

# Biodegradable Polyurethane Foam from Liquefied Waste Paper and Its Thermal Stability, Biodegradability, and Genotoxicity

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Received 21 December 2000; accepted 25 April 2001

**ABSTRACT:** Liquefaction of waste paper (WP) was conducted in the presence of polyhydric alcohols to prepare biodegradable polyurethane foam. The liquefied-WP-based polyol had suitable characteristics such as apparent molecular weight, hydroxyl value, and viscosity for the preparation of rigid polyurethane foam and was successfully applied to produce polyurethane foam with the appropriate combinations of foaming agents. The obtained foams showed satisfactory densities and mechanical properties as good as those of foams obtained from liquefied wood- and starch-based polyols. The foams had almost the same thermal stability at initial weight loss and seemed to be potentially biodegradable because they were degraded to some extent in leaf mold. There were no mutagens or carcinogens in the water extracts of the foams. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1482–1489, 2002

**Key words:** waste; biodegradable; polyurethane

## INTRODUCTION

Recently, due to increased concerns about the limited availability of fossil resources and the environmental problems derived from the excessive use of fossil fuels, a great deal of effort has been made to develop novel techniques to use biomass efficiently and to derive environmentally friendly materials from biomass. Of these efforts, the liquefaction of biomass in the presence of some organic reagents and its application to the preparation of polymeric materials has attracted considerable attention.<sup>1–3</sup> Two types of liquefaction

have been reported for the use of biomass. The first is performed in the presence of phenols, and the resulting liquefaction products are rich in phenol units and, therefore, can be used to prepare adhesives, moldings, and so on, similar to conventional phenolic resin.<sup>4–8</sup> The second liquefaction method is accomplished in the presence of alcohols, especially polyhydric alcohols, and the resulting products can be used as polyols to prepare polyurethane products.<sup>9,10</sup>

Waste paper (WP) is produced in huge amounts every year and is actively recycled, but it is still incinerated or discarded into the environment. It is necessary to develop new methods to produce more valuable materials from recycled WP. Liquefaction techniques may be useful for this purpose. In this study, polyhydric alcohol liquefac-

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*Journal of Applied Polymer Science*, Vol. 83, 1482–1489 (2002)  
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DOI 10.1002/app.10039

tion, as a new technique for the use of recycled WP, was used to prepare biodegradable polyurethane foam from recycled WP. The thermal stability, biodegradability, and genotoxicity of these foams were also investigated.

## EXPERIMENTAL

### WP and Chemicals

The recycled WP used in this experiment was supplied by Yokohama City, and the wood sample was 20–80 mesh wood meals from birch (*Betula maximowiczii regel*). Poly(ethylene glycol) (PEG400) and glycerol, used together as the liquefaction solvent, were purchased from a commercial source and used without further purification. Diphenylmethane diisocyanate (MDI; Japan Polyurethane Industries Ltd., Osaka, Japan) and silicone surfactant (SH193; Toray Dow Corning Silicone Ltd., Tokyo, Japan) were used for the preparation of polyurethane foam. All other chemicals were reagent grade.

### Liquefaction Procedure and Evaluation of Liquefaction Extent

A mixed solvent of PEG400 and glycerol (4/1 wt %) was used as a liquefaction solvent, and sulfuric acid was used as a catalyst. The solvents and sulfuric acid were premixed thoroughly. Then, the WP (50 g, oven dried) and the premixed solvent (154.5 g), including catalyst, were weighed into a 500-mL three-branched flask. Liquefaction was conducted with constant stirring (200 rpm) and refluxing at 150°C for 30–180 min. The wood, used as a reference, was also liquefied with the same method. The resulting reaction mixture was washed out into a beaker by a mixture of dioxane and water (4/1 v/v). The diluted solution was filtered through Toyo GA100 (Tokyo, Japan) glass filter paper under 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:

$$\begin{aligned} \text{Residue (\%)} \\ = (\text{Weight of residue/Weight of starting WP}) \\ \times 100 \end{aligned}$$

### Characterization of the Liquefied Product

The apparent molecular weights of the liquefied products were determined with a gel permeation

chromatograph (HLC-8020, Tosoh, Tokyo, Japan). Tetrahydrofuran was used as the mobile phase at a flow rate of 1.0 mL/min with 7.0 MPa pressure. The molecular weights were calibrated by the monodisperse polystyrene standards. Unreacted glycerol was calculated from the molecular weight distribution curves as the area ratio of standard glycerol peak and unreacted glycerol peak of the liquefied product.

