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Synergistic effects of sepiolite on the flame retardant properties and thermal degradation behaviors of polyamide 66/aluminum diethylphosphinate composites

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ABSTRACT

The effect of sepiolite as a synergistic agent on the flame retardancy and thermal degradation behavior of polyamide 6,6 (PA66)/aluminium diethylphosphinate (AlPi) composites were investigated by limiting oxygen index (LOI), vertical burning (UL-94) tests, thermogravimetric analysis/infrared spectrometry (TG-IR) and cone calorimeter tests (cone). The morphologies and the chemical compositions of char residue were investigated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectra. The results demonstrated that the specimens with the thickness of 1.6 mm passed UL-94 V-0 flammability rating and the LOI value was as high as 33.4% when the loading amount of AlPi was 14 wt %. However, when sepiolite (3 wt % based on flame retardant) incorporated into the AlPi/PA66 composites and the total loading amount of AlPi/sepiolite mixture was only 10 wt %, the samples with the thickness of 1.6 mm successfully passed UL-94 V-0 flammability rating and the LOI value reached 32.5%. It was deduced that the combination of AlPi with sepiolite possessed an evident synergistic effect and enhanced the flame retardant efficiency for PA66 materials. The TG-IR and FTIR tests of the char residues revealed that the incorporation of sepiolite changed the degradation process of the PA66/AlPi system and possibly formed diethylphosphinic acid, siliconphosphate and magnesiumphosphate in condense phase, which enhanced the thermal stability and char yield of PA66 materials at high temperature. The results of cone tests revealed that AlPi combined with sepiolite efficiently reduced the fire behavior parameters, such as heat release rate (HRR), total heat release (THR) and so on. The digital photographs and morphological structures of char residues demonstrated that sepiolite benefited to the formation of more sufficient, compact and homogeneous char layer on the materials surface during burning. The analysis of XPS indicated that sepiolite promoted the formation of flame retardant elements rich char layer on the materials surface, which increased the strength of the char layer and enhanced the flame retardancy of PA66 polymeric materials.

1. Introduction

Polyamide 6,6 is an important engineering plastics and widely used in many applications such as tire cord, rope, air bag, conveyer belt, bearing and gear due to its excellent properties including chemical resistance, high tensile strength, wear and abrasion resistance [1–5]. However, pure PA66 materials are very flammable and produce a large amount of dripping during combustion, therefore, they can not satisfy some applications which require high flame retardant grade [6]. Thus the flame retardancy of PA66 is becoming an urgent problem and has attracted more and more attention. Traditionally, halogen-containing compounds with antimony trioxide as a synergistic agent has been regard as the main flame retardants for PA66 owning its high flame retardant efficiency and cost-performance ratio [7], but they have been restricted owing to human safety and environmental protection. Thus, the development and application of halogen-free flame retardant has become a subject of extensive investigation for PA66

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materials. Among the halogen-free flame retardants, red phosphorus (RP) is studied most widely as flame retardant for PA66. However, the main disadvantages of red phosphorus as a fire retardant for nylons are its red colors, flammability and the generation of highly toxic phosphine through reaction with water[[1,8,9,18]]. Magnesium hydroxide ($Mg(OH)_2$) is also used in PA66 materials [10], but they exhibit poor compatibility with the polymer matrix and low flame retardant efficiency which deteriorating the mechanical properties of materials [11]. Intumescent flame retardant (IFR) additives have been widely used to enhance the flame resistance of polymers [12,13], the general intumescent system are the phosphorus–nitrogen containing compounds. Y H Chen et al. [14] synthesized nitrogen-phosphorous containing flame retardants (PMOP) and used to prepare the flame retardant glass fiber reinforced PA6 composites, the results shown that the prepared PA 6 composite passed UL-94 V-0 rating (3.2 mm) and UL-94 V-2 rating (1.6 mm) with the loading amount of flame retardant of 30 wt %. However, the IFR additives are susceptible to migration to the polymer surface during the processing owing to their low molecular weight, which decrease the flame retardant efficiency. Meanwhile, they possess lower thermal stability [6,15] and poor water resistance comparing with bromine-containing flame retardants.

Organic phosphinates commercialized as metal salts of phosphinates are a kind of phosphorus based flame retardants for thermoplastics. The reported works reveal that aluminum salt of diethylphosphinic acid (AlPi) is an effective flame retardant for polyamide materials [16,17]. Ulrike Braun et al. [18] reported that PA66/GF-AlPi-MPP and PA66/GF-AlPi-MPP-ZnB composites passed UL-94 V-0 rating and the LOI value reached respectively to 28% and 33% when the total loading amount of flame retardant was 18 wt %. A. R. Horrocks et al. [19] reported that the LOI value of the glass fiber reinforced polyamide beyond 40% and passed UL-94 V-0 rating when the loading amount of aluminum diethylphosphinate (AlPi) was 15 wt %. And, the results revealed that the introduction of zinc stannate into glass fiber reinforced polyamide/AlPi composites and preformed excellent synergistic effect to flame retardant polyamide materials. Some previous researches indicated that the synergistic agents can effectively enhance the strength and stability of the char layer and promote the catalyzing reactions among flame retardant components, further enhanced the flame retardant efficiency [20–23].

