Liquefaction of Corn Bran (CB) in the Presence of Alcohols and Preparation of Polyurethane Foam From Its Liquefied Polyol

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ABSTRACT: Liquefied corn bran (CB)-based polyol was obtained by the liquefaction of CB in the presence of a poly(ethylene glycol) (PEG400)/glycerol mixed solvent. The effects of liquefaction parameters on the degree of liquefaction were evaluated. The catalyst content and solvent/CB ratio have a greater influence on the percent residue than does the reaction temperature. Polyurethane foams were successfully prepared from the liquefied CB-based polyol. Molecular weights of CB-based polyol have no effect on the reaction time, and its hydroxyl numbers and viscosities were suitable for the preparation of foam. Furthermore, the acid value increased to about 34 during the liquefaction. The densities and mechanical properties of the foams showed comparable values to those of conventional polyurethane foams. The amount of additive (PCL303) in the liquefied CB-based polyol had a significant effect on the properties of the resulting foams. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 319–325, 2000

Key words: liquefaction; corn bran; polyol; poly(ethylene glycol); glycerol; polyurethane foam

INTRODUCTION

Polyurethane foams are generally prepared by the reaction of isocyanates and polyols obtained mainly from fossil resources. Also, they have wide application (structural, electrical, packaging materials, and so on) due to their ease of processing and excellent properties.[1,2] However, with increasing concern about environmental problems and shortage of fossil resources, there has been interest in replacing petroleum-based products with renewable and biodegradable materials.[3–5]

A series of experiments on the liquefaction of biomass to prepare polyols were conducted and applied to polyurethane foams.[6,7] It was found that the biomass-based polyols have suitable characteristics (hydroxyl numbers, viscosities, and so on) for making polyurethane foams with comparable properties to conventional polyurethane foams.[8,9]

In this study, effort was focused on the preparation of polyols from corn bran (CB), which is one of the food-industry wastes, using the alcohol liquefaction technique. The influence of various reaction conditions on the liquefaction of CB was investigated. The characteristics of liquefied product-based polyol and the properties of the resulting polyurethane foams were also evaluated.

EXPERIMENTAL

Materials

CB was supplied by the Sanwa Starch Ltd. Co. (Nara, Japan). It was dried in an oven at 105°C

for 24 h and kept in a desiccator at room temperature before use.

The poly(ethylene glycol) (PEG400) and glycerol used as the liquefaction solvents were purchased from commercial sources and used without further purification. Diphenylmethane diisocyanate (MDI; Japan Polyurethane Ind. Ltd., Tokyo, Japan), dibutyltin dilaurate (DBTDL; Katsuta Ind. Ltd., Tsukuba, Japan), silicone surfactant (SH193; Toray Dow Corning Silicone Ltd., Tokyo, Japan), and polycaprolactone (PCL303; Daicel Chem. Ind. Ltd., Sakai, Japan) were used for preparing polyurethane foams as received. All other chemicals were of reagent grade.

Liquefaction Procedure and Evaluation of Liquefaction Extent

Liquefaction was carried out by using a mixed solvent of PEG400 and glycerol (4/1 w/w %) as the liquefaction reagent and sulfuric acid as the catalyst. The amount of acid catalyst used was based on the weight percent of the solvent. The liquefaction was conducted under constant stirring and reflux in an oil bath. When the reaction time reached a predetermined value, the resulting reaction mixture was collected in a beaker using a mixture of dioxane/water (4/1 v/v %). The dilute solution was filtered through Toyo GA100 glass filter paper under a vacuum. The residue was dried to a constant weight in an oven at 105°C, and the percent residue was calculated by the following equation:

Residue (%)

= weight of residue/weight of starting CB × 100

Unreacted glycerol was calculated from the molecular weight distribution curves as the area ratio of the standard glycerol peak and the unreacted glycerol peak of the liquefied product.

Characterization of the Liquefied Product

The molecular weight and the molecular weight distribution of the liquefied products were determined using a gel permeation chromatograph equipped with a differential refractometer R401 detector. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min under 7.0 MPa pressure. The concentration of the samples was 0.5 wt % in the THF solution, and the amount injected was 150 μL. The molecular weights of the samples were calibrated by use of monodisperse polystyrene standards.

