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A fully bio-based waterborne polyurethane dispersion from vegetable oils: From synthesis of precursors by thiol-ene reaction to study of final material

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ABSTRACT

A new linear saturated terminal diisocyanate was synthesized from castor oil-derived undecylenic acid by thiol-ene coupling (TEC) and Curtius rearrangement. The structure of the diisocyanate was carefully examined using Fourier transform infrared spectroscopy, ^{1}H nuclear magnetic resonance (NMR), and ^{13}C NMR. This diisocyanate was used as a starting material for the preparation of a fully bio-based waterborne polyurethane dispersion (BPUD) by reacting with castor oil and castor oil-based carboxylic acid-type hydrophilic chain extender, which was prepared from castor oil by using 3-mercaptopropionic acid via TEC. The thermal/mechanical properties of the formed BPUD film were characterized via differential scanning calorimetry, thermogravimetric analysis, tensile test, hardness test, and water resistance test. The fatty acid-derived diisocyanate and the castor oil-based hydrophilic chain extender were used to produce BPUD with favorable properties.

1. Introduction

Waterborne polyurethane (WPU) has gained increasing attention because of its overall balance of properties and environmental-friendliness. WPU can be found in products such as coating, adhesive, finishing agents, paper surface treatment agent, and fiber surface treatment agent [1,2]. Commercial WPU can be obtained from the reaction of a diisocyanate (or a polyisocyanate) with a polyol and a hydrophilic chain extender obtained from petroleum-based resources; however, finite fossil resources will be arguably diminished within a few generations. Thus, replacing petroleum-based raw materials with renewable resources constitutes a major contemporary challenge in both economical and environmental aspects [3,4]. Vegetable oil is considered as one of the most important classes of renewable sources that can be used as a reliable starting material to obtain new products with a wide variety of possibilities for chemical transformations [5–14]. The abundance and the relative low price of vegetable oils make it an industrially attractive raw material for the polyurethane industry.

Polyurethane (PU) is a unique class of polymer that can have various properties by selecting different components as starting materials. Vegetable oil-based PU is often produced from chemically modified triglycerides and their fatty acids. Vegetable oils are mostly triglycerides and contain several reactive sites, such as double bonds and ester groups. Thus, the use of vegetable oils opens up various possibilities of obtaining new structures [8–13] and achieving well-defined functionalities. Many efficient methodologies can be performed to modify double bonds, such as epoxidation [6,15], ozonolysis [16], acyclic diene methathesis (ADMET) polymerization [13,17], and TEC [9,14,15,18,20]. Among all reported reaction pathways, TEC is one of the most important reactions for the functionalization of double bonds. Over the past few years, a variety of plant oil-based monomers for PU, such as polyols [6,14,15,20,22–24], diisocyanates [20,21], and polyamine [9], have been prepared via TEC. The use of these precursors to produce a PU system has been demonstrated; however, most studies only involve solvent-borne PU [20–23]. Studies on fully bio-based WPU are few or even non-existent.

Castor oil naturally possesses both C=C and hydroxyl bonds and is used to produce fine chemicals as well as for the preparation of monomers and polymers [25]. In the present study, we describe the functionalization of castor oil and undecylenic acid (UDA) with carboxyl groups via TEC. Carboxyl-functionalized castor oil (CCE) was designed as a bio-based hydrophilic chain extender; dicarboxyl based on UDA was used to prepare bio-based diisocyanates (BDI) via Curtius rearrangement. We modified and improved an analogous Curtius rearrangement of a previous study [21], performed liquid–solid phase transfer synthesis of isocyanate, and efficiently

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catalyzed the reaction between sodium azide and acyl chloride by using tetrabutylammonium bromide (TBAB). The second originality of this study results in the synthesis of a WPU system, where all the raw materials are based on vegetable oil. The renewable carbon content of BPUD in theory is 87.3%. The use of carboxylated castor oil as a hydrophilic chain extender and a UDA-based diisocyanate for a fully bio-sourced WPU is detailed, and the thermal/physical properties of the formed film are investigated. The detailed method is expected to combine the advantages of TEC reaction, vegetable oil, and WPU.

