent years, it has been, therefore, considered as an attractive alternative to halogen-based flame retardants and has become the major trend in the development of flame retardant polyolefins^[1–3]. However, $\text{Al}(\text{OH})_3$ must be present at high loadings for PE in order to confer adequate fire retardancy^[4, 5]. The high loading of $\text{Al}(\text{OH})_3$ hydroxide in PE results in significant deterioration of mechanical and processing properties. This is possibly due to insufficient interactions between PE with non-polar, hydrophobic molecular chains and $\text{Al}(\text{OH})_3$ with polar and hydrophilic groups. It is well known that the interfacial properties between inorganic compounds and polymer matrix play an important role in determining the overall properties of the filled composite. Ethylene vinyl acetate copolymer (EVA) has been suggested as an effective approach for improving the mechanical properties of $\text{Al}(\text{OH})_3$ filled PE^[5]. $\text{Al}(\text{OH})_3$ treated with fatty acid and their derivatives is also an effective approach for improving the mechanical properties of polypropylene (PP) loaded with the filler. Titanate is also reported to effect a marked improvement of mechanical properties for CaCO_3 , talc, and fiber glass filled high-density PE and PP^[6–9].

Another drawback of PE used in the electric cable industry is its relatively low upper usable temperature. By crosslinking the material, the upper usable temperature is increased^[10–12]. The most common way is through the

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use of peroxide crosslinking agents added to the PE. The peroxides provide a source of free radicals when heated above their decomposition temperatures. These free radicals are capable of extracting hydrogen atoms from the PE backbone, thus transferring the free radical sites to the PE. By so doing, two polyethylene chains can crosslink together. A second method of crosslinking PE is through the use of irradiation. In this case, the free radical formed on the PE backbone is the result of electron beam irradiation. The third way of crosslinking PE is through the grafting of a silane onto the PE and, subsequently, through the condensation reaction of the silane grafts by moisture. The method of making crosslinkable PE through silane grafting has attracted much attention in recent years because of its various advantages, such as easy processing, low cost and capital investment.

Generally, the bigger the particle size of $\text{Al}(\text{OH})_3$ inorganic compounds used, the lower is the cost. In this paper, $\text{Al}(\text{OH})_3$ of average particle size 400 mesh is used to modify linear low-density PE in order to reduce the filler cost. Isopropoxy tri(dioctyl pyrophosphoryl) titanate which is used as coupling agent for PE highly filled with $\text{Al}(\text{OH})_3$ has not been reported, and the effects of the titanate on the mechanical properties and microstructure of PE loaded with 140 phr $\text{Al}(\text{OH})_3$ were investigated here. Silane crosslinked PE is used to replace PE matrix in the composite in order to improve the matrix's upper use temperature and the mechanical performance. The relationship between mechanical properties and microstructure of the composites is also discussed.

EXPERIMENTAL

Materials

Polyethylene used here was linear low-density polyethylene (LLDPE) with a melt index (GB 3682-83) of 2 g/10 min and density of 0.918 g/cm^3 , obtained from Saudi Arabia. $\text{Al}(\text{OH})_3$ powder having a mean particle size of 400 mesh was provided by Fengyang Powder Corporation, China. Vinyl triethoxy silane (A151) was received from Union Carbide. Isopropoxy tri(dioctyl pyrophosphoryl) titanate was obtained from Jiangnan Reagents Corporation, Changzhou, China.

Sample Preparation

Materials were mixed in a Haake internal mixer at a temperature of 170°C and a rotor speed of 80 rpm. Dicumyl peroxide (DCP) as a free radical initiator was mixed and compounded with the silane and PE are compounded in the internal mixer under the same conditions. $\text{Al}(\text{OH})_3$ pretreated with some reagents was then added and mixed till torque stabilization. The mixture was then crosslinked through hydrolysis of the ethoxysilane group with water, followed by condensation of the formed hydroxyl groups. All the mixtures were then transferred to a pre-heated compression mould and hot pressed at 180°C under pressure of 20 MPa to the form of sheets 1.0 mm in thickness, then punched to dumbbell shape. The dumbbell shape samples were subsequently crosslinked in hot water before the tensile test.