Sepiolite is layer-chain structure with the chemical formula of $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 8H_2O$, and it is usually used as synergist for flame retardant polymers due to its good catalytic actions [24]. Therefore, recent studies on thermal stability of polymer/sepiolite systems have shown a strong catalytic effect on the degradation of polymer; it is observed that the accumulated amount of silica particles on the sample surface, and their coverage over the exposed sample surface during burning, have a significant effect on the reduction of heat release rate of polymer [11,25]. Rahmat Gul et al. [26] reported that a synergistic effect on flame retardancy, thermal stability and mechanical properties was found when sepiolite was incorporated into a linear low-density polyethylene (LLDPE)/magnesium hydroxide (MH) composite, and the LOI value reached 36.5% with the sepiolite percentage of 15 wt % in the LLDPE/MH formulation. However, few literature reported the effect of sepiolite in PA66/AlPi system, moreover, the mechanism of synergistic effect need further investigate.

In this work, the AlPi combined with sepiolite was incorporated into PA66 matrix to prepared flame retardant PA66 materials. The flame retardant properties, the formation of charred layers and their microstructure, the synergistic effect of sepiolite in PA66/AlPi systems, the thermal degradation behavior and its flame retardant mechanism of PA66/AlPi/sepiolite composites were investigated by the means of limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter (CONE), scanning electron microscopy (SEM), thermogravimetic analysis/infrared spectrometry (TG-IR) and X-ray photoelectron spectroscopy (XPS) etc.

2. Experimental

2.1. Materials

The PA66 was purchased from DUPONT Company Ltd., USA. Aluminium diethylphosphinate (AlPi) was purchased from Tianjin Zhenxing Chemicals Company and sepiolite was offered by Yunying trading Co. Ltd., China.

2.2. Preparation of PA66 composites

Flame retardants and PA66 were firstly heated in drying oven under vacuum at 80 °C and then mixed homogeneously with a high-speed mixer. Granules of the flame retardant PA66 composites were obtained by extruding the mixtures of PA66, AlPi and sepiolite with different mass fraction in a twin-screw extruder (D: 20 mm, L/D: 32, model: SLJ-20 Nanjing Jieya Chemical Engineering Equipment Co., China) at a temperature profile of six heating zones (265 °C, 270 °C, 275 °C, 275 °C, 270 °C, and 270 °C). Testing samples were molded by an injector (HTF86X1, Zhejiang Haitian, China) at a temperature profile of five heating zones (270 °C, 275 °C, 280 °C, 280 °C, and 275 °C). The contents of flame retardants in flame retardant PA66 composites were listed in Table 1.

2.3. Characterization methods

The LOI values were measured on a JF-3 oxygen index instrument (Jiangning, China) with sheet dimensions of 130 mm × 6.5 mm × 3 mmaccording to ISO 4589-2:1996. The vertical burning ratings were measured on a CZF-2-type instrument (Jiangning, China) with sheet dimensions of125 mm × 12.5 mm × 1.6 mm and 125 mm × 12.5 mm × 3 mm according to the American National Standard ANSI/UL 94-2010.

Cone data were acquired with a dual cone calorimeter (manufactured by FTT) at an incident heat flux of 50 kW/m^2 according to ISO5660-1 standard. The samples were measured on the sheet dimensions of 90 mm × 90 mm × 4 mm. All samples were laid on a horizontal holder.

Thermogravimetric analysis/infrared spectrometry (TG-IR) of the samples was performed on the TGA Q5000 IR thermogravimetric analyzer interfaced to the Nicolet 6700 FTIR spectrophotometer. FTIR was directly connected to TG and measured the gaseous decomposition products from TG by real time. About 5.0 mg sample was put in an alumina crucible and heated from 50 to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere with a flow rate of 20 ml min^{-1}. The temperature of the transfer line is 270 °C.

Fourier transform infrared (FTIR) spectra were characterized on potassium bromide discs and Perkin Elmer 400 spectrometer (USA).

Table 1
Formulation and flame retardancy results of the PA66/AlPi composites.

Samples	PA66	AlPi (wt %)	LOI (%)	UL-94	
				UL-94 rating (3.2 mm)	UL-94 rating (1.6 mm)
S0	100	0	21.5	No rating	No rating
S1	90	10	30.5	No rating	No rating
S2	88	12	32.2	V-0	No rating
S3	86	14	33.4	V-0	V-0