Polyol Recovery from Biomass-Based Polyurethane Foam by Glycolysis

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ABSTRACT: Biomass-based polyurethane foams (PUFs) were degraded by glycolysis and the polyols recovered were reused to prepare a rigid polyurethane foam. Biomass-based PUFs were prepared from liquefied wood or starch polyols and grafted products with polycaprolactone. The glycolysis was conducted using diethylene glycol (DEG) as a solvent and potassium acetate as a catalyst under various reaction conditions. The effects of reaction conditions on the properties of the polyols recovered were examined. The average-weight molecular weight (Mw) and viscosity decreased as the reaction time, temperature, and ratio of DEG/PUF increased, whereas the hydroxyl value increased. It was found from IR measurements that the conversion of the urethane functional group (–NCOO–) increased as the glycolysis proceeded. The PUF prepared from the recovered polyols had properties comparable to those of the raw PUF used in glycolysis. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 975–980, 2005

Key words: biomass; glycolysis; liquefaction; polyol; polyurethane foam
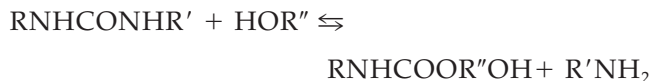
INTRODUCTION

Polyurethanes (PUs) generated from the reaction of a polyol and a diisocyanate are general-purpose materials with an extremely versatile range of properties and apply for foams, films, and molded products.

Recently, the polyols used for PUs have been developed from natural resources.[1–8] For example, vegetable oils such as safflower oil, soybean oil, and castor oil can be used as a polyol for PUs. Lee et al.[3,4] also studied the development of polyols from biomass resources using liquefaction technology. In addition to these efforts, trials were conducted to obtain polyol from waste PUs through chemical recycling. In particular, glycolysis is a representative and industrially established method. There has been much research on the glycolysis of PUs.[9–15] Basically, PU can react with a glycol to yield essentially linear products with a low molecular weight, although the chemistry of glycolysis is complicated because there are a variety of chemical groups in the polyurethane foams (PUFs) such as urethane, allophanate, and urea groups. For example, the glycolysis of PU (with diphenylmethane diisocyanate (MDI) as an isocyanate) in the presence of an excess of glycol at 195°C includes the following reactions.
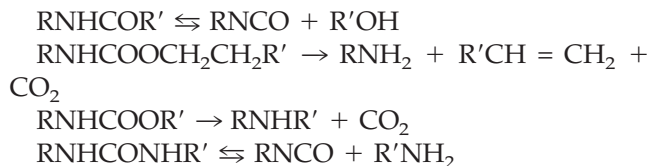
The glycolysis reaction for the benzyl phenyl carbamate is

$$RNHCOOR' + HOR''OH \leftrightarrows$$
$$RNHCOOR''OH + R'OH$$
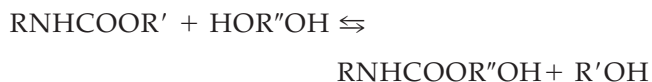
The glycolysis reaction for the disubstituted ureas resulting in urethanes and amines is

$$RNHCONHR' + HOR'' \leftrightarrows$$
$$RNHCOOR''OH + R'NH_2$$

Furthermore, the pyrolysis of urethanes and ureas is

$$RNHCOR' \leftrightarrows RNCO + R'OH$$
$$RNHCOOCH_2CH_2R' \rightarrow RNH_2 + R'CH = CH_2 + CO_2$$
$$RNHCOOR' \rightarrow RNHR' + CO_2$$
$$RNHCONHR' \leftrightarrows RNCO + R'NH_2$$

Other reactions between urethane groups and pyrolysis products are also suggested.

In this study, the glycolysis of biomass-based PUFs was conducted to establish an effective method for chemical recycling and the effects of reaction conditions on the properties of the glycolysis products were investigated.

TABLE I
Properties of Liquefied Biomass Polyols and PUFs Used in This Study

Kind of polyols	Properties of polyols			Properties of PUF		
	Molecular weight (Mw)	Hydroxyl value (mgKOH g^{-1})	Viscosity (mPa · s)	Density (× 10^3 g/cm^3)	Compressive strength (Kpa) at 10% strain	Elastic modulus (MPa)
LW[a]	—	342	18,400	47	179	2.98
LS[b]	—	405	5200	37	225	2.38
LW-g-PCL[c]	3818	128	142,300	40	233	4.85
LS-g-PCL[d]	2214	330	27,542	44	276	4.66

[a]Liquefied wood.
[b]Liquefied starch.
[c]Liquefied wood-grafted polycaprolactone.
[d]Liquefied starch-grafted polycaprolactone.

