

Synthesis of Soy-Polyols Using a Continuous Microflow System and Preparation of Soy-based Polyurethane Rigid Foams

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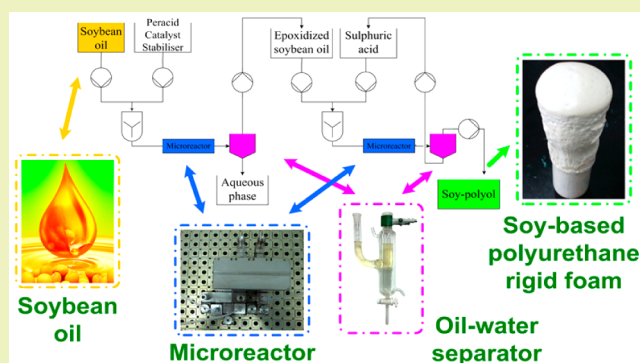
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ABSTRACT: A soy-polyol labeled Polyol-m was synthesized directly from soybean oil in a continuous microflow system equipped with self-designed oil–water separators and using a reported scheme for epoxidation under following the optimized conditions for hydroxylation: sulfuric acid concentration of 10 wt %, residence time of 13 min, and temperature of 75 °C. Another soy-polyol labeled Polyol-f was also synthesized in a conventional flask from commercially available epoxidized soybean oil as a raw material for the purpose of comparison. Polyol-f had a wider molecular weight distribution, higher viscosity, and lower hydroxyl number than Polyol-m because of the more substantial oligomers introduced by oligomerization, which was confirmed by Fourier transform infrared (FTIR) and gel permeation chromatography (GPC). In addition, the corresponding soy-based polyurethane rigid foams labeled PU-m and PU-f were prepared. PU-m had fine, uniform, and closed-cell morphology, and it contained higher cross-linking due to such characteristics as lower viscosity and higher hydroxyl number; these characteristics were beneficial for the foam properties, including compression strength, thermal insulation, dimensional stability, and thermostability.

KEYWORDS: Soy-polyol, Polyurethane foam, Epoxidation, Hydroxylation, Microflow system, Oil–water separator



INTRODUCTION

With the impending exhaustion of fossil fuel resources, the uses of renewable, biodegradable, agricultural resources have attracted considerable attention. Soybean oil is an inexpensive and abundant renewable resource containing multiple reactive sites providing an excellent matrix for polyols synthesis.^{1,2} Polyurethanes (PUs) are the most versatile polymer prepared from polyols and isocyanates including foams, elastomers, adhesives, surface coatings, artificial leathers, fibers, and so on. With increasing consideration of environmental impacts and sustainability, vegetable oil-based PUs are gaining popularity.^{3–5}

Currently, possible synthetic routes from vegetable oils to polyols are ozonolysis, hydroformylation, transesterification, and epoxidation with epoxy ring opening; the epoxidation–hydroxylation method is an effective way to introduce a vicinal secondary alcohol at the double bond location via in situ ring opening.^{5,6} There are several literature examples on the synthesis of soy-polyols using the method.^{2,7} However, the synthesis methods were carried out in conventional flasks, which can introduce problems such as long reaction time,

increased risks from peroxide, and other disadvantages caused by a heterogeneous reaction. Additionally, the unavoidable side reaction, oligomerization, consumed newly formed hydroxyl groups, which generated polyols with low hydroxyl numbers and high viscosities, characteristics that were not conducive to PU preparation.⁸

Microreaction technology, a technological innovation based on process intensification, is expected to make a revolutionary change in chemical synthesis. Microreactors are generally made of silicon, quartz, glass, metals, or polymers. Compared with conventional batch reactors, microreactors exhibit many advantages including lower operating cost, easier modulation, easier scale-up for industrial production, and better safety. Due to the high surface-to-volume ratio, microreactors also demonstrate efficient mass and heat transfer, which are well suited for highly exothermic reactions. Furthermore, the

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relatively precise control of reactive intermediates favors the application of microreactors in highly selective reactions.^{9–12}

In consideration of the deficiencies of previously published research,^{2,7} microreactors would be promising instruments for soy-polyol synthesis. In the early stages, we carried out fundamental research on the epoxidation of soybean oil using a continuous microflow system, and a high-quality epoxidized soybean oil (ESO) with an epoxy content of 7.3% (close to the theoretical value of 7.58%) was obtained.⁹ Although it is not uncommon to synthesize polymers in microreactors,¹³ the application for polyol synthesis for PUs has rarely been reported.

In this study, soy-polyols were synthesized by concatenating epoxidation and hydroxylation in a microflow system. A type of self-designed oil–water separator was employed to make the procedure continuous and convenient. Three parameters including catalyst concentration, residence time, and temperature were experimentally discussed. By optimizing the process, a high quality soy-polyol was prepared directly from soybean oil. In addition, another soy-polyol was synthesized in a conventional flask using commercially available ESO as the raw material for the purpose of comparison. By replacing a desired amount of the conventional petrochemical polyether polyol with each synthesized polyol, two PU rigid foams were obtained using isocyanate, surfactants, and the blowing agent cyclopentane. Several experimental techniques were applied to characterize the samples: mainly, Fourier transform infrared (FTIR), gel permeation chromatography (GPC), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA).

