Powder Technology 320 (2017) 14–21

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Structural modification of ammonium polyphosphate by DOPO to achieve high water resistance and hydrophobicity

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ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form 2 July 2017
Accepted 7 July 2017
Available online 13 July 2017

Keywords:
Phosphorus heterocycles
Nitrogen heterocycles
Hydrophobic ammonium polyphosphate
High water resistance

ABSTRACT

As one of the important flame retardants, ammonium polyphosphate (APP) usually needs surface modification or microencapsulation to lower its solubility in water and to improve its compatibility with polymers before being applied to the flame retardant system. Herein, we reported a new way to obtain highly water-resistant hydrophobic APP by introduction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) into its molecular structure. The contact angle of obtained DOPO-modified APP is 105°, and its solubility in water at 25 and 80 °C was 0.08 and 0.2 g·100 mL^{-1} H_2O, respectively, lower than that of the commercial microencapsulated APP (0.2 and 0.4 g·100 mL^{-1} H_2O). The hydrophobic mechanism of DOPO-modified APP was discussed in detail. For PP loaded with 30% of DOPO-modified APP or commercial APP, the former could pass V0 rating (1.6 mm) at the vertical burning test (UL-94), while the latter failed. The LOI value of the former increased to 30.1% and that of the latter was only 24.2%. Moreover, cone calorimeter (CC) testing results also indicated that the former exhibited better flame retardant performance.

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1. Introduction

Ammonium polyphosphate (APP), being an acidic source of intumescent flame retardant system, has attracted much more attention due to its low price, low toxicity and higher thermal stability. However, some unsuitable qualities of APP, such as low water resistance and poor compatibility with the polymer matrices, constrain its application. In other words, the problems with the dispersion of inorganic flame-retardant additives into organic medium should be well resolved [1–4]. Surface modification and microencapsulation are usually adopted to alter water solubility and hydrophobicity or hydrophilicity of particles [5–9]. Shao et al. [10] employed ethylenediamine to modify APP via ion exchange reaction and used the modified APP to prepare intumescent flame-retardant polypropylene. The water solubility of modified APP dropped from 1.8 to 1.24 g·100 mL^{-1} H_2O (tested at 25 °C according to Chinese Chemical Industry Standard HG/T 2770-2008). But this value still failed to comply with the standard of water solubility (<0.5 g·100 mL^{-1} H_2O) of APP in HG/T 2770-2008. Sun et al. [11] prepared surface-modified APP with melamine (MA) and 2,4-toluene diisocyanate (TDI) in turn, whose water solubilities at room temperature were decreased from 0.3680 to 0.2975 (MA-APP) and 0.2123 g·100 mL^{-1} H_2O (MA-TDI-APP). Hu et al. [12–15] coated APP with different resins, such as polyurethane, melamine-formaldehyde resin, urea–melamine–formaldehyde resin, melamine-formaldehyde resin and urea–formaldehyde resin, to enhance its water resistance. The water solubilities of all microencapsulated APPs were <0.5 g·100 mL^{-1} H_2O, even in hot water. Nevertheless, some noxious monomers such as formaldehyde would be released not only in production but also in plastics processing, and would cause noticeable health risks.

Liu et al. [16] prepared cross-linked APP by diammonium hydrogen phosphate (DAP) and melamine (MEL) with a water solubility of 0.19 g·100 mL^{-1} H_2O, suggesting that a cross-linked structure by a triazine ring gave rise to better water resistance. In view of these, we put forward a new idea of structural modification on cross-linked APP via introducing an organic small molecule so as to fundamentally alter its hydrophilicity, with the result that subsequent surface modification or microencapsulation is not necessary before APP is loaded in polymer matrices.

This study is aimed to introduce 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) into the APP molecular structure to achieve high water resistance and hydrophobicity. DOPO is a type of cyclic phosphate with a diphenyl structure and active groups (P—H), possessing high thermal stability, good oxidation resistance,

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http://dx.doi.org/10.1016/j.powtec.2017.07.029
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and good water resistance [17,18]. Meanwhile, the flame-retarding effect of DOPO-modified APP on PP was also investigated.

