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Capitalizing on the molybdenum disulfide/graphene synergy to produce mechanical enhanced flame retardant ethylene-vinyl acetate composites with low aluminum hydroxide loading

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ABSTRACT

We have engineered a flame retardant ethylene-vinyl acetate (EVA) composite which has the similar mechanical properties as polyvinyl chloride (PVC) and therefore may prove to be an alternative material for cable sheathing. Four composites were studied, EVA with aluminum hydroxide (ATH), EVA with ATH and molybdenum disulfide (MoS_2), EVA with ATH and graphene nanoplatelets (GNPs), and EVA with all three components. Tensile testing showed nearly identical results for the EVA/ATH and EVA/ATH/MoS_2 compounds, while the EVA/ATH/GNPs compound had higher mechanical properties. The compound containing all three components showed further enhanced mechanical properties, indicating that a synergy was established. This was further confirmed using Scanning Electron Microscopy (SEM) where GNPs were seen to increase the dispersion of the MoS_2 and ATH components within the polymer matrix. Cone calorimetry test clearly showed a large decrease in heat release rate when GNPs were added, which was further enhanced by adding GNPs and MoS_2 together. Application of the UL-94 test showed that only the compound containing 36 wt% of ATH and 2 wt% each of MoS_2 and GNPs can achieve the UL-94 V0 rating.

1. Introduction

Ethylene-vinyl acetate (EVA) is an elastomeric copolymer known for its excellent tactile properties in the adhesive industry. Its high ductility also makes it an attractive component of polymer blends where it can provide a very large range of thermos-mechanical properties with broad applications in areas ranging vastly from footwear to electronics. In particular, EVA blends have been promoted as an environmentally friendly alternative to polyvinyl chloride (PVC) in cable sheathing. PVC has been traditionally used for producing the insulation and sheathing of cables due to its resistance to corrosion, flame retardancy, and ductility. However, processing PVC involves the release of a toxic by-product, dioxin, a highly dangerous and carcinogenic chemical. Another potential hazard of using PVC is the plasticizers leaking. Adding plasticizers can further enhance the ductility of PVC to fulfill the requirements of cable sheathing, but these chemicals are suspected carcinogens and easily leak out from the PVC matrix, where they can enter the environment, pollute water systems, and cause significant harm to animals and humans. As a result, there has been an intensive effort to find a sustainable replacement. EVA was proposed since it is corrosion resistant, and even more ductile than PVC which would obviate addition of plasticizers. Unfortunately, though the neat polymer is also highly flammable and the incorporation of halogenated compounds which used to be an effective and way to render EVA flame retardant, are also found to have high toxicity and hence are no longer permitted [1]. Therefore, alternative non-halogenated flame retardants such as phosphate-based, nitrogen-based and metal hydroxide-based compounds have been developed and integrated into EVA for cable sheathing [2–15]. Currently, the most common flame retardant to produce EVA based cable sheathing is aluminum hydroxide (ATH) due to its relatively high efficiency and low cost. If ATH is used alone, the general weight ratio of ATH in the EVA/ATH composite needs to be as high

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as 60% to acquire the desired flame retardancy. Such high loading of filler negatively affects the physical properties of the composite, weakening the mechanical properties and shortening the durability. Numerous attempts have been reported to minimize the total ATH loading of the EVA composite without sacrificing its flame retardancy [16–21]. Addition of melamine borate (MB) assisted the EVA/ATH composite to form more rigid protective layer, shielding the heat source effectively during burning, hence decreasing the total ATH weight ratio to 47% [16]. Incorporating 2 wt% of Cloisite 30B nanoclay was able to improve the thermal stability and mass transport barrier effect of the EVA/ATH composite, thereby decreasing the concentration of ATH to 48 wt% [18]. In order to further decrease the ATH weight ratio, more effective flame retardant synergism formulation must be developed.

It has been reported that molybdenum disulfide (MoS_2) nanoplatelets was able to increase the thermal stability of the polymeric matrices and assist the formation of the compact protective char layer, suppressing the thermal spreading during burning [22–25]. Another nanoplatelets structure filler, graphene nanoplatelets (GNPs), has been widely proven to be an effective charring agent and heat suppressor [26–33]. Inspired by the flame retardant mechanism of these nanoplatelets, we used GNPs and MoS_2 together to replace part of ATH, expecting to render EVA composite with higher thermal stability and to yield more char during burning. In the study, we show that addition of 2 wt% of GNPs and 2 wt% of MoS_2 in the EVA/ATH system produces a composite with only 36 wt% of ATH, yet passes the stringent UL-94 V-0 criteria. To our best knowledge, 36 wt% of ATH is the lowest value thus far reported which allows the EVA/ATH system to attain a UL-94 V-0 rating. Here we present a detailed study of the mechanism involved, where we discuss how the formulation was optimized to enhance the filler dispersion, increase thermal stability, and facilitate char formation. Furthermore, we also elaborate on the interplay between filler composition and mechanical properties, where we demonstrate that incorporating GNPs and MoS_2 together, produces a synergy which also tremendously enhances the tensile strength of the composite, which is a very desirable outcome for the application of cable sheathing.

