

Production of Polyols and Waterborne Polyurethane Dispersions from Biodiesel-Derived Crude Glycerol

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ABSTRACT: This study investigated the preparation of polyols and waterborne polyurethane dispersions (CG-WPUDs) from biodiesel-derived crude glycerol. The polyols were produced from biodiesel-derived crude glycerol via a thermochemical conversion process, which converted crude glycerol components such as glycerol, free fatty acids, and methyl esters of fatty acids (FAMES) into polyols under optimized reaction conditions. CG-WPUDs with different hard segments (41.0% to 63.2 wt %) were prepared from the crude glycerol-based polyols produced. PU coating films cast from CG-WPUDs showed increasing glass transition temperatures (T_g) from 63°C to 81°C when hard segment content increased from 41.0% to 63.2% and had good thermal stability up to 240°C. CG-WPUD-based coatings showed excellent adhesion to steel panel surfaces, pencil hardness as high as F, but relatively low flexibility. This study demonstrated the potential of biodiesel-derived crude glycerol for the production of bio-based polyols and WPUDs. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41425.

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INTRODUCTION

Polyurethane (PU) coatings have been widely used in various commercial applications because of their excellent chemical, solvent, and abrasion resistance, as well as toughness combined with good low-temperature flexibility.¹ Traditionally, PU coatings are solvent-based, which lead to significant emissions of volatile organic compounds (VOCs) upon application. In recent years, the use of solvent-based coating systems has been largely reduced because of increasingly stringent VOC emission regulations. As a result, environmentally friendly PU coating technologies, such as waterborne PU dispersions (WPUDs), have been gaining increasing attention and experiencing rapid development in recent years.^{2–4}

WPUDs are binary colloidal systems in which PU particles with very small sizes (i.e. 20–200 nm) are dispersed in a continuous phase of water.⁵ The high surface energy resulting from the small particle size distribution facilitates film formation on substrate surfaces after water evaporation, with little or no VOC emissions.³ Compared to their solvent-based analogs, WPUDs have advantages such as low toxicity, low viscosity at high molecular weights (M_w), and low environmental hazards.^{3,6} In recent years, there has been widespread research interest in developing bio-based WPUDs from renewable sources, among which vegetable oils, especially soybean oil, have been the most

commonly studied.^{3,7–9} The production of bio-based WPUDs usually begins with the production of bio-based polyols, from which WPUDs are produced. The properties of bio-based WPUDs largely depend on the properties of bio-based polyols. Lu and Larock³ prepared WPUDs with different hard segments (39.3–49.0 wt %) from soy-based polyols with different hydroxyl numbers (135–200 mg KOH/g) and functionalities (2.4–4.0). Their results suggested that polyols with higher functionalities and higher hydroxyl numbers led to PU coating films with higher rigidity and higher mechanical strength.³ In a later study, Ni et al.⁸ used six soy-based polyols with hydroxyl numbers ranging from 100 to 164 mg KOH/g to prepare WPUDs, and their results also showed that the rigidity of PU coating films increased with increasing polyol hydroxyl number. To further improve the properties of bio-based WPUDs, crosslinkers and nanocomposites have been used along with polyols to prepare WPUDs with improved mechanical strength.^{10,11} In addition, the properties of vegetable oil-derived WPUDs were improved or tailored through the preparation of hybrid PUs.^{12–14} Generally, previous researches have shown that vegetable oils are promising feedstocks for the production of bio-based WPUDs with potential applications in various areas.

Our previous studies have shown that crude glycerol, a low-value biodiesel byproduct, has potential for liquefying

Table I. Formulation of Crude Glycerol-Based Waterborne Polyurethane Dispersions (CG-WPUDs) Prepared from the Crude Glycerol-Based Polyol

Samples ^a	Relative molar ratio to hydroxyl groups in CG-POL ^b				HS ^c (wt %)	DMPA ^d (wt %)
	NCO	OH (CG-POL)	OH (DMPA)	OH ^e		
CGPU-63.2	1.6	1	0.6	0	63.2	10.8
CGPU-58.2	1.4	1	0.4	0	58.2	8.1
PCGPU-51.5	1.43	1	0.4	0.03	51.5	6.6
PCGPU-41	1.5	1	0.4	0.1	41.0	5.0

^aCGPU-63.2 and -58.2: WPUDs based solely on crude glycerol-based polyol; PCGPU-51.5 and -41: WPUDs based on a mixture of crude glycerol-based and petroleum-derived polyether polyol (Voranol 4701, hydroxyl number: 34 mg KOH/g); number after dash indicates hard segment content in Pus.

^bCG-POL: crude glycerol-based polyol produced in this study.

^cHard segment.

^dDimethylol propionic acid.

