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Effects of microencapsulated APP-II on the microstructure and flame retardancy of PP/APP–II/PER composites

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ABSTRACT

In this study, crystalline form II ammonium polyphosphate (APP-II) was microencapsulated with melamine-formaldehyde (MF) resin, which was prepared by *in situ* polymerization. The results of Fourier transform infrared spectra (FTIR), thermogravimetry (TG), energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) analyses demonstrated that APP-II was successfully microencapsulated with the MF resin. Polypropylene (PP)/APP-II/pentaerythritol (PER) and PP/MFAPP-II/PER composites were prepared and the flame retardancy, thermal stability, and microstructure of the corresponding composites were investigated based on the limiting oxygen index (LOI), UL-94 testing, TG, EDS, SEM, and cone calorimetry. Compared with PP/APP-II/PER composites, the PP/MFAPP-II/PER composites had a higher LOI value and passed the V-0 rating more easily. The results of the TG, EDS, SEM, and cone calorimetry analyses demonstrate that MFAPP-II is beneficial for forming a compact and strong intumescent char, thereby reducing the rates of the maximum-rate decomposition temperature (T_{max}), heat release rate (HRR), total heat release rate (THR), and mass loss (ML) for the PP/MFAPP-II/PER composites, as well as improving the thermal stability, compatibility, and dispersion of MFAPP-II in PP/MFAPP-II/PER composites.

1. Introduction

Polypropylene (PP) has excellent mechanical and physiochemical properties and is used in a wide variety of applications, such as the automobile industry, electricity, engineering, housing materials, and transportation [1–4], but its inherent combustibility limits the range of its application. Thus, it is necessary to improve the flame retardancy of PP.

In general, flame retardants, particularly intumescent flame retardants (IFRs), are effective in reducing the flame retardancy of PP [5]. IFRs have attracted much attention in recent years because they are more environmentally friendly [6] than traditional halogen-containing flame retardants, as well as being more efficient flame retardants. For example, their anti-dripping property means that they tend to emit less smoke and toxic gases during combustion, so they conform to current development trends for flame retardants. However, IFRs have some disadvantages compared with halogen-containing flame retardants [7–9], i.e., they are moisture-prone, have low flame retardant efficiency, and have low compatibility with polymer matrices. Many previous studies have attempted to overcome these disadvantages. For example, previous researchers [10–12] found water resistance could be enhanced by improving the polymerization degree of ammonium polyphosphate (APP) and by the surface modification of APP particles with surfactants.

Microencapsulation is an important method for the surface modification of APP particles. For example, Wu et al. [13–15] reported several methods for producing microencapsulated APP, which are effective for enhancing water resistance. Lei [16] developed a method for producing microencapsulated APP coated with hydroxyl silicone oil and melamine-formaldehyde, where the limiting oxygen index (LOI) value could reach 32% when the APP content was 30%. The microencapsulated APP was incorporated into an ethylene vinyl acetate copolymer and the LOI value could reach 31% when the APP content was 22.5%, which allowed it to pass the V-0 rating [17]. A type of modified APP was prepared by reacting melamine and APP at 250 °C, where its thermal stability and water resistance were improved

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greatly [18]. Modifying APP with melamine obviously improved the thermal stability and the PP composite exhibited a superior flame retardant effect when the added concentration was 25% [19]. The Chisso Corporation of Japan developed a method for modifying melamine-APP, which further improved the properties of melamine-APP [20].

In the present study, APP-II microencapsulated with melamine-formaldehyde (MF) resin was prepared by *in situ* polymerization and it was characterized by Fourier transform infrared spectra (FTIR), thermogravimetry (TG), energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) analyses. The APP-II microencapsulated with MF resin was then used to produce PP/MFAPP-II/pentaerythritol (PER) composites. Microencapsulation of APP-II may improve the flame retardant efficiency and compatibility of PP/MFAPP-II/PER composites. The effects of MFAPP-II on the microstructure and flame retardancy of PP/MFAPP-II/PER composites were determined by LOI, UL-94, TG, SEM, and EDS. The effect of APP-II microencapsulation was also analyzed by cone calorimetry to assess its use as an intumescent coating during the combustion of PP/MFAPP-II/PER composites.

2. Experimental

2.1. Materials

PP (white powder, isotactic index = 96%, melt flow index = 3.5 g/10 min, apparent density = 0.43 g/ml) was provided by Kaikai Petroleum chemical company.

37% formaldehyde, pentaerythritol (PER) and melamine were provided by the Kelong Chemical Reagent Factory (Chengdu, China).

APP-II (average degree of polymerization was about 1000) was kindly donated by Shanghai Xushen Nonhalogen Smoke Suppressing Fire Retardants Co. Ltd.

