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Aluminum hydroxide filled ethylene vinyl acetate (EVA) composites: effect of the interfacial compatibilizer and the particle size

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Abstract Ethylene vinyl acetate (EVA) copolymer was filled with aluminum hydroxide (ATH) with three different sizes of 1.8, 1.2 and 0.8 μm in various volume fractions. The effect of interfacial compatibilizer on the properties of the composites was studied by morphology observation, dynamic mechanical analysis, tensile and flame tests. The results illustrated that the incorporation of functionalized polyethylene combined with dicumyl peroxide (DCP) and the silane coupling agent led to a pronounced improvement in the tensile strength compared to the composites with ATH untreated or treated by silane coupling agent alone. It was found that good dispersion and interfacial adhesion between the ATH particles and the matrix can improve the flame properties of composites. The particle size has a great effect on the flammability of the EVA/ATH composites. ATH with smaller particle size can increase the LOI value and improve the UL-94 flammability of the composites.

Introduction

In recent years, fire protection receives greater attention and importance because of various disasters caused by fires in public buildings. A world-wide innovation of substituting the halogenated flame retardants with halogen-free retardants is an important trend in the plastics products [1, 2], especially in cable materials [3–5].

Ethylene vinyl acetate (EVA) copolymer is extensively used in insulation compounds of wires and cables. EVA/alumina trihydrate (ATH) composites have attached much attention [6–9]. To obtain adequate fire retardance, high loading of approximate 60 wt% of ATH is always needed, which leads to the deterioration of mechanical and processing properties. Addition of polymeric compatibilizers can improve the compatibility of the filler with the matrix, which has a great effect on the mechanical properties of the composites [10, 11]. Hippi et al. [12] has studied the usefulness of functionalized polymers as compatibilizers for polyethylene (PE)/ATH and PE/MH blends. They found that the improved adhesion with use of funcitonalized copolymers could improve the stiffness and toughness without deterioration of flame retardancy of the composites. Chiang and Hu [13] obtained improvement in tensile strength and impact resistance in polypropylene (PP)/MH composites by adding PP-g-AA. Interfacial chemistry of PP/ATH composites has been studied by Ren and Wang [14], who suggested that the interface between ATH and PP disappeared when PP-g-AA and silane coupling agent were added. The siloxane group of the KH-792 ($H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$)coupling agent can bond chemically with the ATH surface, and amine group at the other side of the coupling agent can bond chemically with the acrylic acid of the PP-g-AA. Liauw et al. [15] treated ATH filler with silane systems consisting of a vinylsilane and organic peroxide, resulting in a crosslinked encapsulating layer around the filler

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particles. Elastomeric encapsulation of the filler particles leads to a significant improvement in the mechanical properties of highly filled impact modified PP based composites. Studies on polyolefin/ATH composites were focused on the effects of coupling agents or compatibilizers. The aim of this paper is to investigate the combination effect of coupling agent, organic peroxide and compatibilizers on the interfacial adhesion and the effect of the paritcle size and content of ATH on the mechanical properties of EVA/ATH composites.

Experimental

Materials

Ethylene vinyl acetate (ESCORENE UL7765), produced by EXXON with melt flow index = 2.3 g/10 min, contains 28 wt% of vinyl acetate. $Al(OH)_3$ was Martinal OL104/LE, OL107/LE and OL111/LE from Albemarle Corporation, which have the average diameter of 1.8, 1.2 and 0.8 μm, respectively. Dicumyl peroxide (DCP) is analytical grade. The γ-methylacryloxypropyl trimethoxy silane (KH570) was supplied by Yaohua Chemical Company, China. The LLDPE-g-MAH CMG9904 with 0.9% MAH and MFI = 0.8 g/10 min was supplied from Shanghai Sunny New Technology Development Co., Ltd.

Sample preparation

The EVA composites with desired amounts of ATH were prepared by melt mixing in a corotating twin-screw extruder (TSE-35A/600-15-40, D = 35 mm, L/D = 40, Nanjing Ruiya Polymer Processing Equipment Co. Ltd.). The extrusion process was preformed at 100 rpm in the 140–150 °C temperature range. The sheets about 3 mm thickness were prepared by compressing at 170 °C under a pressure of 14.5 MPa for 3 min and quenching to 40 °C by a cold press. The basic formulations of these blends are listed in Table 1.