$\text{Al}(\text{OH})_3$ treated with titanate was prepared by using a mixing method. Titanate dissolved in toluene was added to aluminum hydroxide and mixed, then dried to a constant weight.

Characterization

Flammability behavior of the sample was characterized using the limiting oxygen index (LOI) according to ASTM D2863. The LOI instrument (HC-2) was made by Jiangning Analytic Instrument Corporation, Jiangsu.

Tensile properties were measured on an Instron-4302 Tensile tester, according to Chinese standard GB/T 1040-92. Testing was done at a temperature of 25°C and a speed of 50 mm/min.

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

SEM Observation

The phase morphology of the composites was examined by scanning electron microscopy (Hitachi S520 SEM). Specimens were prepared by immersing test pieces in liquid nitrogen before breaking. Surfaces of the test pieces were coated with gold.

RESULTS AND DISCUSSION

Flammability of Al(OH)₃ Filled LLDPE

The dependence of LOI of Al(OH)₃ filled LLDPE samples on Al(OH)₃ concentration is shown in Fig. 1. Similar to those results reported previously^[13, 14], the LOI of Al(OH)₃ filled LLDPE sample is improved with the increase of filler concentration, while LOI of the neat LLDPE and LLDPE filled with 140 phr Al(OH)₃ are 17.1 and 28.9, respectively. It demonstrates that the LOI of LLDPE filled with 140 phr Al(OH)₃ can confer an adequate level of flame retardancy.

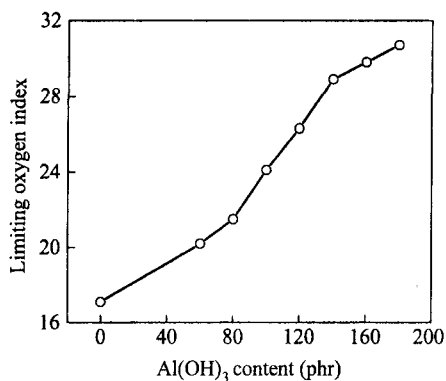


Fig. 1 Limiting oxygen index of polyethylene and polyethylene filled with various amount of Al(OH)₃ samples

Mechanical Properties

Figure 2 shows the dependence of tensile strength and elongation at break of LLDPE/Al(OH)₃ composite on the filler concentration. The tensile strength of LLDPE/Al(OH)₃ composite decreases sharply when Al(OH)₃ concentration is over 60 phr, due mainly to stress concentration and poor stress transfer in the composite. It is also noted that tensile strength changes slightly with further increase of Al(OH)₃ concentration, indicating the effect of reinforcement of the filler in LLDPE/Al(OH)₃ composite. Figure 2(b) shows that the elongation at break of LLDPE/Al(OH)₃ composite is rather poor when the filler concentration exceeds 60 phr, owing to the poor interface adhesion between the filler and the matrix.