The viscosities of the liquefied products were measured using a Brookfield viscometer (TOKMEC INC.) at 25°C and 60% RH. The amount of acid produced during liquefaction was measured by titration and expressed as the number of milligrams of potassium hydroxide required to neutralize the acid in 1 g of the sample. The hydroxyl number of the liquefied products is defined as the number of milligrams of potassium hydroxide equivalent to the phthalic anhydride consumed in the phthalification of 1 g of the sample and was determined according to the JIS standard (JIS K1557).

## Polyurethane Foam Preparation

The liquefied CB-based polyol was used directly to prepare polyurethane foams by reaction with diphenylmethane diisocyanate. Thus, the predetermined amounts of the liquefied CB-based polyol, catalyst, surfactant, water, and additive (PCL303) were mixed thoroughly in a paper cup before the prescribed amount of isocyanate was added, followed by mixing at a stirring speed of 8000 rpm for 10–15 s. The resulting mixture was poured immediately into a 12 × 12 × 10-cm box and was allowed to rise at room temperature. The rise time of the foam usually was about 1–2 min, and the foam obtained was allowed to cure at room temperature for 1 h before being removed from the box. The isocyanate index was calculated as follows:

$$\text{Isocyanate index} = M_{\text{MDI}} \times W_{\text{MDI}}/M_{\text{LC}} \times W_{\text{LC}}$$

$$\times M_{\text{add}} \times W_{\text{add}} + W_{\text{w}} \times 100$$

where M_{MDI} is the number of moles of isocyanate groups per gram of MDI; W_{MDI}, the weight of MDI (grams); M_{LC}, the number of moles of hydroxyl groups per gram of liquefied CB based-polyol; W_{LC}, the weight of liquefied CB based-polyol (grams); M_{add}, the number of moles of hydroxyl groups per gram of the additives; and W_{add} and W_{w}, the weight of the additives and water in the foam formulation (grams), respectively. The hydroxyl groups in the surfactants and catalysts were not taken into account.

Mechanical Properties

Measurements of the mechanical properties of the foams are based on the JIS standard (JIS K7220). The foams were cut into 50 × 50 × 50-mm specimens. The specimens were conditioned for 48 h at 20°C and 60% RH before the density was de-
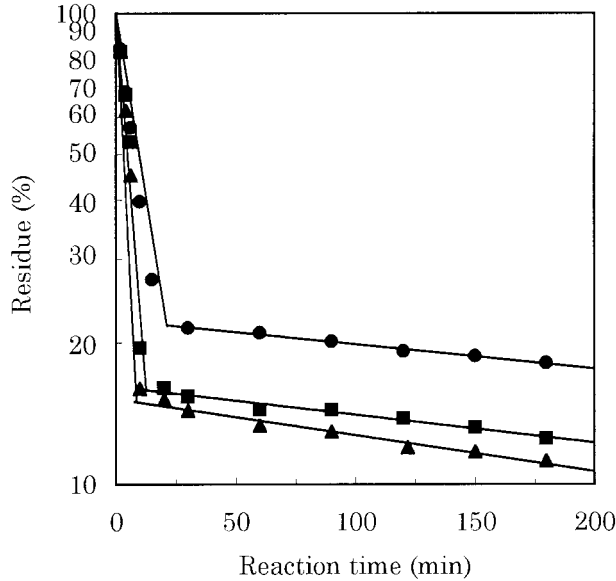
Figure 1 Effect of temperature on the liquefaction of CB. Solvent mixture/CB ratio 3; catalyst content 3%; liquefaction temperature: (●) 130°C; (■) 150°C; (▲) 170°C.
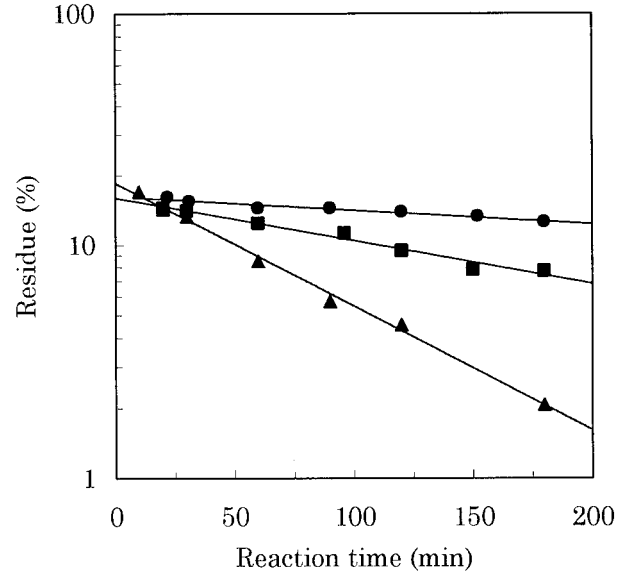

