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Aluminum phosphate microcapsule flame retardants for flexible polyurethane foams

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ABSTRACT

In this study, highly efficient flame-retardant aluminum phosphate (ALP) microcapsules were synthesized from ALP and ammonium phosphomolybdate trihydrate. The chemical structure of the ALP microcapsules was characterized by scanning electron microscopy and elemental analysis, and the thermal degradation behavior was investigated by thermogravimetric analysis (TGA). Subsequently, flexible polyurethane (PU) foams were prepared with the ALP microcapsules. Limiting oxygen index (LOI) tests, vertical burning tests, smoke density rating (SDR), and cone calorimetric tests were employed to investigate the combustion of the materials. The results showed that the flexible PU foams with 15 parts per hundred polyol by weight (pphp) ALP microcapsules passed the vertical burning test and they had an increased LOI value of 28.5%. The SDR value for PU/20 pphp ALP microcapsule composites was about 16.0% and the SDR value for the pure PU was about 29.0%. The corresponding flame-retardant mechanism was investigated by Fourier transform infrared spectroscopy, TGA, Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) tests, and energy-dispersive X-ray spectrometry.

1. Introduction

Flexible polyurethane (PU) foam is a type of polymeric material that comprises chains with repeating units containing the characteristic urethane group, which is normally manufactured from isocyanates and polyols. The main applications of flexible PU foams are in automobiles and electronic products such as cushions, interior decorations, sofas, and mattresses [1,2]. Unfortunately, flexible PU foams also have some disadvantages, especially their flammability and the toxicity of the gas products emitted during thermal degradation and combustion [3]. Pristine flexible PU foam is highly flammable with a limiting oxygen index (LOI) values as low as 20.0%. Thus, flexible PU foam can combust and spread fires easily without flame-retardant treatment. Effective and commercially available flame retardants for flexible PU foam include halogen-containing flame retardants. However, halogen-containing flame retardants usually produce corrosive and toxic gases during combustion [4,5]. Considering their health and environment risks, halogenated flame retardants are limited or even banned in many areas. The use of halogen-free flame retardants as additives is a simple and green alternative to enhance the fire safety of flexible PU foams. Ammonium phosphomolybdate trihydrate and ammonium molybdate tend to form char structures and they can also release inert gases in combustion environments, so these materials are used widely as flame retardant additives [6]. Many studies have aimed to develop effective non-halogenated flame retardants for PU foam [7,8].

Achieving high flame retardancy and non-dripping for flexible PU foams by adding a low loading of flame retardants is a challenging problem. Furthermore, the addition of large amounts of flame retardants may degrade the mechanical properties and cause poor compatibility. Thus, it is very important to develop an economical, environmentally friendly, and highly efficient flame retardant for flexible PU foams [9,10]. To address this problem, Chen et al. [11] prepared flame-retardant flexible PU foam using a 2-carboxyethyl-(phenyl)phosphinic acid melamine salt, which exhibited self-extinguishing capabilities and good flame retardancy. Rao et al. [12] also prepared a melamine salt (DPPMA: Product of diphenylphosphinic acid and melamine) where flexible PU foam containing DPPMA exhibited self-extinguishing capabilities and good flame retardancy. Nevertheless, it is difficult to prevent the toxic gases comprising CO, NOx, and HCN from being released during the combustion of PU foam. Choking smoke containing these highly toxic gases is the main cause of fatalities during fires [13,14]. Therefore, smoke suppression must be considered when designing flame retardants for flexible PU foams.

In the present study, we prepared novel aluminum phosphate (ALP)

