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Smoke suppression properties of ferrite yellow on flame retardant thermoplastic polyurethane based on ammonium polyphosphate

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HIGHLIGHTS

- Smoke suppression of FeOOH on flame retardant TPU composites has been investigated.
- FeOOH has excellent smoke suppression abilities for flame retardant TPU composites.
- FeOOH has good ability of char formation, hence improved smoke suppression property.

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ABSTRACT

This article mainly studies smoke suppression properties and synergistic flame retardant effect of ferrite yellow (FeOOH) on flame retardant thermoplastic polyurethane (TPU) composites using ammonium polyphosphate (APP) as a flame retardant agent. Smoke suppression properties and synergistic flame retardant effect of FeOOH on flame retardant TPU composites were intensively investigated by smoke density test (SDT), cone calorimeter test (CCT), scanning electron microscopy (SEM), and thermal-gravimetric analysis (TGA). Remarkably, the SDT results show that FeOOH can effectively decrease the amount of smoke production with or without flame. On the other hand, the CCT data reveal that the addition of FeOOH can apparently reduce heat release rate (HRR), total heat release (THR), and total smoke release (TSR), etc. Here, FeOOH is considered to be an effective smoke suppression agent and a good synergism with APP in flame retardant TPU composites, which can greatly improve the structure of char residue realized by TGA and SEM results.

1. Introduction

It has been reported that most fire deaths are due to toxic gases, oxygen deprivation, and other effects that have been widely referred to as smoke inhalation instead of burns in the United States [1]. In many cases, the visibility impairing and narcotic irritating effect of fire gases are regarded as the decisive factor preventing many fire victims from perceiving their possibilities of escape [2]. Choking smoke poisoning is the leading cause of fire deaths. There are mainly three aspects of fire smoke hazards. First, the high temperature smoke containing a lot of heat can cause thermal damage to people. In addition, the heat can accelerate the spread of fire. Second, fire smoke contains large amounts of toxic gases that are easy to cause poisoning and suffocation, such as CO, HCl, HCN, and so on. Third, fire smoke can affect people's sight and reduce the visibility, so that impact evacuation and rescue [3,4]. As a consequence, the science of understanding how fire smoke and toxic gases generate has progressed substantially in the last half century [5]. In particular, certain problems, such as the corrosiveness, smoke emissions, and toxicity of the combustion products, have always been important issues [6].

TPU is one of the most versatile engineering thermoplastics with elastomeric properties. Because of its high performance, including excellent abrasion resistance, high tensile strength, high compressive and tear strength, good flexibility, and good hydrolytic stability, TPU has been widely used in much industrial area, such as wires and cables, conveyor belts, and protective coatings. However, its flammability and molten dripping nature restrict its applications. Therefore, it is important to improve the flame retardancy of TPU [7]. Many investigations demonstrated that halogen-containing flame retardants show effective flame retardant properties in TPU and a high price-performance. However, the utilization of such retardants has been limited due to generation of toxic gas, causing life and environmental problems. Thus, a wide range of halogen-free flame retardants has been developed and used in TPU, which are mostly phosphorus-containing flame retardants and achieve good improvement. Currently, due to the rise of intumescent system, the majority applied in TPU are halogen-free intumescent flame retardants. However, due to the large amount of addition, there is a great impact on mechanical

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Table 1
Formulations of flame retardant TPU composites.

Sample code	TPU (wt%)	APP (wt%)	FeOOH (wt%)
TPU-0	100.00	–	–
TPU-1	80.00	20.00	–
TPU-2	80.00	19.375	0.625
TPU-3	80.00	18.75	1.25
TPU-4	80.00	17.50	2.50
TPU-5	80.00	16.25	3.75
FeOOH1.25	98.75	–	1.25
FeOOH3.75	96.25	–	3.75
FeOOH20	80.00	–	20.00

properties of TPU and a negative impact on its application [8,9]. Furthermore, there is also a large amount of toxic smoke released from intumescent flame retardant TPU composites during combustion. Thus, developing the retardants with good flame retardancy and smoke suppression is the key to further explore the TPU applications. To the best of our knowledge, no work has been reported the synergistic effects between FeOOH and APP on achievement of smoke suppression and flame retardant properties in TPU composites.

This paper mainly studies the synergistic smoke suppression properties and flame retardant effect between FeOOH and APP in flame retardant TPU. And, the effect was investigated by smoke density test (SDT), cone calorimeter test (CCT), and thermalgravimetric analysis (TGA), respectively. Additionally, to further explore how the structure of char determines smoke suppression properties, the residue chars of TPU composites left after cone calorimeter test were examined by scanning electron microscopy (SEM) analysis.