MATERIALS AND METHODS

Materials. Formic acid (98%), hydrogen peroxide (30%), sulfuric acid (98%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were reagent grade or better. FULINMEN soybean oil with an iodine value of 130 mg I₂/100 g was supplied by COFCO (Beijing, China). ESO with an epoxy content of 6.2% was purchased from Aladdin Industrial Corp. (Shanghai, China). H4110III, H6305SA, and H403 are petrochemical polyols with hydroxyl numbers of 430, 460, and 740 mg KOH/g, respectively, and were supplied by Nanjing Hongbaoli Co., Ltd. (Nanjing, China). WANNATE PM-200, a polymeric diphenylmethane diisocyanate (MDI) with 30.5 wt % NCO, was obtained from Wanhua Chemical Group Co., Ltd. (Yantai, China). AK-8803, a foam stabilizer, was obtained from Jiangsu Maysta Chemical Co., Ltd. (Nanjing, China). The catalysts Polycat 8 and Polycat 41 were obtained from Air Products and Chemicals, Inc. The blowing agent cyclopentane was obtained from MEILONG Cyclopentane Chemical Co., Ltd. (Foshan, China).

Microflow System. The microflow system was supplied by Ehrfeld Mikrotechnik BTS and consisted mainly of sandwich microreactors, LH25 slit-plate type mixers, and plunger pumps. A Petite Fleur dynamic temperature control system (Huber Kältemaschinenbau GmbH, Germany) was employed to regulate the reaction temperature. For process convenience and continuity, a simple and practical oil–water separator was designed and produced, as shown in Figure 1. The bottleneck at a is an inlet for oil–water mixture; the bottleneck at b is an outlet for the oil phase; the aqueous phase flows away from the outlet at c; the prominences at e and d are the inlet and outlet for reflux condensing water, respectively; f refers to an inner tank for holding the oil–water mixture, and where the mixture stratifies; the polytetrafluoroethylene tube for the oil–water mixture infusion should be extended to the position at g.

The process included two parts: the epoxidation of soybean oil and the subsequent hydroxylation, which was illustrated in Scheme 1. The epoxidation has been reported previously,⁹ and the scheme for

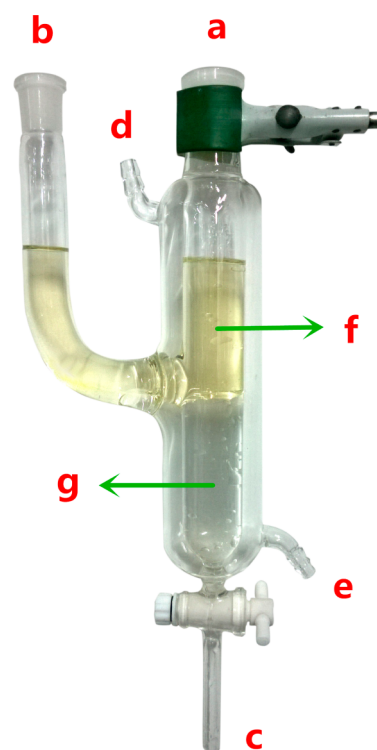


Figure 1. Self-designed oil–water separator.

synthesizing ESO with an epoxy content of 7.2% was adopted in this study. The molar ratio of hydrogen peroxide to formic acid was 1:1, and the sulfuric acid (catalyst) and EDTA-2Na (stabilizer) account for 5 and 3 wt % of the soybean oil mass, respectively. The rate of flow of soybean oil was 0.8 mL/min, whereas the other mixture including hydrogen peroxide, formic acid, catalyst, and stabilizer, flowed at a rate of 4.7 mL/min. The two flows were pumped through the micromixer into the microreactor and held for a residence time of 6.7 min at 75 °C. Next, the resultant was transferred into the oil–water separator. Following the stratification process, the oil phase (ESO) was pumped into a beaker while the aqueous phase was drained off.

Because the oil volume remained largely unchanged after epoxidation, the rate of flow of ESO was also set as 0.8 mL/min to maintain equilibrium. The hydroxylation procedure was nearly the same as the epoxidation procedure, and the sulfuric acid solution used as a ring-opener and catalyst was recyclable because the concentration was almost stable during the reaction. The generated crude soy-polyol was diluted using a certain amount of ethyl acetate and then washed with a 5% sodium carbonate solution and distilled water until the pH of the aqueous phase reached approximately 7.0. Next, the sample was dried by anhydrous sodium sulfate and purified from the residual organic phase on a rotary evaporator to obtain the refined soy-polyol.

