Water-Absorbing Polyurethane Foams from Liquefied Starch

YAOGUANG YAO, MARIKO YOSHIOKA, and NOBUO SHIRAISHI*

Department of Wood Science and Technology, Kyoto University, Kyoto 606, Japan

SYNOPSIS

Water-absorbing polyurethane foams were prepared from liquefied starch polyols and diphenylmathane diisocyanate (MDI) by using a cell-opening foaming surfactant. The liquefied starch polyols were obtained by the liquefactions of starch in the presence of polyethylene glycol-dominant reaction reagents by using sulfuric acid as a catalyst under either a refluxing condition or a reduced-pressure condition. The influences of the liquefaction conditions on the properties of the liquefied starch polyols were investigated, taking into account the requirements for preparing appropriate polyurethane foam. Feasible formulations for the preparation of the water-absorbing foams were proposed and the properties of the foams obtained were investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Preparation of low-cost polyols from abundant and renewable biomass resources has long been an interesting subject in the polyurethane industry. It was known that by the hydroxyalkylation reaction polyols could be prepared from hydroxyl-containing biomass such as sorbitol,[1] sucrose,[2] methyl glucoside,[3,4] lignins,[5,6] and starch,[7,8] and these polyols could be used for preparation of the rigid polyurethane foams[4,7-9] because of their great functionalities. However, the biomass substances mentioned above usually possess large hydroxyl numbers (e.g., 1500). For obtaining desirable hydroxyl numbers for polyurethane preparation (typically, 300–500), it was necessary to incorporate large amounts of alkylene oxide (e.g., four times of the weight of the biomass) into the biomass molecules. As a consequence, the contents of the biomass components in the resulting foams usually became very low.

For realizing a more extensive utilization of biomass, many efforts have also been made to incorporate directly the plant components such as starch, cellulose powder, lignocellulosics materials, lignins, and so forth into polyurethane formulations.[10-14] However, in many of these cases, the plant components of solid state were incorporated and, therefore, they indeed acted as solid fillers in the foam but not as reactive components, and as a result, foams having high density were apt to be obtained.

Recently, the liquefactions of wood, starch, and other biomass materials in the presence of some organic reagents, such as polyhydric alcohols and phenols, were developed.[15-20] It was found that if polyhydric alcohols with appropriate molecular weights were used in the liquefaction of biomass the resulting liquefied mixtures could be directly used as polyols to prepare polyurethane foams without any additional reaction or treatment.[21,22] This discovery is technologically simple and offers a method to incorporate substantial amounts of biomass into the foam.[23,24]

Among the organic reagents which were used in the liquefaction of biomass, poly(ethylene glycol)s showed great advantages by their large capacities for liquefying biomass[22,23] and inexpensive prices. On the other hand, it was known that if the backbone structure of the polyurethane is rich in ethylene oxide units, water can associate with the chain oxygens via hydrogen bonding and, therefore, the polyurethane obtained will exhibit a hydrophilic character.[25-27] Based on this fact, attempts were made in this study to prepare water-absorbing polyurethane foams from the liquefied starch prepared by using poly(ethylene glycol) as the main liquefaction reagent.

Hydrophilic or water-absorbing foams are useful in manufacturing absorbent products or in the agri-

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 60, 1939–1949 (1996)
CCC 0021-8995/96/111939-11

cultural or horticultural purposes. Usually, hydrophilic polyurethane foams are prepared based on filling a separate hydrophilic additive into polyurethane formulations[28,29] or based on the reaction of isocyanate-capped hydrophilic poly(ether polyol) prepolymers, mainly isocyanate-capped poly(ethylene glycol), with water and/or polyhydric polyols.[30,31] In this study, liquefied starches, which were prepared with the poly(ethylene glycol)-dominant liquefaction reagents, were directly reacted with diisocyanate for making foams. It has been known that the liquefied starch prepared in the presence of alcohols was composed mainly of the corresponding alcohol–glucosides and their oligomers[32] and, therefore, it was expected that the presence of the liquefied starch components in the foams would not only decrease the cost but also enhance the water absorption of the foams because of the hydrophilic nature of the carbohydrate. Furthermore, the presence of the starch components in the foams will also enhance a possibility of biodegradability,[33] which becomes much more striking especially when the foams are used for agricultural purposes.

EXPERIMENTAL

Chemicals and Materials

Cornstarch was received from Sanwa Starch Ltd. and was dried in an oven at 105°C for 4 h before use. Poly(ethylene glycol), PEG #400 ($\bar{M}_w$ = 400), glycerin, sulfuric acid, and sodium hydroxide were of reagent grade and were used without further purification. The ingredients used in the foam formulations are listed in Table I and they were used as received.

Preparation of the Liquefied Starch Polyol

Liquefaction of starch was conducted using sulfuric acid as a catalyst. PEG #400 was used as the primary liquefaction reagent, to which 0–20 wt % of glycerin, as an assistant liquefaction reagent, was incorporated. The liquefaction reagent mixtures, including sulfuric acid (henceforth called liquefaction solvent for convenience) were premixed thoroughly. Then, definite amounts of starch and the premixed liquefaction solvent were put in a 500 mL separable flask. Liquefactions were done under stirring at 150°C by using either of the following two methods: One is with the liquefaction conducted at atmospheric pressure under refluxing, called the refluxing method, and the other is with the liquefaction done under a reduced-pressure condition to remove the volatile substances produced during liquefaction, called the reduced-pressure method. Moreover, in the cases in which the desired incorporated amounts of starch were greater than the amounts of the liquefaction solvent, a stepwise liquefaction procedure[23] was used, i.e., the liquefaction first was done at a starch-to-solvent ratio of 1 to 1 by weight for 30 min, and then the remaining starch was added in the reaction mixture and the liquefaction was continued for a desired period. After the liquefaction, the temperature of the reaction mixture was allowed to decline and then a sodium hydroxide aqueous solution (48 wt %) was added to neutralize the sulfuric acid and the liquefied starch polyol was obtained.

