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Synthesis and characterization of a novel organic-inorganic hybrid char-forming agent and its flame-retardant application in polypropylene composites

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ABSTRACT

A novel organic-inorganic hybrid char-forming agent (SCTCFA-ZnO) was synthesized and characterized by Fourier transform infrared spectrometry (FTIR) and solid state nuclear magnetic resonance (SSNMR). SCTCFA-ZnO was combined with ammonium polyphosphate (APP) to prepare intumescent flame retardant polypropylene (PP) composites. The flame retardancy and thermal degradation behaviour of composites were investigated by the means of limited oxygen index (LOI), vertical burning test (UL-94), cone calorimeter test (CONE) and thermogravimetric analysis (TGA). The flame retardant pattern and mechanism of PP composites were studied by thermogravimetric analysis/infrared spectrometry (TG-IR), scanning electron microscopy (SEM), laser Raman spectroscopy analysis (LRS), FTIR and X-ray photoelectron spectroscopy (XPS). The results indicated APP/SCTCFA-ZnO system with the mass ratio of 2:1 showed the best flame retardant properties and smoke suppression performance in PP composites. TGA results showed that APP/SCTCFA-ZnO could clearly improve the thermal stability of composites and promote the char residue formation. The residue analysis results further revealed higher graphitic cross-linking structures containing more P, O, N and Si in PP/APP/SCTCFA-ZnO consequently resulted in more obvious reduction of the combustion and smoke production than PP/APP/SCTCFA/ZnO.

1. Introduction

Polypropylene (PP) is widely used in various fields, such as automotive parts, furniture and packages, because of its easy processing, excellent mechanical properties, good chemical resistance, low density and cost. However, its further applications have been restricted greatly because of its easy flammability [1–4]. Therefore, it is important to improve the flame retardant properties of PP. Halogen flame retardants, especially bromine-containing, were once considered as the most effective flame retardants in PP. However, the use of halogen flame retardants has been limited due to safety and environmental problems in recent years. Metal hydroxides as a kind of halogen-free flame retardants were used in PP, but the mechanical properties of polymeric materials were seriously destroyed by high loading. Researchers have made great efforts to develop safer and more environment-friendly flame retardants with higher efficiency, and thereupon intumescent flame retardant (IFR) systems are proposed, which have been regarded as the best candidates to replace the halogen-containing flame

retardants because of its low smoke, non-toxicity, anti-dripping and being environmental-friendly [5,6]. Among these, it was reported that IFR systems with triazine derivatives as charring-forming agents could exhibit better flame retardancy and overcome the inherent shortcomings of traditional IFR systems [7,8].

To further improve the flame retardant efficiency of IFR, metallic oxides as synergistic agents were applied in polymer materials. The existing results revealed different kinds of metal oxides (e.g. ZnO and La₂O₃) could play an effective flame retardant synergist and smoke inhibitor of PP/IFR composites [9–11]. Metallic oxides could catalyse the dehydration, NH₃ elimination and phosphorylation of IFR, and form more stable charring layer consequently improving the flame retardancy of composites during combustion [12,13].

However, metallic oxides were frequently added into polymer matrix by physical blending with flame retardants in the previous work. It was difficult for the mixtures to fully show their synergism because of the low addition amounts of the oxides (< 2 wt.%) and thus the evenness was a big challenge [14]. Besides, the poor compatibility

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between metallic oxides and polymer matrix was another undesirable problem, which worsened the physical and mechanical properties [15]. Therefore, the organo-modification, especially using the organic modifiers with high flame retardancy, is a promising way. Since it not only resolves the problems mentioned above, but also makes the interactions between the flame retardants and metallic oxides more efficient within one molecule unit.

Inspired by the char-forming effectiveness of the triazine derivatives and the synergistic effect of metallic oxides, a novel organic-inorganic hybrid triazine compound (SCTCFA-ZnO) was synthesized and characterized in this paper. The synergistic effects of APP and SCTCFA-ZnO on flame retardancy and thermal stability were investigated by the means of LOI, UL-94, CONE test and TGA. The flame retardant pattern and mechanism were studied by TG-IR, SEM, LRS, FTIR and XPS. The comparisons of the flame retardant properties and thermal degradation between PP/APP/SCTCFA-ZnO and PP/APP/SCTCFA/ZnO composites were also systematically carried out in this work.

2. Experimental

2.1. Materials

Ethylenediamine (analytical) was supplied by Tianjin Fuchen Chemical Reagents Factory, China. Cyanuric chloride (industrial) was purchased from Hebei Chengxin Chemical Co. Ltd. China. 1, 4-dioxane (analytical), γ -aminopropyltriethoxy silane (analytical), triethylamine (analytical), ethanol (analytical) and zinc oxide were purchased from Sinopharm Chemical Reagent Co. Ltd. China. PP (T30 s; melt flow rate = 3.0 g/10 min) was provided by China National Petroleum Corporation, China. APP (average particle size = 15 μ m; degree of polymerization > 1000) was purchased from Polyrocks Chemical Co. Ltd. China.

