Polymer Degradation and Stability 105 (2014) 21–30

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

A preliminary study on the thermal degradation behavior and flame retardancy of high impact polystyrene/magnesium hydroxide/microencapsulated red phosphorus composite with a gradient structure

Jichun Liu [a,*], Zhuoli Yu [a], Yaozhen Shi [a], Haibo Chang [b], Yanbin Zhang [a], Jie Luo [a], Chang Lu [a]

[a] School of Chemical Engineering and Pharmaceutics, Key Laboratory of Polymer Science and Nanotechnology, Henan University of Science and Technology, Luoyang, Henan 471023, PR China
[b] School of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

ARTICLE INFO

Article history:
Received 18 October 2013
Received in revised form
10 February 2014
Accepted 16 March 2014
Available online 1 April 2014

Keywords:
High impact polystyrene
Thermal stability
Flame retardancy
Gradient structure

ABSTRACT

High impact polystyrene (HIPS) based composite filled by magnesium hydroxide (MH) and microencapsulated red phosphorus (MRP) with a gradient dispersion of the flame retardant was successfully prepared through layer-on-layer laminating. The gradient variations of structure and composition of the flame retardant along the thickness direction of the composite were characterized by scanning electron microscopy and energy dispersive spectroscopy. Fire performance of the gradient composite was determined by cone calorimeter test. It has been shown that the flame retardant displays a symmetric gradient dispersion along the thickness direction of the HIPS/MH/MRP composite. Thermo-oxidative degradation of the HIPS/MH/MRP gradient composite is retarded notably. This gradient composite can not only produce more charred residue upon thermal degradation, the residue is also more continuous and compact than its homogeneous counterpart with the same loadings of flame retardant. The time to ignition of the gradient composite is prolonged and the times to peak heat release rate, peak mass loss rate, peak smoke production rate and peak CO yield of the gradient composite are all delayed remarkably. Overall, the gradient composite exhibits significantly improved thermal stability, flame retardancy, smoke suppression and decreased toxic release in comparison with its homogeneous counterpart.

1. Introduction

The corrosiveness and toxicity of smoke and other emission products produced during the combustion of polymer materials containing halogen-based flame retardants have given rise to increasing concern worldwide in the past several decades. Extensive work has been performed to render polymers with good flame retardant and smoke suppressant characteristics without evolution of toxic or corrosive decomposition products originating from the flame retardant additive [1–4]. In particular, some metallic hydroxide fillers, such as magnesium hydroxide (MH) and aluminum trihydrate (ATH), have been studied in detail and have become one of the most popular alternatives as either partial or total replacements for halogen-based flame retardants. For example, $Mg(OH)_2$ (or MH) is well-established as an acid-free, halogen-free and smoke-suppressing fire retardant. It decomposes endothermically, releases water and produces a highly heat-resistant magnesia layer covering on the surface of composites upon thermal degradation. Thus, the flame retardant effect of MH is based on cooling, dilution and protection of the magnesia layer against mass and heat transfer between the gaseous flame area and the pyrolyzing melt. However, these metallic hydroxide fillers have an essential disadvantage in common that more than 60 wt% loading is required in order to achieve sufficient flame retardancy. Such high loading could be detrimental to downstream processing and final mechanical properties of the composites [5–7].

Considering the above situation, the combination of MH with other synergists and adjuvants has become a focus of investigation in the pursuit of halogen-free flame retardant (HFFR) composites. Many studies have been done on MH incorporated with other HFFR synergistic agents [8–12] to enhance the flame resistance and decrease the high loading level of MH. Among the various HFFR

* Corresponding author. Tel.: +86 379 64231914; fax: +86 379 64232193.
E-mail address: liujc@iccas.ac.cn (J. Liu).

http://dx.doi.org/10.1016/j.polymdegradstab.2014.03.034

additives, microencapsulated red phosphorus (MRP) is a type of powerful flame retardant and extensively used in polyethylene [13], poly(ethylene terephthalate) (PET) [14], nylon [15], etc. It has been reported that a small amount of MRP combined with MH can improve the fire retardancy of the polymers significantly [5,10]. There is a good synergistic effect between MH and MRP on the flame retardancy of many polymers, such as EVA [10] and HIPS [11,12]. Schartel et al. [11,12] have conducted detailed investigations on the flame retardant mechanism and degradation residue structure of the HIPS/MH/MRP composite. Significant amounts of phosphorus are found to retain in the condensed phase through a reaction of red phosphorus and MH to mostly amorphous phosphates. The formation of amorphous inorganic magnesium phosphates can act as an additional physical barrier to enhance the flame retardancy of the composite material.

So far, great progress has been made in the development of HFFR polymer composites with practical commercial values. Nevertheless, it is clear from earlier work that all the flame retardants are dispersed homogeneously in the polymer matrix and the obtained material is a homogeneous composite. As both thermal degradation and combustion of polymer materials always start from the outmost surface layers, it might be fair to say that the flame retardants dispersed in the inner part of the composite cannot function when the material is radiated or ignited by heat source. At this stage, only the flame retardants dispersed on the surface area can do its work. Recently, Gallo et al. [16] prepared a bi-layer laminate system based on biodegradable polyhydroxyalkanoates blends by compression molding, in which a thin halogen-free flame-retarded layer was located at the top of a kenaf-fiber-reinforced core. They found that this special skin-core composite exhibits better fire retardancy and mechanical performance with a small amount of flame retardants than conventional homogeneous composite. This provides a new way to increase the efficiency of traditional flame retardants. In this paper, a new method is devised to prepare a special composite with the flame retardant displaying a symmetric gradient dispersion along the thickness direction. In this gradient composite, some of the flame retardants were enriched on the surface layer and the loading of flame retardants in the inner part of the composite was decreased.

