Performance Evaluation of Synthesized Acrylic Acid Grafted Polyethylene in Aluminum Hydroxide Highly Filled Polyethylene Composites

Genlin Wang, Pingkai Jiang, Zikang Zhu, Jie Yin

School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai, 200240, China

ABSTRACT: A polymeric agent acrylic acid grafted polyethylene (AAgPE) was synthesized and used as a coupling agent in aluminum hydroxide [$Al(OH)_3$] highly filled linear low-density polyethylene (LLDPE) composite. It is found that AAgPE improves the interfacial adhesion between the filler and the polyethylene matrix, which results in good mechanical properties of the composite. Silicon oil is an effective additive for improving the impact strength, the elongation at break, and the rheological property of the filled composite, but it decreases the tensile strength remarkably. The combination of AAgPE and silicon oil can lead to good performance of the composite. Flammability properties and fracture surface morphologies of the composites through scanning electron microscopy were investigated. The relationship between mechanical properties and microstructure of the composites was discussed.© 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2544–2549, 2002

Key words: polyethylene; aluminum hydroxide; acrylic acid grafted polyethylene; silicon oil

INTRODUCTION

Polyethylene (PE) is a combustible material and its limiting oxygen index is about 17.4, which hinders its applications to some extent. Halogen-based flame retardants were used to produce flame-retardant PE for many years, but they give off heavy smoke and hazardous gases during combustion. In recent years, non-halogen flame retardants such as $Al(OH)_3$ and $Mg(OH)_2$ have therefore been considered an attractive alternative to halogen-based flame retardants and have become a major trend in the development of flame-retardant polyethylene.

Aluminum hydroxide was proven to be an effective flame retardant for polyethylene when used at high concentrations (usually >50% by weight).[1] As is common with most other inorganic fillers, the high loading of aluminum hydroxide in polyethylene results in significant deterioration of mechanical properties such as impact strength and elongation at break, which are essential for meeting the needs in many fields of application.

The interfacial behavior between inorganic compounds and polymer matrices was recognized as a key factor influencing mechanical properties of composites.[2,3] Unfortunately, the high loading of $Al(OH)_3$ in PE leads to the reduction of impact strength and elongation at break, due primarily to the poor interfacial adhesion between the two components. Coupling agents act to provide a means of transferring stress from the polymer matrix to the filler particles, which ultimately result in better mechanical properties. Fillers treated with coupling agents such as titanate, fatty acids, and their derivatives were suggested as an effective approach for improvement of interfacial adhesion of polymer composites.[4,5] Functional polymeric agents have the ability to strongly interact with both filler and polymer matrix, inducing a significant improvement in mechanical properties.[6,7] In addition, it is quite necessary to understand the modifying mechanisms of particulate-filled PE to design and develop an advanced linear low-density polyethylene (LLDPE)/$Al(OH)_3$ composite with good mechanical performance and processibility.

In the present study, acrylic acid grafted polyethylene (AAgPE) was synthesized and used as a coupling agent in $Al(OH)_3$-filled PE. The effects of AAgPE and silicon oil on the mechanical, rheological properties and microstructure of polyethylene loaded with 140 phr (part of reagent per hundred parts of LLDPE) $Al(OH)_3$ were studied. The correlation between mechanical properties and microstructure of the composites was also discussed.

EXPERIMENTAL

Materials

Polyethylene used here was LLDPE (Saudi Arabian Basic Industries (SABIC)) with a melt index (GB 3682-

83) of 2 g/10 min and a density of 0.918 g/cm^3 obtained from Saudi Arabia. Al(OH)$_3$ powder of mean particle size of 1.2 μm and specific surface of 6 m^2/g was provided by Sou Le Enterprise Co., Ltd., Hong Kong. Acrylic acid (AA) used was supplied by Yonghua Chemical Reagent Co. (China). 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. Silicon oil (201, degree of polymerization of 35°) was received from Shanghai Resin Corp., China.

Sample preparation

A certain amount of PE powder, AA, and DCP was added and mixed in a Rheocord Haake internal mixer at 170°C and 60 rpm. The residence time was 8 min.

   PE and other raw materials were compounded in a Haake internal mixer under the same conditions presented above. Aluminum hydroxide was pretreated with silicon oil before mixing.

