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

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ABSTRACT

A novel ricinoleic acid (RA) based phosphorus and nitrogen-containing flame retardant polyols (FRPE) was successfully synthesized and characterized by FTIR, ^{1}H NMR and ^{13}C NMR. The flame retardant polyurethane sealants (FR-PUS) were prepared by curing FRPE with methylene diphenyl diisocyanate (MDI-50). The flame retardant properties and thermal decomposition of FR-PUS were investigated by the limiting oxygen index (LOI), cone calorimeter testing (CCT) and thermogravimetric analysis (TGA). The results showed that FRPE could enhance the thermal stability and improve the flame retardancy of polyurethane sealants (PUS) without any other flame retardant. Moreover, the gaseous degradeation products of FR-PUS were analyzed by thermogravimetric analysis/infrared spectrometry (TG-IR), providing insight into the thermal degradation mechanism. FTIR and dynamic mechanical analysis (DMA) were used to explore the chemical components of the char after CCT and mechanical properties of PUS.

1. Introduction

In recent years, the use of renewable sources in the preparation of polyurethane materials is gaining more and more attentions due to their renewability, lower cost and less environmental pollution [1]. Among them, polyurethane sealant (PUS) plays a dominant role due to its excellent chemical resistance, mechanical strength and affordable cost. Therefore, PUS has been widely used in a broad range of applications, especially in electronics industry [2,3].

Among different renewable resources, many hydroxylated vegetable oils (castor oil) and vegetable oil derivatives (fatty acid) based polyurethane materials were reported in many literatures and found applications in adhesives, foams and elastomers, etc [4,5]. Ricinoleic acid (RA), a renewable resource, is a relatively inexpensive fatty acid obtained from the hydrolysis of castor oil (CO). RA has a secondary hydroxyl groups in the 12th position, a double bond in the 9th position and a carboxylic group [6,7]. Because of its carboxyl、double bond and hydroxyl functionality, RA was used to synthesize polyols to prepare bio-based PUS [8]. However, bio-based PUS is also highly flammable, which restricts its application in some fields like building, electrical and transport. Therefore, it is urgent and imperative to develop flame-retardant bio-based PUS to reduce the risk of fire [9,10].

In order to endow bio-based PUS with good flame retardancy, adding phosphorus-containing compounds is an effective way. However, flame retardant PUS with additive-type flame retardants can reduce the mechanical properties of PUS [11]. Thus, it is essential to develop reactive-type flame retardants to replace additive-type flame retardants. Normally, the reactive-type flame retardants with flame retardant elements and active groups are introduced into the rigid backbone of polyurethane materials to increase the flame retardancy of materials [12,13]. Recently, some studies have indicated that flame retardant efficiency is significantly enhanced when both phosphorus and nitrogen were presented in the polymers due to the synergistic effect between phosphorus and nitrogen. However, there are rarely used for PUS.

In this study, a new flame retardant bio-based polyols containing phosphorus and nitrogen was successfully synthesized, characterized and used for PUS. The flame retardancy of castor oil based

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PUS (CO/PUS) and FRPE based PUS (FRPE/PUS) were characterized by the LOI and CCT. The thermal degradation behavior and mechanism were studied by thermogravimetric analysis (TGA) and thermogravimetric analysis-infrared spectrometry (TG-IR). Additionally, chemical components of char and mechanical properties of PUS were analyzed by RTIR and dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials

Ricinoleic acid (RA), methyl alcohol, dibutyltindilaurate (DBTDL), triethylamine, tetrahydrofuran (THF), sodium bicarbonate, sodium sulfite, ether, ethyl acetate (analytical grade) were purchased from Nanjing Chemical Ragents Co., Ltd (Jiangsu, China). 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. Phenyl dichlorophosphate (PDCP) was provided by Shanghai Shunqiang bioscience Co., Ltd (Shanghai, China). Methylene diphenyl diisocyanate (MDI-50, NCO % = 32.6) was obtained from Yantai Wanhua Group Co., Ltd. (Shandong, China). BF-5(moisture scavenger) was supplied by Shanghai Deyude Trade Co., Ltd. (Shanghai, China). Defom 5500 (defoamer) was obtained from Guangzhou Shenggao Chemicals Co., Ltd. (Guangdong, China).