2. Materials and methods

2.1. Materials

Castor oil was obtained from Sigma–Aldrich China, undecylenic acid (97% purity) was obtained from Sinopharm Chemical Reagent Co., Ltd., China, and 3-mercaptopropionic acid was obtained from Alfa Aesar China. N,N-dimethyl formamide (DMF), triethylamine, dichloromethane (DCM), acetonitrile, acetone, and ethanol were obtained from Beijing Chemical Works. Dimethylolpropionic acid (DMPA), 1.4-butanediol (BDO), ditinbutyldilaurate (DBTDL), tetrabutyl ammonium bromide (TBAB), and thionyl chloride were obtained from Aladin China, whereas sodium azide and dichloroethane were obtained from Tianjin Fuchen Chemical Reagent Factory, China. 2-Hydroxy-2-methylpropiophenone (UV1173) was obtained from Jiuri Chemical of China. Polyether glycol (N210, *Mn* = 1000) and isophorone diisocyanate (IPDI) were industrial products, were used as received.

2.2. Preparation of fatty acid-derived dicarboxylic acid

Undecylenic acid (5.9 g, 0.032 mol), 3-mercaptopropionic acid (5.08 g, 0.048 mol), and UV1173 (0.11 g) were dissolved in dichloroethane (25 mL) in a single-necked flask. The reaction mixture was stirred at 70 °C with UV light irradiation (1700 μW/cm^2, 365 nm) for 4.5 h. After confirming the completion of the reaction by the absence of the ^{1}H NMR shift of the C=C group at 5.3 ppm to 5.7 ppm, the cooled mixture was filtered and washed with water to ensure the complete removal of 3-mercaptopropionic acid. The solid was dried in a vacuum oven (80 °C) for 4 h to obtain a white solid (8.55 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.27–1.35 (m, 12H, 6CH_2), 1.52–1.66 (m, 4H, 2CH_2), 2.34 (t, 2H, J = 7.4 Hz, CH_2), 2.53 (t, 2H, J = 7.4 Hz, CH_2), 2.65 (t, 2H, J = 7.4 Hz, CH_2), and 2.78 (t, 2H, J = 7.2 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 24.58 (CH_2), 26.58 (CH_2), 28.77 (CH_2), 28.92 (CH_2), 29.06 (CH_2), 29.22 (CH_2), 29.31 (CH_2), 29.45 (CH_2), 32.16 (CH_2), 34.05 (CH_2), 34.75 (CH_2), 178.21 (COOH), and 180.36 (COOH).

2.3. Preparation of BDI

The solution of the dicarboxylic acid (4.0 g, 0.0138 mol), thionyl chloride (21 mL, 0.276 mol), and DMF (0.1 g) in DCM (25 mL) was stirred for 4.5 h at 45 °C. Excess thionyl chloride and DCM were then removed at reduced pressure, and the mixture was dissolved in CH_3CN (25 mL) with TBAB (0.45 g, 0.0014 mol). Then the reaction mixture was heated to 60 °C, and NaN_3 (2.68 g, 0.041 mol) was then gradually added within 25 min. The mixture was incubated at 60 °C for 2 h and at 80 °C for another 2 h. After filtration, the solvent was removed at reduced pressure. The residue was purified using column chromatography (1:10 ethyl acetate: petroleum ether), and diisocyanate (3.4 g, 76.4%) was obtained as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.20 (s, 8H, 4CH_2), 1.28 (s, 4H, 2CH_2), 1.47–1.52 (m, 4H, 2CH_2), 2.41–2.47 (m, 2H, CH_2), 2.64–2.67 (m, 2H, CH_2), 3.17–3.22 (m, 2H, CH_2), and 3.31–3.36 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.43 (CH_2), 28.67 (CH_2), 28.85 (CH_2), 29.07 (CH_2), 29.32 (CH_2), 29.60 (CH_2), 31.20 (CH_2), 31.79 (CH_2), 33.74 (CH_2), 42.61 (CH_2), 42.87 (CH_2), 121.93 (N=C=O), and 123.86 (N=C=O); IR (cm^{-1}): 2271 (N=C=O) and 2866, 2926 (C—H).

