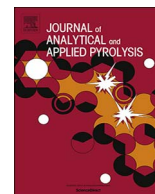




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Synthesis of a novel phosphorus and nitrogen-containing bio-based polyol and its application in flame retardant polyurethane foam

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ABSTRACT

A novel, castor oil (CO)-based, flame-retardant polyol containing phosphorus and nitrogen was successfully synthesized. The novel polyol was characterized by Fourier transform infrared (FTIR), proton nuclear magnetic resonance (¹H NMR), and carbon-13 nuclear magnetic resonance (¹³C NMR) spectroscopies. Flame-retardant polyurethane foams (FRPUF) were prepared by curing flame retardant polyols (FRPE) and flame retardant dihydric alcohol (BHAPE) with polyisocyanate (PM-200). The flame retardant properties and thermal decomposition of FRPUF were investigated using the limiting oxygen index (LOI), cone calorimeter testing, and thermogravimetric analysis (TGA). The FRPE and BHAPE composites were found to enhance the thermal stability and flame retardancy of polyurethane foams (PUF) without the use of other flame retardants. Insight was gained into the gaseous degradation products of FRPUF using thermogravimetric analysis-infrared spectrometry (TG-IR) and thermogravimetric analysis-mass spectrometry (TG-MS). The character of polyurethane foams was explored using FTIR, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Gas-phase pyrolysis products were investigated by TG-IR and TG-MS. Good flame retardancy was observed in FRPUF, which was attributed to the flame retardant FRPE and BHAPE.

1. Introduction

The use of renewable materials in the preparation of polyurethanes has garnered increasing attention in recent years. In addition to renewability, these materials offer lower cost and reduced environmental impact. Polyurethane foams (PUF) have low thermal conductivity, low density, and high strength. They have been widely used in a broad range of applications (particularly building insulation) [1–3].

Many studies have examined hydroxylated vegetable oil-based polyurethane materials and their use in adhesives, foams, and elastomers [4–6]. Castor oil (CO) is a vegetable oil obtained from the seeds of the castor oil plant and is thus a renewable product. Because of its carbonyl, double bond and hydroxyl functionality, CO can be modified to prepare bio-based PUF [7,8]. However, bio-based PUF is highly flammable, which restricts its application as a building material. Thus, it is urgent and imperative that flame retardant bio-based PUF be developed.

Flame retardancy that is achieved through the use of additive-type

flame retardants negatively affects the mechanical properties of PUF [9]. Instead, it is essential that reactive-type flame retardants be developed for use in the production of flame retardant bio-based PUF. Reactive-type flame retardants are normally introduced into the rigid backbone of polyurethane materials. Meanwhile, recent studies have indicated that flame retardant efficiency is significantly enhanced by the addition of phosphorus and nitrogen due to their synergistic effects [10–13]. Yet, these phosphorus and nitrogen-containing polyols are rarely used in PUFs.

In this study, a new flame retardant bio-based polyol containing phosphorus and nitrogen was successfully synthesized, characterized, and blended with flame retardant dihydric alcohol (BHAPE) for use in PUF. The flame retardancy of polyether polyol 4110-based PUF (4110/PUF), BHAPE/4110-based PUF (BHAPE/4110/PUF), and FRPE/BHAPE-based PUF (FRPE/BHAPE/PUF) were characterized by LOI and cone calorimeter testing. The thermal degradation behavior and mechanisms were studied by TGA, thermogravimetric analysis-infrared spectrometry (TG-IR), and thermogravimetric analysis-mass

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spectrometry (TG-MS). Additionally, chemical components of the polyurethane foam (PUF), and flame retardant polyurethane foam (FRPUF) char were analyzed by Fourier transform infrared spectroscopy (FTIR), a scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials

Castor oil (CO) was supplied by Qingdao Fusilin Chemical Science & Technology Co., Ltd. (Jiangsu, China) and dried at 110 °C under vacuum for 2 h before used. Diethanol amine, sodium methoxide, sodium bicarbonate, sodium chloride, dibutyltin dilaurate (DBTDL), tetrahydrofuran (THF), sodium sulfite, triphenyl phosphine, hydrogen peroxide (30%), phosphoric acid, formic acid, carbon tetrachloride, triphenyl phosphine, formaldehyde, sodium hydroxide, diethyl phosphite (DEPP), ethyl acetate (analytical grade) were purchased from Nanjing Chemical Reagents Co., Ltd (Jiangsu, China). Polyisocyanate (PM-200, NCO% = 30.2%) was obtained from Yantai Wanhua Group Co., Ltd. (Shandong, China). Polyether polyol 4110 (Polymer of sucrose, methyloxirane and oxirane, hydroxyl value = 430 ± 30 mg/g) was supplied by Jiangsu Chenhan polyurethane Co., Ltd. (Jiangsu, China). Dichlorofluoroethane (141b, foaming agent) was obtained from Jining Huakai Resins Co., Ltd. (Shandong, China). γ -glycidoxypropyl trimethoxysilane (KH560, foaming agent) was obtained from Nanjing Shuguang Chemical Co., Ltd. (Jiangsu, China). Polysiloxane-polyether copolymer (AK8804, foam stabilizer) was obtained from Nanjing Maysta Chemical Co., Ltd. (Jiangsu, China). 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from Jiangyin Huangfeng Technology Co., Ltd. (Jiangsu, China).