EXPERIMENTAL

Materials

The biomass used were wood (*Tsuga heterophylla* Sarg.) and corn starch, which were donated by Kishu Paper Co. Ltd (Tokyo, Japan) and the Sanwa Starch Co., Ltd. (Nara, Japan), respectively. The polyethylene glycol (PEG), glycerol (Gly), ε-caprolactone (CL), diethylene glycol (DEG), and potassium acetate were purchased from Nakarai Tesque, Inc. (Kyoto, Japan). MDI and silicone surfactants were obtained from Japan Polyurethane Ind., Ltd. (Tokyo, Japan), and Toray Dow Corning Silicone, Ltd. (Tokyo, Japan), respectively. All other chemicals and foaming agents were obtained from commercial sources.

Liquefaction of biomass, graft-polymerization of CL, and preparation of PUF

Liquefaction was carried out according to the conventional method using a PEG/Gly mixed polyol reported previously.[6–8] The reaction temperature and time were 150°C and 60 min for wood liquefaction and 180°C and 120 min for starch liquefaction, respectively. Sulfuric acid and phosphoric acid were used as a catalyst for wood and starch liquefaction, respectively.

After liquefaction, the obtained product was dehydrated at 140°C by vacuum distillation to below 1% water content and was not neutralized. CL was directly added by batch processing to the liquefied product. Graft polymerization was conducted at 140°C under constant stirring and refluxing for 60 min.

These biomass-based polyols were used directly to prepare polyurethane foams by reacting with MDI. Silicone oil (SH193) was used as a surfactant and the water contained in the liquefied biomass was used as a blowing agent. A 33% solution of triethylene diamine in ethylene glycol and N,N,N',N'',N''-pentamethyldiethylenetriamine were used as gelling and blowing catalysts, respectively. The MDI index was 105 in all samples.

The properties of the liquefied biomass polyol and PU samples used in glycolysis are listed in Table I.

Glycolysis and the preparation of PUF from glycolysis product

Glycolysis was conducted under atmospheric pressure in the presence of DEG and potassium acetate as a solvent and catalyst, respectively. The PUF used was cut into dimensions of 5 × 5×5 mm. The reaction temperature and time were from 133 to 195°C and from 30 to 180 min, respectively. The ratio of DEG/PUF was changed from 1 to 3, and the catalyst content was 2%. The recycled PUF was prepared from the glycolysis product (GP) using the same foaming agents introduced above.

Characterization of the liquefied biomass, GP, and PUF

The molecular weight was determined using a gel permeation chromatograph equipped with a differential refractometer RID-10A detector (Shimadzu Co.). Tetrahydrofuran was used as the mobile phase. The molecular weights of the samples were calibrated using monodisperse polystyrene standards. The hydroxyl value was determined by the titration method (JIS K1557). The viscosity was measured using a Brookfield viscometer (Brookfield Laboratories, Inc.) IR spectra were obtained using a FTIR System 2000 (Perkin-Elmer) spectrometer. Compressive properties of PUF were measured with a Shimadzu Autograph AG-I 5kN in the direction perpendicular to the foam rise at a constant crosshead speed of 5 mm/min, based on the JIS standard (JIS K7220). The PUFs were cut into 50 × 50 × 50 mm specimens. The compressive strength of the foams was determined as the stress at 10% strain.

RESULTS AND DISCUSSION

Figure 1 shows the effect of reaction time on the molecular weight distributions of the polyols recovered
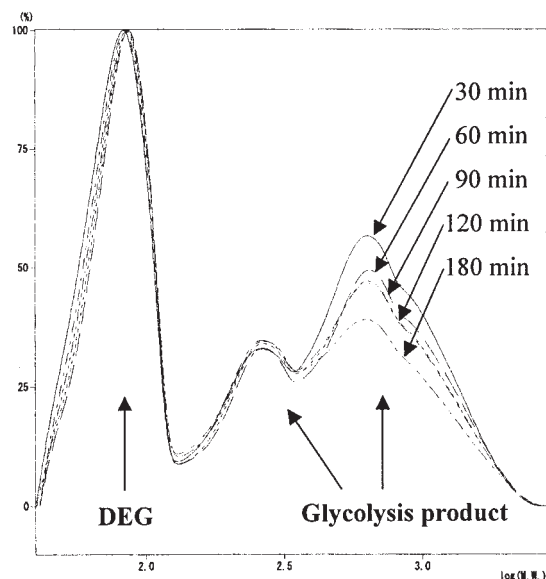
Figure 1 Effect of reaction time on the molecular weight distribution of the polyols recovered from LW-based PUF. Ratio of DEG/PUF, 3; reaction temperature, 195°C; catalyst content, 2%.