Preparation of Soy-Polyol in a Conventional Flask. The soy-polyol in conventional flasks was prepared via the method as reported in the literature.⁶ A 150 g sample of commercially available ESO, 900 mL of THF, and 450 mL of a 6% sulfuric acid solution were added to a 2 L three-neck flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The flask was placed in a 65 °C oil bath and allowed to react for 8 h. After cooling to room temperature, the aqueous phase was removed using a separatory funnel. The post-treatment process of the residual mixture was the same as previously mentioned, and a soy-polyol labeled Polyol-f was obtained.

Foam Formulation. The PU rigid foams were prepared using a free-rise method according to the formulation in Table 1, and an isocyanate index of 110 was adopted. Soy-polyol was mixed with the other ingredients, namely petrochemical polyols, surfactant, catalysts, blowing agent, and water, in the required proportions under ambient conditions for approximately 120 s; then, polymeric MDI was added and mixed with a high-speed stirrer for another 8 s. Next, the mixture

Scheme 1. Reaction Scheme of Test Rig for Soy-Polyol Synthesis

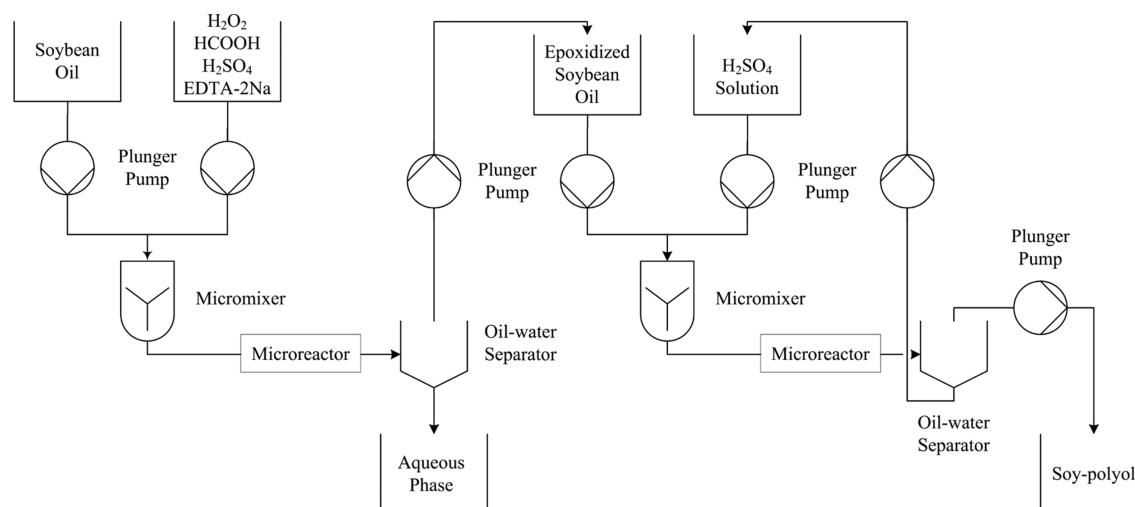


Table 1. Rigid Foam Formulation

ingredients	soy-polyol	H4110III	H6305SA	H403	AK-8803	Polycat 8	Polycat 41	KAc solution (30 wt %)	water	cyclopentane
formulation (parts by weight)	50	21	24	5	2.0	2.6	1.0	0.1	1.2	13

was poured into an open mould, was allowed to expand freely and was cured at room temperature (25 °C) for 7 days. Samples were cut into specific shapes as per the test requirements. The foams were named PU-m and PU-f according to the type of soy-polyol that was involved in the foaming.

Determination of Acid and Hydroxyl Numbers, Epoxy Content, and Viscosities of Soy-Polyols. The acid numbers of soy-polyols were determined in accordance with ASTM D4662-08. The epoxy content was analyzed by an official method, AOCs Cd 9-57 (2009), Oxirane Oxygen in Epoxidised Materials. The viscosities of the soy-polyols were measured at 25 °C using an SNB-1 digital viscometer (Techcomp Jingke Scientific Instruments Co. Ltd., China) according to ASTM D4878-08.

The determination of hydroxyl numbers of polyols is usually measured using ASTM D4274-05, Test Method C (phthalic anhydride reflux), with acidity correction. However, epoxy groups are capable of reacting with some acylation reagents, which affects the hydroxyl number determination of epoxy-containing polyols. Therefore, in this study, acetyl chloride was chosen as the acylation reagent to open efficiently the epoxy rings; a relatively accurate hydroxyl number was obtained with a correction according to a previously reported equation.¹⁴

