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Research Paper

Remarkably improving the fire-safety of polypropylene by synergism of functionalized ZrP nanosheet and N-alkoxy hindered amine

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A B S T R A C T

Realizing the high efficiency of halogen-free flame retardant is one of the biggest challenges and the most urgent issues in the development of high performance polypropylene (PP). Coupling the catalytic carbonization and free-radical quenching mechanism is proposed to be an efficient method to address this issue. In this work, a functionalized zirconium phosphate (F-ZrP) with good catalytic carbonization capability was synthesized, and was combined with N-alkoxy hindered amine (NOR) to flame-retard PP. The composition showed high flame-retardant efficiency. When the content of NOR, F-ZrP and ammonium polyphosphate were 0.2 wt%, 4.95 wt% and 14.85 wt%, respectively, the flame retardant PP reached a limiting oxygen index of 36.0% and achieved a UL-94 *V*-0 rating. Meanwhile, the peak heat release rate, average heat release rate, total heat release, peak smoke production rate and total smoke production were declined by 95.6%, 90.6%, 73.3%, 93.5% and 80.6%, respectively. It revealed that F-ZrP formed closed micron-scale char-cages *via* interfacial carbonization. In the char-cages, the nitroxyl radicals generated by NOR efficiently quenched the active free-radicals produced by PP and induce their cyclization reaction. Under the further catalytic effect of ZrP, graphitized crystalline char with extraordinary thermostability and barrier effect was generated quickly and protected the polymer from burning.

1. Introduction

Polypropylene (PP) is widely used in our daily life due to its outstanding mechanical properties, corrosion resistance and electrical isolation. Nevertheless, it is highly combustible, which brings huge safety risk to people's lives and properties. Therefore, it is imperative to improve the flame retardancy of PP. As is known, PP mainly undergoes free-radical chain degradation reactions during combustion, and there is a close relationship between the combustion intensity and the active free-radical concentration (Fu et al., 2016; Turku and Kärki, 2016; Liu et al., 2016). Accordingly, halogen flame retardants can efficiently inhibit the combustion of PP by quenching active free-radicals in the gas phase. However, they generate lots of corrosive gas and poisonous smoke in the fire, which causes heavy casualties (Xu et al., 2015). Therefore, the application of halogen flame retardants are gradually restricted and even forbidden in many countries. In recent years, halogen-free flame retardants, such as intumescent flame retardants (IFR), phosphorus flame retardants, layered double hydroxides (LDH) and metal oxides, are widely investigated and used (Ribeiro et al., 2018; Xiao et al., 2017; Kaul et al., 2017; Pan et al., 2017). Unfortunately, the efficiency of the existing halogen-free flame retardant is unsatisfactory and there is still a great gap comparing with the halogen flame retardant. Realizing the high efficiency of halogen-free flame retardant in polypropylene is an enormous challenge.

IFR is considered to be one of the most promising halogen-free flame retardant because it can effectively block the flame and suppress the melt-dropping by forming multicellular swollen char (Jin et al., 2017). The efficiency of IFR was mainly depended on the quality of the char layer. Unfortunately, the forming char is often defective and thermal instability, which greatly limited the significant improvement of the flame-retardant efficiency. Although the intumescent char can insulate against heat and oxygen, it can't effectively suppress the free-radical chain degradation reactions of PP during combustion, especially in the high temperature condition of a fire scene (Bauer et al., 2017). Therefore, a high amount of IFR (≥25 wt%) is still required to endow PP with satisfying flame retardancy (Zheng et al., 2016a, 2016b).

How to effectively inhibit the free-radical chain degradation reactions of PP is proposed to be the key factor to significantly improve the flame retardancy of PP/IFR. Simultaneously endowing IFR with catalytic carbonization and free-radical quenching capability is an effective

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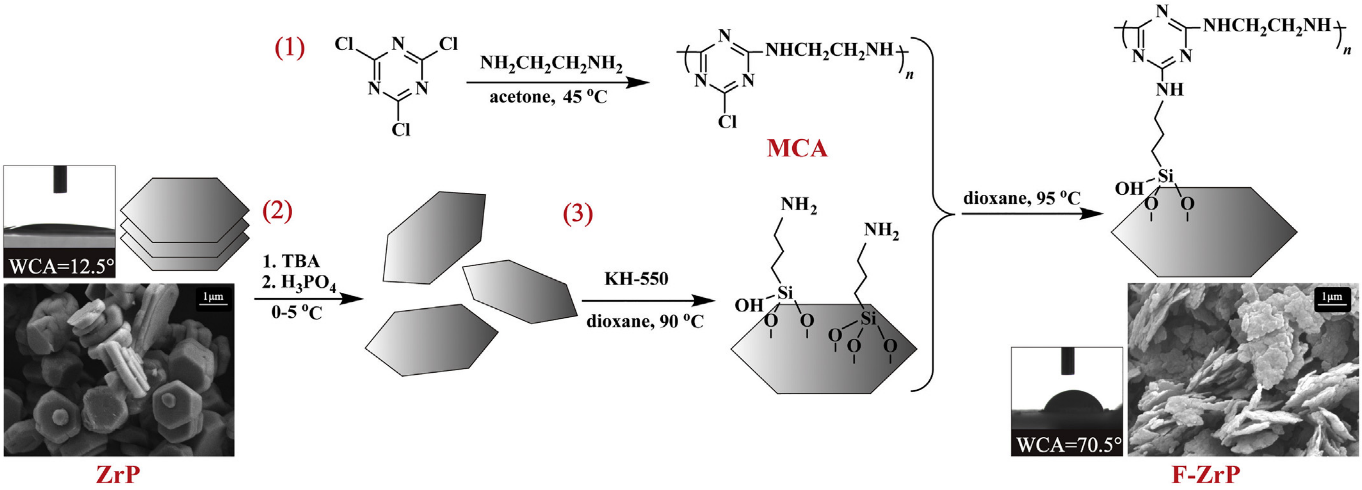

Scheme 1. Synthesis route of F-ZrP.

way to achieve this objective. No matter catalyzing PP into thermostable char or quenching the active free-radicals generated by PP can efficiently inhibit the degradation reactions of PP, which reduces the combustible gases and lessens the burden of the char layer (Song and Ren, 2016; Song et al., 2009; Fu et al., 2010). Additionally, catalyzing carbonization of PP can also supply more carbon source for IFR to improve the quality of the intumescent char.

