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Effect of alkyl groups in organic part of polyoxo-metalates based ionic liquids on properties of flame retardant polypropylene

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ABSTRACT

The structure-property relationship of a series of polyoxo-metalates based ionic liquids (PILs) modified polypropylene (PP)/Intumescent flame retardant (IFR) composites were studied. The results showed that the chemical structure of PILs has a great effect on properties of PP composites. The flame retardancy of PP/IFR/PILs composites with a shorter alkyl group are better than that with a longer alkyl group. The PP/IFR/PIL composite with 0.5 wt% PIL with 1-butyl-3-methyl imidazole and 14.5% IFR gets the UL-94 V-0, but achieving the same UL-94 grade needs no less than 19.5 wt% IFR and 0.5 wt% PIL with 1-octyl-3-methyl imidazole. In addition, PILs modified by different groups have great effects on the mechanical properties, the PP/IFR/PIL composites containing 1-dodecyl-3-methyl imidazole obtain the best notch impact strength. The results show that the flame retardant and mechanical properties of PP/IFR/PILs composites can be tailored by changing the cation structure of PIL.

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1. Introduction

Polypropylene (PP) is one of the most popular resins among all plastics due to its excellent properties and high cost performance. However, the flammability of PP limits its applications in many fields. So it is necessary to improve the flame retardant properties of PP. A lot of work have been done in the past several decades to overcome this drawback of PP and great progresses have been achieved [1–10]. Usually the flammability of PP is modified by adding flame retardants into PP or grafting flame retardant elements onto PP. The used flame retardants include halogen, phosphorus, silicon etc.

Intumescent flame retardant (IFR) is one of the most suitable halogen-free candidates for PP because of matched thermal and chemical performance between them. IFR is usually a compound including acid source, carbon source and blowing agent. It shows lots of excellent advantages and environmentally friendly characteristics. However, its flame retardant efficiency is not high enough because only covered by a char layer with good quality and high quantity, can good flame retardancy be obtained. Generally the loading of commercial IFRs is needed more than 25 wt% to achieve the UL-94 V-0 as shown in many literatures [11–15]. And the addition of IFRs will deteriorate the mechanical properties of polymers. Besides, the cost of materials will be increased also. So, increasing the efficiency and cost performance of IFR in PP is an important research topic.

Designing novel flame retardants or introducing catalysts/synergists into the traditional IFRs systems are usual methods to increase the flame retardant efficiency of IFRs [16–22]. Among all methods, adopting catalysts/synergists is more convenient and most of them are inorganic materials. Though these catalysts/synergists have good effects on flame retardancy, they are difficult to be dispersed uniformly into the resin because of their low content and poor compatibility. Organic-inorganic hybrid materials show better potential as synergist than single inorganic materials due to they are composed of inorganic and organic parts. Polyoxometalate based ionic liquid (PIL) is a kind of organic-inorganic hybrid material and can behave as efficient catalyst in many reactions, also in flame retardant fields in our previous work [23,24]. It is found that good synergistic effect exists in PP/IFR/PIL system. The anion of PIL affects the flame retardant properties of PP greatly. However, the effects of organic structure of cation in PILs on the flame retardant performance of PP composites are still confused. What is even more important is that the cation structure may modify the compatibility between PILs, IFR and PP and influence the mechanical performance of PP composites. Therefore, it is a feasible method to balance the flame retardant and mechanical performance of PP/IFR/PILs composites by changing chemical structure of PILs.

This paper focuses on the effect of organic structure of cation in PILs on the flame retardant and mechanical properties of

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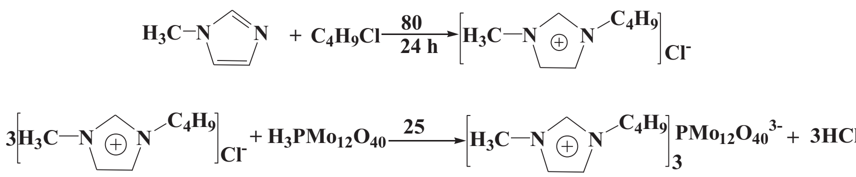

(1)

(2)

Scheme 1. Preparation road of PIL4.

PP/IFR composites. PILs with different chemical structure were prepared based on the reactions between 12-phosphomolbdic acid (PMoA) and 1-butyl-3-methyl imidazolium ([C4]) chloride, 1-octyl-3-methyl imidazolium ([C8]) chloride, 1-dodecyl-3-methyl imidazolium ([C12]) chloride and 1-octadecyl-3-methyl imidazolium ([C18]) chloride, respectively. The synergistic effects of these catalysts on the thermal, flame retardant and mechanical properties of PP composites were investigated by using UL-94 vertical burning tests, limiting oxygen index (LOI), thermogravimetric analyzer (TGA) and notched impact strength tests. Scanning electron microscopy (SEM) was adopted to observe the morphology of char residues after combustion and crack surface of PP composites.

