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Synergistic effects of layered double hydroxide with hyperfine magnesium hydroxide in halogen-free flame retardant EVA/HFMH/LDH nanocomposites

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Abstract

The synergistic effects of layered double hydroxide (LDH) with hyperfine magnesium hydroxide (HFMH) in halogen-free flame retardant ethylene-vinyl acetate (EVA)/HFMH/LDH nanocomposites have been studied by X-ray diffraction (XRD), transmission electron spectroscopy (TEM), thermogravimetric analysis (TGA), limiting oxygen index (LOI), mechanical properties' tests, and dynamic mechanical thermal analysis (DMTA). The XRD results show that the exfoliated EVA/HFMH/LDH can be obtained by controlling the LDH loading. The TEM images give the evidence that the organic-modified LDH (OM-LDH) can act as a disperser and help HFMH particles to disperse homogeneously in the EVA matrix. The TGA data demonstrate that the addition of LDH can raise 5−18 °C thermal degradation temperatures of EVA/HFMH/LDH nanocomposite samples with 5−15 phr OM-LDH compared with that of the control EVA/HFMH sample when 50% weight loss is selected as a point of comparison. The LOI and mechanical tests show that the LDH can act as flame retardant synergist and compatilizer to apparently increase the LOI and elongation at break values of EVA/HFMH/LDH nanocomposites. The DMTA data verify that the T_g value (−10 °C) of the EVA/HFMH/LDH nanocomposite sample with 15 phr LDH is much lower than that ($T_g = -2$ °C) of the control EVA/HFMH sample without LDH and approximates to the T_g value (−12 °C) of pure EVA, which indicates that the nanocomposites with LDH have more flexibility than that of the EVA/HFMH composites.

Keywords: Layered double hydroxide; Hyperfine magnesium hydroxide; Ethylene-vinyl acetate; Synergistic effect; Nanocomposites

1. Introduction

Ethylene-vinyl acetate copolymers (EVA) with different vinyl acetate (VA) contents are extensively used in many fields, especially in the cable industry as excellent insulating materials with good physical and chemical properties [1]. However, EVA resins are particularly flammable and emit a large amount of smoke while burning. Magnesium hydroxide (MH) is one kind of toxic-free and smoke-suppressing halogen-free flame retardant additive with high decomposition temperature in flame retardant polymeric materials. But its fatal disadvantages are low flame retardant efficiency and thus very large usage amount, which lead the mechanical properties of flame retardant materials to drop down sharply [2]. In order to minimize this effect, the hyperfinization and surface treatment of MH are two important methods to improve its dispersion and compatibility with polymer matrix. Most commonly used surface modifiers include silane coupling agents, stearates, titanate coupling agents, elastomer, etc [3−6]. However, all these surface modifiers of MH are organic reagents or polymer, which could be detrimental to the combustion properties such as limiting oxygen index (LOI). The hyperfine magnesium hydroxide (HFMH) has been verified to be very effective to improve the flame retardant and mechanical properties of

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polymeric materials, but its dispersion in polymer matrix is very difficult [7,8].

In recent years, the intercalated or exfoliated polymer/LDH nanocomposites have attracted great interest in the field of material science because of their excellent thermal stability, flame retardance, and physico-chemical properties [9–16]. The organically modified LDH (OM-LDH) inorganic compounds have nanosized dispersion in the exfoliated polymer/LDH nanocomposites [11,13,17]. In our previous work, we have prepared several kinds of polymer/LDH nanocomposites by direct melt intercalation [18–20]. The melt intercalation is a very promising method for extending the practical applications of polymer/LDH nanocomposites. Recently, Ristolainen [21] and Bourbigot [22] reported that the nanosized layered silicates as cationic clay have the ability to improve the dispersion of MH or aluminum trihydroxide in the polymer matrix. However, the dispersion ability of LDH as anionic clay to inorganic additives in polymeric materials has not reported yet.

In the present work, we used hyperfine MH and organic-modified LDH layers as halogen-free flame retardant system and studied their synergistic effects on morphological structure, thermal property, flame retardant property, and mechanical properties of the EVA/HFMH/LDH nanocomposites by X-ray diffraction (XRD), transmission electron spectroscopy (TEM), thermogravimetric analysis (TGA), limiting oxygen index (LOI), mechanical properties' tests and dynamic mechanical thermal analysis (DMTA). The main purpose of this study is to develop a new type of low smoke and halogen-free flame retardant polymeric nanocomposites and to be applied for the halogen-free flame retardant EVA insulated wire and cable.