Characterization

Grafting degree

First, the melt grafting of AA onto LLDPE was performed in a Haake internal mixer. Second, AA-grafted polyethylene 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. Finally, the sheets were extracted with distilled water in a Soxhlet extractor for 3 days to exclude nonreacted AA and homopolymer (PAA) and then dried in a vacuum oven for 24 h. The grafting degree and grafting efficiency were determined by the following equation:

$$\text{Grafting degree} = (W_t - W_0)/W_0 \times 100\%$$

where W_t represents the weight of the grafted PE sample after elimination of PAA, and W_0 represents the weight of the original PE sample.

Flammability properties

Flammability behavior was characterized by using the limiting oxygen index (LOI) according to ASTM D2863. The LOI was defined as the minimum mole percentage of oxygen in a mixture of oxygen and nitrogen necessary to barely support flaming combustion of a material initially at room temperature under the conditions of the test method.
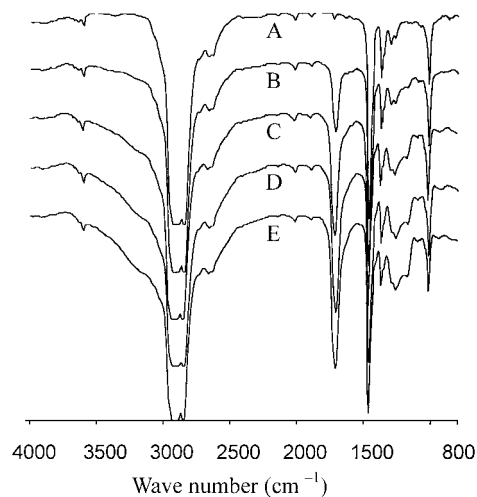

Figure 1 FTIR spectra of polyethylene samples that have reacted with acrylic acid (A) 0 phr acrylic acid; (B) 2 phr acrylic acid; (C) 4 phr acrylic acid; (D) 6 phr acrylic acid; (E) 8 phr acrylic acid.

Fourier transform infrared spectroscopy

First, the synthesized coupling agent AAgPE was pressed into films in 100-μm thicknesses. Next, the films were dipped in distilled water for 24 h to remove the nonreacted acrylic acid, and then, followed by a Soxhlet extraction with ethanol for 24 h to remove any adhering homopolymer (PAA). Finally, samples were dried in an oven under vacuum at 70°C for 24 h before test, using a Perkin–Elmer FTIR.

Mechanical properties

Tensile and elongation-at-break properties were measured on an Instron-4302 Tensile tester, according to Chinese standard GB/T 1040-92. Notched specimens of a thickness of 3 mm with a V-shape notch (the depth of the notch was 2.7 mm and the radius of the notch tip 0.25 mm) were tested in a RAYRAN impact tester at a hammer speed of 3.5 m/s and pendulum weight of 0.818 kg according to ASTM D256.

SEM microscopy

The phase morphology of the composites was examined using SEM (Hitachi S520). Some specimens were prepared by immersing test pieces in liquid nitrogen before breaking. Surfaces of the test pieces were coated with gold to avoid charging under the electron beam.

RESULTS AND DISCUSSION

FTIR study

Figure 1 shows FTIR spectra of PE before (spectrum A) and after (spectrum B–E) reaction with various
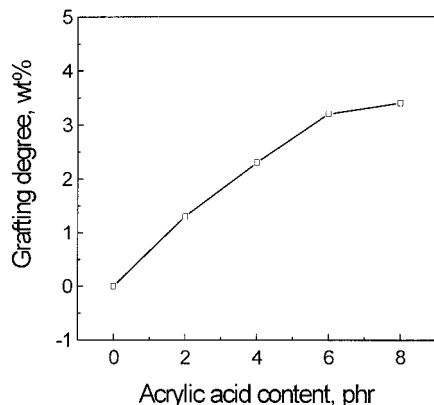
Figure 2 Effects of acrylic acid content on grafting degree when DCP remains 0.2 phr.

amounts of AA when the extent of DCP remains constant (0.2 phr). In comparison between spectrum A and other spectra (B–E), the AA grafting reactions are thus demonstrated to occur because the peaks at 1730 cm^{-1} are assigned to the functional group carbonyl. From the figure, it can also be clearly seen that the extent of AA grafting reaction in a Hakke internal mixer increases as the amounts of AA used increases. It still can be found that the intensity of the functional group carbonyl absorbance increases with the AA used and levels off when the content of AA reaches 6 phr. From Figure 2, it can be seen that the grafting degree increases with AA and levels off at 6 phr AA, and this is consistent with the results obtained from FTIR study.