^eHydroxyl groups from Voranol 4701 (hydroxyl number: 34 mg KOH/g).

lignocellulosic biomass for the production of bio-based polyols and PU foams.^{15–18} Compared to vegetable oils, crude glycerol is a low-value and inexpensive byproduct and generally does not compete directly with food supplies. In this study, the feasibility of using crude glycerol for polyol and WPUD production was investigated. Thermochemical conversion of crude glycerol to polyols was optimized to prepare crude glycerol-based WPUDs (CG-WPUDs). CG-WPUDs were prepared in anionic form using dimethylol propionic acid (DMPA) as an internal emulsifier, and the effect of hard segment content on the properties of WPUDs was investigated.

MATERIALS AND METHODS

Materials

Chemicals purchased from Fisher Scientific (Pittsburgh, PA) included imidazole and standard NaOH solutions (0.1N and 10N, respectively). Chemicals purchased from Sigma Aldrich (St. Louis, MO) included phthalic anhydride, dibutyltin dilaurate (DBTDL), DMPA, and isophorone isocyanate (IPDI). Chemicals purchased from Pharmco-AAPER (Shelbyville, KY) included pyridine, acetone, triethylamine (TEA), HPLC-grade tetrahydrofuran (THF), and 98% concentrated H₂SO₄. All chemicals purchased above were of reagent grade or higher purity. A commercial petroleum-derived polyether polyol (Voranol 4701, hydroxyl number: 34 mg KOH/g) was obtained from The Dow Chemical Company (Midland, MI). Crude glycerol was obtained from Bio100 Technologies, LLC. (Mansfield, OH) and determined to contain glycerol (23.1%), soap (26.1%), fatty acid methyl esters (FAMES) (24.8%), methanol (7.9%), water (17%), free fatty acids (FFA) (2%), and ash (3%).

Thermochemical Conversion of Crude Glycerol to Polyols

Thermochemical conversion of crude glycerol to polyols was carried out in a 500-mL three-neck flask, which was connected to a vacuum pump (DOA-P707-FB, Gast Manufacturing, Benton Harbor, MI), a condenser, and a thermometer. Crude glycerol and a predetermined amount of 98% concentrated sulfuric acid were added into the flask and then heated to the desired reaction temperature (160–190°C) using a temperature-controlled heating mantle (Thermo Electron, Madison, WI) under vacuum (gauge vacuum: -90 kPa) and constant stirring by a magnetic bar (500 rpm). Then, the reaction temperature was

held constant and the reaction continued for a predetermined time (15–120 min). Upon completion of the reaction, the flask was immediately removed from the heating mantle and cooled to room temperature in a fume hood. Polyols were recovered from the flask.

Characterization of Crude Glycerol-Based Polyols

The acid and hydroxyl numbers of the polyols were determined according to ASTM D4662-08 and D4274-05D, respectively. The molecular weights (M_w) of the polyols were determined using an LC-20 AB high performance liquid chromatography (HPLC) system (Shimadzu, Columbia, MD) equipped with a RID-10A refractive index detector (RID) and a gel permeation chromatography (GPC) column (Styragel HR1 THF, 7.8 × 300 mm, Waters, Milford, MA). The mobile phase used was HPLC-grade THF at a flow rate of 1 mL/min. The column and RID temperatures were maintained at 35°C and 40°C, respectively. The injection volume was 10 μL. An external calibration curve was constructed by analyzing standard polystyrene with M_w ranging from 200 to 2000 g/mol. The data analysis was conducted using Shimadzu LC solution Version 1.25. The composition of crude glycerol-based polyols was characterized according to methods reported in a previous study.¹⁹

Preparation of Crude Glycerol-Based WPUDs (CG-WPUDs)

Table I shows the formulations and hard segment contents (41–63.2%) of the WPUDs produced in this study using crude glycerol-based polyols and/or a commercial petroleum-derived polyether polyols (Voranol 4701, hydroxyl number: 34 mg KOH/g). The preparation of CG-WPUDs was carried out at 80°C in a 250-mL three-neck round bottom flask equipped with a nitrogen inlet, a magnetic stirrer, and a condenser. Polyols (5.0 g) and predetermined amounts of DMPA and IPDI, which varied with different formulations (Table I), were weighed into the flask, followed by the addition of 0.1% DBTDL (based on the total weight of polyols, DMPA, and IPDI) as a catalyst and approximately 30 mL of acetone as solvent. The flask was then immersed into an oil bath, which was kept constant at 80°C. The reaction between polyols and isocyanate was conducted until it was completed, as indicated by the disappearance of the NCO absorption peak under Fourier transform infrared spectroscopy (FT-IR) (Spectrum Two IR spectrometer, PerkinElmer, Waltham, MA).

During the reaction, acetone was added as necessary to decrease the viscosity of the polymer solution. After completion of polymerization, an appropriate amount of TEA (molar ratio of TEA/DMPA: 1.2/1) was added to the polymer solution and the reaction was conducted for 1 h at 50°C. Then, the polymer solution was dispersed into deionized water under vigorous stirring. Acetone in the dispersion was then removed at 40°C by a vacuum-assisted rotary evaporator (Laborota efficient 4001, Heidolph, Schwabach, Germany). The produced CG-WPUDs had solid contents of approximately 20%.