Measurements of the Unliquefied Residues of Starch

The residual amounts of starch after liquefaction were determined according to the method described

Table I Chemicals Used in Foam Formulations

Chemical	Description	Supplier
DBTDL (dibutyltin dilaurate)	Foaming catalyst	Katsuta Ind. Ltd.
L33[a] (triethylene diamine)	Foaming catalyst	Tosoh Ltd.
SH193	Silicone surfactant for rigid foams[b]	Toray Dow Corning Silicone Ltd.
SH192	Silicone surfactant for flexible foams[b]	
GP3000	Poly(ether polyol), $\bar{M}_w$ 3000, functionality of three	Japan Polyurethane Ind. Ltd.
PEG1500	Poly(ether polyol), $\bar{M}_w$ 1500, functionality of two	Commercial source
PCL303	Poly(ester polyol), $\bar{M}_w$ 310, functionality of three	Daicel Chem. Ind. Ltd.
MR100	Diphenylmethane diisocyanate	Japan Polyurethane Ind. Ltd.

[a] 33% triethylene diamine solution in dipropylene glycol.

[b] Silicon–glycol copolymer nonionic surfactants; SH192 has a larger dimethyl polysiloxane ratio than has SH193.

in a previous article,[34] i.e., about 10 g of the liquefied mixture was dissolved in a 200 mL of dioxane/water binary solvent (dioxane/water = 8/2) and stirred for more than 4 h, and then the dilution was filtrated through glass filter paper (Toyo GA100) in a vacuum. The solid residues were dried in an oven at 105°C to a constant weight. The percent residue of the starch was calculated by the following equation:

$$\text{Residue (\%)} = \frac{R}{WC} \times 100$$

where R is the weight of the dried residue; W, the weight of the liquefied mixture used in the measurement; and C, the weight percentage of starch in the liquefied mixture.

Measurements of the Apparent Viscosities of the Liquefied Starch Polyols

The apparent viscosities of the liquefied starch polyols were measured using a GFT-500A flow tester (Shimadzu Co.). Measurements were conducted at 25 ± 1°C using a 0.5 mmϕ × 1.0 mmL die at a fixed apparent shear stress of 1.225×10^6 dyn/cm^2.

Measurements of the Hydroxyl Numbers of the Liquefied Starch Polyols

The hydroxyl number of a liquefied mixture is defined as the number of milligrams of potassium hydroxide equivalent to the phthalic anhydride consumed in the phthalification of 1 g of sample and was determined according to the method described in a previous report.[24]

Foam Preparation

The liquefied starch polyols obtained above were directly used to prepare polyurethane foams by reaction with diphenylmathane diisocyanate (MDI). Thus, the definite amounts of liquefied polyol, catalyst, surfactant, water, and others (such as conventional polyols), if any, were premixed thoroughly in a paper cup, to which the prescript amount of MDI (at a isocyanate index of 85–115) was added and then mixed at a stirring speed of 8000 rpm for 10–15 s. The resulting mixture was poured immediately into a 12 × 12 × 10 cm cardboard box and was allowed to rise at room conditions. The rise time of the foam was usually about 2 min, and the foam then obtained was allowed to cure at room temperature for 1 h before being removed from the box. The isocyanate index was calculated as follows:

Isocyanate index

$$= \frac{M_{\text{MDI}} \times W_{\text{MDI}}}{M_{\text{LB}} \times W_{\text{LB}} + M_{\text{add}} \times W_{\text{add}} + \frac{2}{18} \times W_w} \times 100$$

where M_{MDI} is the number of moles of isocyanate groups per gram of MDI; W_{MDI}, the weight of MDI (g); M_{LB}, the number of moles of hydroxyl groups per gram of liquefied starch polyol; W_{LB}, the weight of liquefied starch polyol (g); M_{add}, the number of moles of hydroxyl groups per gram of other additives, if any; W_{add}, the weight of additives (g); and W_w, the weight of water in the form formulation (g). Here, additives are mainly referred to conventional polyols. The hydroxyl groups in the surfactants and catalysts were not taken into account.

Measurements of Mechanical Properties of the Foams Before and After Absorption of Water

Measurements of mechanical properties of the foams were conducted according to JIS (Japanese Industrial Standard) K7220. The foams were cut into 50 × 50 × 50 mm specimens (eight specimens for every foaming formulation). The specimens were conditioned for 48 h at 23°C and 50% relative humidity and then were calipered and weighted to determine densities. Next, four of the eight specimens were immersed in water for 24 h and then taken out for measuring the mechanical properties in wet state. The compressive properties of the foams either before absorbing water or after saturation-absorbing water were measured using a DCS-500R Shimadzu autograph. The tests were run in the direction perpendicular to foam rise at a constant crosshead speed of 5 mm/min. The compressive strengths of the foams were determined based on the stresses at the yield points of the specimens in the case of specimens showing yield points below 12% strain; otherwise, the strengths were determined based on the stresses at 10% strain.

Measurements of Water Drop Absorption Time of the Foams

Drops of water were dripped on the cut surfaces of a foam which are perpendicular to foam rising direction. The times in which the drops were completely absorbed by the foam were recorded. At least 20 drops in different places were tested for every sample and their average values were reported.

