



Bio-polyols synthesized from crude glycerol and applications on polyurethane wood adhesives



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ABSTRACT

Crude glycerol (CG), a byproduct of the biodiesel process, was converted through a one-pot thermo-chemical process to produce desirable bio-polyols (CG-polyols) which is suitable for polyurethane (PU) wood adhesives application in this study. The operating parameters (molar ratio of crude glycerol to fatty acid ($R_{CG/FA}$), temperature, and reaction time) were optimized to obtain bio-based CG-polyols with preferred properties (hydroxyl number, acid number, and viscosity) for the production of PU-wood adhesives. The hydroxyl number of CG-polyols was greatly affected by the molar ratio $R_{CG/FA}$ and temperature, while the acid number was strongly dependent on temperature and time, and viscosity was associated with all three experimental factors. Reliable quantitative prediction models of hydroxyl number, acid number, and viscosity were then established, affording accurate prediction with the differences between predicted and measured data less than 2%. CG-polyols (hydroxyl number of 322 mg KOH/g, acid number of 1.7 mg KOH/g, and viscosity of 25 Pas) suitable for PU adhesives application was produced under the optimized reaction conditions (molar ratio $R_{CG/FA}$ of 1.5, temperature at 220 °C, and reaction time of 5 h). PU wood adhesives with maximum lap shear strength of 36.8 MPa were achieved from the above optimized bio-polyols through the reaction with isocyanate at a NCO/OH ratio ($R_{NCO/OH}$) of 1.3. Properties of resulting PU wood adhesives presented good thermal stability, comparable lap shear strength and chemical resistance to petroleum based analogies.

1. Introduction

Polyols are considered to be the most valuable compounds for pharmaceuticals, food science, and polymer chemistry (Tuck et al., 2014; Vanlede et al., 2015; Chatterjee et al., 2014). In polymer chemistry, polyols are extensively used as raw chemicals to produce polyurethane (PU) products (foam, coatings, and elastomers) by reacting them with isocyanates (Moser et al., 2013; Hu et al., 2012; Ni et al., 2010). However, the current polyol industry heavily relies on petroleum, which exacerbates the depletion of a limited natural resource. Given the recent focus on global warming and sustainability, the development of bio-based polymers from renewable resources is of high interest (Desroches et al., 2012).

Bio-polyols can be synthesized from vegetable oils via the functionalization of unsaturated sites along the fatty acid chains (Pillai et al., 2016; Alagi et al., 2016). Functionalization can be accomplished through various processing approaches, including epoxidation followed by ring opening (Petrovic et al., 2002), hydroformylation followed by

hydrogenation (Lysenko et al., 2004), ozonolysis followed by hydrogenation (Petrovic et al., 2004), and a thiol-ene coupling route (Desroches et al., 2011). The resulting bio-polyols have been reported to exhibit properties suitable for PU product development, such as PU foams (Sonnenschein and Wendt, 2013). Nevertheless, vegetable oil-based bio-polyols consume large amounts of vegetable oil, thus competing with food supplies and a growing biodiesel industry. Some researchers have turned to the synthesis of bio-polyols derived from lignocellulosic biomass (Hu and Li, 2014a, 2014b; Chen and Lu, 2009; Hu and Li, 2012), which have shown acceptable performance for PU applications. The production of bio-polyols could be achieved via a liquefaction process that involves the addition of appropriate liquefaction solvents under a preferred reaction temperature and time with the presence of a catalyst (Hu and Li, 2012). But, the traditional liquefaction process also consumes a large amount of petroleum-derived solvents, which, consequently, lessens its renewability. Therefore, it is crucial to explore renewable sources of solvents and alternative approaches to obtain bio-polyols.

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Crude glycerol, the primary byproduct of the natural oil and animal fat transesterification process, is a promising renewable bio-feedstock with low cost, approximately \$0.05 per pound (Kerr et al., 2007). Glycerol, an important chemical feedstock, is the predominant compound in crude glycerol; thus, extensive research has been conducted to convert crude glycerol to value-added chemicals through chemical and biological processes. Refined crude glycerol, produced as a result of the above processes, has been used in the applications of pharmaceutical, cosmetics, and PU industries (Clomburg and Gonzalez, 2013; Manosak et al., 2011). But the costly refining technologies for crude glycerol prevent its extended applications. Therefore, it is essential to investigate novel processes that can directly utilize unrefined crude glycerol.

A few studies have reported the direct utilization of crude glycerol to produce crude glycerol based bio-polyols (CG-polyols) and PU products, but there have been no reports on synthesizing CG-polyols that are suitable for PU adhesives. Crude glycerol has been converted to bio-polyols via a one-pot thermochemical conversion process which is a very simple and efficient reaction occurring in a flask to obtain desirable products without requiring further steps (Li et al., 2014; Luo et al., 2013). The obtained CG-polyols were used to produce PU foams that showed properties comparable to those of petroleum-based foams (Ugarte et al., 2017; Gaidukova et al., 2017). However, the properties of CG-polyols required for PU wood adhesive applications are greatly different from those for PU foams. Rigid PU foams are generally produced from polyols with a hydroxyl number around 400–600 mg KOH/g and an acid number less than 5 mg KOH/g (Luo et al., 2013). But, the development of PU adhesives requires CG-polyols with a hydroxyl number between 250 and 350 mg KOH/g, an acid number less than 2 mg KOH/g, and a viscosity around ~25–35 Pas (Kong et al., 2011). To the best of our knowledge, there have been no studies dedicated to investigating the synthesis of CG-polyols suitable for PU wood adhesives.