2. Experimental section

2.1. Materials

Commercial TPU (9380A) was produced by Bayer, German. The basic properties of TPU are as follows, density: 1.110 g/cm^3 (ISO1183); hardness: 82A (ISO868); tensile strength: 40 MPa (ISO527-1,-3); elongation at break: 500% (ISO527-1,-3). APP with particle size of 2500 mesh was purchased from new thin Metal and Chemical Co., Ltd., Guangzhou, China. FeOOH (Bayferrox 4920, particle size of 800 mesh) was purchased from the Qingdao Zhicheng Trade Co., Ltd., Qingdao, China.

2.2. Sample preparation

Before processing experiment, TPU was dried in oven at 80 °C for 8 h. APP and FeOOH were dried in oven at 100 °C for 10 h. A certain amount of TPU was melted in the mixer at 175 °C. Then a certain amount of FeOOH and APP were added into the mixer, respectively. The blends were mixed for 10 min and pressed into sheets using tablet press machine. The formulations of flame retardant TPU composites are listed in Table 1.

2.3. Measurements

2.3.1. Smoke density test

A smoke density test machine (JQMY-2, Jianqiao Co, China) was used to measure the smoke characteristics according to ISO 5659-2 (2006). Each specimen with dimensions of 75 × 75 × 2.5 mm^3 was wrapped in aluminum foil and exposed horizontally to an external heat flux of 25 kW/m^2 with or without the application of a pilot flame. Two tests were carried out for each one sample.

2.3.2. Cone calorimeter

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen with dimensions of 100 × 100 × 3 mm^3 was wrapped in aluminium foil and exposed horizontally to an external heat flux of 50 kW/m^2. Three samples were carried out on the cone calorimeter test. The corresponding values of different parameters are average values of the three tests in this paper.

2.3.3. Scanning electron microscopy

Scanning electron microscopy (SEM) studies were performed using a Hitachi X650 scanning electron microscope.

2.3.4. Limiting oxygen index (LOI)

LOI was measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 10 × 6.5 × 3 mm^3. Each sample was tested for 5 times. And, the LOI value was the average of the 5 values.

2.3.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the sample was performed using a DT-50 (Setaram, France) instrument. About 10.0 mg of sample was put in an alumina crucible and heated from ambient temperature to 750 °C. The heating rates were set as 20 K/min (nitrogen atmosphere, flow rate of 20 mL/min).

3. Results and discussion

3.1. Smoke density test

The smoke density test gives detailed information about the smoke production. Fig. 1(A) presents the luminous flux curves of flame retardant TPU composites with flame in the SDT. In the case of TPU-0, the luminous flux rapidly decreases in the first 200 s and gets the lowest luminous flux value (7.5%) at 480 s, then slightly increases gradually. When APP is added into TPU, the luminous flux mainly decreases in the first 450 s, and attains the lowest value (48.9%) at 600 s in the SDT. The smoke produced by TPU-1 is significantly less than that of TPU-0. The luminous flux increases from 18.7% to 56.0% at the end of the experiments. Here, the addition of APP in TPU decomposes at low temperature to form polyphosphoric acid compounds, which can catalyze the carbonization of TPU to generate condensed carbon shell on the surface of TPU-1, resulted the decrease of smoke production.

In the case of the samples containing FeOOH, the luminous flux can further increase compared with TPU-1 containing only APP. In addition, the luminous flux increases along with the increase of FeOOH content. The luminous flux of TPU-4 and TPU-5 are, respectively, up to 82.7% and 88.6% at the end of experiments, which are much higher than that of TPU-1 (56.0%). It is concluded that there may be an apparently synergistic effect of smoke suppression between FeOOH and APP in TPU composites.

Fig. 1(B) presents the luminous flux curves of TPU composites without flame in the SDT. It can be seen that there is a small amount of smoke produced from TPU-0 at the first 300 s. Then, the luminous flux rapidly reduces, and reaches 8.4% at 1200 s. The sample containing only APP (TPU-1) shows lower luminous flux than the pure TPU (TPU-0) in the initial 720 s. With increase of time, the luminous flux of TPU-1 is higher than that of TPU-0. This is mainly because that APP can decompose at low temperature to form some smoke precursors and char residue shell. The smoke precursors lead to low luminous flux before 720 s. On the other hand, the generation rate of the smoke precursors decreases with the formation of char residue shell, resulting higher luminous flux in TPU-1 than that of TPU-0. It is interesting that when 0.625 wt% FeOOH is incorporated