Preparation and Characterization of CG-WPUD-Derived PU Films

For the preparation of PU films, CG-WPUDs were poured into Teflon-coated metal molds, air-dried in a fume hood for 24 h, and then vacuum-dried at 60°C for 24 h. FT-IR analyses of PU films were conducted on a Spectrum Two IR spectrometer (PerkinElmer, Waltham, MA) using an attenuated total reflectance (ATR) diamond cell. All spectra obtained were ATR and the baseline was corrected using Spectrum 10 software. Differential scanning calorimetry (DSC) was carried out on a Q20 DSC analyzer (TA Instruments, New Castle, DE) equipped with refrigerated cooling. Each PU film sample (5.0–10.0 mg) was first heated to 100°C to erase its thermal history, cooled to -70°C, and then heated again to 200°C at $\pm 10^\circ\text{C min}^{-1}$. An equilibration time of 3 min was applied after each heating and cooling cycle. The glass transition temperature (T_g) was determined as the inflection point in the DSC thermogram obtained in the second heating scan. The thermal stability of the PU film was analyzed using a Q50 Thermogravimetric Analyzer (TGA, TA Instruments, New Castle, DE). Each PU sample (8.0–15.0 mg) was heated from 30°C to 800°C at a rate of 20°C/min under a nitrogen atmosphere. Analyses of both DSC and TGA data were conducted using Universal Analysis 2000 (TA instruments, New Castle, DE).

Characterization of the Coating Performance of CG-WPUDs

CG-WPUDs were applied to phosphated cold-rolled steel panels (R-46-I, $4 \times 6 \times 0.032''$, matte finish, Q-lab Corp., Westlake, OH) by a foam brush. The coated panels were dried in a fume hood overnight and then at 60°C in a vacuum oven for 48 h. The tape adhesion, pencil hardness, and mandrel bending tests on coated steel panels were conducted according to ASTM D3359, ASTM D3363, and ASTM D522, respectively.

RESULTS AND DISCUSSION

Thermochemical Conversion of Crude Glycerol to Polyols

The esterification of glycerol with fatty acids can be catalyzed by metal carboxylates, such as inorganic salts (e.g. sodium, potassium, and zinc) of fatty acids, which can act as emulsifying agents to increase the contact between reactants (i.e. glycerol and fatty acids).²⁰ In this study, it was assumed that the soap present in crude glycerol could act as an emulsifier to improve the contact between FFAs and glycerol, eventually accelerating esterification reactions. In addition, soap, the sodium or potassium salt of fatty acids, is a weak alkali. It may also act as a base catalyst to accelerate the transesterification reactions between FAMES and glycerol. To investigate the effect of soap content on polyol production, crude glycerol (initial soap con-

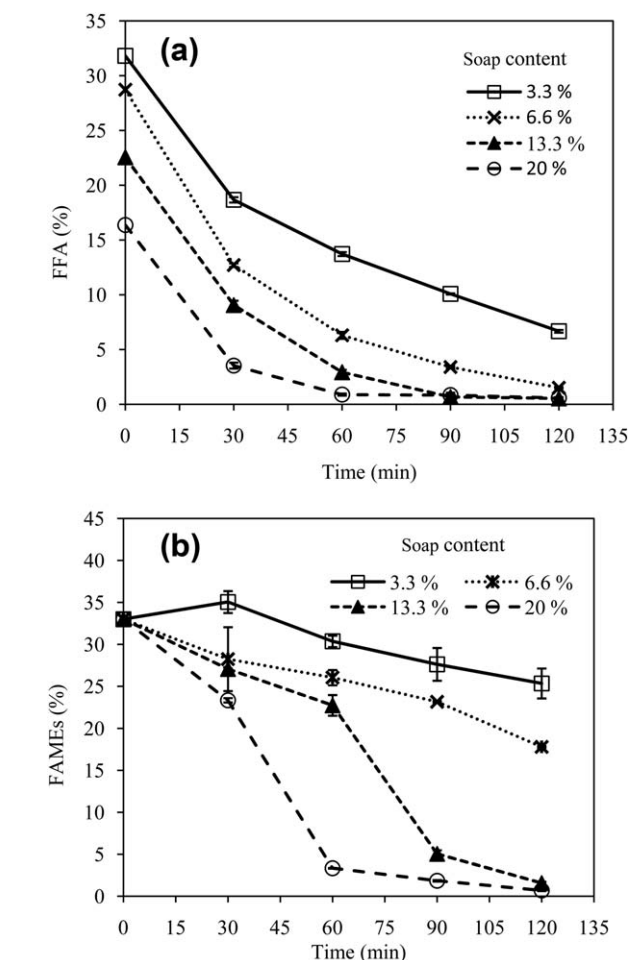


Figure 1. Time-dependent changes of (a) FFA and (b) FAME contents in polyols at different soap levels (3.3–20%, reaction temperature: 180°C).

tent: 26.1%) was partially neutralized by H_2SO_4 to different soap contents (2.5%, 5%, 10%, and 15%) before thermochemical conversion. As crude glycerol was heated to the desired thermochemical reaction temperatures (160–190°C) in this study, almost all of the water (17%) and methanol (7.9%) originally existing in the crude glycerol were gradually evaporated from the reaction medium in a vacuum. As a result, the actual soap contents in the reaction medium at the beginning of the reactions increased slightly to 3.3%, 6.6%, 13.3%, and 20% from their initial contents of 2.5%, 5%, 10%, and 15%, respectively.