Figure 3 Effect of reaction temperature on the molecular weight of the polyols recovered from LW-based PUF. Ratio of DEG/PUF, 3; reaction time, 60 min; catalyst content, 2%.

from liquefied wood (LW)-based PUF by glycolysis. There were three distinct parts, i.e., a low-molecular-weight fraction, attributed to DEG, and two high-molecular-weight fractions with a molecular weight of about 300–500 and a molecular weight higher than 500, which are mainly attributed to GP. The low-molecular-weight fraction showed no change with an increase of reaction time. In the high-molecular-weight fraction, however, the lower parts increased as the reaction time increased, whereas the higher parts decreased. Lower parts in the high-molecular-weight fraction would be mainly composed of raw polyol components, i.e., liquefaction solvent and liquefied wood components, and isocyanates, which were decomposed by glycolysis. The higher parts may be
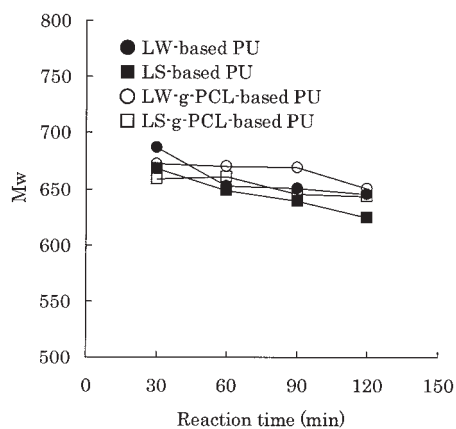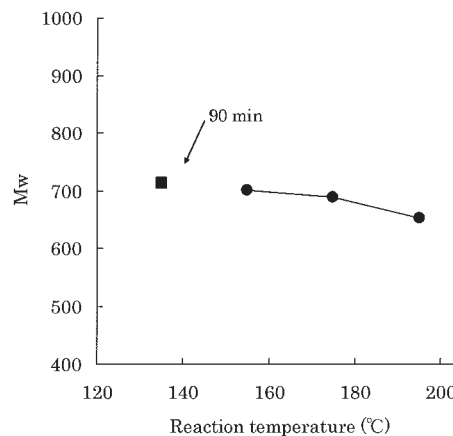
attributed to oligomers with urethane functional groups. The variation in the weight-average molecular weight (Mw) of glycolysis products as a function of reaction time is summarized in Figure 2. In all products, the Mw decreased to less than 700 in a reaction time of 30 min and then gradually decreased further, showing values in the range of 600–700. The decrease in molecular weight indicates the proceeding of glycolysis with the reaction time.

Figures 3 and 4 show the effect of reaction temperature and the ratio of DEG/PUF on the molecular weight of the GP from the LW-based PUF, respectively. At 135°C, the PUF was not completely dissolved in DEG in a reaction time of 60 min, with some solid residue remaining. Thus, the molecular weight of the GP obtained by the reaction for 90 min is shown in Figure 3. The value was about 700. On the other hand, 60 min was enough at temperatures above 155°C. However, there was no significant change in
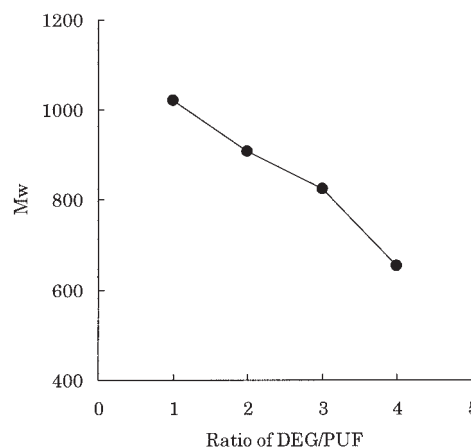

Figure 2 Effect of reaction time on the molecular weight of the recovered polyols. Ratio of DEG/PUF, 3; reaction temperature, 195°C; catalyst content, 2%.