The viscosity of the liquefied products was measured with a Brookfield viscometer (TOKMEC Inc., Middleboro) at 25°C and 60% relative humidity (RH). The acid amount produced during the liquefaction was measured by the titration method and expressed as the number of milligrams of potassium hydroxide required to neutralize the acid in 1 g of sample. The hydroxyl number was 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 JIS K1557 standard.

### Preparation of Polyurethane Foam

The liquefied waste paper (LWP) was directly used to prepare polyurethane foams by reaction with diisocyanate. Thus, definite amounts of LWP, catalyst, surfactant, and water were premixed thoroughly in a paper cup. Then, a certain amount of diisocyanate was added. The combination was then mixed with a rapid agitator (8000 rpm) for 10 s. The resulting mixture was poured immediately into a 12 × 12 × 10 cm box and was allowed to rise at room temperature. The obtained foams were allowed to cure at room temperature for 1 h before being removed from the box. The isocyanate index was calculated as follows:

#### Isocyanate index

$$= \{(M_{\text{MDI}} \times W_{\text{MDI}})/(M_{\text{LWP}} \times W_{\text{LWP}} + W_w)\} \times 100$$

where  $M_{\text{MDI}}$  is the number of moles of isocyanate groups per gram of MDI,  $W_{\text{MDI}}$  is the weight of MDI (g),  $M_{\text{LWP}}$  is the number of moles of hydroxyl groups per gram of LWP,  $W_{\text{LWP}}$  is the weight of LWP (g), and  $W_w$  is the weight of water in the foam formulation (g). The hydroxyl groups in the surfactant and catalysts were not taken into account.

## Mechanical Properties

Measurements of mechanical properties of the foams were based on the JIS K7220 standard. The foams were cut into  $50 \times 50 \times 50$  mm specimens. The specimens were conditioned for 48 h at  $20^\circ\text{C}$  and 60% RH; then, density was determined with the dimensions and weights of the specimens. The measurements were conducted with a Shimadzu Autograph AGS-5kNG (Kyoto, Japan) in the direction perpendicular to the foam rise.

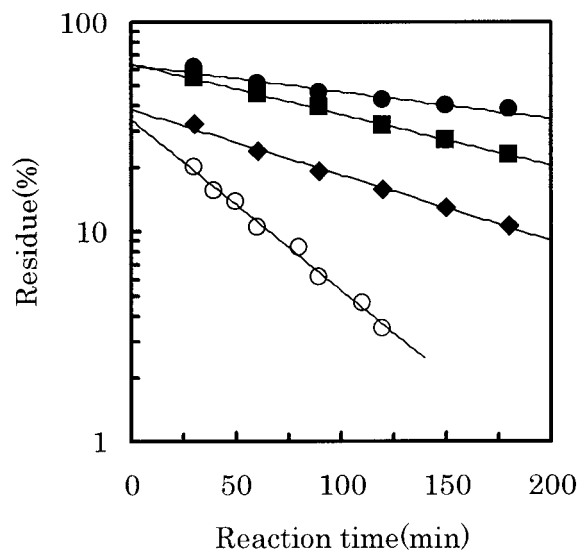
## Thermogravimetric Analysis (TGA)

A thermal gravimetric analyzer (TA instrument TGA 2950, New Castle, DE) was used to measure the thermal degradation of the foams. We obtained powder from the foam by freezing crushing the foam under liquid nitrogen with Cryogenic Sample Crusher JFC-300 (Japan Analytical Industry Co., Ltd., Tokyo, Japan). The foam powder was put into an aluminum capsule and located automatically in the TGA instrument. We conducted degradation under an air atmosphere by increasing the temperature from  $30$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## Umu Test Procedure

The powder from the foam (0.5 g) was extracted with 5 mL of distilled water at  $100^\circ\text{C}$  for 15 min and at 65, 40, and  $28^\circ\text{C}$  for 24 h, respectively. After extraction, each supernatant was concentrated by freeze drying. The test samples were obtained by the addition of 10% dimethyl sulfoxide (DMSO) solution to the dried supernatants and subjected to umu testing.