At different soap contents, the reaction medium had different initial FFA contents [Figure 1(a)] because of acidification of the soap in crude glycerol.¹⁹ As shown in Figure 1(a), the FFA content in polyols decreased with increasing reaction time at all soap levels, because of the esterification occurring between glycerol and FFAs. After 120 min, polyols produced at 6.6%, 13.3%, and 20% soap levels exhibited low FFA contents (<2%), while a relatively high residual FFA content (6.7%) was observed at a 3.3% soap level. The higher residual FFA content at the 3.3% soap level could be largely explained by the reaction medium's higher initial FFA content (31.8%). Similarly, the FAME contents in polyols also decreased gradually with increasing reaction time at all soap levels, because of the occurrence of

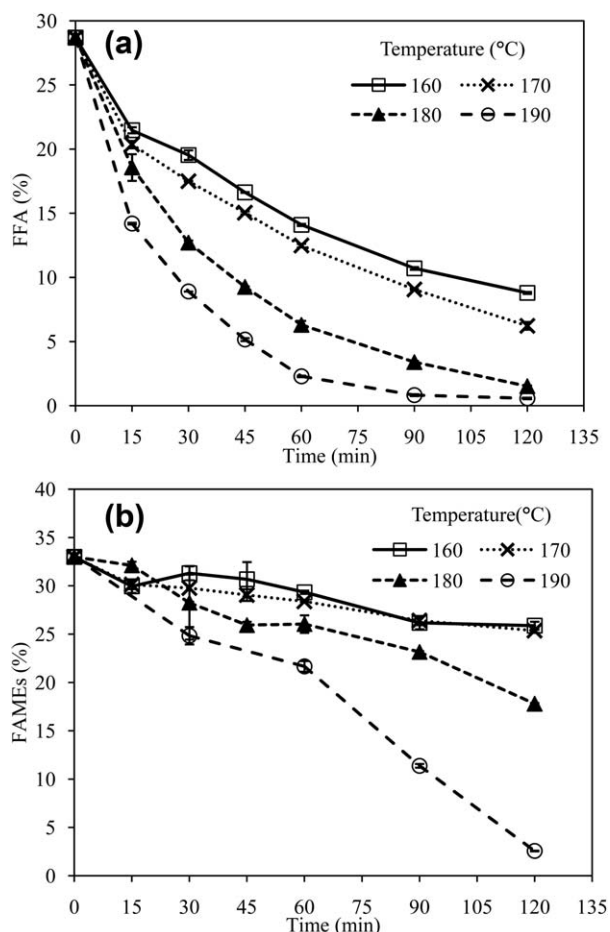


Figure 2. Time-dependent changes of (a) FFA and (b) FAME contents in polyols at different reaction temperatures (160–190°C, soap content: 6.6%).

transesterification reactions between FAMES and glycerol [Figure 1(b)]. FAME content decreased faster at higher soap levels, indicating the strong catalytic effect of soap. After a reaction time of 120 min, the polyols produced at 13.3% and 20% soap levels had very low FAME contents (<1%), whereas those at 3.3% and 6.6% soap levels had high residual FAME contents (>15%). These higher residual FAME contents at 3.3% and 6.6% soap levels could be explained by the lower catalytic effect of the soap and/or by the stronger competition from the esterification between FFAs and glycerol at lower soap levels (i.e. higher initial FFA contents). In addition, it was observed that the FFA content decreased faster than the FAME content at the beginning of the thermochemical process (Figure 1). This most likely resulted from the different rate of reactions (i.e. esterification of FFAs with glycerol and transesterification of FAMES with glycerol).

The time-dependent changes of FFA and FAME contents in polyols at different reaction temperatures (160–190°C) are shown in Figure 2(a,b), respectively. The decrease of FFA content with increasing reaction time was relatively slow at 160°C and 170°C, and the residual FFA content was 8.8% and 6.3%, respectively, after a reaction time of 120 min [Figure 2(a)]. Significant

improvements in FFA conversion rates were observed when the temperature increased to 180°C and 190°C, and the polyols produced at 120 min showed low FFA contents [<2%, Figure 2(a)]. The decrease of the FAME content with increasing time was relatively slow at 160°C, 170°C, and 180°C, and the produced polyols had high contents of residual FAMES (>15%) after a reaction time of 120 min [Figure 2(b)]. A dramatic increase in the FAME conversion rate was observed when the reaction temperature was increased to 190°C, and the produced polyols had a low FAME content of approximately 2.5%.