Figure 4 Effect of the ratio of DEG/PUF on the molecular weight of the polyols recovered from LW-based PUF. Reaction temperature, 195°C; time, 60 min; catalyst content, 2%.
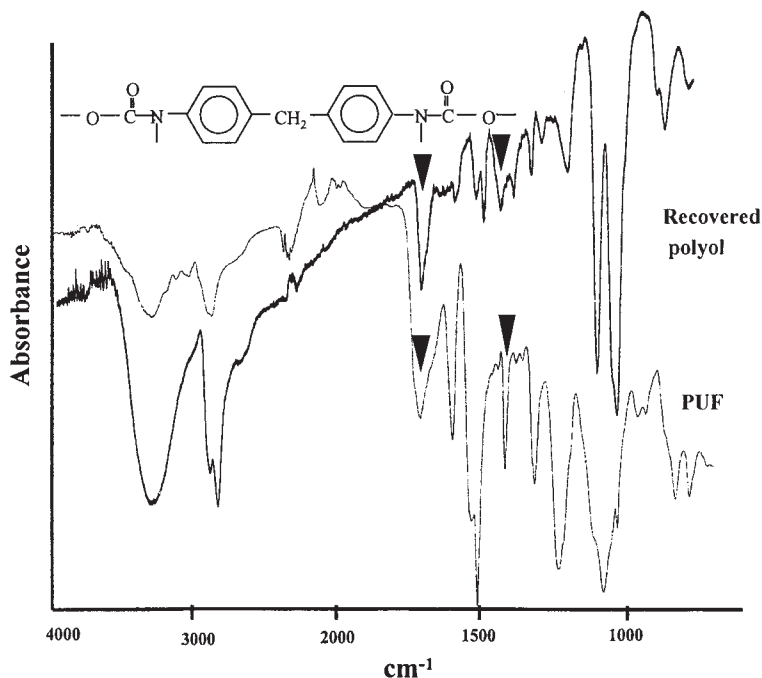
Figure 5   IR spectra of LW-based PUF and the recovered polyols.

molecular weight with increasing reaction temperature, with values in the range of 650–700. This indicates that the GP was not decomposed to a molecular weight less than about 650, even if the temperature rose to 195°C. As shown in Figure 4, the molecular weight decreased as the ratio of DEG/PUF increased, i.e., a higher ratio of DEG/PUF resulted in a lower molecular weight.

The extent of glycolysis can be estimated from the conversion of the urethane functional group (–NCOO–), using the following equation.

Conversion of urethane group (%)

$$= 1 - ([-NCOO-]_r \text{ of } GP/[-NCOO-]_r \text{ of } PUF)$$
$$\times 100, \quad (1)$$

where $[-NCOO-]_r$ is $[-NCOO-]/[-Ar-]$, $[-NCOO-]$ is the IR absorption intensity of urethane group, and

[-Ar-] is the intensity of the aromatic ring. It is known that the aromatic ring due to MDI is more stable than the urethane functional group and is not destroyed in the glycolysis temperature range in this study.[1] Severe glycolysis condition can involve the decomposition of the urethane group. Thus, it is necessary to control the glycolysis condition for obtaining the GP with higher urethane groups.

Figure 5 shows IR spectra of LW-based PUF and the polyol recovered from it. The IR absorbance peaks of the aromatic ring and urethane functional group in both samples appeared at 1450 and 1720 cm^{-1}, respectively. The values for the conversion of the urethane functional group in LW- and LS-based PUF are summarized in Table II. In both samples, the conversion values for the urethane functional group increased as the reaction time increased. The values for the polyol recovered from LW- and LS-based PUF were 73.8 and

TABLE II
Effects of Reaction Time on the Conversion of the Urethane Functional Group(–NCOO–)

Sample	Glycolysis time (min)	Intensity of IR absorbance			Conversion of [–NCOO–] (%)
		[–NCOO–]	[–Ar–]	[–NCOO–]	
LW-based PUF	—	0.258	0.185	1.395	—
	30	0.163	0.286	0.570	59.1
	60	0.101	0.276	0.366	73.8
LS-based PUF	—	0.271	0.166	1.632	—
	30	0.100	0.270	0.370	77.3
	60	0.099	0.407	0.243	85.1