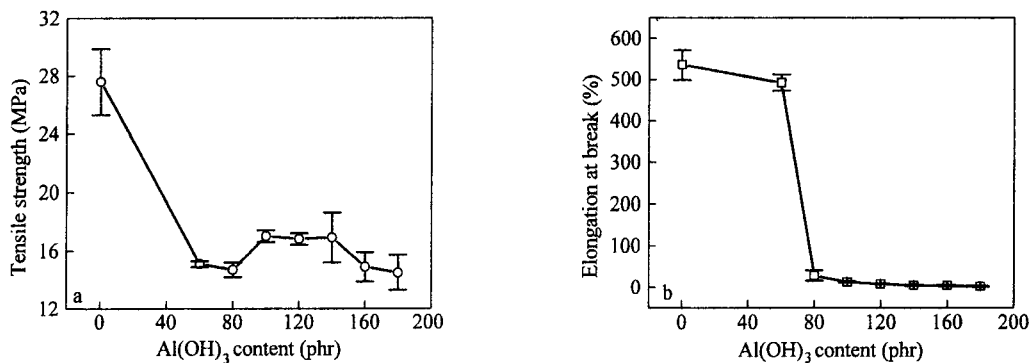


Fig. 2 Tensile strength and elongation at break of LLDPE and LLDPE filled with various amounts of aluminum hydroxide

Interfacial property plays a crucial role in determining the mechanical properties of polymer filled with inorganic compound. Phase dispersion and interfacial adhesion between polymer and filler particles are of importance for filled polymers^[15]. Titanate compound is a good coupling agent^[16–19] for aluminum hydroxide filled LLDPE. In principle, titanate is chemically bonded to the filler through the reaction between the

hydrophilic group in titanate and the hydroxyl group in $\text{Al}(\text{OH})_3$, which improves the interfacial adhesion between PE matrix and $\text{Al}(\text{OH})_3$ remarkably. In addition, the hydrophobic groups in titanate are exposed on the outside surface of $\text{Al}(\text{OH})_3$, thus reducing the surface energy of the inorganic compound, which gives better dispersion of $\text{Al}(\text{OH})_3$ particles and good compatibility between $\text{Al}(\text{OH})_3$ filler and LLDPE matrix.

Figure 3 represents the effects of titanate on the mechanical performance of LLDPE/ $\text{Al}(\text{OH})_3$ composite. Elongation at break of LLDPE and LLDPE filled with 140 phr $\text{Al}(\text{OH})_3$ are found to be 534.8% and 2.1%, respectively, as shown in Fig. 2(b). A significant increase in elongation at break is observed for LLDPE filled with 140 phr $\text{Al}(\text{OH})_3$ when the titanate concentration is 1.5% by weight (Fig.3b). It is also noted that the tensile strength of LLDPE filled with 140 phr $\text{Al}(\text{OH})_3$ decreases slowly with the increase of titanate concentration used in the composite (Fig. 3a). A better interface resulting from the interactions between $\text{Al}(\text{OH})_3$ filler and LLDPE matrix may account for the rapid increase in elongation at break. But a part of titanate diffusing into LLDPE matrix and acting as chain extender can lead to the slow decrease in tensile strength of the composite.

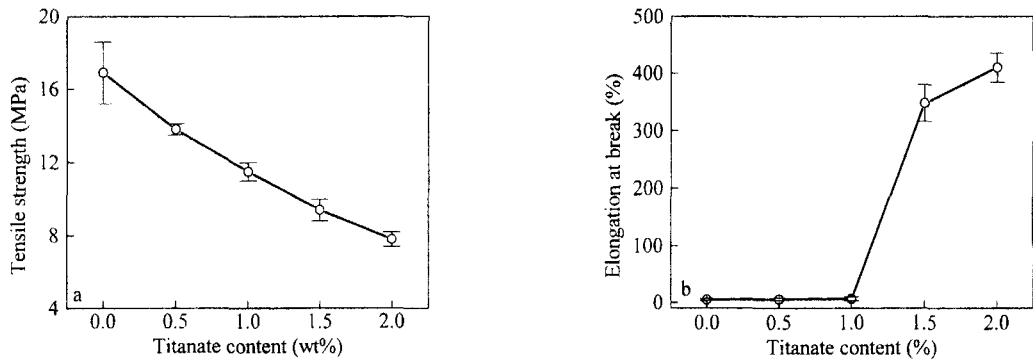


Fig. 3 Influence of titanate used to pre-treat $\text{Al}(\text{OH})_3$ on mechanical properties of LLDPE/ $\text{Al}(\text{OH})_3$ (100/140) composite

Poor interfacial adhesion at the filler-polymer interface is the major problem in particulate filled composites, which results in poor stress transfer. Stress concentrations will be created around the particles and reduce the composite strength. From the results listed in Table 1, when titanate in the composites exceeds 1.5%, LLDPE/ $\text{Al}(\text{OH})_3$ (100/140) and LLDPE/silane/DCP/ $\text{Al}(\text{OH})_3$ composites exhibit a significant increase in notched Izod impact strength, suggesting a transition from brittle to ductile material occurs.