Mechanical and rheological properties

Table I summarizes the effect of grafting degree of AAgPE on tensile strength and elongation at break as well as notched Izod impact strength of PE/Al(OH)$_3$/ AAgPE (90/140/10) composite. It is found that AAgPE improves the tensile strength and elongation at break as well as impact strength of the filled composite; this may be attributed to a better interface resulting from the addition of AAgPE in the filled composite. By increasing the grafting degree of AAgPE, the tensile strength of the composite has a slight increase, whereas the elongation at break and impact strength improve markedly, as can be observed from the table.

The effects of AAgPE and silicon oil on mechanical and rheological properties of PE/Al(OH)$_3$ composite are presented in Table II. As to the PE/Al(OH)$_3$ composite, when the filler loading reaches 140 phr, elongation at break and impact strength were 2.6% and 3.2 KJ/m^2, respectively, demonstrating that high loading of aluminum hydroxide in PE leads to very poor mechanical properties compared with that of pure PE. This is obviously due to the presence of fillers, which

act as defects and stress raiser in the composite because of weak interface adhesion between the filler and the PE matrix. Generally, the way to overcome the defect is to enhance the interfacial adhesion or to form an interfacial layer around the filler particles.[8] In the study, adding AAgPE copolymer the PE/Al(OH)$_3$ composite can introduce an interfacial layer between the aluminum hydroxide filler and the PE matrix. It is based on the following mechanisms. The carboxyl acid groups in AAgPE can react with aluminum hydroxide, causing AAgPE to chemically bond on the filler surface. On the other hand, the PE segments in AAgPE are compatible with PE. A new interfacial layer is thus formed in the PE/Al(OH)$_3$ composite. From the results listed in the table, the PE/Al(OH)$_3$ (100/140) composite exhibits a moderate increase in tensile strength, elongation at break, and impact strength with the addition of $\sim$ 11 phr AAgPE, compared with that without AAgPE. Good mechanical performance of the composite obtained suggests the occurrence of good interfacial adhesion due to the presence of AAgPE-coupling agent.

Silicon oil here was used to modify the PE/Al(OH)$_3$ (100/140) composite and its effects on mechanical properties are presented in the table also. It can be clearly seen that a significant improvement in impact strength and elongation at break was observed when silicon oil was added at $\sim$ 8.9 phr. The tensile strength of the composite, however, is decreased drastically because of the softening effect of silicon oil.[9,10] The increase in elongation at break and impact strength suggest better stress transfer across the interface, which is ascribed to silicon oil. Good dispersion of the filler particles and PE matrix is thus obtained, due primarily to reducing the surface energy of aluminum hydroxide and weakening the interaction of aluminum hydroxide particles on addition of silicon oil. With the addition of AAgPE and silicon oil, it is found that finer dispersion of the filler and good interfacial adhesion are available, and not only the tensile strength but also the impact strength of PE highly loaded with 140 phr aluminum hydroxide can meet the desired levels of mechanical performance, as shown in the table.

As the balance torque is in direct proportion to the viscosity of the material,[11,12] the rheological behavior

TABLE I
Effects of Grafting Degree of AAgPE on Mechanical Properties of PE/Al(OH)$_3$/AAgPE (90/140/10) Composite

Grafting degree of AAgPE (%)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (KJ/m^2)
0	14.5	2.6	3.2
1.3	16.2	7.6	3.5
2.3	17.0	10.1	4.1
3.2	17.4	11.6	5.8

TABLE II
Mechanical Properties of PE/Al(OH)₃ Composites

Composition (wt/wt)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (KJ/m^2)	Balance torque (N m)
PE	23.5	820.1	Nonbreaking	9.9
PE/Al(OH)₃ (100/140)	14.5	2.6	3.2	20.6
PE/Al(OH)₃/AAgPE (90/140/10)	17.4	11.6	5.8	17.3
PE/Al(OH)₃/silicon oil (90/140/8)	6.1	422.4	19.5	10.5
PE/Al(OH)₃/AAgPE/silicon oil (90/140/10/8)	12.2	283.3	17.2	12.1

Note. AAgPE used here was 3.2% (grafting degree).

of PE/Al(OH)₃ composites prepared under predetermined conditions with a Haake internal mixer was investigated. The values of compounding balance torque of PE/Al(OH)₃ composites are listed in Table II. According to the values of balance torque, PE mixed with 140 phr Al(OH)₃ exhibits higher balance torque in comparison with that of PE. The experimental results also indicate that the balance torque in the compounding of a small amount of silicon oil with PE/Al(OH)₃ is much lower than that in the blending of PE and Al(OH)₃ and demonstrate that silicon oil is an effective additive for improving process property of PE highly filled with Al(OH)₃. In comparison with silicon oil, AAgPE has less effect on the balance torque of the filled composite.