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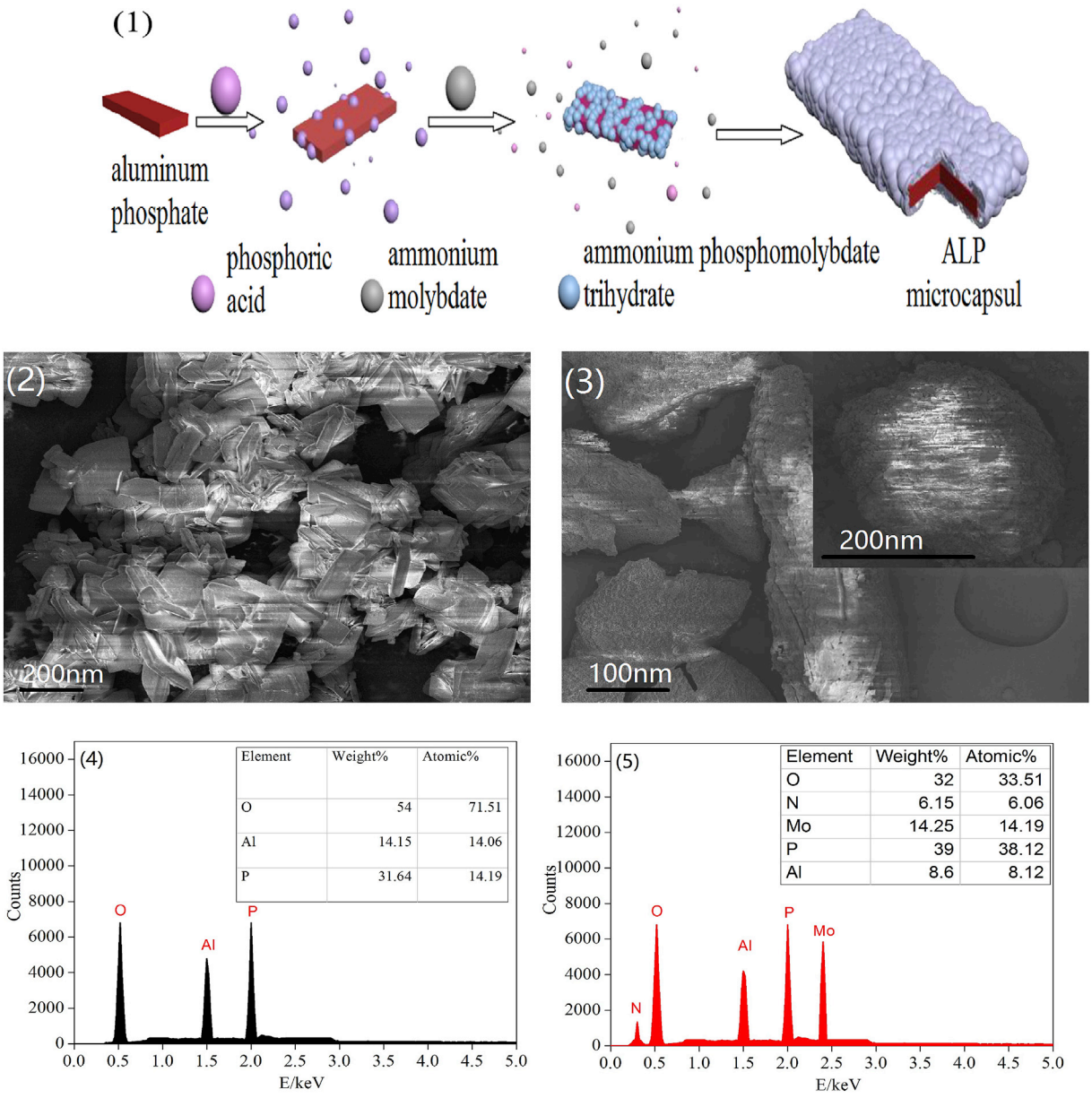

Fig. 1. 1) Synthetic route for the ALP microcapsules; 2) SEM micrographs of ALP; 3) SEM micrographs of ALP microcapsules; 4) EDX analysis of ALP; 5) EDX analysis of ALP microcapsules.

microcapsules and this flame retardant was added to flexible PU foam to obtain flame-retardant flexible PU foam. Furthermore, the smoke density was significantly reduced. The results of this study are beneficial for the design of ALP microcapsules to obtain flame-retardant PU materials.

2. Experimental

2.1. Materials and chemicals

ALP and diethanolamine were purchased from Hangzhou Gaojing Fine Chemical Co., Ltd (China). Phosphoric acid (H_3PO_4) and nitric acid (HNO_3) were purchased from Hangzhou Gaojing Fine Chemical Co., Ltd (China). Polyether polyol (GEP-330 N; average molecular weight = 3000, average functionality = 3.0, OH content = 56 mg of KOH/g, technical pure grade) was purchased from Gaoqiao Petrochemical Company, Shanghai, China. The catalyst A-33 (a dipropylene glycol solution of triethylenediamine at a mass fraction of 33%) and 2,6-toluene diisocyanate (TDI80; average functionality = 2.6–2.7, viscosity ~ 0.22 Pa/s at 25 °C, technical grade) were purchased from Shanghai Deyin Chemical Co., Ltd (China). The surfactant (AK-6680, technical grade) was purchased from Jiangsu Maysta Chemical Co., Ltd (China). Distilled water was used as a chemical blowing agent. Ammonium molybdate was purchased from Anqing Yuetong Molybdenum Co., Ltd (China).

2.2. Preparation of ALP microcapsules

The microencapsulation process used in this study is illustrated in Fig. 1(1). In a typical procedure, the ALP (10 g) was dispersed in 45% phosphoric acid aqueous solution (10 mL) and stirred at room temperature using a magnetic stirrer for 6 h. Ammonium molybdate (3 g) and nitric acid were then added to the suspension, before adjusting the pH to 1.0. The mixture was allowed to sit for 24 h and the precipitate obtained was then filtered, washed, and dried.

2.3. Preparation of PU foams

The isocyanate index (NCO/OH in mol) was 1.05. Briefly, the polyether polyol (100 parts per hundred polyol by weight; pphp), surfactant