Based on the results discussed above, FAMES were converted more rapidly at higher soap levels, because of the intensified emulsifying and/or catalytic effects of soap. However, the residual soap itself did not participate in conversion reactions for the production of polyols after the partial acidification of soap by sulfuric acid. The presence of high soap content in polyols is unfavorable for PU production. Thus, soap content in crude glycerol needs to be optimized to balance these two contradictory effects. In this study, the suitable soap content was determined to be 6.6%, at which the polyols produced at 190°C and 120 min showed low FFA (<1%) and FAME (ca. 2.5%) contents. Table II shows the compositions of original crude glycerol, crude glycerol after the removal of water and methanol, and the crude glycerol-based polyol produced under optimized reaction conditions. Compared to crude glycerol, crude glycerol-based polyols had obviously decreased glycerol, FAME, and FFA contents while significantly increased monoglyceride and diglyceride contents. This agrees with previous findings¹⁹ that the esterification and transesterification among the components of crude glycerol were successfully carried out during the thermochemical conversion process. After characterization, the produced polyols were shown to have a hydroxyl number of 378 mg KOH/g, functionality of 4.7, acid number of <5 mg KOH/g, and M_w of 702 g/mol. Figure 3 shows the GPC curve of crude glycerol-based polyols. The appearance of multiple peaks indicated that polyols consisted of multiple components, which agreed well with the results in Table II.

Production of CG-WPUDs

The crude glycerol-based polyols produced from the optimized thermochemical process had a relatively high hydroxyl number (378 mg KOH/g) and a high functionality (4.7), which may lead to gelation and high crosslinking of PU networks that make the PUs difficult to disperse in water.³ Previous studies on the synthesis of petroleum-derived WPUDs mostly used polyols with low functionalities (ca. 2.0) and a prepolymer process that used excess isocyanates.^{21–23} The use of low-functionality polyols and the prepolymer process ensured a low viscosity of the polymer solution/melt, which reduced the use of organic solvents, such as acetone and methyl ethyl ketone, during the polymerization process. Similarly, the synthesis of WPUDs from bio-based (i.e. mostly vegetable oil-based) polyols has been previously reported and the polyols used also had low functionalities of around 2.0.^{12,14} Most of these bio-based WPUDs were synthesized using NCO/OH ratios equal or close to 1.0, unlike the excess isocyanates used in the prepolymer process.^{3,7,8} By applying a NCO/OH ratio of 1 : 1, WPUDs from soybean oil-

Table II. Composition of Crude Glycerol and Crude Glycerol-Based Polyols

Samples	Crude glycerol	Crude glycerol after the removal of water and methanol ^a	Crude glycerol-based polyols
Free glycerol (wt %)	23.1 ± 0.2 ^b	30.8 ± 0.2	11.0 ± 0.2
Methanol (wt %)	7.9 ± 0.5	0	BDL ^b
Water (wt %)	17.0 ± 0.1	0	BDL
Soap (wt %)	26.1 ± 0.2	34.8 ± 0.2	6.1 ± 0.1
FAMEs (wt %)	24.8 ± 0.3	33.0 ± 0.3	2.5 ± 0.0
FFAs (wt %)	2.0 ± 0.2	2.7 ± 0.2	0.6 ± 0.1
Monoglycerides (wt %)	BDL ^a	BDL	33.8 ± 1.0
Diglycerides (wt %)	BDL	BDL	21.1 ± 0.4

The composition was calculated by subtracting the amounts of methanol and water from the total amount of crude glycerol.

^aMean ± standard deviation of two replicates.

^bBelow the detection limit.

based polyols with high crosslinking density and functionality as high as 4.0 were also prepared and reported.³

In this study, the synthesis of crude glycerol-based WPUDs (CG-WPUDs) was first conducted using a literature-described prepolymer process that uses excess isocyanates.²¹ However, it was observed that a large amount of acetone-insoluble compounds were produced within the first 30 min of the reaction at 80°C (data not shown), probably because of the formation of highly crosslinked PU thermosets caused by the high functionality of the crude glycerol-based polyols produced in this study (f_{ii} : 4.7). When the polymerization was conducted at a NCO/OH molar ratio of 1 : 1, this problem was largely resolved as long as acetone was added as necessary to keep the polymer solution at a low viscosity. Through this approach, no significant formation of acetone-insoluble compounds was observed during the polymerization process, and the produced CG-WPUDs showed good stability under ambient conditions.

