



Polyurethane foams based on crude glycerol-derived biopolyols: One-pot preparation of biopolyols with branched fatty acid ester chains and its effects on foam formation and properties



Cong Li ^a, Xiaolan Luo ^a, Tao Li ^b, Xinjie Tong ^a, Yebo Li ^{a,*}

^a Department of Food, Agricultural and Biological Engineering, The Ohio State University/Ohio Agricultural Research and Development Center, 1680 Madison Ave, Wooster, OH 44691-4096, USA

^b X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

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ABSTRACT

Environmentally friendly biopolyols have been produced with crude glycerol as the sole feedstock using a one-pot thermochemical conversion process without the addition of extra catalysts and reagents. Structural features of these biopolyols were characterized by rheology analysis. Rigid polyurethane (PU) foams were obtained from these crude glycerol-based biopolyols and the foaming mechanism was explored. Investigations revealed that partial carbonyl groups hydrogen-bonded with N–H were replaced by aromatic rings after the introduction of branched fatty acid ester chains in the “urea rich” phase, and that distinct microphases had formed in the foams. Studies showed that branched fatty acid ester chains in the biopolyols played an important role in reducing the degree of microphase separation and stabilizing bubbles during foaming processes. PU foams with thermal conductivity comparable to commercial products made from petroleum-based polyols were obtained. These studies show the potential for development of PU foams based on crude glycerol, a renewable resource.

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1. Introduction

As one of the most widely used polymeric materials, polyurethane (PU) plays an important role in modern life and its global demand is growing every year. However, most commercial PU products are derived from non-renewable resources. Increased environmental concerns have led to increased research focus by industry and academia on utilizing renewable resources to replace the traditional petroleum-based resources [1,2].

Renewable biomass-derived materials have shown promise as feedstocks for PU products. Significant progress has been made and many feedstocks derived from biomass for PU production have been developed. Polyols, one of the most important feedstocks in the PU industry, have been intensively investigated. A variety of vegetable oil-based polyols have been successfully developed for PU preparation in the last decade [3]. By taking advantage of the unsaturated sites in fatty acid chains, vegetable oils can be functionalized and polymerized by the classic epoxidation route [4–6], hydroformylation/reduction route [7,8], ozonolysis/reduction route

[9–11], and the newly developed thiol-ene coupling route as well as the metathesis route [12–15], which results in many possibilities for use in PU production.

While vegetable oil-based biopolyols have been successfully commercialized, expansion of commercial production is not anticipated as it would compete with food consumption. A more sustainable and economic approach that produces biopolyols from crude glycerol, a byproduct of the biodiesel process, has been developed in our group [16]. These biopolyols, which have been produced from crude glycerol using a one-pot thermochemical process, have been used for rigid PU foam applications. Crude glycerol is a low-value byproduct with a cost as low as \$0.11/kg [17]. Compared to pure glycerol, crude glycerol contains many components such as methanol, water, soap, free fatty acids (FFAs), fatty acid methyl esters (FAMES), and glycerides [18]. High quality biopolyols can be obtained by properly taking advantage of these components [16]. The expanding biodiesel market and increasing demand for biofuels is expected to create a large supply of crude glycerol. Therefore, utilizing crude glycerol for the production of biopolyols has the potential to significantly impact the PU industry.

In thermochemical conversion of crude glycerol, esterification and transesterification reactions among components in crude glycerol were shown to occur and biopolyols with branched fatty

* Corresponding author. Tel.: +1 330 263 3855; fax: +1 330 263 3670.
E-mail address: li.851@osu.edu (Y. Li).

acid ester chains were obtained [16]. Nevertheless, the complex components in crude glycerol and the complicated reactions in biopolyol synthesis have restricted the application of crude glycerol in biopolyols and polyurethanes. By now, the mechanism for the production of PU foams from crude glycerol-derived biopolyols is still unclear. A in-depth study of the biopolyol conversion process and PU foam preparation from crude glycerol-based polyols is necessary, which will provide insights and guidance for the fundamental understanding of foaming mechanism and rational design of materials from these biopolyols. The purpose of this study was to investigate the microstructure characteristics of PU foams made from crude glycerol-derived biopolyols, study the effects of properties of biopolyols on foam structure and performance, and illustrate the mechanism of successful foaming using crude glycerol-derived biopolyols. An improved method, which controlled the reaction temperature at 150 °C to avoid side reactions such as glycerol dehydration [19,20] and applied a high vacuum (0.001 MPa) condition to accelerate the removal of methanol and water and the conversion of glycerol, was used to prepare crude glycerol-derived biopolyols. Two different types of crude glycerol-derived biopolyols were synthesized by adjusting the reaction time and the rheological characteristics of the crude glycerol, and these derived biopolyols were studied. Microstructures of PU foams from the crude glycerol and its derived biopolyols were characterized, and the possible origins of distinct morphologies were investigated. Thermal and mechanical properties of the produced PU foams were comprehensively evaluated. The relationships between these properties and PU microstructures were studied to help understand foaming mechanisms during the production of PU foams from crude glycerol-derived biopolyols.

