



Solvent-free two-component polyurethane conjugated with crosslinkable hydroxyl-functionalized ammonium polyphosphate: Curing behaviors, flammability and mechanical properties

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ARTICLE INFO

Keywords:

Polyurethane
Ammonium polyphosphate
Flame retardancy
Mechanical property
Curing behavior
Solvent-free

ABSTRACT

To simultaneously improve the compatibility, flame retardancy and mechanical properties of ammonium polyphosphate (APP) based polyurethane, an efficient and facile strategy was developed, in which hydroxyl-functionalized APP (HAPP) was synthesized through ion-exchange reaction between APP and 3-aminopropanol, and then utilized as a multiple-function excipient for solvent-free two-component polyurethane (2K-PU) by chemical cross-linking. The curing behavior, mechanical and flame-retardant performances of HAPP cured 2K-PU, designating as 2K-PU/HAPP, were elaborately evaluated. Cone calorimeter results indicated that the conjugation of 15 wt% HAPP into 2K-PU significantly reduced the peak heat release rate (PHRR), total heat release (THR) and total smoke production (TSP) by 68.7%, 42.8% and 9.3%, respectively. Intriguingly, mechanical tests illustrated that the chemical incorporation of HAPP definitely improved the tensile strength of 2K-PU/HAPP while well-maintained the elongation at break, highlighting its attractive potential for industrial application. In addition, a flame-retardant mechanism for 2K-PU/HAPP was proposed. All aforementioned results distinctly demonstrate a feasible yet promising paradigm for fabricating APP-containing polyurethane.

1. Introduction

Polyurethane (PU) is an extensively exploited versatile polymer with overall balance and controllable features, which has considerable application prospects in leather finishing, synthetic leather manufacturing, coatings, textile laminating, adhesives, foams, and many other industrial fields [1,2]. With ever-increasing legislative restriction on volatile organic compounds (VOCs) emission, the solvent-based polyurethane (SPU) has gradually been substituted by eco-friendly counterparts, such as waterborne polyurethane (WPU) and solvent-free two-component polyurethane (2K-PU) [3]. In industry, to obtain WPU dispersions, usually 10–30 wt% (based on the total feed of reactants) of organic solvents like *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP) or acetone are necessarily to reduce the viscosity of prepolymer mixtures [4,5]. That is to say, certain VOCs are virtually emitted during the synthesis and commercial processes of WPU. Moreover, some property profile of WPU, especially the water and chemicals resistance are inferior to SPU [6]. From this point, the solvent-free 2K-PU, which offers ecofriendly solutions for high-performance PU, has progressively received attention.

In fact, the intrinsic combustibility is another intractable problem

facing PU, which frequently precludes its application in some areas. Under this consideration, plentiful approaches have been devoted to enhance the flammability of PU. The halogenated compounds have long seized an indispensable role in flame retardant PU owing to their advantages of high-efficiency and economic competitiveness. Nevertheless, lots of halogen-containing flame retardants are currently eliminated since they emanate numerous poisonous gases and smoke during a fire, which may cause secondary damage to both humans and environment [7]. Hence, developing more environmentally compatible alternatives is highly desirable. In the last decades, phosphorus-, phosphorus-nitrogen, silicon-, sulfur and chitosan-phosphorous based flame retardants [8–13] as well as nanofillers including carbon nanotubes, graphene oxide, layered double hydroxide and montmorillonite [14–17] have been investigated to improve the fire safety of PU. Among multitudinous candidates, the phosphorus-nitrogen containing intumescent flame retardant (IFR) is recognized as one of the promising alternatives in terms of unmatched efficacy and low-toxicity. It is well-established that a typical IFR system normally consists of an acid source, a char source combined with a gas source [18]. Up to present date, ammonium polyphosphate (APP), which simultaneously serves as acid source and blowing agent, has been widely applied in IFR systems.

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As reported, APP was mostly used as additives by physically blending with PU [18–20]. However, APP tends to exude towards the surface of PU during the service life as a result of the poor compatibility between solid APP particles and PU matrix, thus resulting in a decrease of the flame-retardant efficiency and other properties of PU.

To circumvent this shortcoming, a commonly utilized method is microencapsulation at APP surface, the microcapsule substances of which involve cellulose acetate butyrate [21], polyurethane [22], epoxy resin [23], cyclodextrin [24], and oxydianiline-formaldehyde resin [25]. Indeed, the microencapsulation process has been proven to encourage satisfactory improvements in the interfacial interaction between APP and polymeric matrices. Unfortunately, its damage to the mechanical properties of PU composites has not been effectively solved. Therefore, how to reconcile the contradiction between the mechanical properties and fire resistance of PU still remains a challenge. Quite recently, Chen and Wang et al. modified the APP by cation exchange reaction with diethylenetriamine, piperazine and polyethyleneimine, respectively, through which the organic-inorganic mono-component flame-retardant amine hardeners were synthesized and cured with epoxy resins [26–28]. Results confirmed that the modified APP bestowed the resulting epoxy resins with excellent flame retardancy and smoke suppression efficiency, while the impact strength was improved as well. However, to the best of our knowledge, no literature has yet reported that APP could contribute to flame-retardant PU through irreversible chemical method.

Considering the inadequacies mentioned above, we herein demonstrate a facile procedure for fabricating hydroxyl-functional ammonium polyphosphate (HAPP) by grafting 3-aminopropanol on the surface of APP via ion-exchange reaction. Subsequently, HAPP was utilized as crosslinkable reinforcing agent for solvent-free 2K-PU. It is anticipated that the covalent conjugation of multifunctional HAPP can effectively enhance the flame-retarding, smoke suppression, and simultaneous, the mechanical properties of 2K-PU.