118 mL of acetyl chloride and an appropriate quantity of toluene were added to a 1 L volumetric flask, mixed well, and used as the acylation reagent. A magnetic stirring bar, 5 g of sample, and 10.0 mL of dioxane were added to a 250 mL conical flask with a ground glass stopper, and the flask was shaken until the sample completely dissolved. Next, the conical flask was placed in an ice–water bath; after cooling to 0 °C, 5.0 mL of the acylation reagent and 2.0 mL pyridine were added to the conical flask, which was subsequently plugged with a straight drying tube containing anhydrous calcium chloride. Then, the conical flask was placed in a 40 °C water bath and stirred for the reaction to take place. After 1 h, the conical flask was removed and placed in the previous ice–water bath with stirring, and 25.0 mL of cold distilled water was added to decompose the surplus acetyl chloride. After 30 min, 25.0 mL of dichloromethane and a few drops of cresol red were added, and the mixture was titrated using a 0.5 M alcoholic sodium hydroxide solution. A blank test was also carried out. The hydroxyl number was calculated by the following equation:

$$\text{OHV} = [56.1 \times c \times (V_0 - V_s)/m] - 2 \times 56.1 \times \text{EC} \times 100/16 + \text{AN}$$

where OHV is the hydroxyl number of the sample (mg KOH/g), c is the concentration of the alcoholic sodium hydroxide solution (mol/L), V_0 is the volume of the standard solution consumed in the blank test (mL), V_s is the volume of the standard solution consumed in the sample test (mL), m is the sample mass (g), EC is the epoxy content of the sample (%), and AN is the acid number of the sample (mg KOH/g).

Characterization of Soy-Polyols. Fourier transform infrared (FTIR) spectra were collected on a TENSOR 27 FTIR spectrometer (Bruker Corp., Germany) equipped with a MIRacle single reflection ATR accessory (PIKE Technologies, US). The test range was 4000–600 cm^{-1} , the resolution was 4 cm^{-1} , and the number of scans was 32.

Gel permeation chromatography was performed in THF at 40 °C on a Viscotek 270max system (Malvern Instruments Ltd., UK) using a VE 1122 solvent pump equipped with a ShodexTM GPC KF-802 column (8.0 × 300 mm) at a flow rate of 1.0 mL/min. A 270 dual detector in conjunction with a VE 3580 RI detector provided two detection means including right angle light scattering and refractive index. A VE 7510 GPC degasser and a GPC heated column oven were also used. The calibration curves for the GPC analysis were obtained from polystyrene standards.

Characterization of Soy-based PU Rigid Foams. The foam morphologies were examined using an S-3400N scanning electron microscope (Hitachi High Technologies Inc., Japan) at an acceleration voltage of 20 kV. The apparent foam densities were measured according to ASTM D1622-08. The compression strength was tested with a CMT4204 wicket computer-controlled electronic universal testing machine (MTS Systems Co. Ltd., China) according to ASTM D1621-10. The measurement of thermal conductivity was conducted using an HFM 436 Lambda heat flow meter (Netzsch, Germany), and test specimens with dimensions of 300 × 300 mm × 25 mm were needed; the two opposing surface temperatures were set as 13 and 23 °C. The dimensional stability was measured according to ISO 2796:1986.

Thermogravimetric analysis (TGA) of the PU rigid foams was carried out at a heating rate of 10 °C/min from 25 to 800 °C under nitrogen atmosphere using a Pyris 1 thermogravimetric analyzer (PerkinElmer Inc., US). The dynamic properties of the PU rigid foams were evaluated by a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA). A disk (15 mm diameter × 10 mm thickness) was cut from the foam and tested in compression mode. The storage modulus (G') and loss modulus (G'') were recorded at 1 Hz and 0.1%

strain over a temperature range of 25 to 220 °C and at a temperature ramp rate of 3 °C/min.

RESULTS AND DISCUSSION

The theoretical hydroxyl number was calculated based on the assumption that all the epoxy groups were converted to two –OH groups each, according to the following equation:

$$\text{theor OHV} = 56.1 \times f \times 1000/M$$

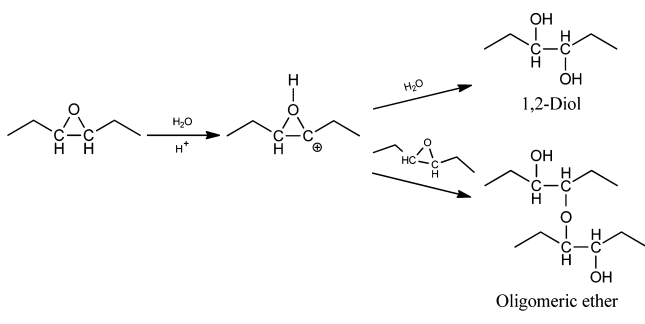
where M is the relative molecular weight of the polyol, and f is the functionality of the polyol, which is calculated by

$$f = (\text{EC} \times 100 \times 2/16)/(100/M')$$

where M' is the relative molecular weight of ESO, and EC is the epoxy content of ESO, e.g., 7.2%. Because the relative molecular weight changes insignificantly during the hydroxylation process in an ideal situation, M and M' were eliminated, and theor OHV was calculated as 504.9 mg KOH/g.

Under the conditions of hydroxylation, two significant competing reactions take place, and oligomerization is unavoidable,¹⁵ as shown in Scheme 2. Therefore, there was a

Scheme 2. Ring-Opening Pathways of ESO



difference between the theoretical and experimental hydroxyl numbers. For better analysis of the factors affecting the hydroxylation, the conversion ratio (ratio of “experimental hydroxyl number” to “theoretical hydroxyl number”) was defined and is represented in Figures 2–4.