Water-absorption Curves and Equilibrium Water Uptakes of the Foams

The water-absorption curves (time dependence of the water absorptions) and the equilibrium water uptakes of the foams were tested by the following procedures: Preweighed foam cubes (5 × 5 × 5 cm), in triplicate, were totally immersed in water and just below the level without any crushing. The cubes were periodically taken out, put on a screen for 5 s to trickle the water covering the foam surfaces, weighed on an electronic balance, and then put back in water. This treatment was repeated until there was no further change in the weights of the samples. The equilibrium water uptake of the foam was calculated as follows:

$$\text{Gravimetric water uptake (\%)} = (W_\infty - W_0)/W_0 \times 100$$

$$\text{Volumetric water uptake (\%)} = (W_\infty - W_0)/V_0 \times 100$$

where W_∞ is a weight of the foam at the equilibrium absorption; W_0, the weight of the foam before absorbing water; and V_0, the apparent volume of the foam before absorbing water.

Water Retentions of the Foams

After reaching the equilibrium water absorption as described in the previous section, the specimens were taken out of the water, weighed, and then put into an oven set at 60°C. A cup of water also was put into the oven as a control. The weight changes of the foams and the water in the cup were recorded until the foams reached constant weights. Then, the weight changes of the foam and free water were calibrated on the basis of the unit apparent surface area of the foams, i.e., the surface area of the foam cube, and free water. It should be noted that the actual area of the evaporation surface of a cellular material is always larger than its apparent area and, therefore, the water retention values evaluated by this method are conservative ones.

Accelerated Tests for Water Leaching of the Foams

Preweighed foam specimens (5 × 5 × 5 cm) were immersed in water and washed by crushing occasionally. The water was replaced by fresh water once a day and the washing was continued for 1 week. Then, the foams were taken out and dried in an oven at 60°C until constant weights were obtained. Percent leaching was calculated based on the difference in weight between the original foam and the leached foam.

RESULTS AND DISCUSSION

Liquefaction of Starch by Refluxing Method and Properties of the Liquefied Starch Polyols

The purpose of liquefaction is to convert a solid starch into liquid polyol. Figure 1 shows the changes in the residual amounts of starch and the hydroxyl numbers of the liquefied starch mixtures with liquefaction time in different liquefaction solvent compositions. It can be seen that starch can be liquefied by the polyols under the catalysis of sulfuric acid within 30 min. Moreover, compared with the case of using PEG #400 alone as the liquefaction solvent, the use of the PEG/glycerin mixed solvent speeds up the liquefaction of starch and depresses the repolymerization (gelation) reaction which occurs at about 115 min of the reaction time in the absence of glycerin. The hydroxyl numbers of the liquefaction mixtures, before reaction, are almost the same as those for the liquefaction solvents alone, indicating that the hydroxyl groups in the solid starch granules almost are inaccessible to the phthaloylating agent. In the beginning period of the liquefaction, the hydroxyl numbers of the mixtures increase with the progress of the liquefaction of starch and reach the maximum values around the times when the starches are completely dissolved, indicating that the hydroxyl groups of starch are

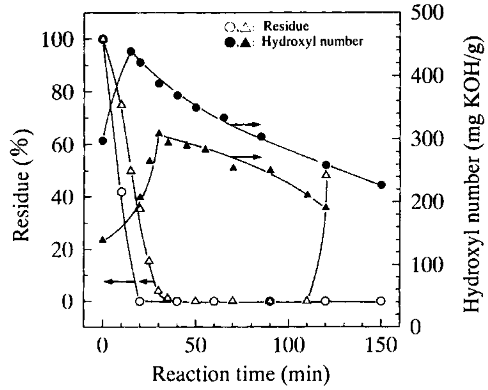

Figure 1 Effects of reaction time on the amount of residue and the hydroxyl number of liquefied starch. Solvent/starch ratio, 1; reaction temperature, 150°C; solvent composition: (●, ○) PEG #400/glycerin/H_2SO_4 = 80/20/3; (▲, △) PEG #400/H_2SO_4 = 100/3.

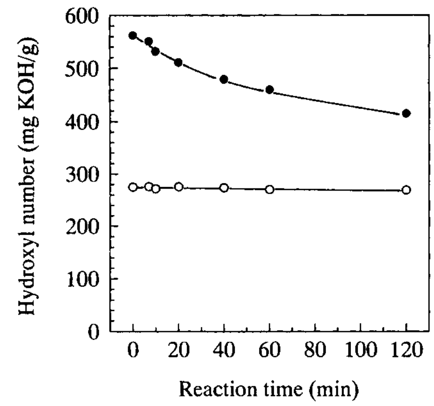

Figure 2 Variation of hydroxyl numbers of liquefaction solvents with reaction time. Reaction temperature, 150°C; solvent compositions: (●) PEG #400/glycerin/H_2SO_4 = 80/20/3; (○) PEG #400/H_2SO_4 = 100/3.

liberated by the liquefaction and dissolution. After obtaining the maxima, the hydroxyl numbers decrease rapidly and monotonously with the reaction time.

The significant decreases in the hydroxyl numbers of the liquefaction mixtures with reaction time after the maximum values (as shown above) reveal that there exist losses in the hydroxyl groups of the polyols solvents and/or liquefied starch components during the reaction. For comparison, the liquefaction solvents alone without adding starch were subjected to the same liquefaction conditions and the changes in hydroxyl number of the liquefaction solvents are shown in Figure 2. It can be seen that in the case of mere PEG #400 the hydroxyl number does not change with liquefaction time, and in the case of the PEG #400/glycerin binary solvent, the hydroxyl number decreases to some extent but not so significantly as those shown in Figure 1. These results suggest that the decreases in hydroxyl number of the liquefaction mixtures during reaction are largely due to the dehydration and/or oxidation reactions of the liquefied starch components.