2. Experimental methods

2.1. Materials

Ammonium polyphosphate (APP, form II, $n > 1000$) was provided by Jinan Taixing Fine Chemicals Co., Ltd. (Shandong, China). Polypropylene glycol with average molecular weight of 2000 and 1000 (N220 and N210, CP), 3-aminopropanol (AP, AR), and 1,3-butanediol (1,3-BDO, AR) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). HDI trimer (HT-100, containing ~22.0% NCO functionality), isophorone diisocyanate (IPDI, purity 99.5%), and methylene-bis(4-cyclohexylisocyanate) (H_{12} MDI, purity > 99.5%) were kindly supplied by Wanhua Chemical Group Co., Ltd. (Shandong, China). 1,4-Butylene glycol (1,4-BDO, AR), stannous octoate ($Sn(Oct)_2$), and anhydrous ethanol (AR) were obtained from Kelong Chemical Reagent Co., Ltd. (Sichuan, China).

2.2. Preparation of HAPP

Hydroxyl-functionalized ammonium polyphosphate (HAPP) was fabricated via cation exchange reaction between APP and AP as illustrated in Scheme 1. Typically, a certain volume ratio of ethanol to deionized water (200 mL: 9 mL) was introduced into a 500 mL three-neck glass flask equipped with a thermometer, magnetic stirrer, nitrogen inlet and a circumference condenser. Then 3-aminopropanol (6.97 g) was poured into the solution under gentle agitation at room temperature for 10 min. Subsequently, 30 g APP was added into the flask, and the mixture was gradually heated up to 90 °C, refluxing for 4 h. After cooled to ambient temperature, the precipitate was filtered, washed thrice with anhydrous ethanol. Successively, the resulting white solid was dried in a vacuum oven at 80 °C to constant weight, having a yield of 89%.

2.3. Synthesis of hydroxyl-terminated prepolymer (HTP)

A 250 mL three-necked reactor was charged the following reactants: IPDI (39.96 g, 0.18 mol), N220 (80 g, 0.04 mol), N210 (20 g, 0.02 mol), 1,4-BDO (3.6 g, 0.04 mol), and catalyst $Sn(Oct)_2$ (0.05 wt%). Then the homogeneous mixture was gradually increased to 80 °C and continued till the theoretically calculated free NCO content was reached, which was determined using the standard dibutylamine back-titration method (ASTM D1638). After cooling to 60 °C, 1,3-BDO (14.4 g, 0.16 mol) as blocking agent was added, and the reaction was proceeded at constant temperature until the complete disappearance of NCO absorption signal at 2267 cm^{-1} in FTIR spectrum (see Fig. S1), yielding a hydroxyl-terminated prepolymer.

2.4. Curing procedure of two-component polyurethane

A stoichiometric amount of the synthesized hydroxyl-terminated prepolymer and HAPP, as listed in Table S1, was mixed in a one-neck flask as component A, and then the component B (molar ratio of H_{12} MDI to HT-100 6:1) was introduced into the premix, upon which the NCO/OH value was fixed at 1.2. Thereafter, stannous octoate (0.05 wt %) as curing accelerator was added, and the blend was stirred steadily in vacuum at room temperature. When the mixture became homogeneous and no bubbles generated, the viscous liquid was transferred rapidly into a fresh mold and cured in an oven at 100 °C for 1 h. To avoid stress crack, the cured flame retardant polyurethanes (2K-PU/HAPPx, herein x denotes the mass fraction of HAPP) were cooled slowly to ambient temperature after the thermo-curing procedure. For comparison, the 2K-PU + APP15 sample which cured by a physical mixture of 2K-PU and 15 wt% APP was prepared.

2.5. Measurements

Fourier transform infrared (FTIR) spectra were collected on an IS10 FTIR spectrometer (USA) using KBr pellets over the wavenumber range from 4000 to 400 cm^{-1} .

The 1H NMR and ^{13}C NMR were recorded on a Bruker AV500M NMR spectrometer (Switzerland) with D_2O as solvent and tetramethylsilane as an internal standard.

X-ray photoelectron spectroscopy (XPS) was obtained on a Thermo Escalab 250XI spectrometer (USA) equipped with Al K α excitation radiation ($h\nu = 1486.6$ eV).

Elemental analyses of C, H and N were performed on a Euro-EA 3000 elemental analyzer (HEKAtech, Italy). While phosphorus content was carried out using a PerkinElmer Optima 2100DV based on inductively coupled plasma-atomic emission spectrometer (ICP-AES, USA).

X-ray diffraction (XRD) patterns were taken on an X-ray diffractometer (XPERT Pro MPD DY129, Holland) equipped with a Cu-K α tube and Ni filter ($\lambda = 0.1542$ nm).

Scanning electron microscope (SEM) micrographs of APP, HAPP, char residue and the freeze-fractured surfaces of 2K-PU films were acquired using a JEOL JSM-5900LV scanning electron microscope (Japan) with an acceleration voltage of 15 kV. Samples were sputter-coated with a conductive gold layer before examination.

Thermogravimetric analysis (TGA) was conducted using a TG 209 F1 thermal analyzer (NETZSCH, Germany) under N_2 with a constant heating rate of 10 °C min^{-1} .

Differential scanning calorimeter (DSC) was recorded on a DSC 200 PC analyzer (NETZSCH, Germany), operating at a heating rate of 5, 10 and 20 °C min^{-1} under N_2 atmosphere.

The limiting oxygen index (LOI) values were assessed by an HC-2C oxygen index meter (Jiangning, China) with sample dimensions of 127 × 10 × 3 mm^3 following the procedures in ASTM D 2863-2009. All specimens were repeated in quintuple.

The UL-94 vertical burning tests were determined using a CZF-II

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