Flammability properties

The dependence of LOI of PE/Al(OH)₃ on the Al(OH)₃ filler concentration is shown in Figure 3. Similar to those results presented by other authors previously,[1,13] the LOI of the composites improves significantly with the increase of the filler concentration. It demonstrates that the LOI of PE filled with >140 phr Al(OH)₃ can confer adequate flame retardancy, as shown in Figure 3.

The LOI and compositions of PE/Al(OH)₃ composites are summarized in Table III. It is found that the
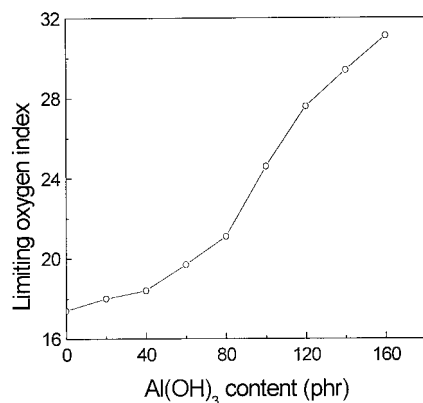
LOI of PE filled with 140 phr Al(OH)₃ improved significantly compared with that of neat PE. The LOI of samples C and D are somewhat lower than that of sample B (as observed in Table III), indicating that silicon oil has a slightly negative effect for flame retardancy of PE filled with 140 phr Al(OH)₃. In comparison between sample B and samples C, D, and E, it can be demonstrated that the LOI of PE filled with 140 phr Al(OH)₃ changes little when a small amount of AAgPE and silicon oil was used, which was essential to meet the desired level of flammability properties for PE filled with 140 phr Al(OH)₃. The presented results indicate the excellent combination of mechanical, rheological, and flammability properties of PE/Al(OH)₃/AAgPE/silicon oil (90/140/10/8) composite studied.

Morphologies of the composites

The influence of AAgPE-coupling agent and silicon oil on the filler dispersion and phase morphology of the PE/Al(OH)₃ (100/140) composite was studied through SEM. As shown in Figure 4(A), the interface adhesion and dispersion of the filler particles in the matrix are rather poor. Many agglomerated filler particles can be found in the PE/Al(OH)₃ composite, implying that the filler is not well dispersed in the PE matrix. The filler particles, however, seem to be well dispersed without agglomeration in the PE matrix with addition of silicon oil, as observed in Figure 4(C).

It is well known that coupling agents improve the adhesion by forming a thin interfacial layer that

Figure 3 Limiting oxygen index of polyethylene filled with various amounts of aluminum hydroxide.

TABLE III
Limiting Oxygen Index of the PE/Al(OH)₃ Composites

Sample code	Composition (wt/wt)	Limiting oxygen index
A	PE	17.4
B	PE/Al(OH)₃ (100/140)	29.4
C	PE/Al(OH)₃/AAgPE (90/140/10)	28.9
D	PE/Al(OH)₃/silicon oil (90/140/8)	28.1
E	PE/Al(OH)₃/AAgPE/silicon oil (90/140/10/8)	28.5