The relationships between liquefaction compositions and the properties of the resulting liquefied starch polyols are summarized in Table II. It demonstrates that about 1% sulfuric acid (based on the weight of the total mixtures) is enough for obtaining complete liquefactions even if the content of starch is up to 60 wt %. The viscosities of the liquefied mixtures are somewhat large compared with those of the conventional polyols (e.g., 1930 cp for PCL 303) and increase with increasing starch contents. However, even containing starch up to 60 wt %, the resulting liquefied mixtures still have feasible viscosities for the preparation of the urethane foams. When the starch content is as large as 70%, the liquefied mixtures are pastelike and have very poor fluidity at room temperature and therefore cannot be used as foaming polyol. From this table, it can be found that the hydroxyl numbers of the liquefied starch polyols fall in the range between 270 to 369, being in the suitable range for the preparation of polyurethane foams.[9] Replacements of parts of PEG #400 with glycerin in the liquefaction compositions result in decreases in the viscosity and increases in the hydroxyl number of the resulting mixtures, but the latter is within acceptable ranges as described above. In addition, the liquefied starch mixtures are almost completely soluble in water except for those obtained from a long liquefaction time (e.g., 2 h), indicating that these liquefied starch mixtures have a great hydrophilic nature.

Table II Liquefaction Compositions and Conditions for the Preparation of Liquefied Starch Polyols and the Properties of the Resulting Products (Refluxing Method)

Liquefaction Compositions (%)				Liquefaction Time	Residue	Hydroxyl No.	Apparent Viscosity
PEG 400	Glycerin	H_2SO_4	Starch	(min)	(%)	(mg KOH/g)	(cp)
49	0	1	50	45	1.3	289.5	35230
44	5	1	50	45	0.3	325.6	30210
39.2	9.8	1	50	45	0.4	369.1	25140
39.2	0	0.8	60	30 + 60[a]	2.8	270.1	52170
35.2	4	0.8	60	30 + 60[a]	1.6	302.4	41250
31.4	7.8	0.8	60	30 + 60[a]	1.2	332.2	36520
23.3	5.8	0.9	70	30 + 60[a]	5.2	302.4	457000
PCL 303	—	—	—	—	—	580	1930

[a] Stepwise liquefaction method: liquefaction first was done at a solvent/starch ratio of 1 for 30 min, then the additional amount of starch was added, and the reaction was continued for additional 60 min.

Preparation of Polyurethane Foam from the Liquefied Starch Polyols

The liquefied starch polyols obtained above were directly used to prepare polyurethane foams by reaction with MDI using two different silicon–glycol copolymer foaming surfactants, SH192 and SH193, individually. The foam formulations and the properties of the resulting foams are shown in Table III. It was found that foams with good cell structures and substantial mechanical properties could be obtained by using SH193, a surfactant usually used for rigid foam preparation, and resulted in high closed-cell contents, regardless of the compositions and hydroxyl numbers of the liquefied starch in the range studied as shown in Table I except for the one with 70 wt % starch content which could not mix with MDI because of its very large viscosity. However, these foams did not show evident water absorptivity, i.e., the water drops could not be absorbed until they disappeared by evaporation, and the water uptakes of the foams were as low as below 5 w/v %. These results are considered to be due to the independent cell structures of the foams which restrain the permeation of water in the foams. However, it was found that satisfactory foams could not be obtained by using the cell-opening surfactant, SH192, based on the formulations listed in Table III, i.e., the expanding masses tended to collapse in the early stage of the foaming process, probably resulting from the occurrence of the intercommunication and coalescence of the bubbles (cell linkage) before the expanding masses have reached enough gelation stage. It is known that liquefied biomasses are generally suitable for the preparation of rigid urethane foams[8,17,21,22,24,35] because of the large hydroxyl numbers, great functionality, and cyclic molecular structures of the biomass components.

On the other hand, the cell-opening surfactant SH192 is such a surfactant developed specifically for preparation of flexible foams by using the polyols with relatively high molecular weights (several thousands) and small hydroxyl numbers (e.g., 50).[36] Therefore, the failure in foaming of the above liquefied starch with the cell-opening surfactant is considered to be due to the difficulty in establishing the balance between gelation and blowing. To improve the foamability of the liquefied starch polyol under using the cell-opening surfactant, each of the following three kinds of polyol, GP3000, PEG #1500, and PCL303, are incorporated into the foam formulations as modifiers and their effects are shown in Table IV. It can be seen that additions of GP3000, a triol for making conventional flexible urethane foams, remarkably improve the foamability of the liquefied starch polyols. The mass can be blown smoothly to a relatively large volume. A slight healthy bubbling and relaxation can be observed at the end of the expansion process, indicating that the foam has continued cell structures. As contrasted with GP3000, incorporating either PEG #1500, which also has high molecular weight ($\bar{M}_w$ = 1500) but functionality is only two, or PCL 303, which has three hydroxyl groups but low molecular weight ($\bar{M}_w$ = 310), cannot improve the foamability of the liquefied starch polyol.

These results indicate that the foaming of the liquefied starches under the act of cell-opening surfactants can be facilitated by the addition of a high molecular weight triol, GP3000. The improved foamability probably could be ascribed to the increased resilience and viscosity of the foaming mass imparted by the high molecular weight triol and which protect the foaming mass from coalescence and collapse. It was found that the suitable addition amount of GP3000 was 5–20% based on the weight of the liquefied starch, depending on the hydroxyl number of the liquefied starch. The liquefied starch with a greater hydroxyl number required a somewhat larger amount of addition. However, the suitable range was not critical and an increased addition amount only resulted in a more flexible foam.