Figure 2 Effect of catalyst content on the liquefaction of CB. Solvent mixture/CB ratio 3; reaction temperature 150°C; catalyst content: (●) 3%; (■) 4%; (▲) 6%.

termined using the dimensions and using the weight of the specimens. The strength measurements were conducted by a Shimadzu Autograph AGS-5kNG in the direction perpendicular to the foam rise at a constant crosshead speed of 5 mm/min. The compressive strength of the foams was determined as the stresses at 10 and 25% strain.

RESULTS AND DISCUSSION
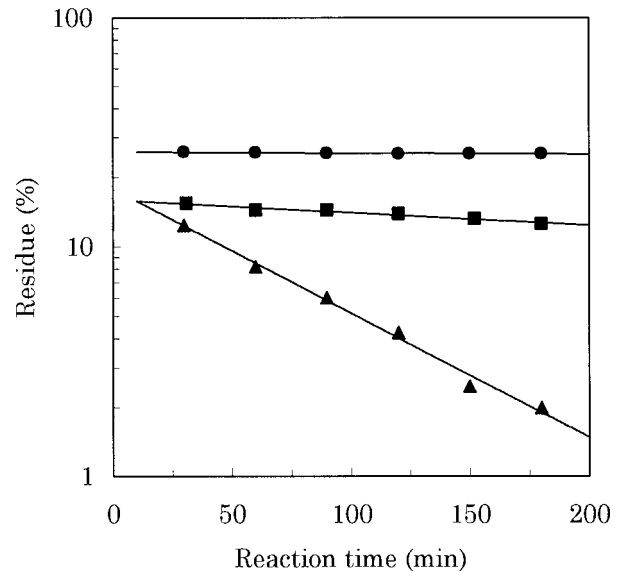
Figure 1 shows the time dependencies of the per-

cent residue obtained at different temperatures in the liquefaction of CB. As shown in Figure 1, the liquefaction of CB progressed very fast in the initial stage (within 30 min) in which the percent residue declined to about 15–22%. Thereafter, the percent residue decreased at a much slower rate. The relationship of the residue to the reaction

Table I Effect of Reaction Conditions on the Rate Constant of Liquefaction and Minimal Residue

Reaction Condition		Rate Constant ($\times 10^{-3}$/min)	Minimal Residue (%)
Temperature	130	1.2	18.1
(°C)	150	1.4	12.5
	170	1.8	11.2
Catalyst content	3	1.4	12.5
(%)	4	4.3	7.7
	6	12.2	2.1
Solvent/CB ratio	2	0.1	25.4
(w/w)	3	1.4	12.5
	5	12.4	2.0

Figure 3 Effect of solvent mixture/CB ratio on the liquefaction of CB. Catalyst content 3%; reaction temperature 150°C; solvent/CB ratio: (●) 2; (■) 3; (▲) 5.
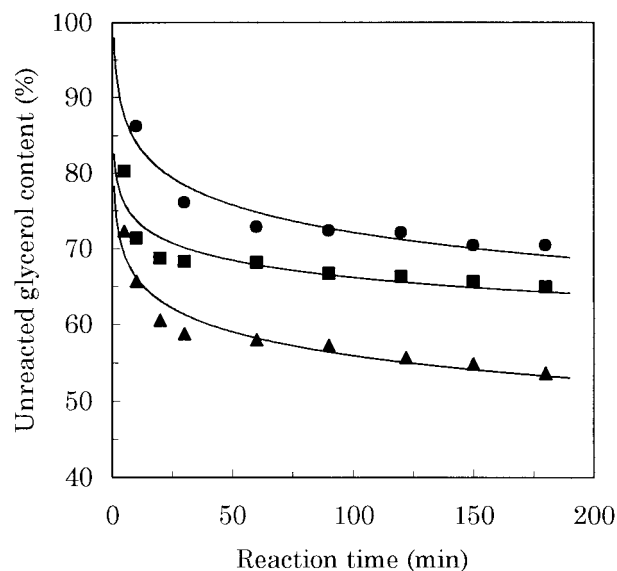
Figure 4 Effect of liquefaction temperature and time on the content of unreacted glycerol. Liquefaction temperature: (●) 130°C; (■) 150°C; (▲) 170°C.