2.2. Synthesis of flame retardant fatty acid (FRFA)

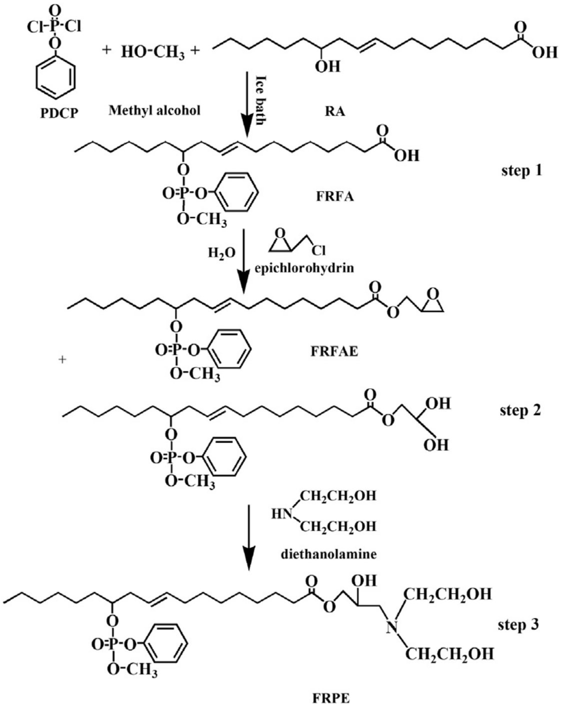
The FRFA was synthesized by charging PDCP (21.1 g) and 30 mL dried THF into a four-necked flask equipped with thermometer, nitrogen inlet, dropping funnel and mechanical stirrer. Triethylamine (20.2 g) was slowly added into to the above flask, the system was cooled to 0–5 °C and stirred for 30 min. Then, methyl alcohol (3.0 g) in dried THF (10 mL) was added dropwise into the above flask over 2 h and stirred at room temperature for 4 h. RA (29.8 g) in dried THF (30 mL) was added the system and stirred at room temperature for another 12 h. Finally, the mixture was filtered and rotary evaporated to remove the salt and solvent. The obtained product was referred as FRFA. The schematic process of the reaction is presented in Scheme 1 (step 1).

2.3. Synthesis of flame retardant fatty acid glycidyl ester (FRFAE)

FRFAE was synthesized by reaction of FRFA with epichlorohydrin using benzyl triethyl ammonium chloride as a catalyst. A mixture of FRFA (4.68 g), epichlorohydrin (9.2 g) and of benzyl triethyl ammonium chloride (0.025 g) were charged into a four-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel and a thermometer. The mixture was heated slowly to 117 °C and stirred for 2 h. Then, the mixture was cooled to 60 °C, sodium hydroxide (25 g) was added into the mixture and reacted for another 3 h. After that, the reaction mixture was mixed with 100 mL ethyl acetate and washed to PH = 7 with sodium bicarbonate solution and distilled water. The ethyl acetate in the reaction mixture was removed with a vacuum rotary evaporator. The obtained product was referred as FRFAE. The schematic process of the reaction is presented in Scheme 1(step 2).

2.4. Synthesis of flame retardant polyols (FRPE)

FRFAE (5.2 g) and diethanolamine (1.05 g) were charged into a four-necked round-bottomed flask equipped with mechanical stirrer, a thermometer and a water condenser. The mixture was slowly heated to 70 °C and maintained at 70–75 °C for 4 h. The reactant mixture was cooled and dissolved in ether. The solution was washed to PH = 7 with sodium sulfite and distilled water. Finally, the solvent evaporated in a rotary evaporator. The FRPE was obtained. The schematic process of the reaction is presented in Scheme 1(step 3).



Scheme 1. Synthesis Route and Structure of FRPE.

2.5. Preparation of polyurethane sealants

The polyurethane sealants were prepared by a three-step procedure. The procedure was described as: Firstly, a certain proportion of FRPE, DBTDL, BF-5 and Defom 5500 were added into a 500 mL plastic beaker at room temperature. The mixture was stirred immediately with high-speed mechanical mixer for 10 s. Then, MDI-50 was added into the mixture and stirred for 10 s. Finally, the obtained viscous mixture was poured into a foaming mould quickly, and cured at 60 °C for 4 h. The compositions of polyurethane sealants were summarized in Table 1. Other samples were prepared by the similar procedure.

2.6. Measurements

Fourier transform infrared (FTIR) spectroscopy: 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.

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

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 × 10 × 10 mm^3.

Thermogravimetric analyses (TGA): Thermogravimetric