Table III Effects of the Kinds of Surfactant on the Foamability of the Liquefied Starch Polyols and the Properties of the Resulting Foams (Refluxing Method)

Ingredients	Parts by Weight
Liquefied starch polyol	100 (starch content 50–60%)
Catalysts	DBTDL, 0.2–3; L33, 0–1
H_2O (blowing agent)	1–4
MDI	70–170 (index 0.85 to 1.15)
Surfactants	SH193, 0.2–2; or SH192, 0.2–2

	SH193	SH192
Foamability	Good	Collapse
Properties		
Density (g/cm^3)	0.03–0.05	—
Compressive strength	40–100 KPa	—
Modulus of elasticity	0.8–4.6 MPa	—
Water drop absorption time	>150 min	—
Water uptake		
Gravimetric (w/w)	<200%	—
Volumetric (w/v)	<5%	—

Table IV Effects of Additions of Conventional Polyols on Foamability as Well as the Properties of the Resulting Foams (Refluxing Method)

Ingredients	Parts by Weight
SH192 (surfactant)	0.5–2
Liquefied starch polyol	100 (starch content 50–60%)
Catalysts	DBTDL, 0.2–3; L33, 0–1
H_2O (blowing agent)	1–4
MDI	70–170 (index 0.85–1.15)
Conventional Polyols	GP3000, 5–20; or PEG #1500, 5–20; or PCL 303, 5–20

	GP3000	PEG #1500	PCL 303
Foamability	Good	Collapse	Collapse
Properties			
Density (g/cm^3)	0.030–0.050	—	—
Compressive strength			
Dry	25–60 KPa	—	—
Wet	20–40 KPa	—	—
Modulus of elasticity			
Dry	0.4–1.2 MPa	—	—
Wet	0.3–1.0 MPa	—	—
Water drop absorption time	5–300 s	—	—
Water uptake			
Gravimetric (w/w)	1300–2000%	—	—
Volumetric (w/v)	50–90%	—	—
Leaching rate	20–33%	—	—

The mechanical properties, water-absorption properties, and the water-leaching rates of the resulting cell-open foams are also given in Table IV. It is found that the foams can absorb water drops within 5–300 s. The equilibrium water uptakes of the foams range from 13 to 20 times of their dried weights, i.e., 50–90% of the apparent volumes of the foams have been occupied by water. These results indicate that foams with satisfactory water absorptivity can be prepared from the liquefied starch by using a cell-opening foaming surfactant. As for the compressive properties, it is understandable that the foams prepared by using SH192 are relatively flexible compared with those by using SH193 because the former have continued cell structures.

However, the foams prepared by using SH192 have relatively coarse and nonuniform cell structures and a somewhat sticky feeling. In addition, from this table, it can be noticed that the leaching rates of the foams by soaking in water are very large, amounting to 20–30% of the original weight of the foam. These results indicate that the miscibility between the hydrophilic liquefied starch polyol and the hydrophobic diisocyanate is very poor and there exits severe phase-separation in the resulting foams. As a result, the nonreacted liquefied biomass leaches out when the foams are soaked in water. It can be anticipated that an improvement in the miscibility between the ingredients will result in an improvement in the properties of the foams.

Liquefaction of Starch Under a Reduced-pressure System and Properties of the Resulting Foams

It is known that liquefaction of starch is accomplished by alcoholysis, condensation, and oxidation reactions of the starch molecules.[32] Some of these reactions consume the hydroxyl groups and therefore decrease the hydrophilicity of the liquefied starch mixture, which will improve the compatibility of the liquefied starch with the diisocyanate. However, in a reflux reaction system, the water produced in the condensation cannot be removed and therefore it will obstruct the alcoholysis and condensation reactions. Moreover, the presence of water can also promote the hydrolysis of starch or its derivatives to lower polysaccharides and glucose, which results in the production of extra hydroxyl groups. In addition, refluxing of the volatile substances in the flask must result in a decrease in the actual reaction temperature and therefore give an unfavorable effect to the condensation and oxidation reactions.

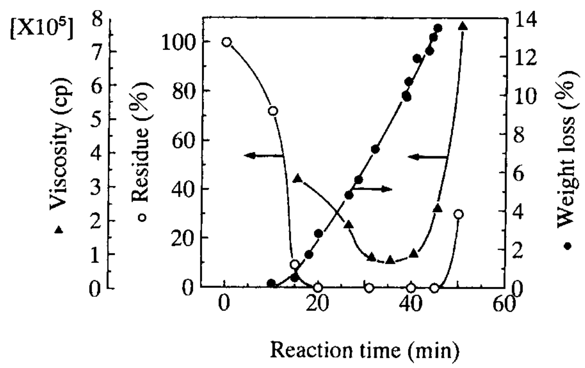

Figure 3 Effects of reaction time on the (O) amount of residue, (▲) viscosity, and (●) weight loss of liquefied starch obtained under reduced pressure. Solvent/starch ratio, 1; reaction temperature, 150°C; solvent compositions: PEG #400/glycerin/H_2SO_4 = 80/20/3.

For depressing the hydrolysis reaction and promoting the alcoholysis and condensation reaction, the reaction flask was connected to a pressure-reducing system in order that the water and other volatile substances produced in the reaction could be removed from the liquefaction mixture. Figure 3 shows the percent residues of starch and the weight losses and viscosities of the liquefied mixture as functions of reaction time under the pressure-reducing reaction conditions. The changes in the percent residue show that there is no evident difference in the liquefaction kinetic compared with that under the refluxing reaction conditions, i.e., starch can be liquefied completely within 20 min as far as the residual rate is concerned. However, when the reaction proceeds to about 50 min, gelation occurs suddenly, which results in a drastic increase in the solvent-insoluble fraction. On the other hand, weight loss, due to evaporation, begins at about 10 min and then increases gradually with the progress of liquefaction. From about 20 min when the starch has been liquefied completely, weight loss increases almost linearly with the increases in the reaction time and reaches about 13 wt % at a reaction time of 45 min (based on the weight of the total mixture). This result indicates that a large amount of volatile substances is produced during the liquefaction. As for the viscosity of the liquefied mixture, it decreases initially with increasing liquefaction time and reaches a minimum value of 81,000 cP at 35 min and then increases at an accelerated rate. When the reaction is conducted for about 45 min, the viscosity of the liquefied mixture increases drastically, which soon resulted in the formation of a gel-like mixture. Compared with Table II, it can be seen that the viscosities of the liquefied mixtures prepared by this method are much greater than those prepared by the refluxing method. This can also be ascribed to the removal of the low molecular weight substances and the condensation reactions.