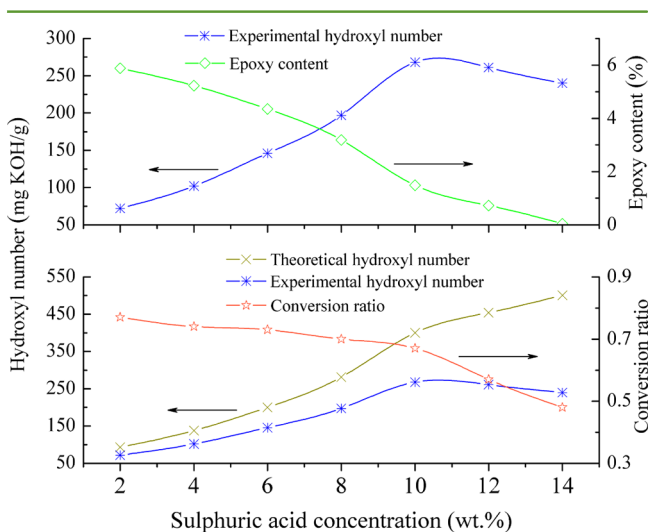


Figure 2. Effect of sulfuric acid concentration on the hydroxyl number of polyols.

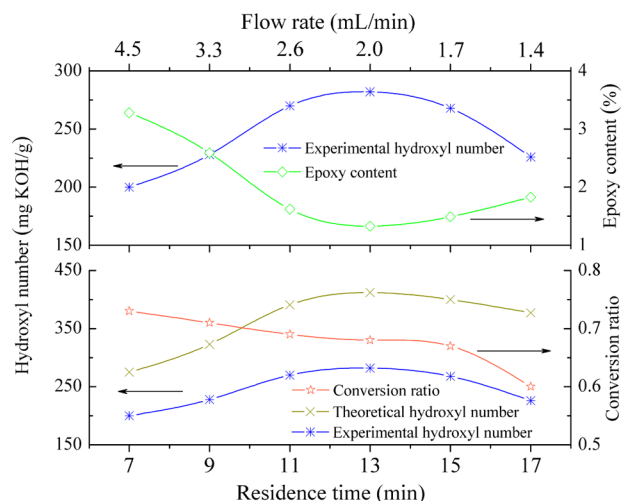


Figure 3. Effect of residence time on the hydroxyl number of polyols.

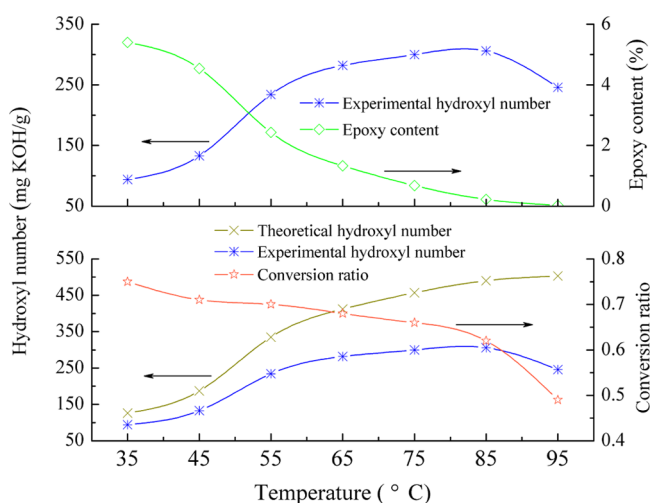


Figure 4. Effect of temperature on the hydroxyl number of polyols.

The optimization of the hydroxylation in the microflow system was performed by investigating the effect of the catalyst concentration, residence time, and temperature on the reaction.

Effect of Catalyst Concentration on the Hydroxyl Number of Polyols. The most common catalysts applied for in situ epoxide ring-opening usually includes sulfuric acid, phosphoric acid,¹⁵ and fluoroboric acid.¹⁶ In this study, sulfuric acid was chosen for cost and safety reasons. The reaction conditions in the flask were as follows: the temperature was set as 65 °C, the residence time was initially set as 15 min, and the flow rate of ESO was consistently set as 0.8 mL/min to maintain equilibrium. Because the volume of the microreactor was 37 mL, the flow rate of the sulfuric acid solution was approximately 1.7 mL/min.

As shown in Figure 2, the epoxy content decreased with increasing sulfuric acid concentration, while the experimental hydroxyl number peaked at a concentration of 10 wt %. Understandably, higher concentrations of sulfuric acid gave rise to progressively shorter reaction times for the completion of the ring opening reaction.¹⁵ Meanwhile, the oligomerization reaction was enhanced by a higher acid concentration because the reaction rate for the formation of oligomeric ether in concentrated acid is first-order.¹⁷ Further, the decreasing trend

of the conversion ratio also indicates the above-mentioned mechanisms.