Measurements

UL-94 test

The UL-94 vertical test was carried out using a CZF-1 type instrument (made in China) on sheets 80 × 12 × 3 mm according to GB/T 2408-96.

Limiting oxygen index (LOI)

The LOI value was tested using a HC-2 type instrument (made in China) on sheets 80 × 6.5 × 3 mm according to GB/T 2406-93.

Mechanical properties

Tensile tests were carried out using a dumbbell specimen (GB1040 Type II specimens, 130 mm × 6 mm × 2 mm) and a Shimadzu AG-10TA tensile tester with a crosshead speed of 50 mm/min.

Scanning electron microscopy (SEM)

The dispersion of ATH particles in the matrix was analyzed by scanning electron microscopy (JSM-6360LV, JEOL). The sheets were cryogenically fractured in liquid nitrogen. The fractured surfaces were sputtered with gold before viewing.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out with a Rheogel-E4000 (Japan). Samples of dimension (20 mm × 6 mm × 2.0 mm) were cut from the center of the dumbbell-shaped pressed specimens. Tests were performed over a wide temperature range of –120 °C to 100 °C at a heating rate of 3 °C/min with a frequency of 1 Hz. The viscoelastic properties, such as, the storage modulus (E') and the mechanical loss factor ($\tan \delta = E'/E''$), were recorded as a function of temperature.

Results and discussion

Effect of compatibilizer

The SEM micrographs of the fracture surfaces for the unmodified, the silane coupling agent treated and the compatibilized composites of EVA with OL104 (Sample 104a–d) are respectively shown in Fig. 1(a–d). It is obvious that the untreated ATH dispersed poorly and unregularly in the EVA matrix. And aggregates of ATH were observed in Fig. 1(a). Silane coupling treated ATH dispersed uniformly in the EVA compared to the untreated one. However, the edges of ATH were out and the interface between ATH and EVA were clear in both cases, which indicated that the ATH particles are not bonded to the matrix.

Table 1 Formulation of the EVA/ATH composites

Run	EVA	U*-OL104	T*-OL104	T-OL107	T-OL111	DCP	LLDPE-g-MAH
104a	40	60					
104b	40		60				
104c	39.97		60			0.03	
104d	35.47		60			0.03	4.5
107d	35.47			60		0.03	4.5
111d	35.47				60	0.03	4.5
104e	37.97	57.5				0.03	4.5
107e	37.97			57.5		0.03	4.5
111e	37.97				57.5	0.03	4.5

* U-represents untreated, T-represents treated.

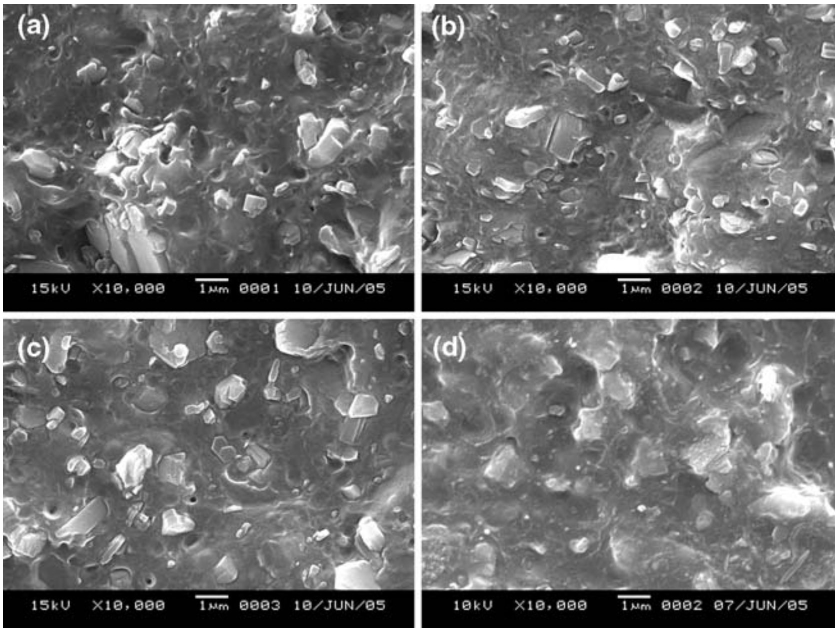

Fig. 1 SEM micrographs of EVA composites with OL104 ATH: (**a**) 104a, (**b**) 104b, (**c**) 104c, (**d**) 104d

