

Different flame retardancy effects and mechanisms of aluminium phosphinate in PPO, TPU and PP



Hongxia Li^a, Nanying Ning^{a,b}, Liqun Zhang^{a,b}, Yanxiang Wang^b, Wenli Liang^b,
Ming Tian^{a,b,*}

^a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

^b Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:

Received 24 October 2013

Received in revised form

2 March 2014

Accepted 24 March 2014

Available online 2 April 2014

Keywords:

Poly(2, 6-dimethyl-1, 4-phenylene oxide)
(PPO)

Thermoplastic polyurethane (TPU)

Polypropylene (PP)

Flame retardancy

Aluminium phosphinate

Fire behaviour

ABSTRACT

The effects of aluminium phosphinate (AlPi) on the flame retardancy of three different polymers, namely, poly(2, 6-dimethyl-1, 4-phenylene oxide) (PPO), thermoplastic polyurethane (TPU) and polypropylene (PP), were investigated through cone calorimeter tests (CONE), vertical burning tests (UL-94), limiting oxygen index (LOI), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) observation. The results showed that the amounts of AlPi needed to reach V-0 UL-94 rating in the PPO, TPU and PP matrices were 0 wt%, 30 wt% and 50 wt%, respectively. Moreover, the addition of AlPi significantly increased the LOI values of PPO and PP, but had almost no effect on that of TPU. With the addition of AlPi, the peak of heat release rate (PHRR) of PPO and TPU decreased whereas that of PP increased. The total heat evolved (THE) of all polymers decreased by adding AlPi into the polymers. With the addition of AlPi, PPO composite formed a dense char layer and showed the best flame retardancy, TPU composite formed a thinner char layer and PP composite did not form char layer during combustion.

Based on the thermal degradation behaviour and the char residue of these composites, the flame retardancy mechanisms of the three systems were discussed. For AlPi/PPO composites, the flame retardancy mechanism was condensed phase charring mechanism because of the formation of continuous char layer during combustion. For AlPi/TPU composites, AlPi acted mainly in gas phase, and a synergistic reaction of phosphorus and nitrogen compounds occurred and diethylphosphoric acid providing flame inhibition was released during the burning process. As a result, the addition of AlPi successfully reduced the melt-dripping and enhanced flame retardancy of TPU matrix. For AlPi/PP composites, AlPi acted as a flame inhibitor in gas phase, decreasing the effective heat of combustion of the volatiles (THE/TML) and increasing the amount of CO.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, the interest in flame retardants used in polymers has been focused on the halogen-free flame retardants because the European Union RoHS (Restriction of the use of certain Hazardous Substances) instruction banned the use of halogenated flame retardant materials [1,2]. Among halogen-free flame retardants, magnesium hydroxide (Mg(OH)₂) is widely used in various polymers, but its flame retardant efficiency is very low. Normally, a content of Mg(OH)₂ higher than 60% is required for excellent flame

retardancy (UL-94 V-0). The mechanical and processing properties of the composites filled with Mg(OH)₂ are declined with increasing Mg(OH)₂ content [3]. Therefore, more efficient flame retardants are required to be developed. Intumescent flame retardants (IFRs) have received considerable attention because of high flame retardant efficiency for most polymers [4,5]. In general, IFRs are composed of three compositions including an acid source (such as ammonium polyphosphate, APP), a blowing agent (such as melamine, MEL) and a carbon source (such as pentaerythritol, PER). It is well known that an intumescent char layer can be formed during combustion and then provide good fire protection for polymers. However, these IFRs are hydrophilic and are very sensitive to corrosive substances, such as water, acid, and alkali [6]. The easy migration of these additives to the polymer surface in moist and corrosive environment significantly restricts their applications [7].

* Corresponding author. Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China.

E-mail address: tianm@mail.buct.edu.cn (M. Tian).

Phosphorus-based flame retardants such as aluminium phosphinate (AlPi) have attracted considerable interest because of high flame retardant efficiency, non-migration, and environmentally amicability. Hence, AlPi has been widely used in various polymers, such as polyamide 6 (PA6) [8], polyamide 6, 6 (PA6, 6) [9], poly(ethylene terephthalate) (PET) [10–12], poly(butylene terephthalate) (PBT) [13–16], poly(methyl methacrylate) (PMMA) [17,18] and thermoplastic polyurethane (TPUs) [19]. Although AlPi has excellent flame retardant efficiency in many polymers, the flame retardancy mechanism of AlPi in various polymers is different. For example, Sullalti et al. [15] reported that AlPi played a major role in the condensed phase, forming a consistent amount of char in PBT. However, Braun et al. [9] reported that AlPi acted mainly in the gas phase in PA6, 6 through the release of diethylphosphoric acid, providing flame inhibition. Hence the flame retardant efficiency and mechanism of AlPi associated with the characteristic of polymer need to be further studied.

In this study, we intentionally chose three types of polymers with potential different flammability, namely, poly(2, 6-dimethyl-1, 4-phenylene oxide) (PPO), thermoplastic polyurethane (TPU) and polypropylene (PP). The flame-retardancy of PPO, TPU and PP systems in the presence/absence of AlPi was evaluated by vertical burning test (UL-94), limiting oxygen index (LOI) and cone calorimeter test (CONE). The corresponding flame retarding mechanisms of AlPi in the above three different polymer matrices were carefully discussed.