Effect of Residence Time on the Hydroxyl Number of Polyols. The temperature of 65 °C was maintained and an acid concentration of 10 wt % was employed. By adjusting the residence time, the flow rate of the acid solution changed from 1.4 to 4.5 mL/min. As shown in Figure 3, the epoxy content decreased first and then increased with increasing residence time, which was the opposite trend observed for the experimental hydroxyl number. Understandably, the decrease of epoxy content during shorter residence time was due to an incomplete reaction. In this study, the solvent-free hydroxylation process was a heterogeneous reaction, which strongly depended on the efficient mass transfer of microreactors. A longer residence time corresponds to a smaller flow rate for fixed-length microreactors, weakening the mass transfer, and thus the epoxy content subsequently increased.⁹ In addition, the slowly decreasing trend of the conversion ratio indicated that longer residence times caused oligomerization, although the corresponding lower flow rate of the sulfuric acid solution means a lower acid concentration in the whole system.

Effect of Temperature on the Hydroxyl Number of Polyols. Combined with the optimization results above (an acid concentration of 10 wt % and a residence time of 13 min), the reaction temperature was altered from 35 to 95 °C. As shown in Figure 4, the effects of temperature on the epoxy content, experimental hydroxyl number, and conversion ratio were similar to the effects of acid concentration. As expected, higher temperatures lowered the oil viscosity, improving the compatibility of the mixture. Although the epoxy ring-opening reaction is an exothermic reaction, both the ring-opening reaction and oligomerization were enhanced. The polyol formed at 85 °C possessed a hydroxyl number of 306 mg KOH/g, an epoxy content of 0.22%, and a viscosity of 9800 mPa·s, whereas the polyol formed at 75 °C possessed a slightly lower hydroxyl number (300 mg KOH/g), a higher epoxy content (0.68%), but a significantly lower viscosity (7550 mPa·s). The parameters at 75 °C were chosen for lower energy consumption and viscosity, and because a smaller number of epoxy groups in the polyol were beneficial for the performance of the corresponding PU rigid foam.¹⁸ The soy-polyol synthesized using the optimal parameters was labeled Polyol-m.

Properties of Soy-Polyols. The FTIR spectra of the soy-polyols are shown in Figure 5. For both Polyol-f and Polyol-m, the peaks at 2927 (2856) and 1461 (725) cm^{-1} were assigned to $-\text{CH}_2$ asymmetric (symmetric) stretching vibrations and in-plane (out-of-plane) bending vibrations, respectively. The bands at 1738 and 1240 cm^{-1} corresponded, respectively, to the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibrations of the aliphatic ester groups, while the peak appearing at 1094 cm^{-1} was assigned to the secondary hydroxyl group. For Polyol-m, the increase in the intensity of the hydroxyl peak at 3400 cm^{-1} indicates that Polyol-m had a higher hydroxyl number, which agrees with the results (Table 2). Similarly, the increase in the intensity of the ether peak at 1167 cm^{-1} for Polyol-f indicates that more substantial oligomerization occurred in the conventional flasks. In addition, the Polyol-m peaks at 843 and 823 cm^{-1} were attributed to the epoxy group, which disappeared after the epoxy group completed the opening reaction, as also noted for the Polyol-f.

Figure 6 shows the GPC chromatograms of the soy-polyols. Combined with Table 2, the chromatograms indicate that side reactions, mainly oligomerization, occurred, causing the polyols

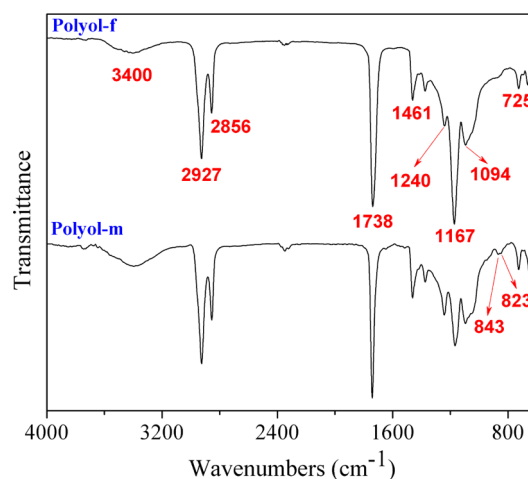


Figure 5. FTIR spectra of soy-polyols.

to have complex structures and a wide molecular weight distribution. For Polyol-f, the weak peak before the dominant peak was due to oligomerization, which was more prominent in Polyol-f than in Polyol-m. The chromatogram of Polyol-m exhibited less fluctuation compared with Polyol-f, proving a lower polydispersity index.

As expected, Polyol-f had a larger molecular weight and higher viscosity than Polyol-m because of the more substantial oligomers introduced by oligomerization. As shown in Table 2, the near-zero epoxy content and lower hydroxyl number of Polyol-f also indicate that oligomerization easily occurred during the hydroxylation process in the conventional flasks.