time in this slow-rate region shows a semilog behavior, and this suggests that the liquefaction of CB progresses according to pseudo-first-order kinetics. Within the range of experiments, the rate constant and the minimal residue at different temperatures are summarized in Table I. It was found that only a slight difference in the liquefaction rate was observed among the reaction temperatures used.

On the other hand, even though a liquefaction temperature of 150°C was used, the percent res-

idue decreased to less than 10% as the catalyst content and the solvent/CB ratio increased from 4 to 6% and from 3 to 5, respectively (Figs. 2 and 3). As shown in Table I, the liquefaction rates increased drastically with an increase in both reaction parameters, catalyst content, and solvent/CB ratio. In summary, the liquefaction rate of CB is only slightly dependent on the reaction temperature, but greatly dependent on the catalyst content and the solvent/CB ratio.

It is also important to note that any recondensation of the liquefied biomass components, which causes an increase in residual amounts, was found not to occur under the reaction conditions discussed. This can be attributed to the absence of the lignin component in CB. In our previous article,[6] on the liquefaction of lignin-containing biomass, the use of the binary solvent mixture (PEG400/glycerol) was found to accelerate the liquefaction because of the presence of PEG400, and it was found at the same time to suppress the recondensation of the degraded components because of the presence of glycerol. The suppression of the recondensation is not complete when the biomass contains lignin.

Figure 4 shows the changes of the unreacted glycerol content as a function of the liquefaction time at different temperatures. Similar to the above-mentioned behavior of the percent residue, the content of unreacted glycerol also decreased sharply within 30 min before leveling off gradually. However, there are significant differences in the absolute values of the unreacted glycerol content among the reaction temperatures. This re-
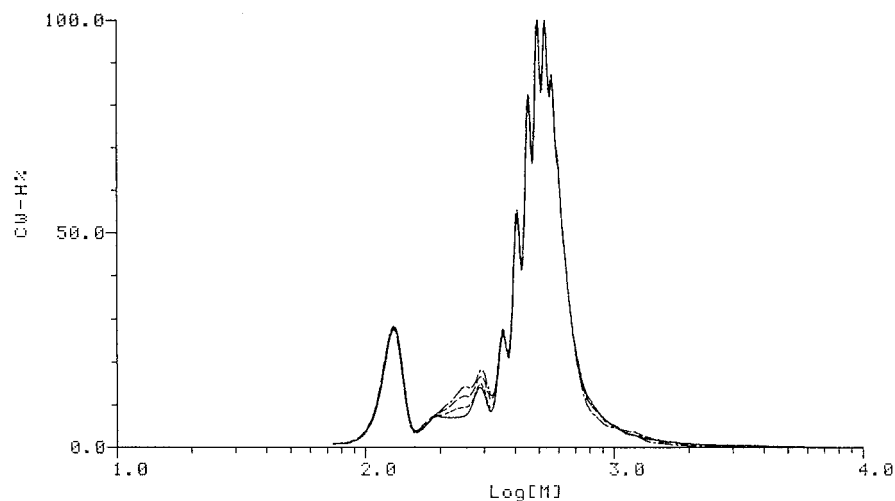
Figure 5 Molecular weights of liquefied CB-based polyols: (—) 30 min: (- - -) 60 min; (— — —) 90 min; (— · —) 120 min.
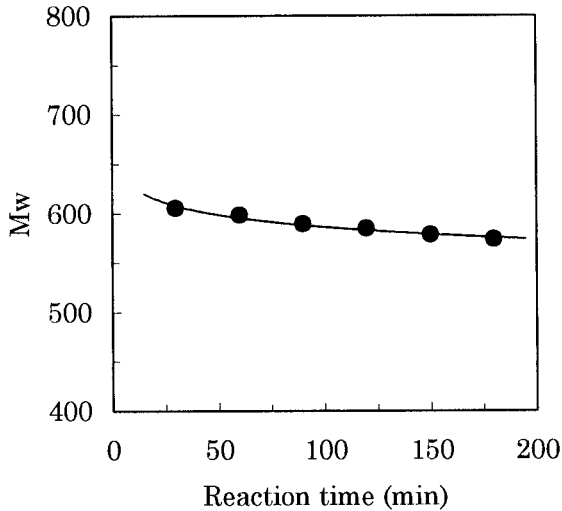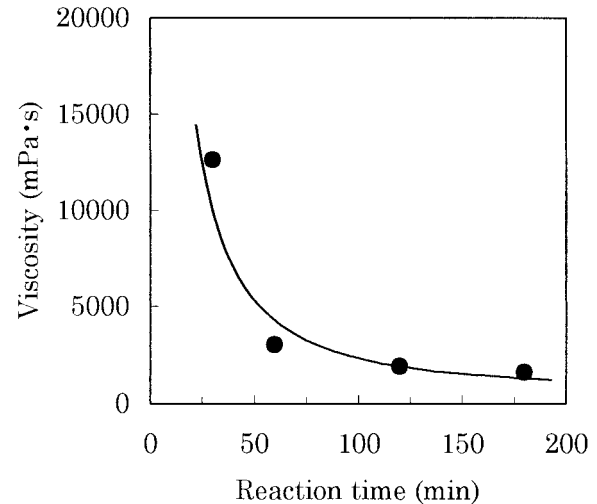
Figure 6 Effect of reaction time on the weight-average molecular weight of liquefied CB-based polyols.

