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Flame retardation of glass-fibre-reinforced polyamide 6 by a novel metal salt of alkylphosphinic acid

Zhi Hu, Li Chen*, Gong-Peng Lin, Yuan Luo, Yu-Zhong Wang*

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

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ABSTRACT

Aluminum salts of phosphinic acid mixture of diisobutylphosphinic acid and monoisobutylphosphinic acid (HPA-2TBA-Al) and glass fibres were compounded with polyamide 6 to prepare a series of flame retardant GF/PA6 composites via melt blending. The flame retardance and burning behaviors of the composites were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), and Cone calorimeter test. The thermal properties and decomposition kinetics were investigated by thermogravimetric analysis (TGA) under N_2 atmosphere. Addition of HPA-2TBA-Al results in an increased LOI value, a UL-94 V-0 rating together with a decrease in both the values of PHRR and THR in Cone calorimetric analysis. Visual observations and scanning electronic microscopy (SEM) after flame retardant tests confirmed the char-formation which acts as a fire barrier in condense phase. Analysis of cone calorimeter data indicates that gas phase flame retardant mechanism exists in the GFPA6/HPA-2TBA-Al system.

1. Introduction

Glass-fibre-reinforced polyamide 6 (GFPA6) is a widely used thermoplastic composite due to its outstanding properties, including high strength over a broad temperature range, wear and abrasion resistance and chemical resistance [1,2]. Numbers of flame retardant GFPA6 systems containing halogen or phosphorus compounds are commercially available; however, due to the environment consideration, development of halogen-free additives for GFPA6 becomes a constant challenge. Furthermore, halogen-free flame retardant GFPA6 systems mostly are badly in need owing to legislative restrictions and ecological problems. Phosphorus-based flame retardants including red phosphorus, inorganic phosphates and organo-phosphorus compounds are developed as the most promising approaches to meet the new regulations, standards and test methods for many years [3,4]. Red phosphorus is found to be an effective flame retardant additive in a wide range of polymer materials and particularly useful in glass-filled polyamide with a low loading, but it has limitations, such as red color, flammability and generation of phosphine during processing [5–8]. Recently, it's reported that aluminum salt of diethylphosphinic acid (AlPi, commercially available as Exolit OP 1312 from Clariant Co., Germany) was effective halogen-free flame retardant for polyamide (PA), poly(butylene terephthalate) (PBT), poly(methyl methacrylate) (PMMA) and especially for their glass-fibre-reinforced products [9–13]. Braun et al. investigated the fire retardance mechanism of AlPi in combination with melamine polyphosphate and zinc borate in glass-fibre-reinforced PA66 and found that the AlPi acts mainly by flame inhibition. Laachachi et al. studied the fire behavior of PMMA blended with AlPi and oxide nanoparticles and proposed that AlPi acts principally in the condensed phase and the presence of oxides playing a reinforcement role in the carbonaceous layer. Gallo et al. investigated the flame retardance of PBT containing AlPi and/or nanometric metal oxides and found that AlPi acts mainly in the gas phase through the release of diethylphosphnic acid. Braun et al. found that in glass-fibre-reinforced poly(butylene terephthalate) (GFPBT), 13–20 wt% of the aluminum salt of diethylphosphinic acid (AlPi) fulfill the flame retardant requirements (UL-94 = V-0; LOI>42%) and the use of AlPi results in flame inhibition due to the release of the phosphinate compounds in the gas phase. The flame retardant effectiveness and mechanism of metal salt of alkylphosphnic acid not only related to the applied polymer, but also related to its chemical structure.

In this paper, the mixtures of aluminum salts of both diisobutylphosphinic acid and monoisobutylphosphinic acid (HPA-2TBA-Al) were used as flame retardants for glass-fibre-reinforced polyamide 6. The flame retardance and the thermal properties of GFPA6/HPA-2TBA-Al were discussed. Condense and gas phase

* Corresponding authors. Tel./fax: +86 28 85410755.
E-mail addresses: l.chen.scu@gmail.com (L. Chen), yzwang@scu.edu.cn (Y.-Z. Wang).

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mechanisms were investigated by char-formation observation, activation energies (E_α) calculation and cone calorimetric analysis.

2. Experimental

2.1. Materials

PA6 and glass fibre were kindly supplied from DSM Engineering Plastic Company. PA6 was dried in the oven at 100 °C for 4 h prior to blending. The mixtures of aluminum salts of diisobutylphosphinic acid and monoisobutylphosphinic acid (HPA-2TBA-Al, Scheme 1) were supplied from Weili Flame Retardant Chemicals Industry Co. Ltd (Chengdu, China).

2.2. Sample preparation

The PA6 and glass fibre were mixed with the flame retardant by tumbling the ingredients in a tumbler. Then the mixtures were fed into a twin-screw extruder operating at about 230 °C, the extrudates were cut into pellets. The pellets were compression molded and cut into standard testing bars.