Apparently surface treatment with silane coupling agent does not improve adhesion but merely serves the purpose of well dispersal of ATH. Addition of dicumyl peroxide (DCP) leads to little change of ATH dispersion due to so small amount of DCP (0.03 wt%). However, somewhat different morphological appearance is displayed by the presence of the interfacial compatibility agent LLDPE-g-MAH. As can be seen in Fig. 1(d), LLDPE-g-MAH improves the interfacial adhesion between ATH and EVA matrix since particles are coated with a sheath of EVA matrix to yield a smooth fracture surface in the composite.

Apart from SEM observation, DMA was used for 104a–d composites to obtain further information on mechanical properties and molecular motions. Temperature dependences of storage modulus (E') and loss factor (tanδ) peaks of the composites are shown in Fig. 2. The composite 104b of KH570 treated ATH showed little improvement in storage modulus (E'), where the E' values of 104c and 104d were clearly higher than that of 104a. The composites 104d with addition of DCP and LLDPE-g-MAH has the highest storage modulus.

Figure 2b shows the tanδ peaks located at about –10 °C associated with the relaxations of side groups or short branch points. The position of the tanδ peaks of composites 104c–d remains unchanged compared to 104a, while the broadening of tanδ peaks and a reduction of peak intensity were observed. This behavior is because that the strong interaction between ATH and the matrix, resulted from DCP and functionalized polyethylene, hinders the molecular motion. An increase in E', a lowering of the mechanical loss factor and broader peaks indicate improved interfacial adhesion, which convince the observation of SEM.

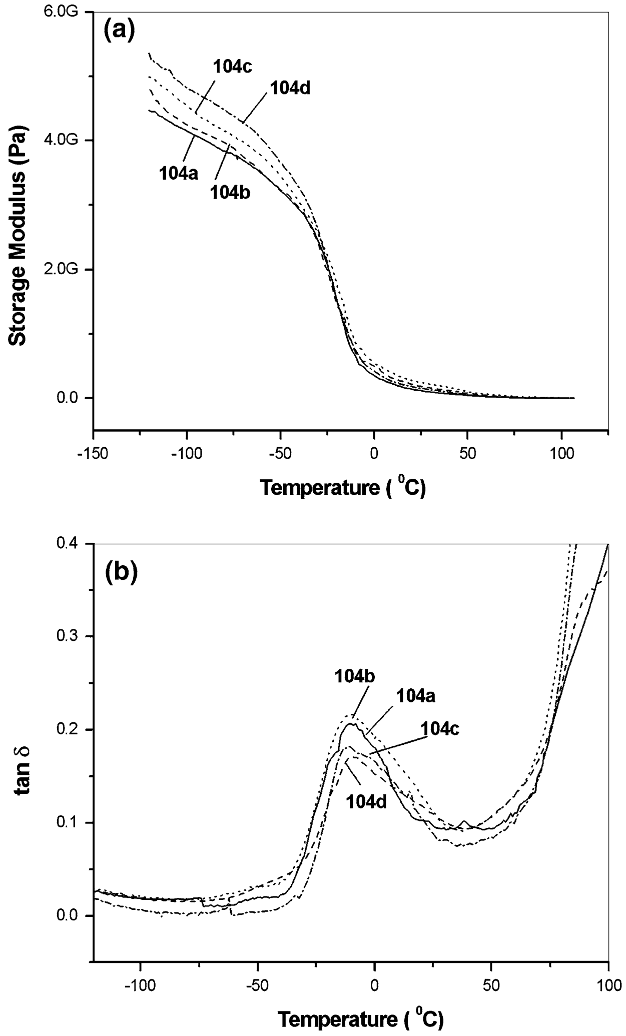

Fig. 2 Temperature dependency of E' and tanδ for composites 104a-104d: (**a**) storage modulus E', (**b**) tanδ