2.4. Preparation of castor oil-based chain extender (CCE)

A reaction mixture of castor oil (5.6 g, 0.006 mol), 3-mercaptopropionic acid (2.29 g, 0.022 mol), UV1173 (0.08 g), and ethanol (30 mL) was stirred at room temperature with UV light irradiation (1700 μW/cm^2, 365 nm) for 6 h. The reaction was monitored via ^{1}H NMR spectroscopy, and the absence of double bond proton peaks was monitored. After completion of the reaction, excess ethanol was removed via rotary evaporation to obtain a viscous liquid. The liquid was washed with water to ensure the complete removal of 3-mercaptopropionic acid. The washed liquid was dissolved in ethyl acetate, and the castor oil-derived chain extender (6.71 g, 92.1%) was obtained after the removal of the solvent via rotary evaporation. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.86 (t, 9H, J = 6.48 Hz, 3CH_3), 4.10–4.28 (m, 4H, 2CH_2), 5.19 (m, H, CH), and 12.24 (s, H, COOH).

2.5. Preparation of polyurethane and films

The synthesis process of BPUD is shown in Scheme 1. BPUD was prepared firstly by reacting castor oil with BDI at molar rations of the OH group to the NCO group (OH/NCO of 1.0/1.6). Then the NCO remained further reacted with CCE completely. The weight percent of carboxyl to polyurethane was designed to be 3%, to ensure the polyurethane disperse in water stably. Typically BPUD was prepared according to the following procedures. Castor oil (1.77 g, 0.0019 mol), BDI (2.37 g, 0.0084 mol), trace DBTDL, and acetone (10 g) were added in turn in a three-necked flask. Subsequently, the mixture was heated to 80 °C for 3 h, and CCE (1.59 g, 0.0013 mol) was then added and reacted for 3 h. Reaction completion was monitored by the absence of infrared (IR) absorption of the free NCO group at 2270 cm^{-1}. After confirming the completion of the reaction, the mixture was cooled to 50 °C, and triethylamine (0.46 g, 0.0046 mol) was added and stirred for 0.5 h. Lastly, the prepolymer was allowed to disperse in deionized water with vigorous stirring. Acetone from the resulting PU dispersions was removed at 35 °C in a rotary evaporator. The solid content of BPUD was 30 wt%.

The fully petroleum-based WPU (PPUD) was prepared according to the following procedures. N210 (7.04 g, 0.007 mol), IPDI (5.16 g, 0.0232 mol), DMPA (1 g, 0.0075 mol) dissolved in DMF (5.1 g), trace DBTDL, and acetone (15 g) were added in turn in a three-necked flask. Subsequently, the mixture was heated to 80 °C for 3 h, and BDO (0.78 g, 0.0087 mol) was then added and reacted for 3 h. Reaction completion was monitored by IR. After confirming the completion of the reaction, the mixture was cooled to 50 °C, and triethylamine (1.20 g, 0.012 mol) was added and stirred for 0.5 h. Lastly, the prepolymer was allowed to disperse in deionized water with vigorous stirring. Acetone from the resulting PU dispersions was removed at 35 °C in a rotary evaporator. The solid content of PPUD was 30 wt%.

The polyurethane films were prepared by casting the PU-waterborne dispersions onto PTFE plates, which had been degreased with acetone. The cast polyurethane films were maintained at a thickness of 0.2 mm to 0.3 mm by a drawbar and were dried at room temperature for 24 h and at 70 °C in a vacuum for 24 h prior to testing and characterization.

2.6. Testing methods

The IR spectra were obtained on a Bruker-Vertex 70 spectrometer by using the attenuated total reflection (ATR) mode. The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AV-400 NMR with