With the purpose of synthesizing CG-polyols with preferred properties suitable for PU wood adhesives, the objectives of this study were to (1) investigate the effects of different operating parameters on the properties of CG-polyols; (2) establish models to predict the properties of CG-polyols and to optimize the operating parameters to produce desirable CG-polyols suitable for PU wood adhesives; (3) develop a suitable procedure to produce PU wood adhesives from CG-polyols; and (4) characterize the properties of CG-polyols obtained under the optimized experiment conditions and the properties of corresponding PU wood adhesives.

2. Methods and materials

2.1. Materials

Crude glycerol samples with two separated fractions (crude fatty acid and glycerol fractions) were obtained from a biodiesel plant in Cincinnati, Ohio. The compositions of the two fractions are shown in Table 1. Imidazole, phthalic anhydride, phenolphthalein, standard hydrochloric acid (HCl) solutions (0.1 N), sodium hydroxide (NaOH) solutions (0.1 N and 10 N), Polyethylene glycerol with an average molecular weight of 400 (PEG 400), polymeric methylene-4-4'-diphenyl isocyanate, potassium hydroxide and Dibutyltin dilaurate were

purchased from Fisher Scientific (Pittsburgh, PA). Pyridine, ethyl alcohol, acetone, 98% concentrated H₂SO₄, and toluene were purchased from Pharmco-AAPER (Shelbyville, KY). All chemicals above were of reagent grade or higher purity, and they were used without further treatment.

2.2. Synthesis of bio-polyols from crude glycerol

The crude glycerol fraction was first distilled using a rotary evaporator at 60 °C under vacuum to remove volatiles (mainly methanol). Thermochemical conversion of crude glycerol to bio-polyols was carried out in a 250-mL three-necked flask equipped with a magnetic stirring and heating system (Thermo Electron Corp., Madison, WI), vacuum pump (DOA-P707-FB, Gast Manufacturing, Inc., Benton Harbor, MI), thermometer, and condenser. Designated amounts of distilled crude glycerol and fatty acids, at ratios R_(CG/FA) of 1, 1.5 and 2, were added into the flask, and a catalyst (1% NaOH based on the total weight of reactant) was added subsequently. The reactions were conducted at different operating temperatures (180 °C ~ 220 °C) with 15 inches of Hg vacuum and constant stirring (450 rpm) for 3 ~ 6 h. The flask was then immediately removed from the heating panel and cooled to room temperature. Water and other volatiles generated during the thermal conversion process were collected by a glass Graham condenser. Crude glycerol-based bio-polyols, i.e. CG-polyols, were recovered from the flask. All CG-polyol production tests were conducted in triplicate.

2.3. Synthesis of PU adhesives

The synthesis of PU adhesives was carried out at room temperature under nitrogen protection by mixing the synthesized CG-based polyols or PEG400 with polymeric methylene-4-4'-diphenyl isocyanate in the absence of chain extenders using dibutyltin dilaurate as a catalyst (0.1 wt% based on the total weight of polyols and polymeric methylene-4-4'-diphenyl isocyanate). In this study, Dibutyltin dilaurate, which is a general-purpose catalyst, promoted the polymer forming and gelation reaction between the isocyanate and CG-based polyol. PU adhesives based on optimized CG-polyols under different molar ratios of NCO/OH (R_{NCO/OH}) from 1.0 to 1.7 were prepared to investigate the effect of R_{NCO/OH} on the properties of PU adhesives. The preparation of PU adhesives from PEG400, a petroleum-based glycerol, was similar to the procedure of PU adhesive from CG-polyols. The synthesis of PEG400-based PU wood adhesives was carried out at a certain molar ratios of R_{NCO/OH} of 1.3.

2.4. Determination of hydroxyl number, acid number, and viscosity

The hydroxyl number and acid number of obtained CG-polyols were measured following the standards of ASTM D4274-05D and D4662-08, respectively. The viscosity of obtained CG-polyols was measured using a digital Viscometer (Brookfield viscometer LVDV-II + PRO, Brookfield Ameter, Middleboro, MA) at a speed of 60 rpm, 35 °C.

2.5. Experimental design and data analysis

Response surface methodology (RSM) with a central composite

Table 1
Compositions of crude glycerol sample.

Crude samples	Glycerol (wt%)	Methanol (wt%)	Free fatty acid (wt%)	FAMES ^b (wt%)	Soap (wt%)	Water (wt%)	Ash (wt%)	Others (wt%)
Fatty acid fraction	0.4	BDL ^a	63.0	5.3	0.2	0.6	0.5	30.0
Glycerol fraction	81.3	BDL ^a	0.4	BDL ^a	0.3	10.5	3.0	4.5

^a : Below detection limit (BDL).

^b : Fatty Acids Methyl Esters (FAMES).

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