Reaction temperature, 195°C; ratio of DEG/PUF, 3; catalyst content, 2%.
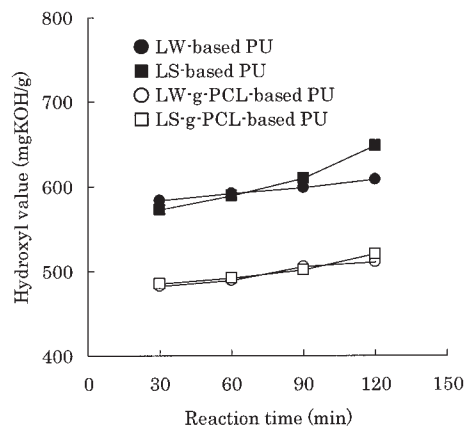
Figure 6 Effect of reaction time on the hydroxyl value of the recovered polyols. Ratio of DEG/PUF, 3; reaction temperature, 195°C; catalyst content, 2%.

Figure 8 Effect of the ratio of DEG/PUF on the hydroxy value of the polyols recovered from LW-based PUF. Reaction temperature, 195°C; time, 60 min; catalyst content, 2%.

85.1% at a reaction time of 60 min, respectively, which are considered high.

The change of hydroxyl values for the glycolysis products as a function of reaction time is shown in Figure 6. For the products from the liquefied biomass (LW or LS)-based PUF, the values were in the range of 550–650 mgKOH/g. On the other hand, the values for the glycolysis products from the liquefied biomass-g-PCL-based PUF were in the range of 450–550 mgKOH/g. This difference may be ascribed to the graft polymerization of PCL into the liquefied biomass, i.e., the hydroxyl values of the grafted polyols are lower than those of the liquefied biomass. Because glycolysis products were mainly composed of the raw polyols for PUF and oligomers with urethane groups, the hydroxyl value of glycolysis products would be largely affected by the hydroxyl value of raw polyol. It is natural that the hydroxyl value increases with the advance of glycolysis. In all samples, the hydroxyl values increased with the reaction time.
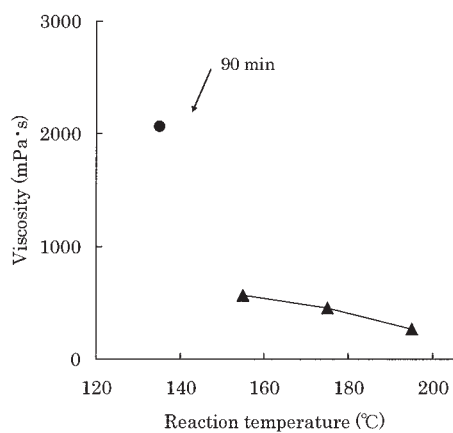
Figures 7 and 8 show the effect of reaction temperature and the ratio of DEG/PUF on the hydroxyl value of the polyol recovered from LW-based PUF, respectively. Similar to the relationship between the molecular weight and reaction time, there was no significant difference in hydroxyl values with increasing reaction temperature. On the other hand, a higher hydroxyl value was obtained at a higher ratio of DEG/PUF. As mentioned above, because DEG with a high hydroxyl value (1057 mgKOH/g) was not separated by the glycolysis, the content of DEG would be affected by the hydroxyl value of the glycolysis product.

Figure 9 shows the effect of reaction temperature on the viscosity of the polyol recovered from LW-based PUF. The viscosity of the polyol obtained at low temperature (135°C) was high, even if the reaction was prolonged to 90 min. At a temperature of greater than 155°C, the viscosity was less than 1000 mPa's, which was lower than the values for raw polyols shown in

Figure 7 Effect of reaction temperature on the hydroxy value of the polyols recovered from LW-based PUF. Ratio of DEG/PUF, 3; reaction time, 60 min; catalyst content, 2%.
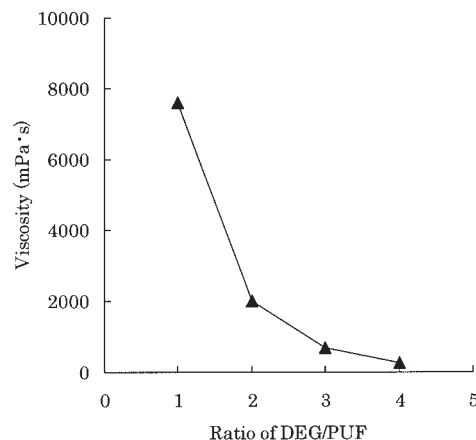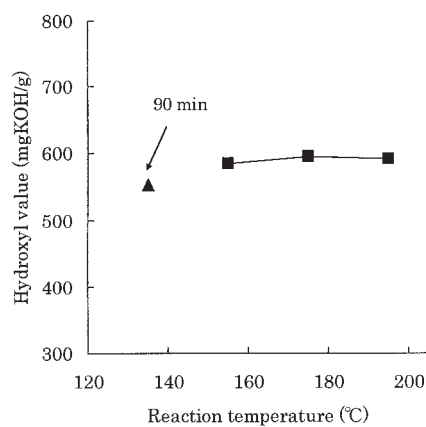