2.2. Preparation of microencapsulated APP-II

First, 63 g melamine, 110 ml 37% formaldehyde solution, and 250 ml distilled water were placed into a triple-necked flask, which was equipped with a condenser and a stirrer. The mixture was adjusted to pH 8–9 by adding 25% ammonia in water and heated to 85 °C, where the temperature was maintained for about 15 min. Next, the solution was transferred to another triple-necked flask, which contained 100 g APP-II and 100 ml distilled water. The temperature of this system was maintained at 85 °C for 2.5 h. The mixture was then filtered, washed with distilled water, and dried at 100 °C. Finally, the MFAPP-II powder was obtained. The phosphorus (P_2O_5) contents of MFAPP-II and APP-II were determined using a weighing method [21]. The phosphorus content of APP-II was 70.36% and that of MFAPP-II was 29.63%. Therefore, the APP-II content was about 42.11% in MFAPP-II.

2.3. Preparation of the composites

All the PP, PP/APP-II/PER and PP/MFAPP-II/PER composites with different APP-II or MFAPP-II content are prepared on a two-roll mill at about 180 °C, and then molded into plates. The mixed samples are hot-pressed at about 180 °C under 10 MPa for 10 min into sheets of suitable thickness and then cooled to ambient temperature at the cooling rate of 30 °C/min in the mold at 10 MPa [22,23]. The blend compositions with their sample codes were listed in Table 1.

Table 1
Composition of samples and the flame retardancy of composites.

Sample code	PP (wt%)	APP-II (wt%)	MFAPP-II (wt%)	PER (wt%)	LOI (%)	UL-94
Pure pp	100	0	0	0	19	NR*
PP/APP-II/PER-1	86.7	5	0	8.3	22.8	NR
PP/APP-II/PER-2	81.7	10	0	8.3	26.7	NR
PP/APP-II/PER-3	76.7	15	0	8.3	30.5	V-1
PP/APP-II/PER-4	71.7	20	0	8.3	35	V-0
PP/APP-II/PER-5	66.7	25	0	8.3	37.3	V-0
PP/APP-II/PER-6	61.7	30	0	8.3	39	V-0
PP/MFAPP-II/PER-1	86.7	0	5	8.3	23	NR
PP/MFAPP-II/PER-2	81.7	0	10	8.3	29.8	V-1
PP/MFAPP-II/PER-3	76.7	0	15	8.3	34.4	V-0
PP/MFAPP-II/PER-4	71.7	0	20	8.3	37	V-0
PP/MFAPP-II/PER-5	66.7	0	25	8.3	38.1	V-0
PP/MFAPP-II/PER-6	61.7	0	30	8.3	39.7	V-0

NR means no rating.

2.4. Measurements

2.4.1. FTIR

All the specimens measured with FTIR are prepared by the following steps: powder samples are mixed with KBr powders, and the mixture is pressed into a tablet. FTIR analysis is conducted with a Nicolet 6700 spectrophotometer (Nicolet Co. USA).

2.4.2. Thermogravimetry

Thermogravimetric analysis was performed employing TA Instruments NETZSCH TG 209 F1 Iris (Germany). The samples are heated from room temperature to 800 °C at the heating rate of 10 °C min^{-1} under nitrogen atmosphere with a flowing rate of 10 ml min^{-1}.

2.4.3. Limiting oxygen index

LOI is measured as per GB 2406.2-2009 (China) with an XZT-100A oxygen index meter (Kecheng, China).

2.4.4. UL-94 testing

UL-94 vertical burning tests are carried out with a CZF-3 instrument (Jiangning Analysis Instrument Company, China). As per UL-94 test standard [16], dimension of specimens in the test shall be 127 mm × 12.7 mm × 3 mm.

2.4.5. Scanning electron microscopy and energy dispersive spectroscopy

The SEM and EDS of particles and PP composites are obtained by adopting a Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) and Oxford IE250 (Oxford, England) energy dispersive spectroscopy (EDS). Surface elemental composition analysis is performed with EDS. The operating voltage of SEM is 20 kV.

2.4.6. Analysis of the water solubility

First, 10.0000 ± 0.0001 g of APP-II or MFAPP-II were weighed and mixed with 100 ml water in a beaker. The mixture was stirred in a water bath at 25 ± 0.1 °C for 30 min, separated in a centrifuge at a speed of 3000 rpm for 15 min, and filtered. Next, 20 ml of the clear supernatant was transferred to another beaker and dried to constant weight at 115 ± 5 °C. The solubility (g/100 ml) was calculated using the following equation.

$$S = (m_1 - m_2)/20 \times 100$$