The umu test was conducted three times with an umu test kit (Japan Immunoresearch Laboratories Co. Ltd., Takasaki, Gunma, Japan), which included the bacterial strain (*S. typhimurium* TA1535/pSK1002), culture solution, S-9 mix, and so on. The culture solution (1 mL) was added to the bacterial strain, and the mixture was incubated at  $37^\circ\text{C}$  for 3 h. The bacterial culture was subdivided into 0.1-mL portions in test wells, and 0.01 mL of the test sample was added to each well. Then, S-9 Mix containing 0.1 mL of distilled water was added to estimate the genotoxic potential by metabolic activation. After 2 h of incubation at  $37^\circ\text{C}$ , the  $\beta$ -galactosidase solution (0.1 mL) was added to each well and then incubated at  $37^\circ\text{C}$  for 1 h. The reaction was stopped by the addition of DMSO solution (0.1 mL) of sodium



**Figure 1** Liquefaction of (●) BP, (■) BNP, (□) NP, and (○) wood (reaction temperature =  $150^\circ\text{C}$ , catalyst concentration = 3%).

dodecyl sulfate, and the absorbance at 625 nm ( $\text{OD}_{625}$ ) of the mixture was measured.

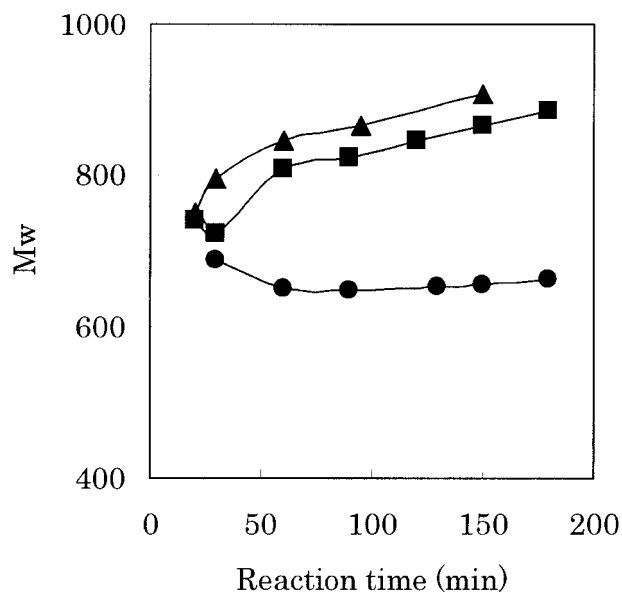
## RESULTS AND DISCUSSION

### Liquefaction of WP

Fundamental studies of liquefaction behavior were conducted with three kinds of WP and wood as references, and the results are summarized in Figure 1. Liquefaction of all materials progressed according to pseudo first-order kinetics, and there were differences in the slopes among them. We reported previously that the differences in liquefaction behavior of WPs are due to their different chemical compositions.<sup>11</sup> That is, newspaper (NP) with high lignin content can be readily liquefied, whereas box paper (BP) and business paper (BNP) are difficult to liquefy because of their high cellulose content. Yao et al. also reported that the rapid liquefaction stage was mainly dependent on the components of lignin and hemicellulose, whereas cellulose mainly affected the slow liquefaction stage in which the residue slowly decreased.<sup>3</sup>

### Characteristics of LWP-Based Polyol

Changes in the apparent molecular weights of liquefied BP, NP, and wood versus reaction time

