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Synthesis of rigid polyurethane foams with castor oil-based flame retardant polyols

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ABSTRACT

A new method of introducing castor oil based flame-retardant polyols (COFPL) into polyurethane foams was explored in this paper. Castor oil was alcoholyzed with glycerol. And epoxidation of glycerolysis castor oil was carried out by formic acid and hydrogen peroxide (H_2O_2). The flame-retardant polyols were gotten though ring-opening reaction with diethyl phosphate. A novel castor oil-based polyurethane foam has been prepared by a one-shot process with and without COFPL. The structure of COFPL was characterized by FT-IR and ^{1}HNMR and the two studies exhibited characteristic peaks for COFPL. The thermal degradation and fire behaviour of polyurethane foams were investigated by limiting oxygen index (LOI), cone calorimetry test and thermogravimetry analysis. It has been shown that although the content of *P* element is only about 3%, the fire retardant incorporated in the castor oil molecule chain increased thermal stability and LOI value of polyurethane foam can reach to 24.3% without any other flame retardant. The compression strength of polyurethane foam was also improved with the increase of flame-retardant polyols. Morphology of polyurethane foams was examined by scanning electron microscope (SEM) and found to be displayed the regular size and high percentage of close area of the cell. Therefore, rigid foams from castor oil-based flame retardant polyols appear suitable for a wide range of applications.

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1. Introduction

The main aim of this research was to form flame-retardant polyols with castor oil. The rapid depletion of fossil and petroleum resources is encouraging current and future chemists to orient their research toward designing safer chemicals, products, and processes from renewable feedstock. In this way the replacement of petroleum-based raw materials by renewable resources has become a major contemporary challenge in terms of both economical and environmental aspects (Bozell and Patel, 2006). The chemical industry is increasingly looking toward sustainable technology to reduce the environmental impact. Castor oil (CO) which is obtained from extracting or expressing the seed of a plant which has the botanical name *Ricinus communis* of the family *Eurphorbiacae* (Kirk-Othmer, 1979) is a versatile vegetable oil due to its unique composition in which the main component is the 12-hydroxy-9-*cis*-octadecenoic acid. The rich chemistry of raw CO is attributed to its structure (one double C=C and one –OH group perfatty acid chain), which makes it a good starting material for a wide range of applications (Luca et al., 2006). Due to its unusual structure, this oil is very versatile in its applications (Cassidy and Schwank, 1979).

Castor oil is a raw material used extensively in varnishes, paints, coatings, inks, lubricants and a wide variety of other products. Because of its hydroxyl functionality, the oil is suitable for use in isocyanate reactions to make polyurethane millable (Yeganeh and Mehdizadeh, 2004), polyurethane elastomers (Gao et al., 2012; Stefan, 2010), coatings (Trevino and Trumbo, 2002; Mülazim et al., 2011) and adhesives (Somani et al., 2003; Fiorelli et al., 2012), interpenetrating polymer network from castor oil-based polyurethane (Athawale and Kolekar, 1998) and polyurethane foam (Tibério et al., 2012). A recent work (Mitha and Jayabalan, 2009) reported the synthesis of crosslink-able and biodegradable crosslink-able poly(castor oil fumarate)/poly(propylene fumarate) composite adhesive as a potential injectable and for orthopedic applications.

The improvement of the thermal stability and fire behaviour of polyurethane is today the aim of numerous studies, as there are a number of important issues that need to be solved. So far, the application of polyols is limited by their high flammability. Any solution of this problem will increase their application in industry. For these reasons, studies to find effective flame retardants have been carried out by many researchers in industry and universities over a long period of time, but so far there is a limited success. Polyurethane generated from reactive flame-retardant monomer exhibit more excellent flame-retardant properties than those with additive flame retardants, for the flame retardants molecule linked

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Table 1
The hydroxyl value and yield.

Hydroxyl value (mg KOH/g)	408
Yield of castor oil monoglycerides (%)	56.96
Yield of castor oil diglycerides (%)	35.58
Total yield (%)	92.54

to the polyurethane by covalent bond. The covalent bond makes it more stable while additive flame retardants in the polyurethane were easier to infiltrate out. The flame retardant compounds which have good flame retardant property, but hardly pollute the environment are particularly needed (Thirumal et al., 2010).

In our work, castor oil was first time to convert to flame-retardant polyols by reaction with glycerol, H_2O_2 and diethyl phosphate. The flame-retardant polyols can be used to polyurethane foams, polyurethane elastomer, polyurethane films and polyurethane coating. With the P element, the flame-retardant properties can be improved and the application of castor oil will be enlarged. The structure of the castor oil-based flame retardant polyols was confirmed by spectroscopic techniques like FT-IR and ^{1}HNMR spectroscopy and thermal properties were determined by TGA. The thermal degradation and fire behaviour of polyurethanes prepared from COFPL have been studied by thermogravimetric analysis, limiting oxygen index (LOI) and cone calorimetric measurement.

2. Experimental

2.1. Materials

Castor oil (industrial grade) was purchased from Sinopharm Chemical Reagent. Glycerol, hydrogen peroxide, phosphoric acid and thriethylamine were obtained from Nanjing Chemical Reagent Co. Ltd. Triphenylphosphine and sodium methoxide was from Shanghai Zhanyun Chemical Co. ltd.