Performances of Soy-based PU Rigid Foams. SEM images of the cross section of soy-based PU rigid foams, shown in Figure 7, illustrate closed-cell structures regardless of the polyol type. As observed from the micrograph of PU-m, the cell size was elliptical but uniform, and the foam consisted of closed cells with negligible broken-walled cells. The cell structures of PU-f were not uniform, and the number of broken cells increased. The polyol viscosity is critical to the formation of the foam cellular structure. Higher viscosity could cause problems when mixing the foam ingredients and affect the generation and distribution of the cells formed by the blowing agent.^{19,20} The alteration in the cell morphology caused by nonuniform cell structures and increased broken cells could result from the higher viscosity affecting the process of cell nucleation.

The foam properties are summarized in Table 3. Both the density and compression strength of PU-m were higher than that of PU-f. For PU rigid foams, the variability of the compression strength depends on the foam morphology and foam density.^{7,21} Foam compression strength usually increases linearly with foam density in many cellular foam systems.²² The specific compression strength (the ratio of “compression strength” to “density”) was defined for better analysis of the factors affecting the foam compression strength. Compared with PU-f, PU-m still had a higher specific compression strength, which was attributed to the uniform cell structure and higher hydroxyl number of Polyol-m and created a higher degree of cross-linking. In addition, a hydrogen-bonded urethane group was formed when fewer epoxy groups were introduced into the foam, making the foam firmer and stiffer.¹⁸

Thermal conductivity (k value) is an important property for PU rigid foams. A low k value results from a low foam density, a small average cell size, and a high closed-cell content.²³ As

Table 2. General Properties of Polyols

polyol	hydroxyl number (mg KOH/g)	acid number (mg KOH/g)	epoxy content (%)	M_n (Da)	polydispersity index	viscosity (mPa·s)
Polyol-f	232	1.1	<0.1	4980	2.122	12500
Polyol-m	300	1.5	0.68	3013	1.445	7550

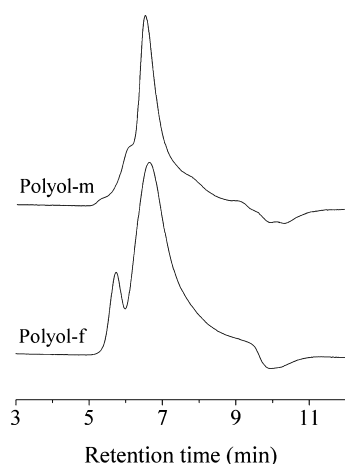


Figure 6. GPC chromatograms of soy-polyols.

shown in Table 3, PU-m had a lower k value due mainly to its fine, uniform, and closed-cell morphology despite having a greater foam density.

Dimensional stability is another important characteristic of PU rigid foams. Standard specifications for dimensional stability have been reported to be less than 3% of the linear change at 70 °C for 24 h.²¹ As shown in Table 4, the dimensional changes of PU-f and PU-m were considered to be mild and acceptable for manufacturing purposes. PU-f exhibited more notable shrinkage

than PU-m; this is likely due to the nonuniform cell structure with many broken walls caused by higher viscosity and less cross-linking as a result of the lower hydroxyl number of Polyol-f.

TGA weight loss curves for soy-based PU rigid foams are shown in Figure 8, and the corresponding data are summarized in Table 4. The decomposition of the PUs occurred in three stages: (1) dissociation of the unstable urethane bond at a temperature between 150 and 330 °C, (2) decomposition of the soft polyol segments at a temperature between 330 and 400 °C, and (3) further degradation of the fragments produced after the second stage.²⁴ Both foams exhibited slight weight losses below 150 °C, due mainly to the volatilisation of additives and water. In other temperature ranges, PU-m exhibited better thermal stability attributed to the greater cross-linking.

Storage modulus, loss modulus, and $\tan \delta$ can be measured directly through dynamic mechanical analysis, and the glass-transition temperature (T_g) can be extrapolated from the data. As shown in Figure 9, T_g was determined by the peak maximum of $\tan \delta$ (see Table 4). PU-m exhibited a higher T_g , which was also attributed to greater cross-linking.

CONCLUSIONS

A soy-polyol labeled Polyol-m was synthesized in a continuous microflow system using a reported scheme for epoxidation and under the following optimized conditions for hydroxylation: sulfuric acid concentration of 10 wt %, residence time of 13