Figure 9 Effect of reaction temperature on the viscosity of the polyols recovered from LW-based PUF. Ratio of DEG/PUF, 3; reaction time, 60 min; catalyst content, 2%.
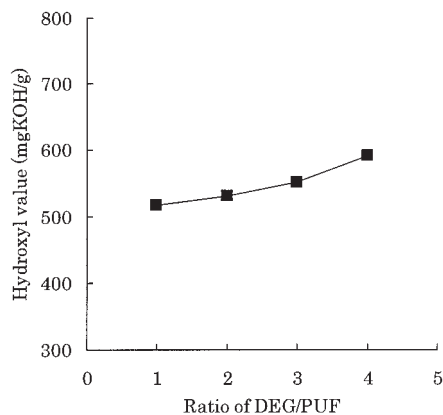
Figure 10 Effect of the ratio of DEG/PUF on the viscosity of the polyols recovered from LW-based PUF. Reaction temperature, 195°C; time, 60 min; catalyst content, 2%.

Table I. It can be stated from this result that the optimum temperature of glycolysis is greater than 155°C.

The effect of the ratio of DEG/PUF on viscosity is shown in Figure 10. Although the viscosity showed a high value (7600 mPa·s) at a ratio of DEG/PUF of 1, it decreased with increasing DEG content, showing values of less than 3. These low values of viscosity in the recovered polyol would be of merit when it was again used in the preparation of PUF.

The properties of polyols recovered in this study are summarized in Table III. The Mw, hydroxyl value, and viscosity of the polyols were in the range of 459–651, 512–649 mgKOH/g, and 202–603 mPa·s depending on the kind of raw PUF, respectively. These properties were suitable for the preparation of rigid PUFs. From the recovered polyols, rigid PUFs were prepared with the appropriate combinations of foaming agents. Table IV summarizes the properties of the PUFs obtained. The density of the foams showed values with a range of 48–54 g/cm³, which are slightly higher than those of raw PUF used in glycolysis. Compressive strength at 10% strain and elastic modulus were in the range of 204–283 kPa and 3.50–496 MPa, respectively. These values were also comparable to those of raw PUF used in glycolysis.

TABLE III
Properties of the Glycolysis Product

Kind of PUF	Molecular weight (Mw)	Hydroxyl value (mgKOHg^{-1})	Viscosity (mPa · s)
LW-based PUF	645	608	270
LS-based PUF	459	648	202
LW-g-PCL-based PUF	651	512	603
LS-g-PCL-based PUF	643	520	565

Reaction temperature, 195°C; time, 60 min; ratio of DEG/PUF, 3; catalyst content, 2%.

TABLE IV
Properties of the PUFs Prepared from the Glycolysis Product Polyols

Kind of glycolysis product	Properties of PUFs		
	Density ($\times 10^3$ g/cm^3)	Compressive strength at 10% strain (Kpa)	Elastic molulus (MPa)
Glycolysis product			
LW-based PUF	51	267	4.23
LS-based PUF	48	276	4.59
LW-g-PCL-based PUF	54	283	3.50
LS-g-PCL-based PUF	48	204	4.96

CONCLUSION

Glycolysis of biomass-based PUFs was conducted to provide an effective method for chemical recycling. Biomass-based PUFs were prepared from the liquefied wood or starch polyols and their grafted product with polycaprolactone. DEG as a solvent and potassium acetate as a catalyst were used. The Mw and viscosity decreased as the reaction time, temperature, and ratio of DEG/PUF increased, whereas the hydroxyl value increased. The conversion of the urethane functional group (–NCOO–) increased as glycolysis proceeded. Rigid PUFs were prepared from the recovered polyols and their properties were comparable to those of the raw PUF used in glycolysis.

In addition to the advantage of using a biomass component that can be degraded in the natural environment, it was found from these results that biomass-based PUF was chemically recyclable.

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