Figure 7 Effect of reaction time on the viscosity of liquefied CB-based polyols.

sult suggests that the reactivity between the decomposed CB components and the liquefaction solvents can be controlled by changing the reaction temperature. It has been known that alcohols can react with liquefied components during liquefaction, resulting in a decrease in the number of hydroxyl groups.[10] Therefore, the unreacted glycerol amount as well as the hydroxyl number could be considered as an important index for the preparation of polyurethane foams.

Characterization of Liquefied CB-based Polyols

Figure 5 presents the molecular weight distributions obtained at different reaction times. It is interesting to note that all curves are very similar and that more than 80% of the molar mass elutes below 1×10^3. Furthermore, the liquefaction time was shown to have little effect on the molecular weight distributions. The calculated weight-average molecular weights (M_w) are summarized in Figure 6. As expected, the M_w did not vary significantly with increasing reaction time. The small difference in the molecular weights indicates that the CB components are decomposed into relatively stable, low molecular weight substances with no sign of recondensation even after prolonged reaction periods.

Figure 7 shows the effect of reaction time on the viscosity of the liquefied CB. The viscosities decreased drastically from 12,600 to 3010 mPa s within the initial 60 min before becoming relatively stable for the remainder of the liquefaction

reaction. Even though these values are slightly larger than those of conventional polyols, they are still satisfactory for the preparation of polyurethane foams.

Because acid values of the resulting polyols are needed for the calculation of hydroxyl numbers, Figure 8 shows the changes of the acid values in liquefied CB-based polyol as a function of reaction time. The acid value increased with liquefaction time. Since acidic substances can be produced during the liquefaction of wood or starch,[11] the increase of acid values can be attributed either to the increase of acidic substances in the depoly-
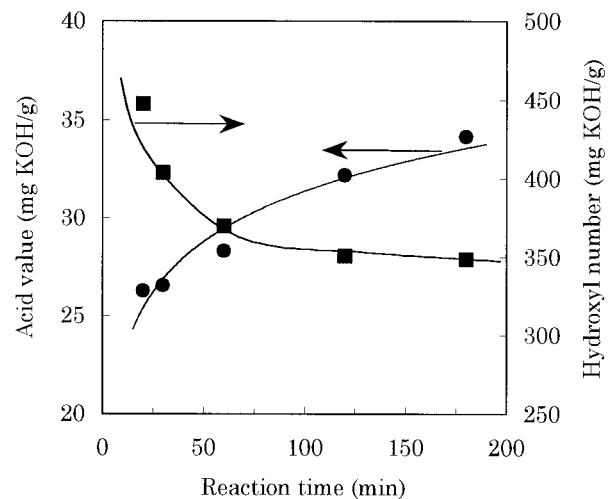
Figure 8 Variation in hydroxyl number and acid value as a function of reaction time.