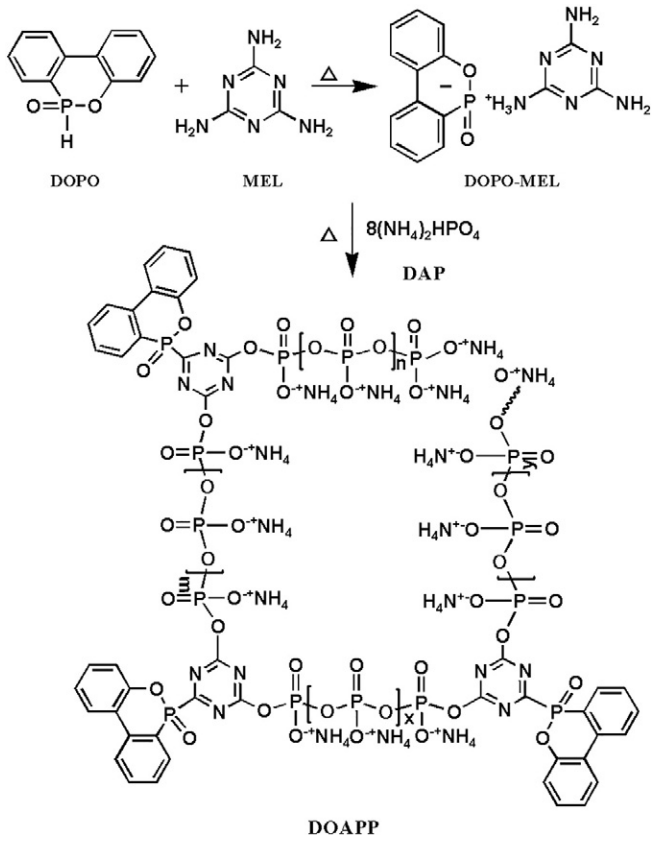
2. Experimental

2.1. Materials

DOPO was purchased from Aladdin Industrial Corporation, China. MEL was bought from Tianjin Hengxing Chemical Reagent Co., Ltd., China. DAP was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd., China. All chemicals were analytical reagents. The commercial APP microencapsulated by melamine-formaldehyde resin with average degree of polymerization $n > 1000$ (Hangzhou JLS Flame Retardants Chemical Corporation) was tested simultaneously for the comparative analysis. Powdered PP (045, Ningbo Yongxing Chemical Co., Ltd., China) was used for the preparation of PP composites.

2.2. Preparation of DOPO-modified APP

DOPO, MEL and DAP were dried at 85 °C for 2 days. Dried DOPO was put into a three-neck round-bottom flask, equipped with a mechanical stirrer, a thermometer and a dry N_2 inlet, and then heated to 150–160 °C for 30 min while N_2 purging. MEL was added into the molten DOPO under stirring and reacted with DOPO for 4 h. Subsequently, DAP was added into the flask under stirring at the rate of 200 r min^{-1}, and the mixture was heated to 250–260 °C. The molar ratio of DOPO:MEL:DAP was 1:1:8. Before full solidification, the resultant product was poured out and rinsed with absolute alcohol and hot deionized water (80 °C) to remove unreacted reactants. The white powdered DOPO-modified APP was obtained after drying at 80 °C for 8 h. In addition, lab-synthesized APP was obtained in the same way without the addition of DOPO.



Scheme 1. Synthesis of DOPO-modified APP.

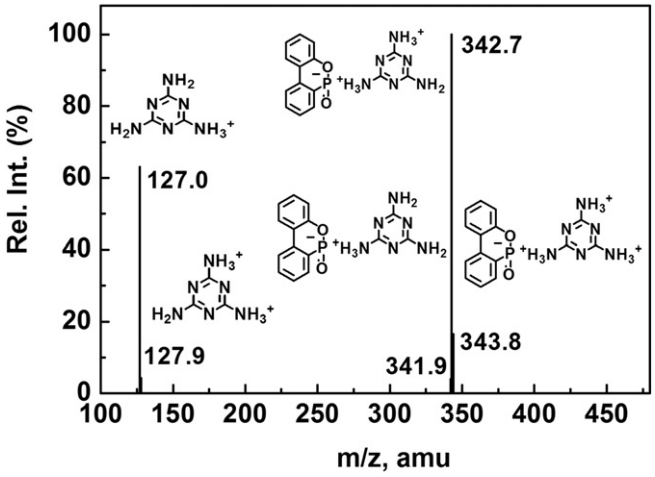


Fig. 1. ESI-MS of DOPO-MEL.

2.3. Preparation of PP composites

All the materials for the composites, including the commercial APP, the prepared DOPO-modified APP and powdered PP were dried in an oven at 80 °C for 24 h. PP composites were extruded by a double conical micro-twin-screw extruder (SJZS-10B-2, Wuhan, China). The 30% of additives (DOPO-modified APP or commercial APP) and powdered PP were fed into the hoppers and then melt compounded. The operating temperature of the extruder was maintained at 190–200 °C from hopper to die. The rotation speed of the screw was 20 rpm. Subsequently, the various specimens were molded by a micro-injection-molding machine (SZS-20, Wuhan, China).

2.4. Characterization and test

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-710 (Nicolet, USA) spectrometer.

The X-ray diffraction (XRD) patterns using Cu Kα radiation and a Ni filter ($\lambda = 1.540600$ Å) were performed with a D8 Advance powder diffractometer (Bruker, Germany) at a scanning rate of $0.02° \cdot s^{-1}$ in the 2θ range of 10–60°.

A field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Tokyo, Japan) was used to observe the morphologies of different samples.

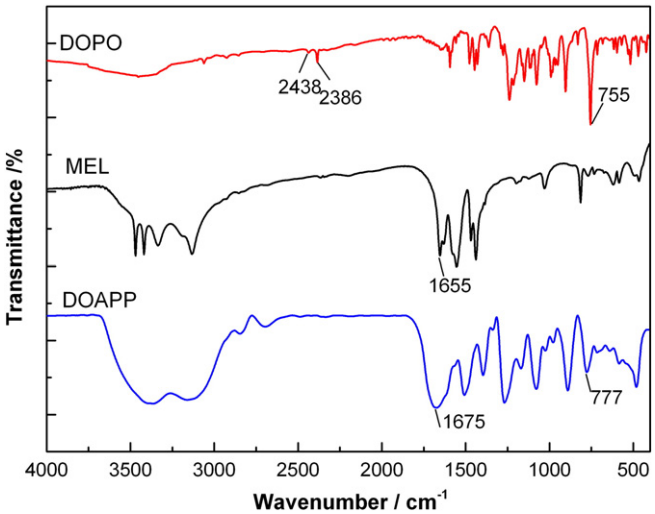


Fig. 2. FTIR spectra of (a) DOPO; (b) MEL and (c) DOPO-modified APP.

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