2. Experimental

2.1. Materials

Commercial EVA with 28 wt% VA was supplied by Sumitomo Chemical Co. Ltd. The hyperfine magnesium hydroxide (HFMH) with a particle size of 0.1–1.0 μm used in this work was supplied by Jingjiang Kexing Nanomaterials Co. Ltd., China. $Mg(NO_3)\cdot 6H_2O$ and $Al(NO_3)\cdot 9H_2O$ (analytical pure) were supplied by Shanghai ZhenXing Chemicals No. 1 Plant. Sodium dodecyl sulfate (SDS) and NaOH (analytical pure) were obtained from China Medicine (Group) Shanghai Chemicals Reagent Corporation.

2.2. Preparation of samples

The OM-LDH was prepared by co-precipitation method described in our previous work [18]. The pH of 300 ml aqueous solution containing 0.03 mol $Mg(NO_3)\cdot 6H_2O$, 0.01 mol $Al(NO_3)\cdot 9H_2O$ and 0.05 mol $C_{12}H_{25}SO_4Na$ was adjusted to pH ∼ 10 with 1 mol L^{-1} NaOH aqueous solution. The slurry was aged for 3 days at 80 °C, then filtered, and washed three times with distilled water. The white powder OM-LDH was obtained by drying at 60 °C in an oven.

The EVA/HFMH/LDH samples were prepared by melt intercalation of two-step blending. Firstly, the OM-LDH powders and the desired amount of EVA were blended for 10 min by a SXX-300 mixer with the rotor speed of 64 rpm at 130 °C. Secondly, HFMH particles were dispersed into the EVA/LDH nanocomposites by blending for another 3 min. The compositions, morphological structures and some flame retardant properties of various samples are summarized in Table 1.

2.3. Measurements

The XRD patterns were recorded using a Rigaku D/Max-rA rotating anode X-ray diffractometer equipped with a Cu Kα tube and Ni filter ($\lambda = 0.1542$ nm). The TEM images were obtained on a Hitachi H-800 transmission electron microanalyzer with an accelerating voltage of 200 kV and camera length of 0.8 m. The samples were ultramicrotomed with a diamond knife on an LKB Pyramitome to give 100-nm thick slices. And the slices were transferred from water to Cu grid. The TGA profiles were performed on a Shimadzu TGA-50H thermoanalyzer under an airflow rate of 6×10^{-5} m^3/min at a scan rate of 10 °C/min. The LOI values were measured using a HC-2 type instrument (made in China) on sheets 120 × 6.5 × 3 mm according to the standard oxygen index test ASTM D2863-77. The mechanical properties of tensile strength (TS) and elongation at break (EB) were measured by a universal testing machine (DCS500, Shimadzu) with the crosshead speed of 25 mm/min at temperature 25 ± 2 °C. The dumbbell-shaped specimens were prepared according to ASTM D412-87. The DMTA data of the loss tangent (tan δ) and the storage modulus (E') with the changes of temperature were recorded on a Diamond DMTA analyzer (Perkin Elmer) in a temperature range of −80 to 80 °C at a constant frequency of 5 Hz and at a heating rate of 5 °C/min.

3. Results and discussion

3.1. Structural characterization

Fig. 1 gives the low-angle XRD patterns of the OM-LDH, EVA/HFMH, and EVA/HFMH/LDH samples with different loadings of OM-LDH. The basal spaces of the OM-LDH sample are measured to be 2.75 nm from (001) diffraction peak at $2\theta = \sim 3.2°$ and 1.38 nm from (002) diffraction peak at

Table 1
Compositions, morphological structures and LOI of various samples

Sample code	EVA (phr)	HFMH (phr)	LDH (phr)	Morphological structures	LOI (%)
EM-0	100	100	0	–	29
EM-2	100	98	2	Exfoliated	31
EM-5	100	95	5	Exfoliated	32
EM-10	100	90	10	Intercalated	32
EM-15	100	85	15	Intercalated	34
Pure EVA	100	0	0	–	18
E-10	100	0	10	Intercalated	–
E-15	100	0	15	Intercalated	–