2.3. Measurements

The LOI value was performed according to ISO 4589-1984 and the dimension of all samples was 130 mm × 6.5 mm × 3 mm. The vertical burning test was performed according to UL-94 and the dimension of all samples were 125 mm × 13 mm × 3.2 mm, 125 mm × 13 mm × 1.6 mm, 125 mm × 13 mm × 0.8 mm, respectively. The flammability of the sample was measured with a cone calorimeter device (Fire Testing Technology). The samples with a size of 100 mm × 100 mm × 6 mm were exposed to a radiant cone (50 kW m^{-2}). Scanning electronic microscopy (SEM, JEOL JSM-5900LV) was used to investigate char residues of the flame retardant GFPA6 after the LOI and Cone test. SEM graphs of the char residues were recorded after gold coating surface treatment. Thermogravimetric analysis (TGA) was carried out on an SDT Q600 thermal analyzer under a 100 mL/min flowing nitrogen and air atmosphere at a scan rate of 20 °C/min, respectively.

3. Results and discussion

3.1. Flame retardance of GFPA6/HPA-2TBA-Al composites

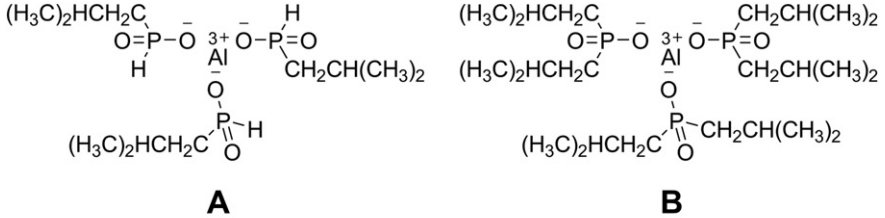
Limiting oxygen index (LOI) values and vertical burning rating (UL-94) rating tests were used to investigate the flame retardance of the composites. The results were summarized in Table 1.

As shown in Table 1, the LOI values increased with the increase of HPA-2TBA-Al contents and reached 30.5 when the HPA-2TBA-Al content was 15 wt%. The LOI values increased slightly when the content of HPA-2TBA-Al increased from 15 wt% to 25 wt%. There are two main effects of glass fibres on the flame retardance: on the one hand, adding glass fibres leads to the so-called "candle-wick effect" reducing the LOI value of GFPA6 compared to the unfilled PA; on the other hand, adding glass fibres leads to "anti-dripping effect" improving the melt flow of FRGFPA [14]. During LOI tests of the composites, charring was observed as shown in Fig. 1: it could be observed that there was no obvious char on the surface of the LOI test bar for the virgin GFPA6; however, for the FRGFPA6, protective char layer on the surface of the LOI test bar was formed. The char layer leads to a significant barrier effect which can isolate flammable gases and heat from the unburned polymer matrix. To further study the char-formation, the morphology of the char obtained from the sample after LOI test was investigated by SEM. As shown in Fig. 2, only glass fibre left on the test bar of the virgin GFPA6 which leads to a low LOI value (22.0). The protective char layer was observed on the test bar of the FRGFPA6 which leads to an increased LOI value (30.5).

Table 1
Flame retardance of GFPA6/HPA-2TBA-Al system with different content.

Samples	LOI (%)	UL-94 rate		
		3.2 (mm)	1.6 (mm)	0.8 (mm)
PA6/30%GF	22.0	NR	NR	NR
PA6/30%GF/15%HPA-2TBA-Al	30.5	V-0	NR	NR
PA6/30%GF/20%HPA-2TBA-Al	32.0	V-0	V-0	NR
PA6/30%GF/25%HPA-2TBA-Al	34.0	V-0	V-0	V-0

UL-94 test measures flammability and flame spread of plastic materials exposed to a small flame [15,16]. Owing to the dripping mechanism, unfilled PA6 achieved a V-2 UL-94 classification [17]. When glass fibre was added to the PA6, the dripping is prevented. The flame retardance of GFPA6 deceased to no rating (NR) because of the "candle-wick effect" and "anti-dripping effect" discussed above. As shown in Table 1, the composite achieved a V-0 (3.2 mm) classification when 15% HPA-2TBA-Al was used as flame retardant; and a V-0 (0.8 mm) classification could be achieved when the content of HPA-2TBA-Al increased to 25%. In UL-94 test, a V-0 classification is given when the material extinguished in less than 10 s after both first and second flame applications, which requires that the flame retardant must be work in a short time. Char-formation was observed during the UL-94 test as shown in Fig. 3. Braun et al. reported that a V-0 GFPBT composite was achieved with 20 wt% content of aluminum diethylphosphinate (AlPi) [10]; however, only HB rating was achieved when 18 wt% AlPi was applied to GFPA66 [9]. The main difference between AlPi and HPA-2TBA-Al probably is the char-formation ability which results a different UL-94 rating. It is noteworthy that the speed of char-formation was fast during the UL-94 test and the formed char layer on the surface of the test bar has a good mechanical property. The unburned polymer matrix was protected well by the char layer. The samples with a thickness of 3.2 mm and 1.6 mm self-extinguish in less than 1 s after both flame applications, 0.8 mm-thickness



Scheme 1. Chemical structures of HPA-2TBA-Al.