2.2. Synthesis of castor oil-based fatty acid amide

Castor oil-based fatty acid amide (CFA) was synthesized by charging CO (9.32 g) and sodium methoxide into a four-necked flask equipped with a thermometer, nitrogen inlet, dropping funnel, and mechanical stirrer. The system was heated to 80 °C, and diethanol amine (1.05 g) was slowly added to the flask. The mixture was then heated to 120 °C and stirred for 3 h. Finally, the reaction mixture was mixed with 100 mL carbon tetrachloride and washed to PH = 7 with sodium sulfite, sodium bicarbonate solution and sodium chloride solution, and rotary evaporated to remove the solvent. The obtained product was referred to as CFA. The reaction process is presented in [Scheme 1](#).

2.3. Synthesis of epoxied castor oil-based fatty acid amide

In the epoxied CO-based fatty acid amide (ECFA) synthesis, CFA was reacted with hydrogen peroxide and formic acid. Phosphoric acid served as the catalyst. A mixture of CFA (3.00 g), formic acid (0.20 g), and phosphoric acid (0.01 g) was charged into a four-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a thermometer. The mixture was slowly heated to 40–45 °C, followed by the slow addition of hydrogen peroxide (2.65 g). The mixture was then slowly heated to 60 °C and reacted for 6 h. The reaction mixture was then mixed with 100 mL ethyl acetate and washed to PH = 7 with sodium hydroxide solution, sodium chloride solution, and distilled water. Finally, the mixture was filtered and the salt and solvent were removed by rotary evaporation. The obtained product was referred to as ECFA.

2.4. Synthesis of castor oil-based flame retardant polyols

The castor oil-based flame retardant polyols (FRPE) was synthesized by charging CFA (4.01 g), DOPO (2.16 g), and triphenyl phosphine (0.12 g) into a four-necked, round-bottomed flask equipped with a

mechanical stirrer, thermometer, and water condenser. The mixture was slowly heated to 155 °C, then maintained at 155 ~ 160 °C for 5 h to obtain FRPE (hydroxyl value = 357 mg/g).

2.5. Synthesis of flame retardant dihydric alcohol

Preparation of flame retardant dihydric alcohol (BHAPE) was done according to the other reports[14]. Diethanol amine and formalin were added into a three-necked flask and stirred at 40 °C for 2 h. The mixture was then heated to 80 °C to remove water generated during the reaction under vacuum. Finally, DEPP was added to the flask and stirred for another 2 h at 60 °C. The product (BHAPE) was obtained after drying in a vacuum at 100 °C. The synthesis routes of FRPE and BHAPE are illustrated in [Scheme 1](#).

2.6. Preparation of castor oil-based flame retardant polyurethane foams

Polyurethane foams were prepared in a three-step procedure. First, FRPE, BHAPE, 4110, AK8804, KH560, DBTDL, and 141b were added to a 500 mL plastic beaker at room temperature. The mixture was stirred immediately with a high-speed mechanical mixer for 10 s. Polyisocyanate (PM 200) was then added and the mixture was stirred for another 10 s. Finally, the obtained viscous mixture was quickly poured into a foaming mold and cured at 70 °C for 2 h. The compositions of polyurethane foams are summarized in [Table 1](#). Other samples were prepared by a similar procedure.

2.7. Measurements

2.7.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of samples were recorded on a FTIR in a range of wave numbers from 4000 to 400 cm^{-1} , using attenuated total reflection fourier transform infrared (ATR-FTIR) method on a Nicolet (USA) IS10 instrument.

2.7.2. Nuclear magnetic resonance spectroscopy analysis (NMR)

Nuclear magnetic resonance (NMR) measurement was performed on an AVANCE 400 Bruker spectrometer at room temperature. The solvent was CDCl_3 .

2.7.3. Limiting oxygen index testing (LOI)

Limiting oxygen index testing (LOI) was carried out with a JF-3 oxygen index instrument (Jiangning Analysis Instrument Factory, Jiangsu, China), the test was measured according to ASTM D2863. The samples used for the test were $120 \times 10 \times 10 \text{ mm}^3$.

2.7.4. Thermogravimetric analyses (TGA)

Thermogravimetric analyses was performed using a TGA Q500 (TA Instruments) instrument. About 4 mg of each sample was scanned from 30 to 800 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen gas at a flow rate of 100 mL min^{-1} .

2.7.5. Cone calorimeter test (CCT)

The cone calorimeter tests were carried out by an Cone calorimeter at a heat flux of 35 kW/m^2 according to ISO 5660-1 standard.

2.7.6. Thermogravimetric analyses/infrared spectrometry (TG-IR)

TG-IR was performed using a TGA Q500 IR thermogravimetric analyzer, which was interfaced to the Nicolet (USA) IS10 FTIR spectrophotometer. About 4 mg of each sample was scanned from room temperature to 700 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in nitrogen atmosphere.

2.7.7. Thermogravimetric analyses/mass spectrometry (TG-MS)

TG-MS measurements were carried out using a 409PC thermal analyzer (Netzsch, Germany) coupled with a QMS403C instrument

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