Table 1. Influence of titanate and silane crosslinking on notched Izod impact strength of LLDPE/ $\text{Al}(\text{OH})_3$ (100/140) composite

Composition	Notched Izod Impact Strength (kJ/m ²)
LLDPE/ $\text{Al}(\text{OH})_3$ (100/140)	3.2 (±0.3)
LLDPE/ $\text{Al}(\text{OH})_3$ /titanate (100/140/0.5)	3.5 (±0.2)
LLDPE/ $\text{Al}(\text{OH})_3$ /titanate (100/140/1)	3.7 (±0.5)
LLDPE/ $\text{Al}(\text{OH})_3$ /titanate (100/140/1.5)	15.3 (±0.6)
LLDPE/silane/DCP/ $\text{Al}(\text{OH})_3$ /titanate (100/2/0.15/140/1.5)	11.3 (±0.6)

The dependence of DCP concentration on the mechanical properties of LLDPE/ $\text{Al}(\text{OH})_3$ /silane (100/140/2) composite was also investigated. Silane was first grafted onto polyethylene, and then was compounded with $\text{Al}(\text{OH})_3$ which was pre-treated by titanate in a Haake internal mixer. The samples taken out from the mixer were then hot pressed into the form of sheets and were crosslinked in hot water. The tensile strength, elongation at break and gel fraction of the composites are summarized in Fig. 4. It can be clearly seen that the tensile strength of 140 phr $\text{Al}(\text{OH})_3$ filled silane crosslinked PE composite increases consistently with the increase of DCP content, while elongation at break of the composite decreases to certain extent. It is also noted that an ideal level of gel fraction will be obtained when DCP concentration attains 0.15 phr, which is essential for improving the

upper-use temperature of the composite. The addition of silane and DCP will improve the tensile strength of composite due to the crosslinking structure formed in the composite. These results also reveal that the addition of excessive DCP (over 0.15 phr) would result in the deterioration of tensile properties owing to the formation of overmuch silane crosslinking structure, which restrains the movement and elongation of the polymer chains.

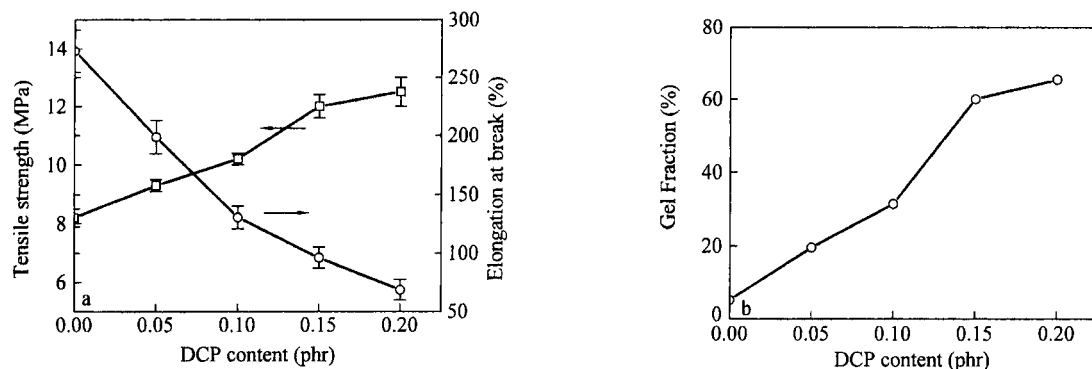


Fig. 4 Influence of DCP content on gel fraction and mechanical properties of LLDPE/Al(OH)₃/silane (100/140/2) composite, Al(OH)₃ was treated with 1.5 wt % titanate before mixing