Figure 4 shows the effects of the liquefaction methods on the relationships between hydroxyl numbers of the liquefied mixtures and liquefaction time. It can be found that before the peaks appear where there are not yet substantial volatile substances to be produced the hydroxyl numbers of the liquefied starch mixtures obtained from the two methods, in either solvent composition, are very similar. After the peaks, however, the hydroxyl numbers of the liquefied starches obtained by the reduced-pressure method decrease rapidly and linearly with the liquefaction time, which is quite different from the results obtained under the refluxing condition. As a result, liquefaction mixtures with much lower hydroxyl numbers are obtained within a reaction time of 40–50 min. Furthermore, for the liquefaction solvent containing 20% (by weight) glycerin, although much greater hydroxyl numbers are observed at the beginning period of the reaction because of the large hydroxyl number of glycerin itself (1800), the hydroxyl number of the liquefaction mixture decreases very fast after 15 min and eventually decreases to lower values than those obtained from the corresponding liquefaction without glycerin. This result suggests that glycerin has higher reactivity than does poly(ethylene glycol), being consistent with the finding that the presence of glycerin accelerates the liquefaction of starch as shown in Figure 1. Moreover, Figure 5 reveals that the hydroxyl number decreases proportionally with an increase in the weight loss.

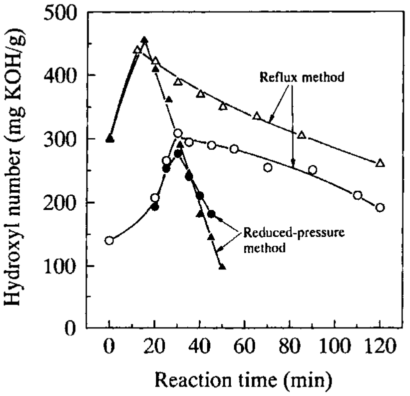

Figure 4 Variations of hydroxyl number of liquefied starches with reaction time by using two liquefaction methods. Solvent/starch ratio, 1; reaction temperature, 150°C; solvent compositions: (▲, △) PEG #400/glycerin/H_2SO_4 = 80/20/3; (●, O) PEG #400/H_2SO_4 = 100/3.

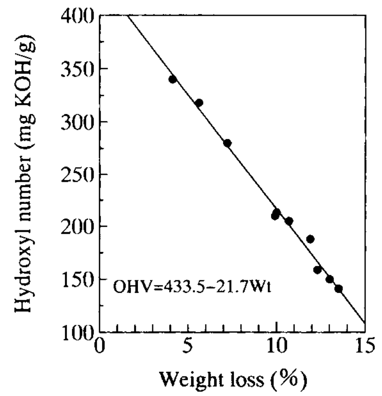

Figure 5 Relation of hydroxyl number in liquefied starches to weight loss under a reduced-pressure condition. Solvent/starch ratio, 1; reaction temperature, 150°C; solvent composition: PEG #400/glycerin/H_2SO_4 = 80/20/3.

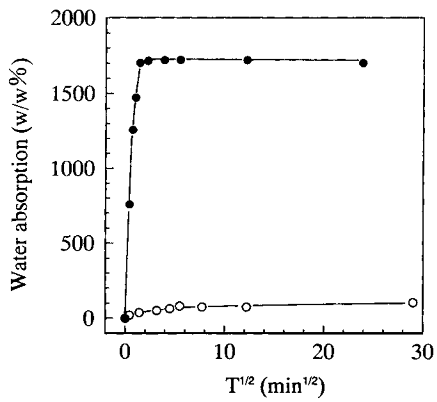

Figure 6 Water-absorption curves of the foams prepared by using foaming surfactant (●) SH192 and (○) SH193, respectively.

The liquefied starch polyols obtained by the above method were used to make foams by using either SH192 or SH193 as a surfactant. However, additions of appropriate amounts of GP3000 in the foaming formulations also were necessary when SH192 was used as a surfactant. It was interesting to find that although the liquefied starch polyols prepared by this liquefaction method had large viscosities they could mix with MDI uniformly, resulting in fine cells and uniform foam structures. The leaching rates of the foams by using SH192 as a foaming surfactant were 5–10% (by weight), as shown in Table V, being much less than those for the foams prepared by the refluxing method. These results indicate that the liquefied starch polyols prepared by the reduced-pressure method have better miscibility with MDI.

Table V Comparison on the Properties of the Foams Prepared Using Different Surfactants (Reduced-pressure Method)

Properties	Surfactant	
	SH192[a]	SH193[b]
Density (g/cm^3)	0.035–0.070	0.030–0.060
Compressive strength		
Dry	25-50 KPa	40-80 KPa
Wet	20-40 KPa	—
Modulus of elasticity		
Dry	0.4-1.0 MPa	0.6-3.8 MPa
Wet	0.3-0.7 MPa	—
Water drop absorption time	1-480 s	>120 min
Water uptake		
Gravimetric (w/w)	1700-2200%	<200%
Volumetric (w/v)	60-90%	<5%
Leaching rate	5-10%	—

[a] Foaming formulations based on Table IV with GP3000 additions.

[b] Foaming formulations based on Table III.

Figure 6 shows the water-absorption curves of the resulting foams. It can be seen that the foam prepared using SH192 as a surfactant absorbs water rapidly and reaches the equilibrium value within 5 min, where the water uptake is 17 times of the dried weight of the foam. However, similar to the result obtained for the refluxing method, the foam prepared using SH193 exhibits a very slow water absorption and a small equilibrium value (also refer to Table V). This result indicates again that continued-cell structures are essential for obtaining satisfactory water absorptivity even though the foams have a hydrophilic nature.