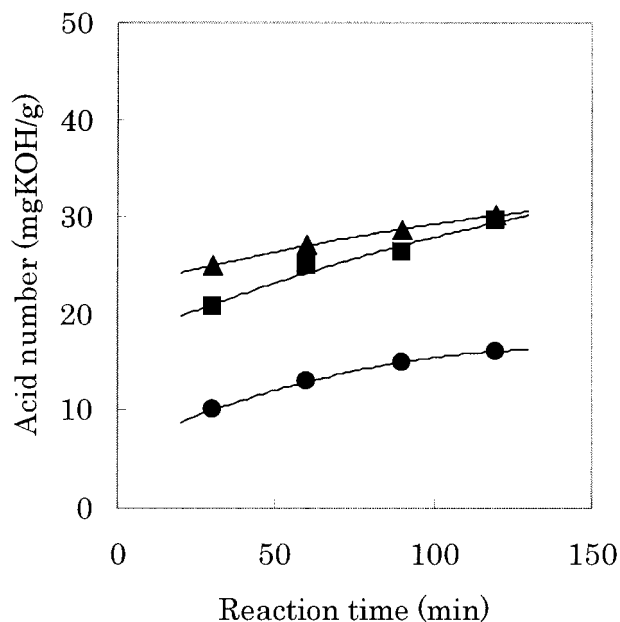


**Figure 2** Effects of reaction time on the apparent molecular weight of liquefied (●) BP, (■) NP, and (▲) wood.

are plotted in Figure 2. The apparent molecular weight of liquefied BP remained relatively constant irrespective of reaction time, whereas the molecular weights of liquefied NP and wood increased with increasing reaction time. This increase in apparent molecular weight during liquefaction was probably due to the recondensation reaction of decomposed components. Decomposed lignin plays a major role in the recondensation reaction during liquefaction.<sup>3</sup> Accordingly, because NP and wood have higher lignin contents than BP, the recondensation reaction of liquefied NP and wood might occur readily, which would result in an increase in the apparent molecular weight.

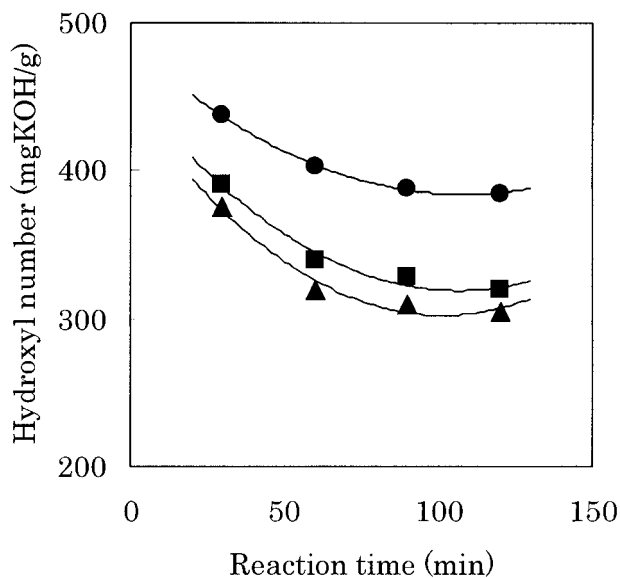
Acid and hydroxyl numbers, which are the important variables in the preparation of polyurethane foam, were determined as estimates of polyol values. Figure 3 shows variations in the acid numbers of LWP- and wood-based polyols as a function of reaction time. The acid numbers of all samples increased as the liquefaction time increased. Acidic substances can be produced by the thermal oxidation of carbohydrates and lignin during the liquefaction of lignocellulosic materials.<sup>10</sup> Likewise, the increase in acid numbers in this study also indicate the generation of acidic substances during liquefaction.

On the other hand, the hydroxyl number decreased with increasing reaction time, as shown

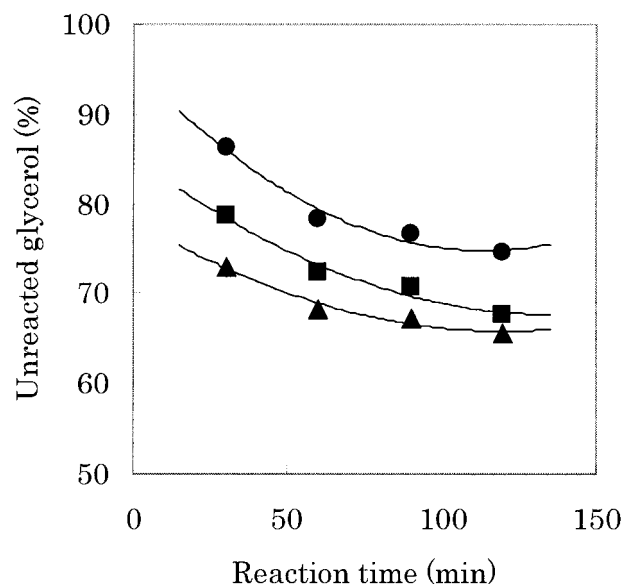


**Figure 3** Acid number of LWP-based polyol as a function of reaction time: (●) BP, (■) NP, and (▲) wood.

in Figure 4. The reduction of hydroxyl number was thought to be caused either by dehydration reactions between liquefied products and polyhydric alcohols or by thermal oxidation that may also occur during liquefaction.<sup>9</sup> Yamada et al. also reported that alcohol-D-glycosides were produced by alcoholysis between polysaccharides and some