Rheological Behavior

The rheological behavior of modified LLDPE/Al(OH)₃ composites prepared under pre-determined conditions in a Haake rotational mixer was investigated. Figure 5 shows the relationship between the compounding torque and compounding time of LLDPE loaded with 140 phr Al(OH)₃. The experimental results show that the balance torque in the compounding of LLDPE with Al(OH)₃ decreases with increasing titanate concentration. As the balance torque is in direct proportion to the viscosity of the material^[19, 20], it is obvious that the viscosity and processing property of LLDPE/Al(OH)₃ composite are improved by the addition of titanate, due to a monolayer of titanate molecules presenting on the filler surface. It can be clearly seen that the titanate additions are effective in reducing the surface energy of the filler particles and particle-particle interaction effects in LLDPE/Al(OH)₃ composite.

Figure 6 presents the influence of DCP content on torque of 140 phr Al(OH)₃ filled composites. The possibility of homopolymerization of vinyl triethoxy silane and crosslinking reaction can be excluded because of low concentration of silane and DCP used in the system^[21]. It was found that the more DCP used, the higher the balance torque, indicating that the extent of silane grafting onto PE increases with increasing DCP concentration. In order to achieve good processing behavior of the composite, degree of silane grafting and DCP concentration should be controlled within a proper level.

Morphologies of the Composites

The phase morphology of polymer composites plays very crucial role in determining their mechanical and rheological properties. The effects of titanate and silane crosslinking structure on stress dissipation, crack initiation and propagation of Al(OH)₃ filled LLDPE composites were studied using SEM (as shown in Fig. 7). As clearly seen in Fig. 7(a), Al(OH)₃ particles are poorly dispersed and many aggregation particles can be found due to incompatibility with the LLDPE matrix. From Fig. 7(b), Al(OH)₃ particles are well dispersed in the polymer matrix, due primarily to the reduction of the surface energy of aluminum hydroxide on the addition of titanate which can weaken the interaction of aluminum hydroxide particles and improve the compatibility of the filler particles and LLDPE matrix. Figure 7(c) shows a much more rough fracture surface when LLDPE matrix is crosslinked through silane. In comparison with Fig. 7(a) and 7(c), it is easy to conclude that a transition from brittle to tough fracture takes place before and after silane crosslinking structure is introduced into the composite.

The results above indicate that surface treatment of Al(OH)₃ particles by titanate coupling agent helps the filler to reduce its surface energy and disperse well in LLDPE matrix. This favors the production of composite with uniform microstructure, improved flexibility and an enhanced elongation at break. It is easy to conclude that

interfacial properties have been changed between LLDPE matrix and $\text{Al}(\text{OH})_3$ when coupling agent and silane are used, leading to the change of mechanical and rheological properties of LLDPE highly filled with $\text{Al}(\text{OH})_3$.

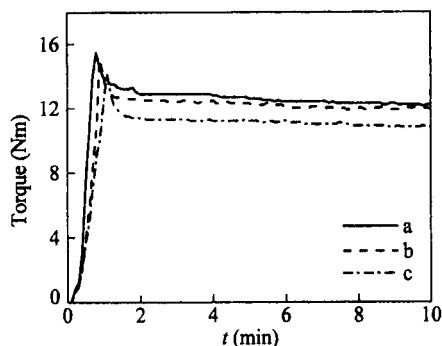


Fig. 5 The rheological behavior of LLDPE/ $\text{Al}(\text{OH})_3$ composites

- a) LLDPE/ $\text{Al}(\text{OH})_3$ (100/140)
- b) LLDPE/ $\text{Al}(\text{OH})_3$ (100/140), $\text{Al}(\text{OH})_3$ was treated with 0.5 wt% titanate
- c) LLDPE/ $\text{Al}(\text{OH})_3$ (100/140), $\text{Al}(\text{OH})_3$ was treated with 1.5 wt% titanate