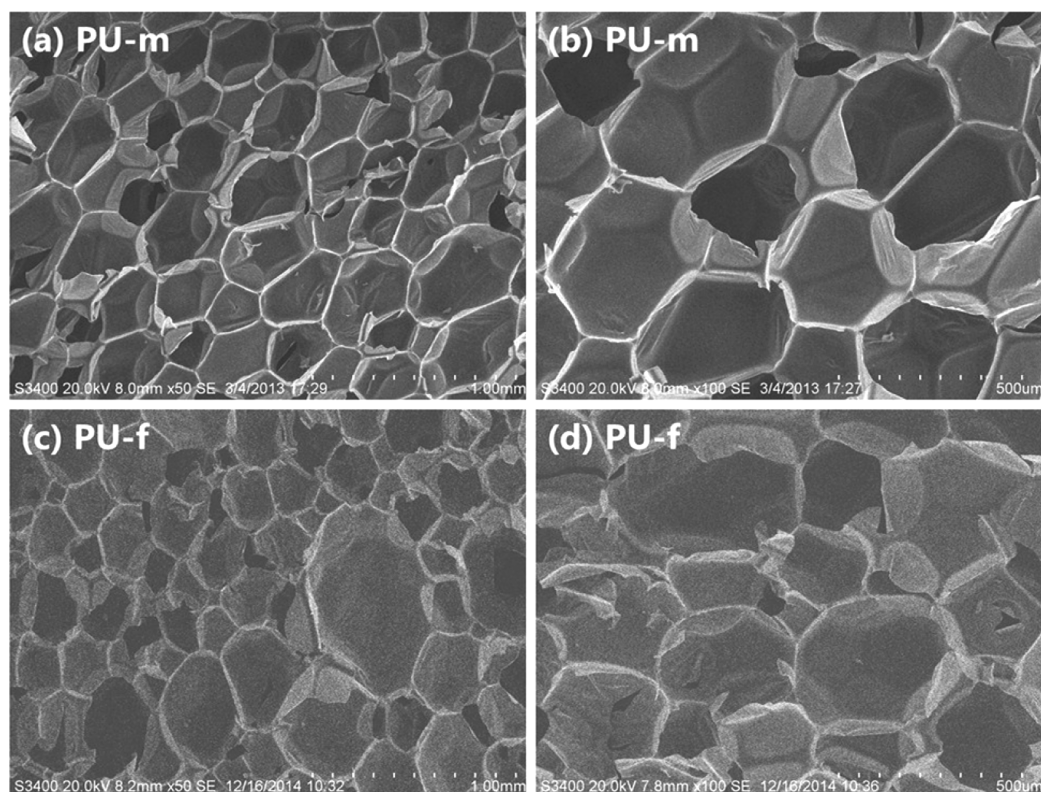


Figure 7. SEM images of soy-based foams.

Table 3. Foam Primary Properties

foam	density (kg/m ³)	compression strength (kPa)	specific compression strength (kPa·m ³ /kg)	k value (mW/(m·K))
PU-f	33.8 (1.3) ^a	156 (2.2)	4.62	22.8 (1.4)
PU-m	36.2 (0.8)	187 (1.6)	5.17	20.1 (0.6)

^aStandard derivation.

Table 4. Dimensional Stability and Thermal Properties

foam	dimensional stability (%)			thermal character				
	length	width	thickness	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)	800 °C (residual/%)	T _g (°C)
PU-f	0.63	0.56	-0.78	247.1	284.7	361.2	8.3	138.5
PU-m	0.39	0.34	-0.55	249.4	291.4	374.5	16.5	155.3

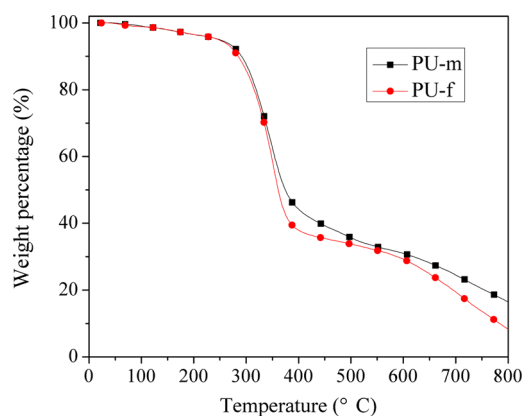
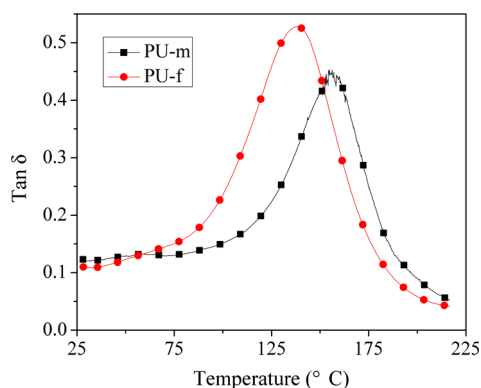


Figure 8. TGA weight loss curves for soy-based foams.

Figure 9. Tan δ vs temperature of soy-based foams.

min, and temperature of 75 °C. Another soy-polyol labeled Polyol-f was also synthesized in a conventional flask from commercially available ESO. Polyol-f had a wider molecular weight distribution, higher viscosity, and lower hydroxyl number than Polyol-m because of more abundant oligomers introduced by oligomerization, as confirmed by FTIR and GPC. Furthermore, one of the corresponding soy-based PU rigid foams, PU-m, had a higher compression strength that can be attributed to the uniform cell structure and higher hydroxyl number of Polyol-m. PU-m exhibited a lower *k* value mainly due to its fine, uniform, and closed-cell morphology. PU-m still exhibited excellent dimensional stability, good thermal stability, and higher *T_g*, which were also attributed to the more abundant cross-linking. The results show that the microflow system has many advantages for the preparation of high quality polyols.

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Notes

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