In this study, the progression of polymerization between polyols and isocyanates was monitored by FT-IR at the wavenumber of 2270 cm⁻¹, which is assigned to the absorption peak of the isocyanate group (-NCO).⁷ It can be seen that the intensity of the -NCO adsorption peak at 2270 cm⁻¹ decreased gradually with

increasing reaction time from 5 to 45 h until its complete disappearance at 45 h, suggesting completion of the polymerization (Figure 4). The reaction time required for completion of the polymerization (45 h) in this study was much longer than the reaction time (ca. 3 h) reported in previous studies, in which WPUDs were synthesized from vegetable oil-based polyols and aromatic isocyanates.^{7,8} This difference could be explained by: (a) the low reactivity of the crude glycerol-based polyols because of the presence of secondary hydroxyl groups, which are much less reactive than primary hydroxyl groups²⁴; (b) the low reactivity of the isocyanate (i.e. IPDI) used in this study, which has the lowest reactivity among all isocyanates and is much less reactive than aromatic isocyanates²⁵; and/or (c) the addition of organic solvent (i.e. acetone) into the reaction system before polymerization may have led to diluted monomer concentrations in this study, while organic solvent was added after certain polymerization times (0.5–3 h) in previous studies.^{3,7,8}

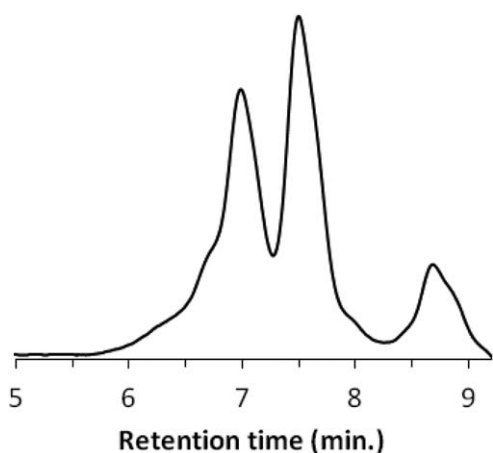


Figure 3. GPC curve of crude glycerol-based polyols.

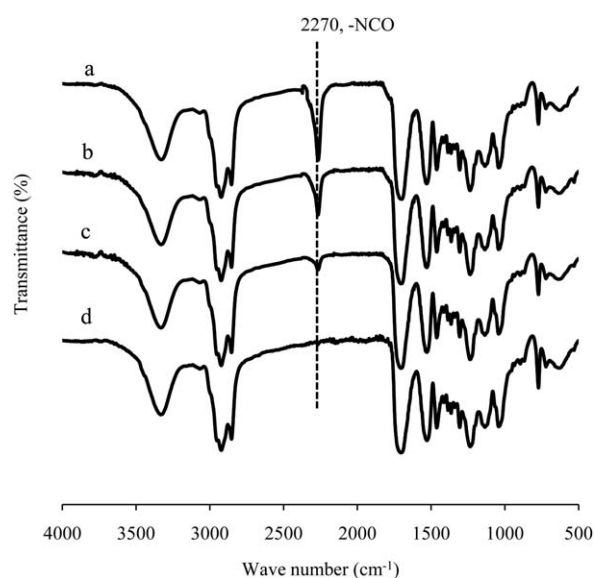


Figure 4. FT-IR spectra of CG-WPUD produced at different reaction times: (a) 5 h; (b) 10 h; (c) 24 h; and (d) 45 h.

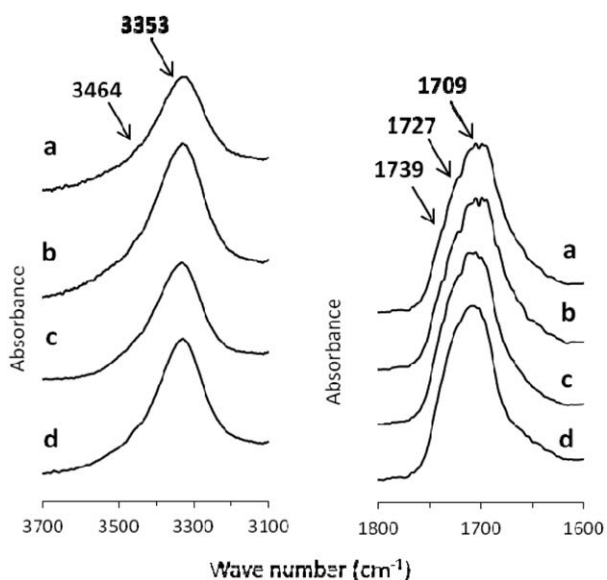


Figure 5. FT-IR spectra of CG-WPUD-derived PU films: (a) CGPU-63.2, (b) CGPU-58.2, (c) PCGPU-51.5, and (d) PCGPU-41.