Table II Formulations for Preparing Foams

Ingredients	Parts by Weight
Liquefied CB-based polyol	100
Catalyst (DBTDL)	1–3
Surfactant (SH-193)	0.5–2
Blowing agent (water)	0–3
MDI (isocyanate index)	104–186

Table III Properties of Foams Obtained from Liquefied CB-based Polyol

Density	0.0346–0.0450 g/cm^3
Compressive strength at 10% strain	38–107 kPa
Compressive strength at 20% strain	70–142 kPa
Elastic modulus	0.22–1.91 MPa

merized CB components or to the oxidation of the saccharides during the liquefaction.

Figure 8 shows that the hydroxyl number of the liquefied CB decreased significantly in the initial reaction stage and almost leveled off with the increase in the liquefaction time. This result reveals that the reaction of the hydroxyl groups of the solvents or the liquefied CB components occurred during the liquefaction. As discussed above, the unreacted glycerol content also showed a similar decrease, suggesting that the reaction between glycerol and the liquefied CB components also occurred during the liquefaction. Yao et al. reported that when the liquefaction solvents alone were subjected to the same liquefaction conditions no significant decrease in the hydroxyl number could be observed.[8] It was suggested that the decrease in the hydroxyl number during the liquefaction could be attributed mainly to either the alcoholysis reaction between solvents and the depolymerized biomass components or to an oxidation reaction that may also occur during the liquefaction.[8] Therefore, it is proposed that the decrease in the hydroxyl number with increasing liquefaction time can be attributed mainly to a reaction between the liquefaction solvent and the depolymerized CB components.

Preparation of Foam and Its Properties

The preparation of polyurethane foams from the liquefied CB-based polyols was conducted by use of various formulations using the ingredients listed in Table II. The density, compressive strength, and modulus of the polyurethane foams were measured and the results are summarized in Table III. Foam densities were found to be in the range of 0.035–0.045 g/cm^3, that is, from hard foams to soft foams depending on the formulation. Foam compressive strengths at 10% strain were between 38 and 107 MPa, and at 25% strain, between 70 and 142 MPa, and they had elastic moduli of 0.22–1.91 MPa. These properties are comparable to those of conventional polyurethane foams and the foams obtained from liquefied wood and starch-based polyols.[8,9]

Effect of Additives (PCL303)

Since PCL303 can be used to improve the foaming properties of liquefied wood or starch-based polyols,[8] a small amount of PCL303 was added. As shown in Table IV, the liquefied CB-based polyols with PCL303 yielded foams with higher density, higher compressive strength, and higher modulus as compared to those of foams without PCL303.

CONCLUSIONS

It was found that acceptable polyols for the preparation of polyurethane foams can be obtained by the liquefaction of CB in the presence of PEG400/glycerol. The liquefaction conditions, liquefaction time, and temperature influenced the character-

Table IV Effect of Addition of PCL303 on the Properties of the Foams

PCL303 Content (%)	Density (g/cm^3)	Compressive Strength (kPa) at 10% Strain	Compressive Strength (kPa) at 20% Strain	Elastic Modulus (MPa)
0	0.038	76	120	1.14
5	0.040	81	148	1.16
10	0.040	149	236	2.46

Liquefied CB-based polyol, 100 parts; catalyst, 3 parts; surfactant, 1 part; blowing agent, 2 parts.

istics of the liquefied CB-based polyol. Polyurethane foams with excellent properties, comparable to those of conventional polyurethane foams, were prepared from the liquefied CB-based polyols. The addition of PCL303 further improved the properties of polyurethane foams made from liquefied CB-based polyols.

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