**Figure 4** Hydroxyl number of LWP-based polyol as a function of reaction time: (●) BP, (■) NP, and (▲) wood.



**Figure 5** Unreacted glycerol content of LWP-based polyol as a function of reaction time: (●) BP, (■) NP, and (▲) wood.

alcohols under the same reaction conditions as used in this study.<sup>12</sup> The same condensation reaction may have taken place in this experiment and reduced the hydroxyl numbers of liquefied products. This suggestion is also supported by the observation that the amount of unreacted glycerol decreased with increasing reaction time, and this decrease showed a good correlation with the decrease in hydroxyl number, as shown in Figure 5. The decrease in hydroxyl number may also have been due to dehydration and thermal oxidative degradation of the polyhydric alcohols alone, but the effects of these reactions were small under the conditions used in this study (data are not shown). Absolute hydroxyl numbers of the liquefied NP- and wood-based polyols were less than those of liquefied BP-based polyol. This difference

**Table I** Properties of LWP-Based Polyols Used for Preparation of Foam

Sample	Hydroxyl Number (mg of KOH/g)	Acid Number (mg of KOH/g)	Viscosity (mPa s)
BP	385	19.0	3810
BNP	396	19.3	3899
NP	336	29.7	2609

**Table II** Combinations of Foaming Agents for Preparation of Foam

Agent	Combination
LWP-Based Polyol	100
Surfactant (SH-193)	0.5–3
Catalyst (DBTDL, TEDA, DT, ETS)	0.5–3
Blowing agent (water)	1–4
MDI (isocyanate index 105)	129–178

DBTL = dibutyltindilaurate; TEDA = triethylenediamine; DT = *N,N,N',N',N''*-pentamethyl diethylene triamine; ETS = bis(2-dimethylaminoethyl)ether.

suggested that the lignin of NP and wood increased reactivity toward polyhydric alcohols.

The properties of the LWP-based polyols used for foaming are summarized in Table I. The ranges for hydroxyl number, acid number, and viscosity were from 336 to 385 mg KOH/g, 19 to 29.7, and 2609 to 3899 mPa s, respectively. These values were regarded as feasible for the preparation of rigid polyurethane foam.

### Preparation of Foam

Foaming was conducted with a combination of foaming agents, as shown in Table II. Surfactant was added from 0.5 to 3% to lower the surface tension of the LWP-based polyol/diisocyanate blend. Too little surfactant fails to stabilize the foam and too much causes the cells to congeal and collapse. Amounts of surfactant added in this study were considered to be suitable because the obtained foams did not show either congealing or collapse. The suitable quantity of catalysts was from 0.5 to 3%, depending on the density and the foaming reaction rates, such as gelling and rising time. Gelling and blowing activities of the catalysts used in this study are summarized in Table III. Water as a blowing agent was added from 1 to 4% to control the density of the resulting foams.

As shown in Table IV, foams with a wide range of properties were obtained from the LWP-based polyols, depending on the compositions of foaming agents. The densities and compressive strengths at 10 and 25% strain were in the range of 35.5–50.6 ( $\times 10^{-3}$  g/cm<sup>3</sup>), 68–195 KPa, and 130–286 KPa, respectively. The densities were somewhat higher and compressive strengths were compared to those from liquefied wood- and starch-based polyols. Elastic moduli were from 0.8 to 3.4 MPa, showing that these foams were somewhat softer than those obtained from wood and starch.