It is reported that the solid acids, such as zeolite, montmorillonite (MMT) and zirconium phosphate (ZrP), can promote the catalytic degradation reactions of PP, generating cross-linkable degradation products, which were further catalyzed into thermostable char (Song et al., 2008; Song et al., 2007; Yang et al., 2008). Our previous research (Xie et al., 2018) found that functionalized zirconium phosphate (F-ZrP) showed a high efficiency in flame retarding PP by catalyzing carbonization. F-ZrP formed high quality intumescent char with micro-nano char cage structure, in which the degraded products of PP was trapped and catalyzed carbonization by ZrP nanosheet. However, even inside the char cage, the temperature was very high, and the free-radical chain degradation reactions of PP were still very violent, which were competing reactions to the catalytic degradation reactions. Therefore, free-radical chain degradation reaction was still a huge obstacle to the catalytic carbonization efficiency of ZrP. Our previous work (Xie et al., 2015) also revealed that N-alkoxy hindered amine (NOR) had a significant free-radical quenching capability, which effectively suppressed the free-radical chain degradation reactions of PP during combustion. Therefore, combination of N-alkoxy hindered amine and functionalized ZrP nanosheet is proposed to be a promising strategy to realize the high efficiency of halogen-free flame retardant PP. On one hand, NOR would quench free-radicals more efficiently in the closed char cages formed by F-ZrP nanosheets. On the other hand, the catalytic carbonization efficiency of F-ZrP on PP would be significantly improved because the free-radical chain degradation reactions of PP are effectively suppressed by NOR.

Herein, a novel IFR system with outstanding catalytic carbonization capability and free-radical quenching capability is proposed. A functionalized zirconium phosphate (F-ZrP) was first synthesized by decorating ZrP nanosheet with macromolecular charring agent. Then it was combined with NOR to flame-retard PP. The catalytic carbonization capability of F-ZrP and the free-radical quenching capability of NOR showed a good synergism. When the contents of NOR, F-ZrP and APP were 0.2 wt%, 4.95 wt% and 14.85 wt%, respectively, the flame retardant PP reached a LOI of 36.0% and achieved a UL-94 *V*-0 rating; most notably, the peak heat release rate, average heat release rate, total heat release, peak smoke production rate and total smoke production of PP decrease by 95.6%, 90.6%, 73.3%, 93.5% and 80.6%, respectively. This work not only enhanced the fire safety and expanded the application of PP, but also provided new method to realize the high efficiency of halogen-free flame retardant for polymer.

2. Experimental

2.1. Materials

Cyanuric chloride, tetra-n-butylammonium hydroxide (TBA) and 3-aminopropyltriethoxysilane (KH550) was purchased from Aladdin Reagent Co., Ltd., China. Zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$) was produced by Tianjin Fuchen Chemical Reagent Factory, China. Ethanediamine and phosphoric acid (H_3PO_4, 85%) was provided by Chinasun Specialty Products Co., Ltd., China. Acetone and dioxane were purchased from Guangzhou Chemical reagent factory, China. Sodium hydroxide (NaOH) was supplied by Sinopharm Chemical Reagent Co., Ltd., China. N-alkoxy hindered amine NOR116 (NOR for short) was produced by BASF SE, Germany. Ammonium polyphosphate (APP, polymerization degree > 1000) was provided by Shifang Changfeng Chemical Co., Ltd., China. Polypropylene (PP, T30S) was purchased from Sinopec Maoming Company, China. There was no further purification for all the reagents.

2.2. Synthesis of functionalized zirconium phosphate (F-ZrP)

F-ZrP was synthesized according to our previous work (Xie et al., 2018), and its synthesis route was shown in Scheme 1. Firstly, a macromolecular charring agent (MCA) was synthesized through the polycondensation between cyanuric chloride and ethanediamine. Secondly, ZrP nanosheet was synthesized by hydrothermal method and exfoliated with TBA. Finally, the F-ZrP was synthesized by grafting the MCA on the exfoliated ZrP nanosheet with KH550.

The chemical structure of F-ZrP was characterized and confirmed by scanning electron microscopy (SEM, Scheme 1), water contact angle (WCA, Scheme 1), Fourier transform infrared spectroscopy (FTIR) and ^{13}C nuclear magnetic resonance (^{13}C NMR). SEM and WCA: After organic modification, the surfaces of ZrP nanosheets became rough and its WCA was increased from 12.5° to 70.5°, indicating that grafting MCA significantly decreased the surface polarity of ZrP nanosheets. FTIR: N–H (3263 cm^{-1}), $-CH_2-$ (2936 cm^{-1}), triazine ring (1556 cm^{-1} and 808 cm^{-1}), P–O (1042 cm^{-1}), Si–O (1072 cm^{-1}) and Zr–O (593 cm^{-1} and 533 cm^{-1}). ^{13}C NMR: 165.7 ppm (the C atom in triazine ring), 41.8 ppm ($-NH_2-\underline{C}H_2$), 23.6 ppm ($Si-CH_2-\underline{C}H_2-CH_2-$) and 10.6 ppm ($Si-\underline{C}H_2-CH_2-CH_2-$).