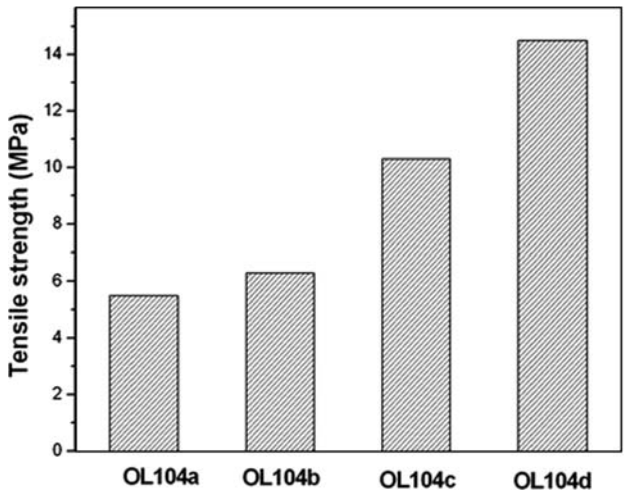

Fig. 3 Tensile strength of the EVA/ATH composites 104a-104d

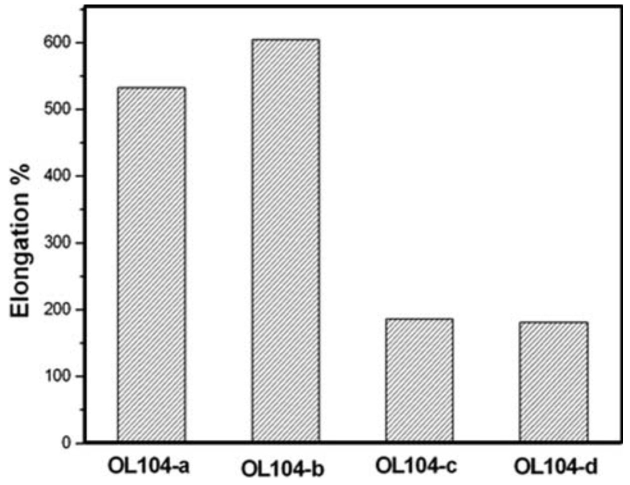

Fig. 4 Elongation of the EVA/ATH composites 104a-104d

Figures 3-4 list the tensile strength and elongation at break of EVA/ATH composites (104a–104d). Addition of silane coupling agent treated ATH produced an increase in the tensile strength and elongation of EVA compared to EVA composites with untreated ATH. However, the tensile strength was only 6.3 MPa, which cannot satisfy the requirement of IEC 60811. When the dicumyl peroxide was incorporated, the tensile strength was increased to 10.3 MPa. It is due to the local cross linkage between the methylacryloxy group of KH570 and the matrix EVA induced by the initiator of DCP. Furthermore, by addition of functionalized polyethylene combined with DCP and the silane coupling agent in the compounding step, pronounced improvement in the tensile strength from 10.3 MPa to 14.5 MPa was achieved. It is due to the improved interfacial adhesion between the ATH particles and the matrix, which has been indicated in the above SEM micrographs in Fig. 1(d).

Figure 4 shows that treatment with silane coupling agent and DCP resulted in composites with lower elongation relative to the composite with filler treated by silane coupling agent alone. A similar phenomenon was observed in polypropylene/magnesium hydroxide composites [15]. It may be because that cross linkage between the filler and the matrix initiated by DCP restrains the motion of the molecule of EVA.

Table 2 presents the LOI and UL-94 data of samples 104a–104d. It is obvious that the sample 104d is the best among the four samples because it can pass the UL-94 V-0 rating with the high LOI value of 34.3. These data illustrate that good dispersion and interfacial adhesion between the ATH particles and the matrix can improve the flame properties of composites.

