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Investigation of interfacial modification for flame retardant ethylene vinyl acetate copolymer/alumina trihydrate nanocomposites

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Abstract

Ethylene vinyl acetate copolymer (EVA)/alumina trihydrate (ATH) nanocomposites were prepared by melt-blending. Two kinds of interfacial modifiers were used in this research, a titanate coupling agent and maleated ethylene vinyl acetate copolymer (MEVA), which acted as a compatibiliser. The effects of modifiers on the properties of EVA nanocomposites were studied by thermogravimetric analysis, tensile and combustion tests. The dispersion and adhesion patterns of the ATH nano-particles in EVA matrix were characterized through Molau solution test, TEM and SEM. The experimental results demonstrated that the use of untreated ATH could clearly decrease the tensile properties of EVA composites. It was found that the combined addition of the two kinds of interfacial modifiers led to a dramatic increase in tensile and flame retardant properties of the nanocomposites. Also the thermal stability of this system, in terms of the thermal degradation test, was enhanced. These effects would be diminished if only one modifier was used. The improvement in the properties of interfacial modified EVA/ATH nanocomposites is mostly attributed to a better dispersion of surface modified filler and a strong adhesion between the filler and matrix.

Keywords: Interfacial modification; ATH; EVA nanocomposites; Mechanical properties; Flame retardancy

1. Introduction

In recent years, a great deal of attention has been paid to the use of flame retardant (FR) polymeric composites with halogen-free (HF) flame retardants, for example conventional alumina trihydrate or magnesium hydroxide, because these materials do not cause environmental pollution, such as toxicity, heavy smoke and corrosion [1–3]. In the wire and cable industry, ethylene vinyl acetate copolymer (EVA)/alumina trihydrate (ATH) composites have been widely researched and used [4,5].

To achieve the required flame retardancy, high loadings of about 60 wt% of ATH are always adopted, which could lead to a poor mechanical performance of the resulting materials [4]. This problem can be solved through improving the dispersion and compatibility of the inorganic filler in polymer matrix. While a variety of surface modifiers can be effective dispersants for fillers, only coupling agents and polymer compatibilisers are found to be able to form a chemical connection between the two phases. The coupling agents are designed to be a molecular bridge, which has limited adhesion effect [6]. The compatibilisers consist of two parts, the hydrophobic polyolefin copolymer or grafting

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with polar hydrophilic monomers, such as acrylic acid (AAC), methyl methacrylate (MMA) and maleic anhydride (MAH). These reactive groups interact readily with functional groups on the inorganic filler, and the polyolefin phase is miscible or compatible with the polymer matrix. A durable connection between the filler and the matrix is thereby established. So compatibilisers are also termed "polymer coupling agents" [6,7]. Many studies about polyolefin/ATH composites were focused on the effects of coupling agents or compatibilisers. Liauw et al. systematically studied the effects of various coupling agents on the mechanical properties of PP/ATH composites [8]. A recent work reported by Hippi et al. showed that the presence of compatibilisers could improve both stiffness and toughness of PE/ATH composites while FR properties of the composites remained unchanged [3].

The present investigation was concerned with the tensile properties and flame retardancy of EVA FR composites with nano-scale ATH, which is a material likely to agglomerate in a polymer matrix. Appropriate coupling agent and compatibiliser were selected in order to enhance the dispersion and adhesion between the filler and matrix, so as to improve the properties of EVA/ATH nanocomposites.

2. Experimental

2.1. Materials

An ethylene vinyl acetate copolymer (EVA14-2) resin, produced by Beijing Organic Chemical Plant with melt flow rate of 2 g/10 min containing 14 wt% vinyl acetate, was used. The alumina trihydrate (ATH), from Zhongzhou Branch, Aluminium Corporation of China Limited, has an average particle size of 100–125 nm. The coupling agent T, isopropyl tris (dioctyl pyrophosphate) titanate (KR-38S, MW = 1310.4, chemical structure shown in Fig. 5), was supplied by Yangzhou Lida Resin Company, China. The compatibiliser MEVA, a type of EVA grafted with 2 wt% maleic anhydride, was manufactured by Ningbo Nengzhiguang New Materials Technology Cooperation, China.

2.2. Sample preparation

2.2.1. Treating the nano-ATH surface with the coupling agent T

The dosage of the coupling agent was 0.5 wt% (based on filler mass), and the modifier was diluted in atoleine to make up a 5 wt% solution. Note that the dosage of the modifier was selected based on the earlier experimental results on flame retardancy and mechanical behaviours of EVA composites [9].

After thorough drying at 100 °C for 10 h, ATH particles were charged into a bench top mixer and the modifier solution was added slowly over a period of 10 min to ensure uniform distribution of the coupling agent. After completion of the titanate addition, the filler was continuously mixed for 25 min, and the temperature was in the range of 100–110 °C. Then the surface treated ATH-T particles were dried at 100 °C for at least 3 h.

2.2.2. Polymer compounding

The EVA cable compositions are shown in Table 1. These raw materials were first mixed using blending equipment. Then they were formed into pellets by compounding the polymer via a Prism 16 mm twin screw extruder at operating temperatures of 110 °C at zone 1, 140 °C at zone 2, 150 °C at zone 3, 160 °C at zone 4 and 60 rpm screw speed. Subsequently the pellets were fed into a single screw extruder to prepare the test specimens, at temperatures of 125 °C at zone 1, 155 °C at zone 2, 170 °C at zone 3, 165 °C at zone 4 and 50 rpm screw speed.

2.3. Analysis of samples

2.3.1. Combustion test

Two standard test methods were used to evaluate the FR properties of all samples prepared.

The limiting oxygen index (LOI) test was adopted to giving a measure of the relative flammability of these samples in which case higher LOI values represented better flame retardancy. Measurements were undertaken within a specimen of a dimension of $120 \times 7 \times 5$ mm using a HC-22 type instrument (made in China) in accordance with ISO 4589-1964.

The UL-94 test was performed to evaluate the flame spread of the test specimens in air atmosphere, using a CZF-1 type instrument (made in China) on sheets according to ISO 1210-1992.

Table 1
Compositions of all samples

Samples	EVA/wt%	ATH/wt%	ATH-T/wt%	MEVA/wt%
1	100	0	0	0
2	80	20	0	0
3	60	40	0	0
4	40	60	0	0
5	80	0	20	0
6	60	0	40	0
7	40	0	60	0
8	90	0	0	10
9	70	0	20	10
10	50	0	40	10
11	30	0	60	10
12	30	60	0	10