2. Experimental

2.1. Materials

EVA copolymer (EDI-240, density: 0.940 g/cm^3) containing 19 wt.% vinyl acetate was donated by Muehlstein International. ATH powders (ATH-6810) with average particle size of 1.5 μm were supplied by J. M. Huber Corporation. MoS_2 powders (234842-500G, particle size less than 2 μm) were purchased from Sigma-Aldrich. GNPs powders (C750, bulk density: 0.2 g/cc, average surface area: 750 m^2/g, average size: 250 nm) were purchased from xGnP Science, Inc.

2.2. Composites preparation

The EVA composites were prepared by melt blending at 150 °C using a C.W. Brabender. The EVA pellets were first poured into the chamber with the rotation speed set at 20 rpm. After the EVA pellets were melted, different combination of fillers was added. After the feeding of all the materials, the rotation speed was increased to 100 rpm and kept for 10 min. The final blends were then molded into different thickness and shapes using a hot press for further characterizations. The composition of each composite used in this study were summarized in Table 1.

Table 1
Composition of EVA composites used in this study.

Sample	EVA (wt%)	ATH (wt%)	GNPs (wt%)	MoS_2 (wt%)
EVA	100	0	0	0
EVA/A	60	40	0	0
EVA/AG	60	38	2	0
EVA/AG′	60	36	4	0
EVA/AM	60	38	0	2
EVA/AM′	60	36	0	4
EVA/AGM	60	36	2	2

2.3. Characterization methods

Tensile Tests: Tensile properties of EVA composites were measured according to ASTM D-638, type M. using an Instron 5542 (Instron Co., Grove City, PA). The extension rate was set at 20 mm/min. Each result was obtained by averaging the values of 10 specimens.

Rheology Measurements: A Bohlin Gemini HR Nano rheometer (Malverm instruments) was employed to evaluate the rheological performance of EVA composites using different test modes. The composites were compression molded into disk-like specimens and measured under frequency sweep mode (0.01–100 Hz at 150 °C with the strain amplitude of 1%) and shear stress sweep mode (10–1000 Pa at 150 °C with a constant frequency of 1 Hz).

Flame Tests: UL-94 vertical burning protocol (ASTM D 3801) was applied on the EVA composites to evaluate self-extinguish ability. The specimens for UL-94 testing were made by 127 mm long, 12.7 mm wide, and 3.2 mm thick. Composites specimens with the dimensions of 100 mm long, 6 mm wide, and 3 mm thick, were measured according to ASTM D 2863 to obtain the limiting oxygen index (LOI) values. A Stanton Redcroft Cone Calorimeter was used to measure the thermal behaviors of EVA composites (specimens are square plates with 75 mm side length and 5 mm thick) including time to ignition (TTI), average heat release rate (AHRR), peak heat release rate (PHRR) and total heat release (THR) at the heat flux of 40 kW/m^2.

Thermogravimetric analysis (TGA): Thermal stability of EVA composites was evaluated using a Mettler Toledo TGA851 under air flow. About 10 mg of the composites was put into an alumina crucible and heated up from 40 °C to 800 °C at the rate of 20° C/min. The raw weight loss data were automatically recorded by the software for derivative thermo-gravimetric analysis.

Transmission Electron Microscopy (TEM): Thin cross-section films (thickness is around 100 nm) of EVA composites were cut by a Lecia FC-7 cryo-microtome at −90 °C (chamber is cooled with liquid nitrogen). The films were then directly lifted onto copper grids and imaged using a JEOL JEM1400 TEM at 80 kV.

Scanning Electron Microscopy (SEM): A JEOL JSM7600F SEM was employed to observe the surfaces of the burnt and unburnt EVA composites samples. The distribution of MoS_2 within the polymer matrix was evaluated by using Energy Dispersive X-ray Spectroscopy (EDXS) mapping on the cross-sectional surface of composites, the mapping element was molybdenum. In order to reach the required electrical conductivity, sample surface was coated by gold with thickness of 10 nm.

Raman Spectroscopy: Raman spectra of GNPs and EVA based composites were obtained by a Renishaw inVia Raman spectrometer. The laser excitation was provided by a Stellar-Pro operating at 514 nm with 10% laser power using a x100 objective lens and a 25 μm slit. The exposure time is 100s. Each curve is an average result of the signals from three different positions on the sample.