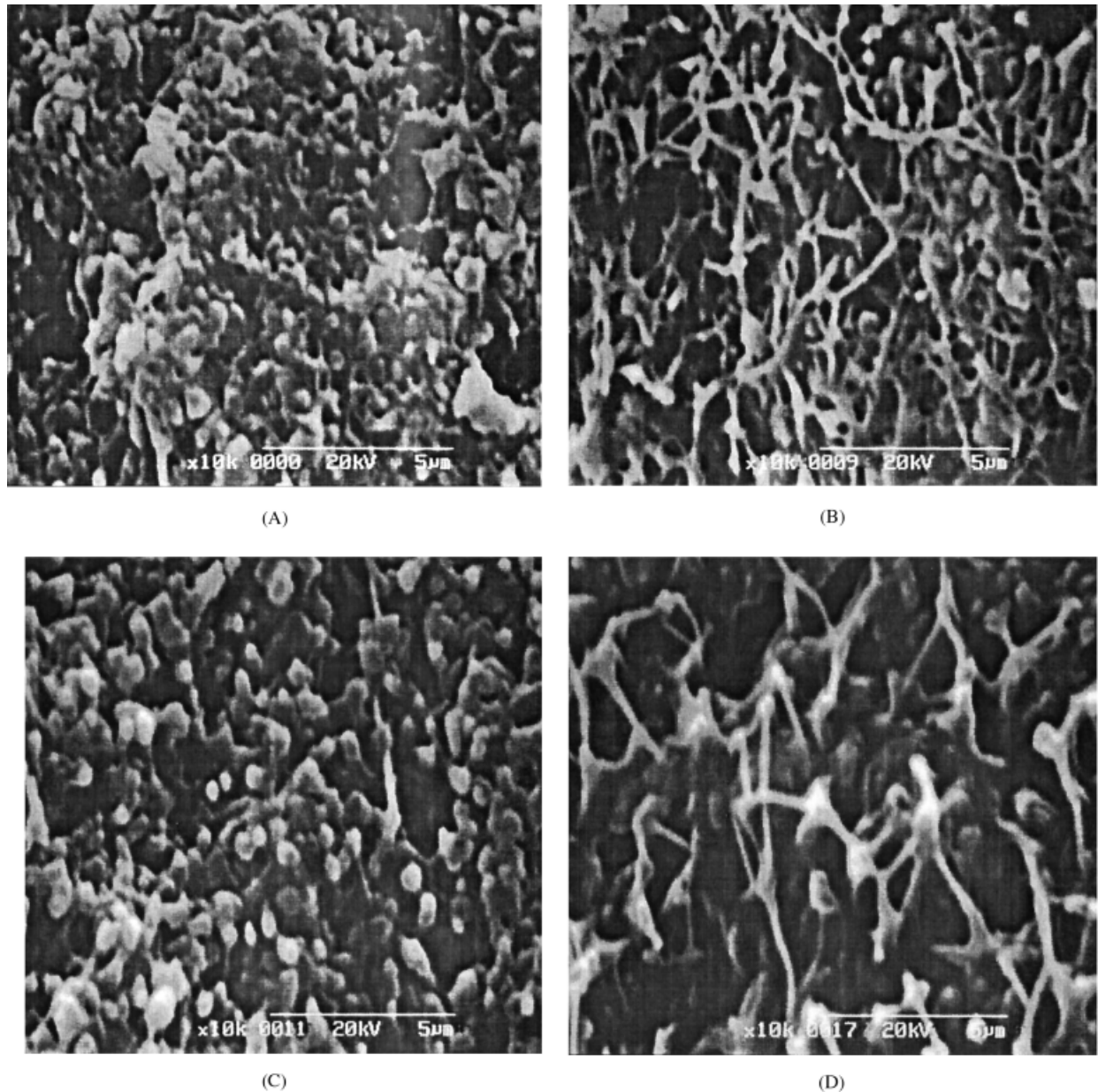*Note.* AAgPE used here was 3.2% (grafting degree).

Figure 4 SEM micrographs of fractured surfaces of aluminum hydroxide filled polyethylene composites under liquid nitrogen: (A) PE/Al(OH)3 (100/140); (B) PE/Al(OH)3/AAgPE (90/140/10); (C) PE/Al(OH)3/silicon oil (100/140/8); (D) PE/Al(OH)3/AAgPE/silicon oil (90/140/10/8).

bridges the filler and the matrix. The bridging effect of the interfacial layer is achieved through chemical and physical interactions among the coupling layer, filler, and polymer matrix.[14–16] As SEM micrographs show above, the interface between the filler particles and PE matrix is blurrier and more complex in Figure 4(B and D) than that in Figure 4 (A and C), indicating good interfacial adhesion is obtained with AAgPE (3.2% grafting degree of AAgPE used here) in the composite. It is also found that, with addition of AAgPE, plastic deformation can be observed (Fig. 4B), whereas it cannot be observed with the addition of silicon oil (Fig. 4C).

The fracture surface morphology of PE/Al(OH)$_3$ composite changes substantially in the presence of AAgPE and silicon oil. Finer dispersion of the filler and plastic deformation of the matrix are clearly found in Figure 4(D), which results in good mechanical performance of the composites. The results are consistent with mechanical properties of the composites mentioned above.

CONCLUSIONS

The influence of synthesized AAgPE and silicon oil on mechanical, rheological, and flammability properties

and microstructure of PE/Al(OH)3 (100/140) composite were investigated. Good interfacial adhesion is obtained with the addition of AAgPE in the composite. Silicon oil is an effective additive for improving process property of the filled PE and can favor the dispersion of the filler and reduce the size of agglomerates.

Finer dispersion of the filler and good interfacial adhesion are available on addition of AAgPE and silicon oil, thus good mechanical and rheological properties of PE highly loaded with aluminum hydroxide composite are obtained. Plastic deformation of the PE matrix observed through SEM is associated with AAgPE-coupling agent.

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