The hysteresis stress–strain curves for a typical water-absorbing foam prepared in this trial before and after the absorption of water are shown in Figure

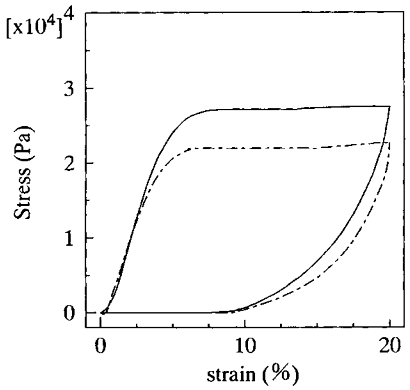

Figure 7 Hysteresis curves of the foams (——) before and (— • —) after absorption of water.

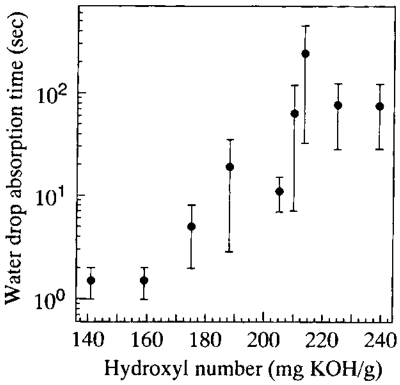

Figure 8 Relation of water drop absorption time of the foam to hydroxyl number of liquefied starch. The bars express the variation ranges of water drop absorption time resulted from the change in foaming formulations.

7. The mechanical properties of the foams are summarized in Table V. It can be seen that the foams have substantial mechanical properties and reveal hysteresis behavior similar to that of the semirigid foam. It is meaningful to notice that the changes in the mechanical properties of the foams resulted from absorbing water are not significant. This characteristic will ensure that the foams can be used in a wet condition with substantial strength.

It can be noticed in Table V that the water-absorption abilities of the foams, especially the water drop absorption time, are changeable in wide ranges, depending on various factors such as the properties of the liquefied starch polyols and the foaming formulations. Based on a statistic analysis on the water drop absorption times of the foams prepared from different liquefied starches and foaming formulations, it was found that among all the factors the hydroxyl number of the liquefied starch was the most significant determining factor for the water drop absorption of the foams. The relationship between water drop absorption time and hydroxyl number is shown in Figure 8. In this figure, the deviation bars represent the variation ranges of the water drop absorption times of the foams prepared by various foaming formulations. It can be seen that when the hydroxyl numbers of the liquefied mixtures are about or less than 200 the foams can absorb water drops in several seconds regardless of the variation of the foaming formulations. With an increase in the hydroxyl number, the water drop absorption time increases rapidly and becomes susceptible to the foaming conditions, i.e., the deviations of the absorption time are very dependent upon the changes in foaming conditions. This phenomenon probably can be ascribed to the fact that polyols with lower hydroxyl numbers require less amounts of isocyanate, a hydrophobic component, which therefore results in an great increase in hydrophilicity of the foams. For instance, in a typical foam formulation, a decrease in the hydroxyl number of the liquefied starch from 360 to 160 leads to a decrease in the MDI content in the resulting foam from 52 to 39% or an increase in the liquefied starch polyol content from 44 to 56% (by weight).

For investigating the water-retention properties of the water-absorbing foams, the weight changes of a water-saturated foam were measured in comparison with those of free water in a cup as a control by allowing them to stand at 60°C for various times, and the results are shown in Figure 9. Based on a regression analysis of the data, it is found that the water in the foam evaporates according to a third-power equation [eq. (1)], whereas the free water in a cup evaporates according to a linear equation [eq. (2)]:

$$W_t = 0.572 - 1.047 \times 10^{-3}t - 3.54 \times 10^{-7}t^2 + 9.98 \times 10^{-10}t^3 \quad (\text{g/cm}^2 \text{ surface})$$
$$(\text{correlation coefficient} = .9999) \quad (1)$$

$$W_t = 0.572 - 3.109 \times 10^{-3}t \quad (\text{g/cm}^2 \text{ surface})$$
$$(\text{correlation coefficient} = .9998) \quad (2)$$

where W_t is the weight of the foam (or free water) at time t. The differences in the evaporation rate of water from the foam and from the cup, respectively, can be seen more clearly from the differential curves of eqs. (1) and (2), as shown in the same figure, i.e., free water evaporates by a constant rate of 3.11 × 10^{-3} g/cm^2/min, while the water in foam evapo-

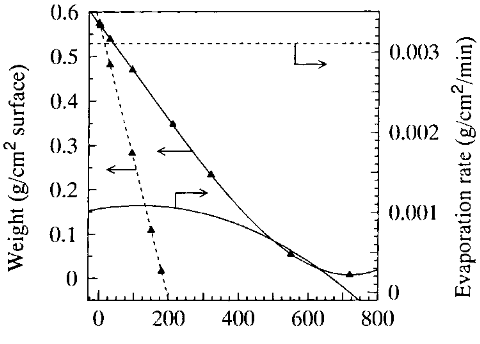

Figure 9 Weight changes and their rates of a water-absorbed foam and the free water at 60°C due to evaporation of water: (— ▲ —) weight change of foam; (———) evaporation rate of foam; (-----△----) weight change of free water; (-------) evaporation rate of free water.

rates at lower rates which decrease with the loss of water. Even in the water-saturated stage, the evaporation rate of water in foams is only one-third of that from the free water. This result indicates that the foams have excellent water-retention properties.