Table 2 Flammability of EVA/ATH composites

Run	UL-94	LOI %
104a	Fail	32.8
104b	FV2	32.7
104c	FV1	33
104d	FV0	34.3

Effect of the size and the content of ATH

To study the influence of particle size of ATH, two particle sizes (OL107-1.2 μm and OL111-0.8 μm) were chosen to compare with OL104 (1.8 μm) in the same composition. Figure 5 shows the dispersion morphologies of samples 107d and 111d. As can be seen in Fig. 5, with decreasing the particle size, no obvious aggregates were observed. The particle dispersion is homogeneous and all the particles are coated to yield a smooth fracture surface, which is similar to sample OL104d in Fig. 1d.

The effect of particle size and content on the tensile properties and LOI values of EVA composites are shown in Figs. 6–8. For the same content of ATH, with decreasing size of ATH particles, tensile strength of the composites changes little, while elongation of the composites decreases. The decrease in elongation with decreasing size of particles is because smaller particles have more active sites in the matrix, which restrains the motion of the molecule of the matrix. For the same type of ATH, EVA composites with 57.5% ATH have higher tensile strength and elongation compared to composites with 60% ATH. It is obvious that the tensile strength is mainly related to the content of filler and elongation is affected by both the size and content of the particles.

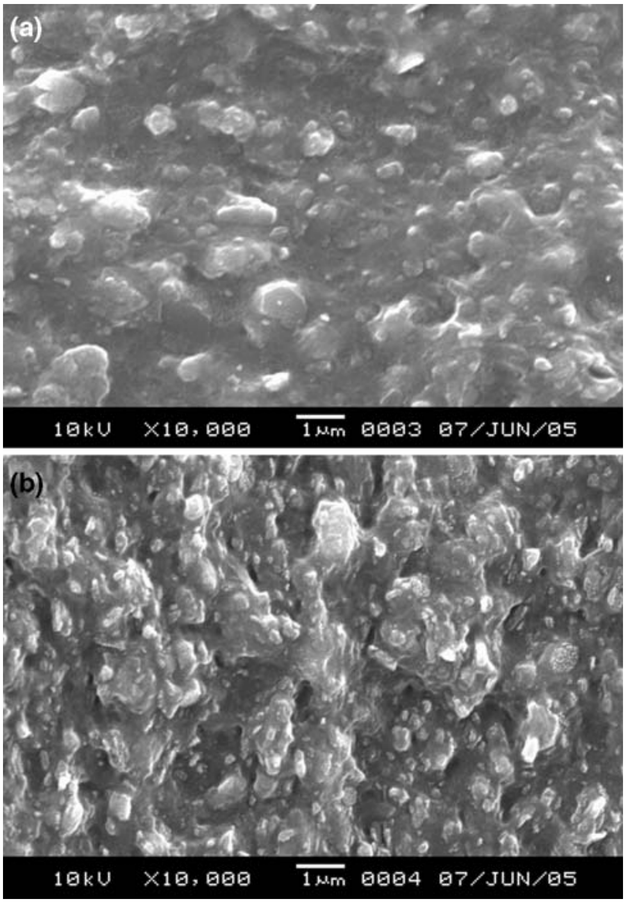

Fig. 5 SEM micrographs of EVA composites with different sizes of ATH: (**a**) 107d, (**b**) 111d

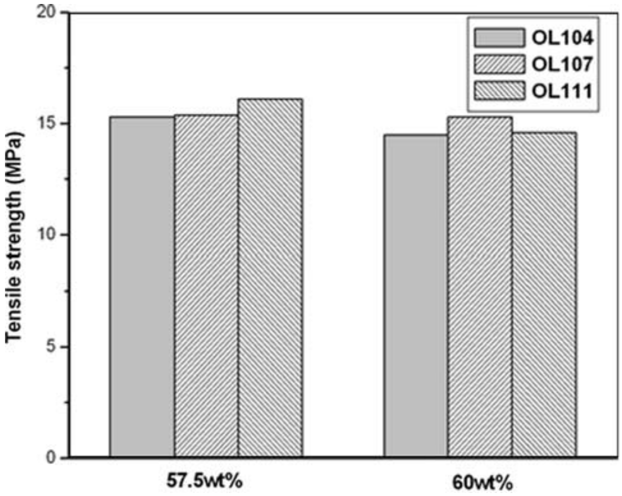

Fig. 6 Effect of filler content and size on the tensile strength of the EVA/ATH composites