Properties of PU Films Cast from CG-WPUDs

Hydrogen bonding, formed between the N-H of the amide group and the urethane carbonyl, the ether oxygen, or the carbonyl group in PUs, has significant impacts on PU properties.³ A higher degree of hydrogen bonding, because of increased polyol functionality or hard segment content in PUs, has been found to lead to stronger crosslinking, higher glass transition temperature (T_g), and higher mechanical strength of PU films.³ FT-IR was used to examine the presence and relative intensity of hydrogen bonding in PUs. The characteristic absorption peaks of the stretching of -NH (3300–3500 cm^{-1}) and -CO (1700–1740 cm^{-1}) groups in PU are particularly useful for this purpose.^{3,7} In this study, the strong absorption peaks at 3353 cm^{-1} and at 1709 and 1727 cm^{-1} in the spectra of four PU films with different hard segment contents were attributed to the stretching of hydrogen bonded -NH and -C=O, respectively (Figure 5).^{3,26} In contrast, the relatively weak absorption peaks at 3464 and 1739 cm^{-1} were assigned to the stretching of free -NH and -C=O groups in PUs, respectively. These results suggest that most -NH and -C=O groups in PUs are hydrogen bonded, which is in agreement with previous reports on soybean oil-derived PUs.^{3,7} The spectra of all four PU films showed similar absorption peaks of -C=O stretching, indicating similar degrees of hydrogen bonding (Figure 5).

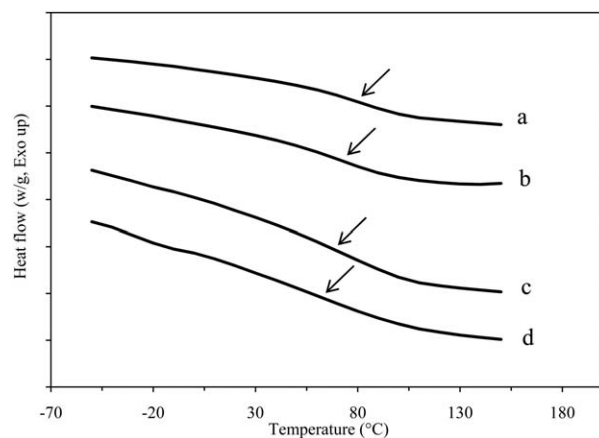


Figure 6. DSC thermograms of CG-WPUD-derived PU films: (a) CGPU-63.2, (b) CGPU-58.2, (c) PCGPU-51.5, and (d) PCGPU-41.

Figure 6 shows the DSC thermograms of the PU films cast from CG-WPUDs. No melting or crystallization peaks were observed in any of the films for temperatures up to 200°C, indicating the amorphous structures of the PU films. The T_g of CGPU-63.5 and CGPU-58.2 were determined to be 81°C and 76°C, respectively. The addition of a petroleum-derived polyether polyol (hydroxyl number: 34 mg KOH/g; f_n : 2.6) into WPUD formulations reduced the T_g of PU films (PCGPU-51.5: 69°C; PCGPU-41: 66°C), because of the increased chain flexibility imparted by polyether chains. In general, the T_g of PU produced in this study increased with increasing hard segment content (Tables I and III), which agrees with previous findings on vegetable oil-based PU.³ The increased T_g at higher hard segment contents was attributed to the increased crosslinking density of hard segments in PU causing a restriction on the mobility of polymer chains.^{3,27} The T_g of prepared PU films cast from soybean oil-based WPUDs increased from 8.9°C to 33.5°C with increasing polyol functionality (f_n) from 2.4 to 4.0 and hydroxyl number from 135 to 200 mg KOH/g.³ The relatively higher T_g (66–81°C) observed in this study were attributed to the higher functionality (f_n : 4.7) and higher hydroxyl number (378 mg KOH/g) of the produced crude glycerol-based polyols. PU networks prepared from high-functionality linseed oil-based polyols (hydroxyl number: 248 mg KOH/g; f_n : 6.4) showed a similarly high T_g of 77°C.²⁷

Figure 7 shows the TGA and derivative TGA curves of PU films cast from CG-WPUDs. Generally, PUs are considered to have low thermal stability because of the presence of labile urethane

Table III. Thermal Properties of CG-WPUD-Derived PU Films and Coating Performance of CG-WPUDs

Samples	DSC	TGA ^a		Coating performance		
	T_g (°C)	T_5 (°C)	T_{50} (°C)	Tape adhesion	Pencil hardness	Mandrel bending at 3/8 in.
CGPU-63.2	81	235	295	5B	F	Fail
CGPU-58.2	76	238	300	5B	F	Fail
PCGPU-51.5	69	243	308	5B	F	Fail
PCGPU-41	66	253	363	5B	2B	Pass

^a T_5 and T_{50} : 5% and 50% weight loss temperature, respectively.