2. Experimental

2.1. Materials

Ammonium polyphosphate (APP) (n > 1500) was supplied by Presafer (Qingyuan, China) Phosphor Chemical Company Limited. Pentaerythritol (PER) was purchased from Aladdin Industrial Inc. (Shanghai, China). PP (F401) was obtained from Yangzi Oil Co., with a melt index of 2.0 g/min (230 °C/2.16 kg). 1-methyl imidazole (MIm) was obtained from Sinopharm Chemical Reagent Co., Ltd. PMoA (Chemical formula: $H_3PMo_{12}O_{40}\cdot nH_2O$) and 1-butyl chloride, 1-octyl chloride, 1-dodecyl chloride, 1-octadecanoyl chloride, of analytical purity were purchased from Aladdin Reagent Chemical Factory. All reagents were used without further purification.

2.2. Preparation of PILs

1-butyl 3-methyl imidazolium chloride ([C4]Cl) was synthesized by stirring1:1 molar ratio of imidazolium and 1-butyl chloride at 80 °C for 24 h in nitrogen atmosphere. After recrystallization from ethyl acetate, the intermediate product was obtained. Then 0.47 g of [C4]Cl and 2.88 g of PMoA were dissolved in deionized water, respectively, and mixed under constant stirring for 12 h. Then a white precipitate was formed. The product was filtered and washed for several times with deionized water until chloride-free ($AgNO_3$ aqueous test). Finally, the obtained [C4]PMo (PIL4) was dried overnight at 80 °C in oven. The preparation road of PIL4 is shown in Scheme 1, the other PILs are similar to PIL4. In addition, [C8]PMo, [C12]PMo, [C18]PMo are marked as PIL8, PIL12, PIL18, respectively. Their HNMR is shown in Fig. S4 and Table S4.

3. Preparation of PP composites

PP composites were prepared by using a Brabender mixer at 200 °C with roller speed 50 rpm for 10 min. The ratio of APP and PER mixture was 3:1 (wt/wt). After mixing, the samples were hot-pressed at about 200 °C under 10 MPa for 3 min into sheets in the dimensions of 100.0 mm × 100.0 mm × 3.2 mm and then cut into suitable sample bars for LOI and UL-94 testing.

3.1. Characterization

LOI values were obtained by a 5801 digital oxygen index analyzer (Kunshan YangYi test Instrument Co., Ltd.) according to ASTM D2863-97. The specimens used for the test were 100.0 mm × 6.5 mm × 3.2 mm in dimension.

UL-94 vertical tests were performed on an AG5100B vertical burning tester (Zhuhai Angui Testing Equipment Company, China) according to ASTM D3801. The specimens used for the test were 100.0 mm × 10.0 mm × 3.2 mm in dimension.

Thermal gravimetric analysis (TGA) experiments were performed on a Mettler Toledo TGA/DSC1 Analyzer. About 5 mg specimens were heated from 25 °C to 800 °C at a heating rate of 10 °C/min under nitrogen (N_2)(50 ml/min).

The SEM morphology of char residue obtained after LOI test was observed by S4800 (Hitachi Corp., Japan). All the samples were coated with a thin layer of conductive gold before examination.

Notched impact strength measurement was carried out with a machine XJ-50Z provided by Chengde Dahua testing machine Co. Ltd. according to ISO180:2000.

4. Results and discussion

4.1. Flame retardant properties

The flame retardant performance of PP/IFR/PILs composites are shown in Table 1.The pure PP has a LOI value of 17.0 and is not classified (NC) in the UL-94 test. When 20 wt% IFR is added, the LOI value increases to 25.7, but is failed in the UL-94 test. All the samples with 0.5 wt% PILs and 19.5 wt% IFR show increased flame retardancy. The PP composites containing PIL4, PIL8 and PIL12 can be classified the UL-94 V-0 without melt dripping and their LOI values are 30.2, 31.3 and 30.0, respectively. However, the PP composites containing PIL18 only passes the UL-94 V-2, and obtains a LOI value 25.2. In addition, the composites with total addition of 15 wt% IFR/PIL4 have a LOI value 28.0 and pass the UL-94 V-0 test. While the PP composites with PILs containing a longer alkyl chain fail in the UL-94 test at the same formulation. The results show that the structure of organic cations in PILs has great effects on the flame retardancy of PP/IFR/PILs composites. The composites containing shorter alkyl chains achieve better flame retardancy than that of longer alkyl chains. It is needed to be noted that the PP11 containing PIL12 can be classified the UL-94 V-0, while that for PP8 is NC.

The effect of PILs content on flame retardancy of PP composites is also researched as shown in Table 2. Though the LOI values change slightly for the four kinds of PP composites, it has a trend of increasing firstly and then decreasing with the content of PILs increasing. However, all PP composites do not pass the UL-94 V-0 tests except PP6. The PIL18 containing the longest alkyl chain possesses the poorest flame retardancy. The PILs may catalyze the charring reaction of PP/IFR during combustion. More or less of PILs do not help to improve the flame retardant properties. Only a suitable dose can increase the flame retardant efficiency. Therefore, only the PP6 achieves the UL-94 V-0. The data suggest that organic structure of PIL plays a great role in the flame retardant properties

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