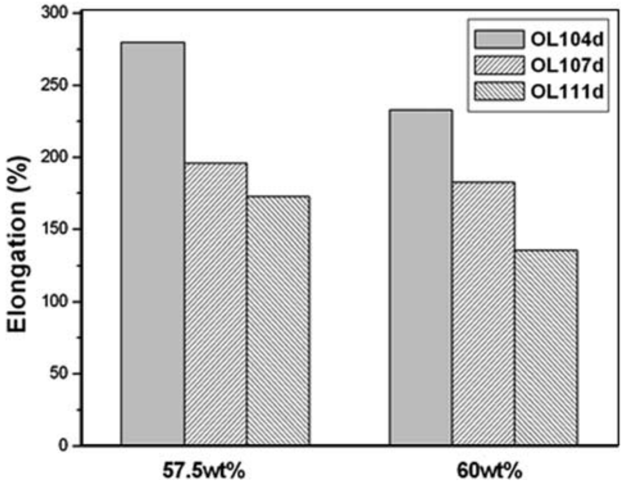

Fig. 7 Effect of filler content and size on the elongation of the EVA/ATH composites

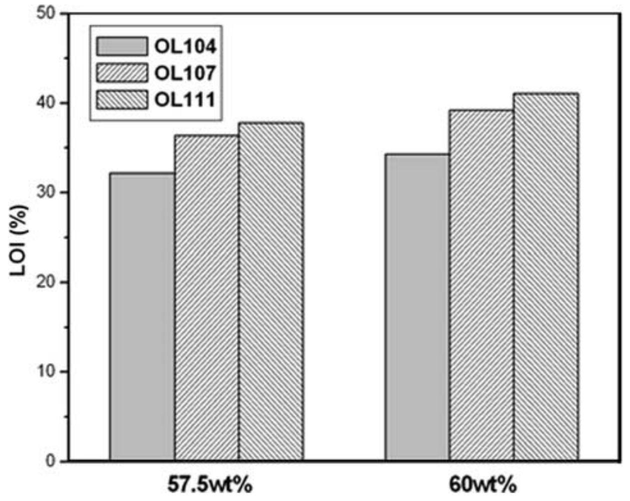

Fig. 8 Effect of filler content and size on the flammability of the EVA/ATH composites

Table 3 UL-94 test of EVA/ATH composites

OL104e	OL107e	OL111e	OL104d	OL107d	OL111d
Fail	FV0	FV0	FV0	FV0	FV0

Figure 8 presents the LOI values of sample104d–111e. LOI values increase greatly as the particle size decreases. As shown in Fig. 5, a better dispersion is observed when difference sizes of particles are incorporated. The smaller the particles, the higher specific surface area of the particles is, which leads to more active sites. In the combustion of these composites, more active sites can accelerate the decomposition of ATH. Compared to samples 107e and 111e with 104d, it is found that samples 107e and 111e with 57.5 wt% of ATH has higher LOI values of 36.4 and 37.8, respectively, while sample 104d with 60.0 wt% of ATH has LOI value of 34.2. Table 3 lists the UL-94 test data of these composites. Samples 107e and 111e can pass the UL-94 V-0 rating, while sample 104e failed. It suggests that, to obtain the same flame retardancy, the content of ATH with small size can be lessened. Less of ATH can improve the processing properties of the composites and the appearance of the products.

Conclusion

Studies were carried out on the effect of the interfacial modifier of functionalized polyethylene and the particle size of ATH on the ethylene vinyl acetate copolymer (EVA)/ATH composites. Adhesion of EVA/ATH composites was dramatically increased by addition of the interfacial modifier, as seen in morphology observation and DMA analysis. The adhesion improvement was particularly reflected in the mechanical properties and flammability, and improvement in both tensile strength and flammability was best achieved by addition of functionalized polyethylene. ATH with smaller particle size can increase the LOI value and improve the UL-94 flammability of the compsoites. Smaller particles of 57.5 wt% ATH has improved flammability than larger particles of 60 wt% ATH.

This work clearly indicates that interfacial adhesion has a great influence on the mechanical properties, while the particle size has a great effect on the flammability. How to obtain good dispersion and adhesion of smaller particles is the key to prepare the halogen-free retardant EVA composites.

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