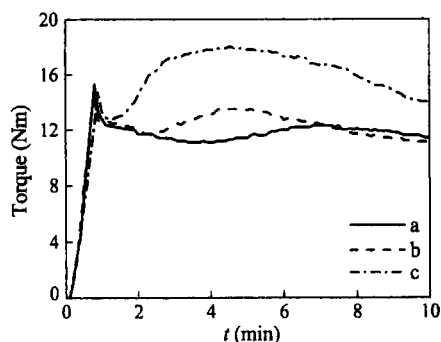


Fig. 6 The rheological behavior of LLDPE/ $\text{Al}(\text{OH})_3$ /silane (100/140/2) composites containing DCP, $\text{Al}(\text{OH})_3$ was treated with 1.5 wt% titanate before mixing
(a) DCP 0 phr; (b) DCP 0.05 phr; (c) DCP 0.15 phr

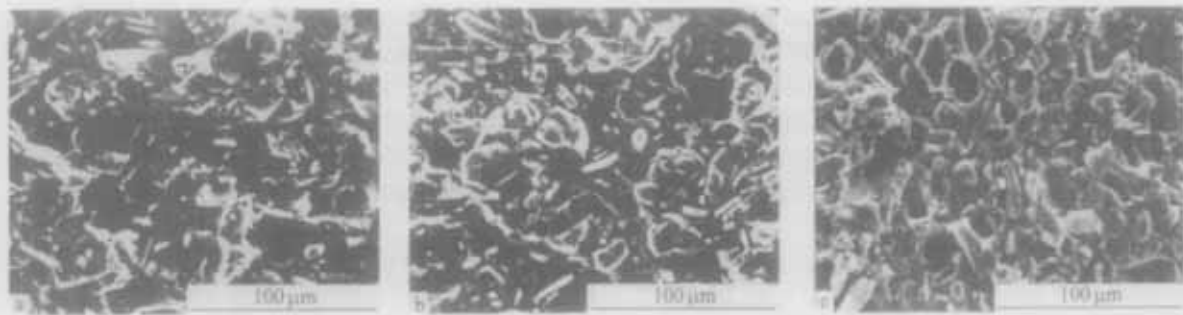


Fig. 7 Scanning electronic micrographs of fractured surfaces of LLDPE/ $\text{Al}(\text{OH})_3$ composites in liquid nitrogen:

- a) LLDPE/ $\text{Al}(\text{OH})_3$ (100/140)
- b) LLDPE/ $\text{Al}(\text{OH})_3$ (100/140), $\text{Al}(\text{OH})_3$ was treated with 1.5% titanate before mixing
- c) LLDPE/silane/DCP/ $\text{Al}(\text{OH})_3$ (100/2/0.15/140), $\text{Al}(\text{OH})_3$ was pre-treated with 1.5 wt% titanate

CONCLUSIONS

Elongation at break of LLDPE/ $\text{Al}(\text{OH})_3$ composite increases significantly with the addition of titanate, while the tensile strength of LLDPE/ $\text{Al}(\text{OH})_3$ composite decreases to some extent. Silane crosslinked PE substituting for PE matrix improves the tensile strength of the composite. Titanate and silane crosslinked structure have a synergistic effect in improving the mechanical performance of the composite.

LLDPE highly loaded with $\text{Al}(\text{OH})_3$ pre-treated with titanate results in superior rheological behavior. SEM micrographs reveal finer dispersion and decreased agglomeration of $\text{Al}(\text{OH})_3$ particles upon treatment of titanate, and a transition from brittle to tough fracture takes place after titanate coupling agent is introduced into the composite.

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