2.2. Preparation of SCTCFA-ZnO

10 g (0.05 mol) cyanuric chloride and 1, 4-dioxane were added in a dry 500-mL three-necked flask equipped with a stirrer and cooling bath. The mixture was stirred and cooled to less than 5 $^{\circ}$ C, a solution of 12 g (0.05 mol) γ -aminopropyltriethoxy silane and 5.48 g triethylamine in

60 mL 1, 4-dioxane was added dropwise for 1 h. Then the reacting mixture was stirred for another 3 h. After the reaction temperature up to 50 $^{\circ}$ C, a solution of 7.17 g (0.12 mol) ethylenediamine and 16.43 g triethylamine in 60 mL 1, 4-dioxane was added dropwise for 0.5 h with vigorous stirring. The reacting mixture was stirred for 3 h and another 3 h with the reaction temperature up to 100 $^{\circ}$ C. Then, the mixture was cooled to room temperature and poured into 300 mL dichloromethane. Next, the filtered solid was washed three times with dichloromethane and dried in a vacuum oven at 100 $^{\circ}$ C for 5 h and the intermediate SCTCFA was obtained.

Then, nano-ZnO dried at 120 $^{\circ}$ C for 6 h was dispersed in 100 mL ethanol with ultrasonic agitation for one hour. Meanwhile, the intermediate SCTCFA was added into 150 mL mixed solution of ethanol and water with the volume ratio of 9/1, and the pH was adjusted to 9. After the mixture was stirred for 3 h, the nano-ZnO/ethanol was added dropwise into the above solution and stirred vigorously at 80 $^{\circ}$ C for 6 h. The reaction mixture was filtered to remove the solvent, and the product was washed three times with hot water and dried in a vacuum oven at 100 $^{\circ}$ C. Finally, a white powder, weighted 20.10 g (yield: 71%), was obtained. The synthesis routes of SCTCFA and SCTCFA-ZnO were shown in Scheme 1.

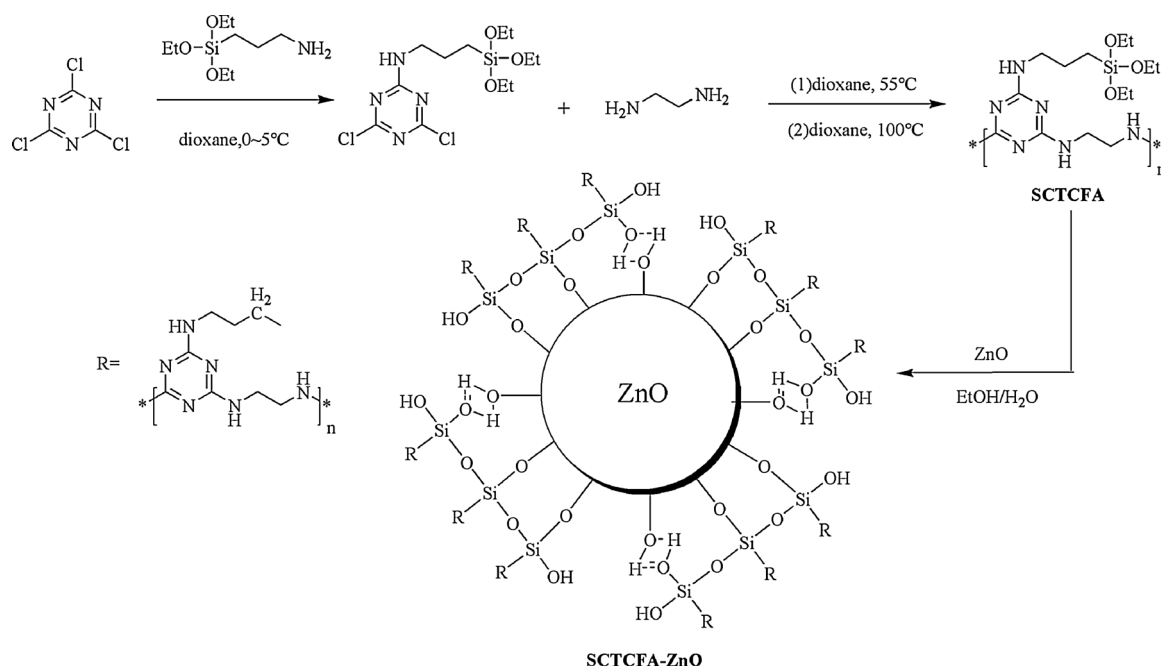
2.3. Preparation of PP/IFR composites

PP, APP, SCTCFA-ZnO, SCTCFA, and nano-ZnO were dried overnight at 100 $^{\circ}$ C in an oven before use. They were melt-mixed in a torque rheometer (KX-160, Jiangsu, China) at 180 $^{\circ}$ C and 40 rpm for 10 min. The formulation of all the samples was listed in Table 1. Then, PP composites were transferred to a mold and hot-pressed into sheets of suitable thickness and size for further testing.

2.4. Characterization

2.4.1. Structural characterization

The infrared spectrum of SCTCFA, SCTCFA-ZnO and char residues were monitored by a Fourier transform infrared (FTIR) spectrometer with KBr pellets (Nicolet iN10MX, USA). 13 C SSNMR and 29 Si SSNMR spectra were performed on Agilent 600 M, USA.



Scheme 1. Synthesis route of SCTCFA-ZnO.

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