**Table III Gelling and Blowing Activities of Catalysts Used in this Study**

Abbreviation	Name	Gelling Activity (l <sup>2</sup> /g mol h) × 10	Blowing Activity (l <sup>2</sup> /g mol h) × 10	Blowing/Gelling Ratio × 10 <sup>-1</sup>
DBTDL	Dibutyltindilaurate	14.4	0.48	0.30
TEDA	Triethylenediamine	10.9	1.45	1.34
DT	<i>N,N,N',N'',N'''</i> -Pentamethyl diethylene triamine	4.26	15.9	37.3
ETS	Bis(2-dimethylaminoethyl)ether	2.99	11.7	39.0

### Thermal Stability

The thermogravimetric curves of the foams from LWP-based polyols are shown in Figure 6. The shapes of the weight loss curves of all samples were almost identical, and initial weight losses were similar, suggesting that degradation started at the urethane bond. Urethanes are known to be relatively thermally unstable materials, primarily due to the presence of urethane bonds. The onset of urethane bond decomposition occurs somewhere between 150 and 220°C, depending on the type of substituents on the isocyanate and polyol side.<sup>13,14</sup>

Although the early stage is dominated by urethane bond decomposition, the polyol component may contribute to weight loss at higher temperatures. When measured by 70% weight loss temperature, liquefied BP polyol-based foam showed the highest thermal stability and then liquefied BNP polyol-based foam, followed by liquefied NP polyol-based foam. This result was considered to be due to the differences in the ash content among the LWP-based polyols. That is, the ash contents of BP, BNP, and NP were 13.3, 5.5, and 3.8%, respectively.

If the onset of degradation or weight loss below 50% was taken as the criterion of stability, the foams produced from LWP-based polyols had almost the same thermal stability.

### Biodegradability

Three foams prepared from liquefied BP- and NP-based polyols and only polyhydric polyols were buried in leaf mold at 30°C and 80% RH for 6 months. As shown in Figure 7, the weight loss of the two foams prepared from LWP-based polyols increased with increasing period of soil-microbial treatment. These foams also showed faster weight loss than that containing polyhydric polyols alone. These results indicate that the biomass component contributed mainly to the biodegradability of the foams.

### Genotoxicity

Early warning systems of environmental hazards have become more important in recent years. Concern has been growing about potential adverse effects of genotoxins on public health. The umu test, which was developed for the detection of chemical mutagens and carcinogens,<sup>15-18</sup> was conducted to estimate the genotoxic potential in water extracts of the foams from LWP-based polyols. The results are summarized in Table V. All samples showed negative values in both the presence and absence of the S9 fraction, indicating that there were no mutagens or carcinogens in the water extracts of the foams.

**Table IV Properties of the Foams from LWP-Based Polyols and Liquefied Wood- and Starch-Based Polyols**

Property	BP	BNP	NP	Wood and Starch
Density (×10 <sup>-3</sup> g/cm <sup>3</sup> )	36–51	42–50	37–47	28–40
Compressive strength (KPa) at 10% strain	82–195	87–189	68–110	84–145
Compressive strength (KPa) at 25% strain	130–286	152–272	130–163	—
Elastic modulus (MPa)	1.1–3.0	1.3–3.4	0.8–1.7	3.7–10.1