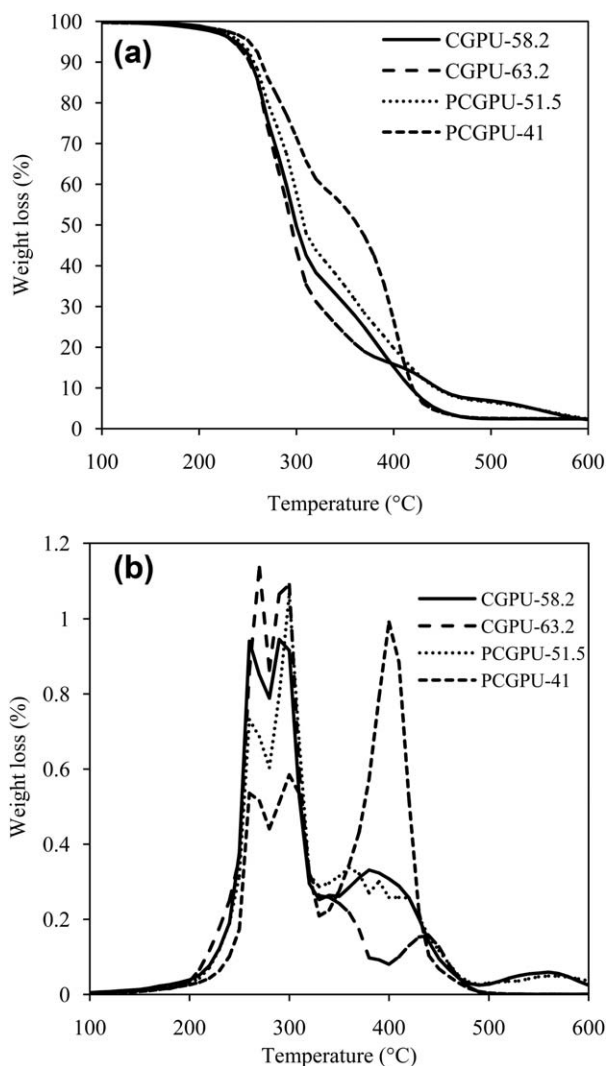


Figure 7. (a) TGA and (b) derivative TGA curves of CG-WPUD-derived PU films.

bonds, which usually start to degrade at temperatures between 150°C and 220°C, depending on the types of isocyanates and polyols used in PU production.²⁸ The dissociation of urethane bonds has been previously proposed to follow three mechanisms: dissociation to isocyanates and alcohol, formation of primary amine and olefin, and formation of secondary amine.²⁹ In this study, PU films exhibited two major degradation stages [Figure 6(b)], similar to the degradation behavior of vegetable oil-derived PU.^{3,8,29} This similarity could be attributed to the fact that crude glycerol-based and vegetable oil-based polyols contain similar structural components such as a glycerol backbone and fatty acid side chains. The first stage, which occurred between 240°C and 310°C, was attributed to the degradation of urethane linkages in the PU, whereas the second stage, which occurred between 310°C and 470°C, was most likely caused by chain scission of the polyol components of CG-WPUDs.³ As shown in Table III, both T_5 (5% weight loss temperature) and T_{50} (50% weight loss temperature) of the PU decreased with increasing hard segment content, because of the higher content of urethane linkages.³ In general, PU films

cast from CG-WPUDs showed thermal stability comparable to their analogs derived from vegetable oils.^{3,8,29}

Coating Performance of CG-WPUDs

Table III shows the tape adhesion, pencil hardness, and mandrel bending performance of CG-WPUDs on phosphated cold-rolled steel panels. All prepared PU coatings showed excellent adhesion to steel surfaces and no coatings were removed from the surface by tape (5B) (Table III). All PU coatings, except PCGPU-41, showed F grade pencil hardness. The lower hardness of PCGPU-41 (2B) was explained by its higher polyether polyol content (Table I), which is more flexible than the crude glycerol-based polyol produced in this study. PU coatings prepared from soybean oil glyceride and hybrid glyceride amide polyols exhibited pencil hardness (F) and tape adhesion properties (5B) similar to the results obtained in this study.³⁰ The Mandrel bending test results showed that incorporation of flexible polyether polyols improved the flexibility of CG-WPUD-based coatings. The low flexibility of CG-WPUD-based coatings largely resulted from the high functionality, high hydroxyl number, low M_w , and relatively rigid molecular chains of the crude glycerol-based polyols produced in this study.

CONCLUSIONS

Thermochemical conversion of crude glycerol to polyols was optimized to produce crude glycerol-based polyols with low contents of residual FFAs (<1%) and FAMEs (<2.5%). PU films cast from CG-WPUDs showed increasing T_g and decreasing thermal stability with increasing hard segment contents. Generally, PU films cast from CG-WPUDs had higher T_g (63–81°C) and similar thermal stability, when compared to vegetable oil-derived PUs. CG-WPUD-based coatings showed excellent adhesion to a steel surface, good hardness, but low flexibility. The flexibility of CG-WPUDs-based coatings can be improved by incorporation of flexible polyether polyols. Overall, the results indicated that crude glycerol-based polyols had a potential for waterborne PU coating applications. Economics and environmental impact analysis on the process of producing waterborne polyurethane coatings from crude glycerol is ongoing.

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