2. Experimental

2.1. Materials

Three kinds of polymers were used in this study. PPE (LXR40) was purchased from China National Blue Star Co., Ltd. Its intrinsic viscosity, measured in chloroform at 25 °C, is 38–42 cm³/g. TPU (ER85A) was obtained from Coating Chemical Industry Co., Ltd. PP (1080) was purchased from Formosa Plastics Corporation. The flame retardant AlPi, Exolit OP 1230, was obtained from Clariant International Ltd. AlPi is based on an organic phosphinate and is insoluble in water and organic solvents. Fig. 1 shows the chemical structure and scanning electron microscopy (SEM) micrograph of AlPi. The phosphorus content of AlPi is 23.3%–24%. The SEM micrograph clearly demonstrates that AlPi exists in the form of spheroidal particles, some of which are irregular, with large particle sizes in the range 20 μm–40 μm.

2.2. Preparation of blends

All the polymers (PPO, TPU and PP) were dried in a vacuum oven at 80 °C for 4 h before melt-mixing. Each polymer and the flame retardant were then mixed in a high-speed mixer for 5 min. The temperature and the rate of mixing were 50 °C and 200 rpm, respectively. Blends of polymer and flame retardant were prepared

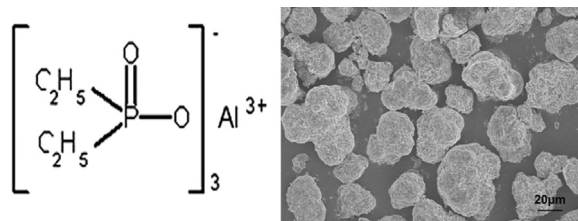


Fig. 1. Chemical structure and SEM micrograph of aluminium phosphinate (Exolit OP 1230).

by using an SJSH-Z-30 co-rotating twin-screw extruder (diameter of screw = 30 mm, $L/D = 44$, Nanjing Rubber and Plastics Machinery Plant Co., Ltd., China). The temperatures of the twelve zones were 260 °C/260 °C/260 °C/265 °C/265 °C/270 °C/270 °C/275 °C/275 °C/280 °C/280 °C/280 °C for PPO–AlPi blends, 160 °C/160 °C/160 °C/165 °C/165 °C/170 °C/170 °C/175 °C/175 °C/180 °C/180 °C/180 °C for TPU–AlPi blends and 170 °C/180 °C/185 °C/195 °C/200 °C/200 °C/200 °C/205 °C/205 °C/210 °C/210 °C/210 °C for PP–AlPi blends. The rotation speed was fixed at 200 rpm. The pellets obtained by extrusion were dried in a vacuum oven for 24 h and then compressed in a pressing machine for 10 min at 15 MPa, at 280 °C for PPO/AlPi composites, 180 °C for TPU/AlPi composites and 200 °C for PP/AlPi composites. The test samples were transferred to another pressing machine and pressed for 10 min at 15 MPa and ambient temperature. For a preliminary study, different amounts of AlPi were used. The compositions of the test samples are listed in Table 1. Among the samples, PPO–10AlPi means PPO composite adding 10 wt% of AlPi, PPO–20AlPi is PPO composite adding 20 wt% of AlPi, and the rest may be deduced by analogy.

2.3. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was conducted on a TGA/DSC simultaneous thermal analyzer (Mettler-Toledo Company, Switzerland). A sample of about 10 mg was put in a silica pan to evaluate the thermal stability of the sample. The sample was heated at a heating rate of 10 °C/min from ambient temperature to 800 °C.

2.4. Fire testing

2.4.1. UL-94 test

Three standard test methods were utilized to evaluate the flame retardancy of the composites. LOI is an indicator of the minimum oxygen concentration that is needed to cause combustion of the material in an oxygen–nitrogen atmosphere through downward burning of a vertically mounted specimen. The test specimen is 70–150 mm in length, 6.5 mm in width and 3 mm in thickness. The LOI test of specimens were proceed according to the Chinese Standard GB/T 2406-93, using a JF-3 instrument (Jiangning Analyzer Plant, China). The horizontal fire test and vertical fire test of specimens (125 mm × 13 mm × 3 mm) were conducted in ambient atmosphere, according to the Chinese Standard GB/T 2408-1996, by using a CZF-3 instrument (Jiangning Analyzer Plant, China). For the horizontal fire test, the samples can be assigned an “HB” rating if the rate of burning is less than 75 mm/min and the flame is restricted to a length of 100 mm. For the vertical fire test, there are three ratings: V-0, V-1 and V-2. If the total flame time is less than

Table 1
Compositions of test samples.

Sample	PPO/(wt%)	TPU/(wt%)	PP/(wt%)	AlPi/(wt%)
PPO	100	0	0	0
PPO–10AlPi	90	0	0	10
PPO–20AlPi	80	0	0	20
PPO–30AlPi	70	0	0	30
TPU	0	100	0	0
TPU–10AlPi	0	90	0	10
TPU–20AlPi	0	80	0	20
TPU–30AlPi	0	70	0	30
PP	0	0	100	0
PP–10AlPi	0	0	90	10
PP–20AlPi	0	0	80	20
PP–30AlPi	0	0	70	30
PP–40AlPi	0	0	60	40
PP–50AlPi	0	0	50	50

Download English Version:

<https://daneshyari.com/en/article/5201882>

Download Persian Version:

<https://daneshyari.com/article/5201882>

[Daneshyari.com](https://daneshyari.com)