2. Experimental section

2.1. Materials

Crude glycerol and biodiesel (fatty acid methyl esters (FAMES)) were obtained from Bio100 Technologies, LLC (Mansfield, OH). Sodium oleate, pure glycerol, ethylene glycol, methanol, and oleic acid were purchased from Fisher Scientific (Pittsburgh, PA). Chloroform was purchased from Pharmco-AAPER (Shelbyville, KY). Standard stock solutions of monopalmitin, monoolein, diolein, triolein, 1, 2, 4-butanetriol, tricaprins, and derivatization reagent *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) were purchased from Restek (Bellefonte, PA). Polycat 5, polycat 8, and DABCO DC5357 used in PU foaming processes were obtained from Air Products & Chemicals, Inc. (Allentown, PA). Polymeric methylene-4, 4'-diphenyl diisocyanate (pMDI) was obtained from Bayer Material Science (Pittsburgh, PA). All chemicals used were of reagent grade or higher purity.

2.2. Synthesis of crude glycerol-based biopolyols

A 200-ml round bottom flask connected with a glass Liebig condenser was used for the preparation of crude glycerol-based biopolyols. An oil vacuum pump was connected to the Liebig condenser with a vacuum connecting tube adapter to maintain the designated vacuum condition. Crude glycerol (80 g) was added into the flask and heated to 110 °C for 60 min under constant magnetic stirring using a temperature-controlled heating mantle (Thermo Electron Corp., Madison, WI). Then it was heated to 150 °C for either 2.5 or 5 h under vacuum conditions (0.001 MPa). The resulting biopolyols prepared at 2.5 and 5 h were designated as polyol-2.5h and polyol-5h, respectively.

2.3. Composition analysis of crude glycerol and its derived biopolyols

The compositions of crude glycerol and its derived biopolyols, such as free fatty acids (FFAs), soap, glycerol, and glyceride contents were determined according to the methods described previously [18]. The hydroxyl number was determined according to ASTM D4274-05D, and the corresponding values for pretreated crude glycerol (i.e., crude glycerol after the removal of water and methanol), polyol-2.5h, and polyol-5h were 456, 391, and 346 mg KOH/g, respectively. The acid number was determined according to ASTM D4662-08, and the corresponding values for pretreated crude glycerol and polyol-2.5h were 20 and 7 mg KOH/g, respectively. The acid number of polyol-5h was below the detection limit.

The FFA content was obtained by conversion of the acid number according to ASTM D5555-95. The soap content was determined according to the AOCS recommended Practice Cc 17-95. The content of FAMES, free glycerol, and glycerides was determined by gas chromatography (GC) using a Shimadzu GC-2010 plus GC system (Shimadzu, Columbia, MD) equipped with a flame ionization detector (FID). Detailed processes were described in our previous report [18].

2.4. Foam preparation

The biopolyol master batch (formula listed in Table 1), which contained polyols, surfactant, catalysts and water, was mixed vigorously in 100 ml plastic cups with a high-speed stirrer for 30 s to achieve homogenous dispersion. Then, pre-weighted polymeric MDI was added into each cup and mixed vigorously for around 10 s. The mixture was rapidly poured into a 1000 ml cylinder mould coated with polytetrafluoroethylene and left to grow at ambient temperature (23 ± 2 °C). Foam samples were allowed to cure overnight before removal from the mould. Foam samples were then cut into specimens of desired dimensions and conditioned for 1 week before testing.

The foams made from pretreated crude glycerol, polyol-2.5h, and polyol-5h were designated as PU-CG, PU-2.5h and PU-5h, respectively. In order to clarify the effect of branched fatty acid ester chains in the foaming process, an artificial polyol was made by mixing pure glycerol, sodium oleate, biodiesel, ethylene glycol, and methanol based on the proportions of free glycerol, soap, FAMES, monoglycerides, and diglycerides in polyol-5h. This artificial polyol was designated as polyol-EG. Ethylene glycol was used for polyol-EG to replace the monoglycerides in polyol-5h, because, except for a lack of branched fatty acid ester chains, ethylene glycol has the same structure as monoglycerides, i.e., both have two hydroxyl groups in a molecule. A similar consideration was also applied to the use of methanol to replace diglycerides. PU foam from the polyol-EG was made following the same procedure as PU foam from polyol-5h.

2.5. Characterization

The rheological properties of crude glycerol and its derived biopolyols were characterized using a TA Instruments DHR-2 rheometer (TA Instruments, New Castle, DE, USA) with a 25-mm plate/plate

Table 1
Components of foam formulation.

Ingredients	Description	Parts by weight
Biopolyols	Donation of hydroxyl groups	100
Polymeric MDI	Donation of isocyanate	Isocyanate to hydroxyl ratio of 1.05
Polycat 5	Catalyst for urea formation	1.26
Polycat 8	Catalyst for urethane formation	0.84
DABCO DC5357	Silicone surfactant	2.5
Water	Blowing agent	3

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