Polymer Degradation and Stability 153 (2018) 325–332

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Improving fire retardancy of ceramifiable polyolefin system via a hybrid of zinc borate@melamine cyanurate

Ying-Ming Li, Cong Deng, Jia-Wei Long, Sheng-Chao Huang, Ze-Yong Zhao, Yu-Zhong Wang*

College of Light Industry, Textile and Food Engineering, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Analytical and Testing Center, Sichuan University, Chengdu, 610064, China

ARTICLE INFO

Article history:
Received 30 October 2017
Received in revised form
24 April 2018
Accepted 10 May 2018

Keywords:
EVA
Melamine cyanurate
Zinc borate
Flame retardancy
Ceramization

ABSTRACT

To achieve a high flame retardancy of ethylene-vinyl acetate copolymer (EVA)-based ceramifiable composites, we prepared a hybrid of zinc borate@melamine cyanurate (ZB@MCA) by depositing zinc borate (ZB) at the surface of melamine cyanurate (MCA) on the basis of their hydrogen bonding, and incorporated the ZB@MCA into the EVA/glass powder/mica powder/organo-modified montmorillonite (EVA/GP/MP/OMMT) system to form a novel flame-retardant and ceramifiable EVA composite (EVA/GP/MP/OMMT/ZB@MCA). For EVA/GP/MP/OMMT/ZB@MCA composite with a weight ratio of 35/23/17/5/20, its ceramic formed at 800 °C has the flexural strength of 13.9 MPa, keeping at a high level. The burning tests confirmed that the limiting oxygen index (LOI) value of the composite reached 27.5%, and the UL-94 V-0 rating was achieved. The peak of heat release rate (PHRR) and the peak of smoke production rate (SPR) decreased remarkably compared with the corresponding value of neat EVA in cone calorimeter test. Thermogravimeter-Fourier transform infrared spectroscopy (TG-FTIR) and X-ray photoelectron spectroscopy (XPS) spectra were used to illustrate the flame-retardant mechanism of ZB@MCA in ceramifiable EVA system, and the result illustrated that the gas-phase flame-retardant mechanism was dominant, meanwhile, the ZB facilitated the formation of ceramic layer as a physical barrier in condensed phase, further leading to the enhancement of flame retardancy of EVA composite.

1. Introduction

Ceramifiable polymer composites are prepared through the incorporation of inorganic fillers, dispersant agent, and other additives into polymers [1,2]. It has been found that for inorganic fillers with high or low melting temperature, such as wollastonite, mica, glass powder, and so on, their ceramics formed at high temperature have high flexural strength, integrity, and low coefficient of expansion. Although these inorganic fillers belong to nonflammable material, the polymer-based ceramifiable composites containing these fillers are still flammable.

Actually, ceramifiable composites with excellent flame resistance are very important. For flame-retarded polymer materials, halogen-free flame retardants are commonly used to improve the flame retardancy of polymers because of its highly effective and environmental friendliness [3–9], mainly including metal hydroxides, intumescent flame retardants [10–13], and nano-inorganic materials [5], etc. However, the pyrolysis residue of flame retardants might greatly weaken the flexural strength of the ceramics formed during burning, so the gas-phase action is dominant in flame-retarding ceramifiable polymer composites to avoid the deterioration of mechanical properties of the formed ceramic. Melamine cyanurate as a gas-phase flame retardant is widely used in flame-retarding polymer materials, which acts through diluting the combustible gases during burning [14,15]. Recently, we prepared a novel ceramifiable flame-retardant EVA composite for cables and insulated wires using glass dust (GD), glass fiber (GF), OMMT, and MCA [16]. The composite resulted in the formation of compact, insulted, and porous ceramics at diverse high temperatures. Meanwhile, it showed excellent flame retardancy. Currently, how to obtain a ceramifiable EVA composite with good flame retardancy is still a challenging work.

Mineral fillers such as zinc borate have attracted considerable attention due to its outstanding synergistic effect with other flame retardants, which may form a glassy layer protecting

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* Corresponding author.
E-mail address: yzwang@scu.edu.cn (Y.-Z. Wang).

https://doi.org/10.1016/j.polymdegradstab.2018.05.012
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polymer materials from further burning [17–21] and facilitate the ceramization of polymer composite. The synergistic effect of ZB on the efficiency of flame retardant was investigated through incorporating it into other flame retardants via physically mixing in past research. A few researchers realized that hierarchical nanostructure might contribute to the enhancement of the synergistic effect for a synergistic flame-retarding system. A novel and efficient flame retardant via synthesizing $Zn_6O(OH)\ (BO_3)_3$ hierarchical nanostructure on the surface of brucite was reported [22], and it was found that the flame retardany of EVA composite containing the brucite with the $Zn_6O(OH)\ (BO_3)_3$ hierarchical nanostructure was much better than that of flame-retarded EVA system containing the physical mixture of brucite and $Zn_6O(OH)\ (BO_3)_3$.

On the basis of the consideration mentioned above, we prepared the ZB@MCA on the basis of their hydrogen bonding to improve the flame retardancy of ceramifiable EVA composite. The structure of ZB@MCA was investigated through scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The flame retardancy of ZB@MCA-filled EVA and the mechanical properties of its ceramics formed at different high temperatures were studied with the aid of different measurements. More importantly, the flame-retardant mechanism of ZB@MCA in ceramifiable EVA composite was also investigated in detail.