2.2. Preparation of glycerolysis castor oil (GCO)

A reaction kettle equipped with a mechanical stirrer, condenser pipe, thermometer and provision for nitrogen flushing was charged with dry castor oil 500 g (0.54 mol) and catalyst 3.75 g. The temperature was raised quickly with continued stirring and maintained at 200 °C after continuous nitrogen for 30 min. Then 123.3 g (1.34 mol) of glycerol was taken in the reaction kettle. The temperature was maintained at 180 °C for 3 h. Finally, polyol was cooled to 40 °C and was washed three times with distilled water. Hydroxyl value of GCO was determined by the acetic anhydride-pyridine method (Cocks and Vanredew, 1976). The properties of the polyols such as hydroxyl value, total yield of GCO are presented in Table 1. The conversion rate was obtained by area normalization. The chemical reaction between castor oil and glycerol producing GCO is shown in Fig. 1.

2.3. Synthesis of epoxidized glycerolysis castor oil (EGCO)

GCO (100 g), formic acid (7.75 g) and phosphoric acid (0.25 g) were mixed in a four-necked round-bottom flask equipped with a tetrafluoroethylene stirrer, a thermometer and a condenser pipe. This was heated to 40 °C in a water bath. After that, hydrogen peroxide was dropped to the reaction flask in 30 min. The mixture was then heated to 60 °C and stirred for 6 h. And then the reaction mixture were cooled to room temperature and washed to pH = 7 with sodium hydroxide solution. The resulting product was dried over anhydrous sodium sulfate. The epoxidation reaction is shown in Fig. 1.

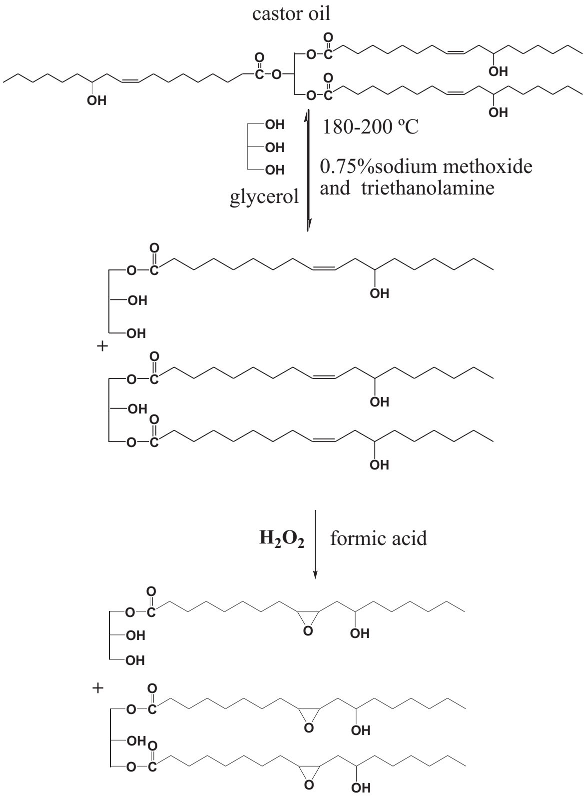

Fig. 1. The alcoholysis reaction and epoxy reaction of castor oil.

2.4. Synthesis of COFPL

Amounts of 100 g EGCO and toluene (75 g) were taken in a 500 ml four-necked round bottom flask provided with a mechanical stirrer, thermometer and a water condenser. The mixture was then heated to 40 °C and the mixture of diethyl phosphate (40 g), toluene (75 g) and triphenylphosphine (0.5 g) were dropped to the reaction flask in 30 min. Then the reaction proceeded with continuous stirring at 70–75 °C for 4 h. The reaction mixture was cooled to room temperature and washed to pH = 7 with sodium hydroxide solution and then washed three times with distilled water. After that it was dried over rotary evaporator under the condition of vacuum. The chemical reaction between EGCO and diethyl phosphate producing COFPL is shown in Fig. 2.

2.5. Preparation of PU foams

The PU foams were prepared by a one-shot process, where all the ingredients were mixed simultaneously and allowed to cure at 80 °C for 24 h. First, a small amount of silicone oil AK8804 (surfactant), *N*,*N*-dimethylcyclohexylamine (catalyst), 141B, and water were mixed with COFPL and GCO. And then the mixture were stirred with a propeller stirrer for 2 min at approximately 1500 rpm to ensure a homogeneous mix,

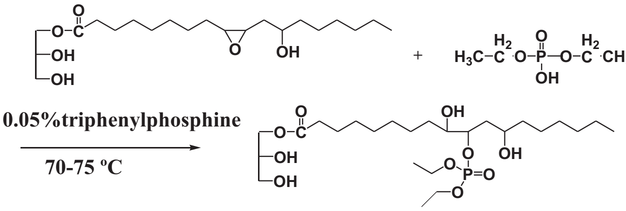

Fig. 2. The chemical reaction between EGCO and diethyl phosphate.

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