The main objective of this paper is to evaluate the preliminary investigation on the thermal degradation and fire performances of the HIPS/MH/MRP gradient composite in comparison with its homogeneous counterpart containing the same loading of MH and MRP flame retardants.

2. Experimental

2.1. Materials

High impact polystyrene (HIPS), with a brand of PH-88 and melt flow rate of 11.9 g/10 min (255 °C, 2.16 kg), was purchased from Zhenjiang Qimei Chemical Corporation (Jiangsu, China). Magnesium hydroxide (MH), with an average particle size of 3 μm and modified with silane coupling agent (dodecyl trimethoxylsilane), was supplied by Jinan Chenxu Chemical Corporation (Shandong, China). Microencapsulated red phosphorus (MRP), with an average particle size of 19 μm, was obtained from Lianyungang Pengrui Chemical Company (Jiangsu, China).

2.2. Sample preparation

First of all, pure HIPS pellets were melted on a two-roll mill at 185 °C, followed by introducing various amounts of MH and MRP flame retardants into the HIPS melt on the rotating rollers. After melt-compounding for 10 min, the as-prepared HIPS/MH/MRP composites with different compositions were hot-pressed in a rectangular mold under 10 MPa for 10 min at 185 °C into sheets of 3 mm and 0.4 mm thick, respectively. The thickness of the sheet was controlled by the mold. The 3 mm thick sheet was used to determine the flame retardancy of the homogeneous composite, while the 0.4 mm thick sheet was used to prepare the gradient composite. By changing the mass ratio of HIPS/MH/MRP, a series of HIPS/MH/MRP homogeneous composites were obtained.

A sketch map to prepare the HIPS/MH/MRP gradient composite is shown in Fig. 1. In this figure, the mass ratios of HIPS/MH/MRP for sheet 1, sheet 2, sheet 3 and sheet 4, which are illustrated with different colors, are 100/80/15, 100/48/9, 100/16/3 and 100/0/0, respectively. The compositions of sheet 1′, sheet 2′ and sheet 3′ are identical with those of sheet 1, sheet 2 and sheet 3, respectively. In each sheet, the mass ratio of MH to MRP is fixed at 16/3. As shown in Fig. 1, thin HIPS/MH/MRP homogeneous composite sheets with different compositions and identical thickness of 0.4 mm, together with a 0.6 mm thick pure HIPS sheet (sheet 4), were first placed in a rectangular mold in turn according to the sequence. The mold was then transferred to a hot press whose templates were set at 185 °C beforehand. The various thin sheets were subsequently melted and hot-pressed under 10 MPa for 10 min at 185 °C into one whole plate of around 3 mm thick. The obtained HIPS/MH/MRP composite plate with a symmetric gradient dispersion of the flame retardant along the thickness direction was used for structural analysis, thermal degradation and fire performance tests. Meanwhile, an HIPS/MH/MRP homogeneous composite containing the same total loading of MH and MRP flame retardants with the gradient composite was prepared and tested for comparison. The mass ratio of HIPS/MH/MRP in this homogeneous composite is 100/27.9/5.2. Moreover, an HIPS/MH/MRP homogeneous composite with a mass ratio of 100/80/15, equal to the surface composition of the gradient composite, was also tested for comparison.

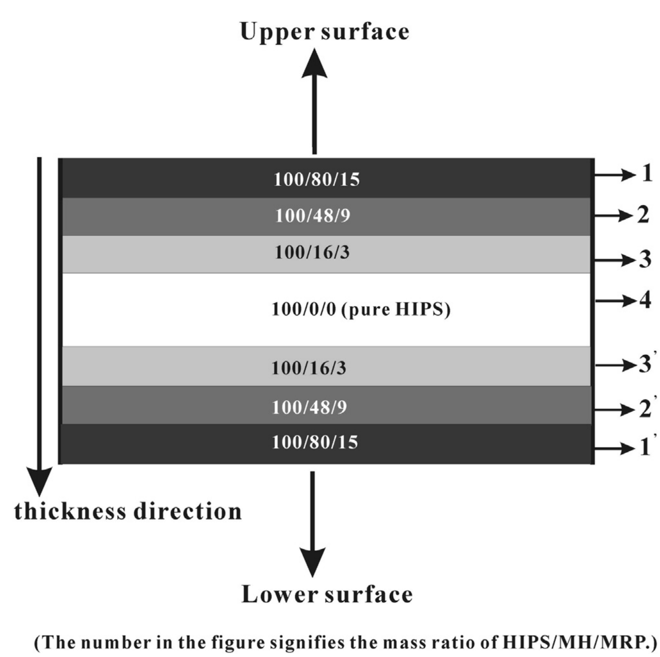

Fig. 1. Schematic diagram showing the preparation of HIPS/MH/MRP gradient composite (The color denotes the loading of flame retardants. The darker the color, the more is the loading of flame retardants. The white area in the center signifies pure HIPS with no flame retardants).