CONCLUSION

Hydrophilic biomass polyols could be obtained by liquefactions of starch in the presence of poly(ethylene glycol)-dominant liquefaction solvents using sulfuric acid as a catalyst. The liquefied starch polyols obtained had feasible viscosities and hydroxyl numbers for the preparation of polyurethane foams. Water-absorbing foams could be prepared by reacting these liquefied starch polyols with diphenylmethane diisocyanate. However, continued cell structures of foams were essential for obtaining excellent water-absorbing properties. The continued cell structures could be facilitated by using a cell-opening type surfactant and by the additions of small amounts of high molecular weight triol in the foam formulations. The foams could absorb water up to 2000 wt % within several minutes and also reveal good water-retention properties and substantial mechanical properties.

REFERENCES

1. J. E. Wilson, H. M. Truax, and M. A. Dunn, *J. Appl. Polym. Sci.*, **3**(9), 343 (1960).
2. M. Wismer and J. F. Foste, U.S. Pat. 3,085,085 (1963).
3. F. Hostettler, R. K. Barnes, and R. W. McLaughlin, U.S. Pat. 3,073,788 (1963).
4. T. E. Yeates and C. L. Mehltretter, *Mod. Plast.*, **39**(3), 151 (1961).
5. G. G. Allan, U.S. Pat. 3,476,795 (1969).
6. L. C.-F. Wu and W. G. Glasser, *J. Appl. Polym. Sci.*, **29**, 1111 (1984).
7. F. H. Otey, B. L. Zagoren, and C. L. Mehltretter, *I & EC Prod. Res. Dev.*, **2**(4), 256 (1963).
8. F. H. Otey, B. L. Zagoren, F. L. Bennett, and C. L. Mehltretter, *I & EC Prod. Res. Dev.*, **4**(4), 224 (1965).
9. T. H. Ferrigno, *Rigid Plastics Foams*, Reinhold, New York, 1967, p. 11.
10. F. Hostettler, U.S. Pat. 4,156,759 (1979).
11. H. Koch and N. Roper, *Starch/Starke*, **40**, 121 (1988).
12. H. Yoshida, R. Morck, K. P. Kringstad, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **34**, 1187 (1987).
13. R. L. Cunningham, M. E. Carr, and E. B. Bagley, *J. Appl. Polym. Sci.*, **44**, 1477 (1992).
14. H. Hatakeyama, S. Hirose, K. Kobashigawa, K. Nakamura, and T. Hatakeyama, *FRI (NZ) Bull.*, **177**, 270 (1992).
15. N. Shiraishi, *Cellulosic Utilization: Research and Rewards in Cellulosics*, H. Inagaki and G. O. Phillips, Eds., Elsevier, London, 1989, p. 97.
16. K. Hirabayashi, M. Yoshioka, Y. Kurimoto, and N. Shiraishi, in *Abstracts of 42th Annual Meeting of Japan Wood Research Society*, Nagoya, 1992, p. 296.
17. N. Shiraishi, M. Yoshioka, and K. Itoh, in *Abstracts of 42th Annual Meeting of Japan Wood Research Society*, Nagoya, 1992, p. 300.
18. S. Pu and N. Shiraishi, *Mokuzai Gakkaishi*, **39**, 446 (1993).
19. L. Lin, M. Yoshioka, Y. Yao, and N. Shiraishi, *J. Appl. Polym. Sci.*, **52**, 1629 (1994).
20. L. Lin, M. Yoshioka, Y. Yao, and N. Shiraishi, *J. Appl. Polym. Sci.*, **55**, 1563 (1995).
21. Y. Uehori, M. Yoshioka, and N. Shiraishi, in *Abstracts of 42th Annual Meeting of Japan Wood Research Society*, Nagoya, 1992, p. 295.
22. Y. Kurimoto, K. Shirakawa, M. Yoshioka, and N. Shiraishi, *FRI (NZ) Bull.*, **176**, 163 (1992).
23. Y. Yao, M. Yoshioka, and N. Shiraishi, *Mokuzai Gakkaishi*, **39**, 930 (1993).
24. Y. Yao, M. Yoshioka, and N. Shiraishi, *Mokuzai Gakkaishi*, **41**, 659 (1995).
25. K. J. Liu and J. L. Parsons, *Macromolecules*, **2**, 529 (1969).
26. B. Bogdanov and M. Mihailov, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 2149 (1985).
27. N. S. Schneider, J. L. Illinger, and F. E. Karasz, *J. Appl. Polym. Sci.*, **47**, 1419 (1993).
28. K. Miki, Jpn. Pat. 2-69536 (1990).
29. K. Miki, Jpn. Pat. 2-47009 (1990).
30. L. L. Wood and K. C. Frisch, U.S. Pat. 3,889,417 (1975).
31. C. E. Garvey, U.S. Pat. 4,731,391 (1988).
32. Y. Yao, M. Yoshioka, and N. Shiraishi, in *Abstracts of 45th Annual Meeting of Japan Wood Research Society*, Tokyo, 1995, p. 287.
33. R. Higashita, K. Shirakawa, M. Yoshioka, and N. Shiraishi, in *Abstracts of 43th Annual Meeting of Japan Wood Research Society*, Morioka, 1993, p. 184.
34. Y. Yao, M. Yoshioka, and N. Shiraishi, *Mokuzai Gakkaishi*, **40**, 176 (1994).
35. K. Nakamura, R. Morck, K. P. Kringstad, and H. Hatakeyama, in *Wood Processing and Utilization*, J. F. Kennedy, G. O. Phillips, and P. A. Williams, Eds., Ellis Horwood, Chichester, 1989, p. 175.
36. L. N. Phillips and D. B. V. Parker, *Polyurethanes Chemistry, Technology and Properties*, Iliffe, London, 1964, p. 34.

Received August 9, 1995
Accepted December 16, 1995