2. Experiment section

2.1. Materials

EVA (Elvax 260, 28% vinyl acetate) was purchased from DuPont Company (USA). Glass powder (GP) with low melting temperature was supplied by Donggu New Materials Co. Ltd. (Nanhai, China), which is composed of P_2O_5 (45.1%), Al_2O_3 (23.8%), K_2O (14.1%), Na_2O (10.0%), SiO_2 (5.5%), CaO (1.0%), TiO_2 (0.2%), SO_3 (0.1%), Fe_2O_3 (0.1%), ZnO (0.1%), volatile compounds (0.1%), and minor oxides. Mica powder (MP) was provided by Huashuo Mineral Products Processing Factory (Lingshou County, China), which is composed of SiO_2 (45.2%), Al_2O_3 (38.5%), K_2O (11.8%), Fe_2O_3, TiO_2 and MaF_2 (4.5%), and minor oxides. OMMT (I.44 P) was purchased from Nano Co. Ltd. (USA), and it was modified by di-methyl, di-hydrogenated tallow ammonium. The zinc vitriol ($ZnSO_4 \cdot 7H_2O$, analytical grade) and borax ($Na_2B_4O_7 \cdot 5H_2O$, analytical grade) were purchased from Chengdu Kelong Chemical Co., Ltd. (China). The sodium hydroxide (NaOH, analytical grade) flakes were purchased from Chengdu Kelong Chemical Co., Ltd. (China). Melamine ($C_3H_6N_6$, analytical grade) and cyanuric acid ($C_3H_3N_3O_3$, analytical grade) were purchased from Chengdu Kelong Chemical Co., Ltd. (China). Melamine cyanurate (MCA) was supplied from Sichuan Fine Chemical Research and Design Institute (Chengdu, China).

2.2. Preparation of ZB@MCA

First, borax aqueous solution (150 ml, 0.33 mol/L) was added into a three-neck flask equipped with a stirrer under nitrogen atmosphere, and then heated up to 90 °C. Then, zinc sulfate aqueous solution (150 ml, 0.33 mol/L) was injected into the flask, and a small amount of sodium hydroxide aqueous solution (0.5 mol/L) was added in the flask in drops to maintain a pH value of 7.5–8.0 for 6 h. Next, 12.61 g (0.1 mol) melamine and 12.91 g (0.1 mol) cyanuric acid were added in the flask. Ten minutes later, 100 ml deionized water was added into the flask. After 2 h, the suspension was immediately filtered and washed with hot deionized water (90 °C) several times to remove the water-soluble impurities until no SO_4^{2-} was detected by 1 mol/L $BaCl_2$ aqueous solution. The prepared solid products were dried under vacuum at 50 °C for 24 h. Finally, the ZB@MCA was obtained.

2.3. Sample preparation

Table 1 shows the formulation of ceramifiable and flame-retarded EVA composites. The ceramifiable filler (CF) in the EVA composite is composed of glass powder and mica powder. Firstly, all raw materials were dried in a vacuum oven at 50 °C for 10 h. Then EVA composites with different weight ratios of additives were prepared by a twin-screw extruder (CTE20, Kebeilong Keya Nanjing Machinery Co., Ltd, Nanjing, China) with a rotation speed of 160 rpm at the following temperature range from the feed zone to the die: 170, 175, 185, 180, 175, and 165 °C. The extruded products were pressed into different samples by plate vulcanizer (Qingdao Yadong Rubber Machinery Co. Ltd. China) at 170 °C and cold-pressed at room temperature for 3 min. The ceramics with the dimension of 30 mm × 4 mm × 3 mm were prepared successfully by muffle furnace (KSL-1200X, Hefei Kejing Material Technology Co. Ltd., China) at 600, 700, 800, 900, and 1000 °C for 1 h, respectively.

2.4. Measurements

Surface morphologies of MCA, ZB@MCA, the ceramics formed at high temperatures, and the residues obtained from CC test were observed using a JEOL JSM 5900 LV scanning electron microscopy (SEM) (JEOL, Japan) at the accelerating voltage of 5 kV.

EDX was employed to analyze the elemental contents of MCA and ZB@MCA. All samples were coated with gold before examined.

The FTIR result was recorded by a Nicolet FTIR 170SX spectrometer (Nicolet, America) using the KBr disk. The wave number range was from 4000 to 400 cm^{-1}.

The XRD analysis was performed by an instrument with the Cu-Ka radiation (DX-1000 CSC, Dandong Fangyuan Instrument Co., Ltd, China) under 40 kV. The test range was from 5° to 80° with the step length of 0.02°.

The flexural strength of ceramic was determined by the 3-point bend method using a Universal Testing Machine (CMT2000, SANS, Inc. Shenzhen, China) according to the procedure in GB 6569–2006 [24]. The load was applied at a rate of 5 mm min^{-1}. All data are the average value of five flexural strengths.

The LOI value was measured by a HC-2C oxygen index instrument (Jiangning, China) according to ASTM D2863-97. The dimension of sheets is 130 mm × 6.5 mm × 3.2 mm.

The UL-94 vertical burning level was tested on a CZF-2 instrument (Jiangning, China) according to ASTM D3801. The dimension of samples is 130 mm × 13 mm × 3.2 mm.

The flammability was measured by a cone calorimeter (CC) device (Fire Testing Technology, UK). Samples with the dimension of 100 mm × 100 mm × 3 mm were exposed to a radiant cone under a heat flux of 50 kW/m^2.

The TG-FTIR instrument consists of a thermogravimeter (TG/1100 L F, METTLER TOLEDO, Switzerland) analysis, a Fourier transform infrared spectrometer (6700, Nicolet, America), and a transfer tube with an inner diameter of 1 mm. The TG-FTIR test was carried out from 40 to 700 °C at a linear heating rate of 10 °C min^{-1} under the nitrogen atmosphere.

The XPS spectra was recorded by a XSAM80 (Kratos Co, UK), using Al Ka excitation radiation (hν-1486.6 eV).