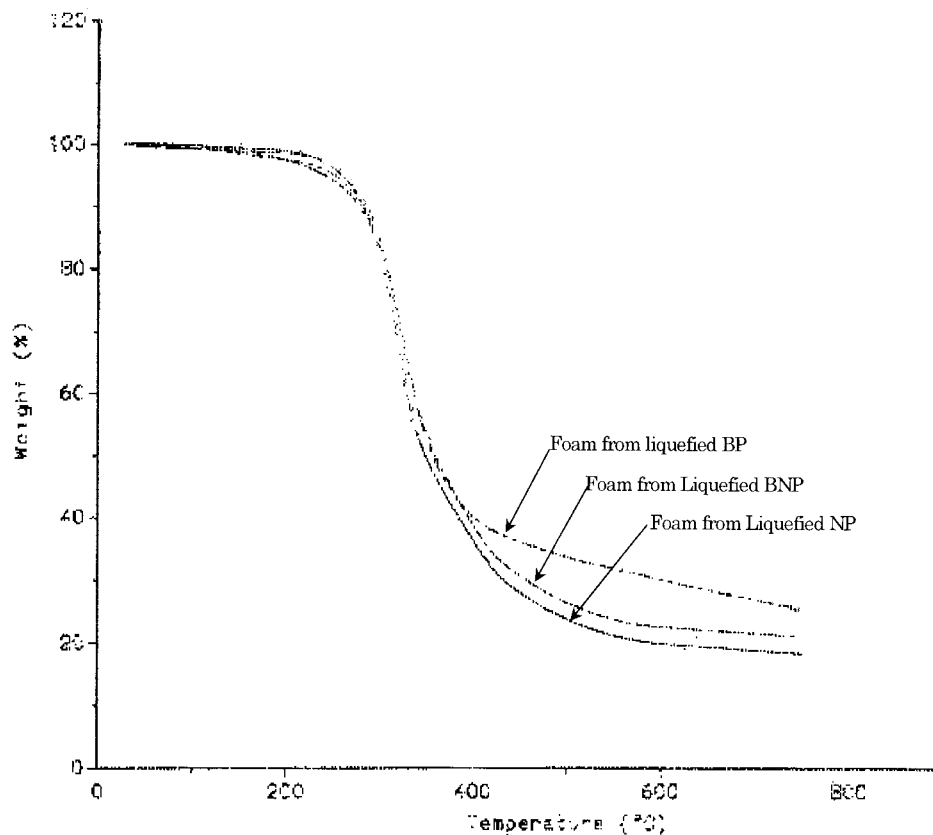


Figure 6 TGA curves of the foams from LWP-based polyols.

## CONCLUSIONS

Polyols were obtained by liquefaction of WP in the presence of polyhydric alcohols. The LWP-based polyols had suitable characteristics for the preparation of polyurethane foams and were successfully applied to produce polyurethane foams with appropriate combinations of foaming agents. These foams showed satisfactory densities and mechanical properties as good as those of foams obtained from liquefied wood- and starch-based polyols. The foams withstood heating at 200°C without significant degradation and had almost the same thermal stability at initial weight loss (0–50%). The foams were biodegradable to some extent because they were degraded by about 20% when buried in leaf mold for 6 months. The results of the umu test showed that there were no mutagens or carcinogens in the water extracts of the foams.

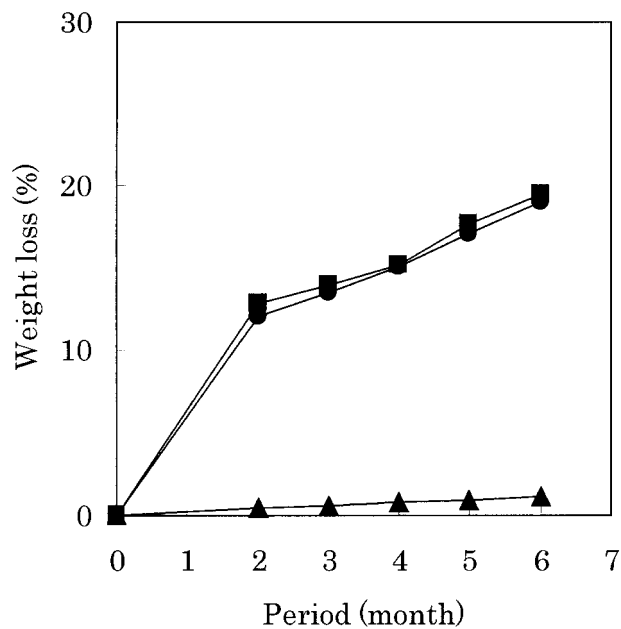


Figure 7 Effects of buried period on weight loss of the foams from LWP-based polyols: (●) BP, (■) NP, and (▲) only polyol (PEG400 and glycerol).

**Table V Genotoxicity in Water Extract of the Foams from LWP-Based Polyols**

Sample			Extracts at 28°C	Extracts at 40°C	Extracts at 65°C	Extracts at 100°C
BP	S9 <sup>a</sup>	(-)	-	-	-	-
		(+)	-	-	-	-
BNP	S9	(-)	-	-	-	-
		(+)	-	-	-	-
NP	S9	(-)	-	-	-	-
		(+)	-	-	-	-
AF2			+ (positive control)			
2AA + S9			+ (positive control for S9)			

<sup>a</sup> In the presence (+) or absence (-) of the S9 fraction.

## REFERENCES

- Shiraishi, N. Cellulosic Utilization, Research and Rewards in Cellulosics; Elsevier: London, 1989.
- Shiraishi, N. Cellul Commun 1998, 5, 2.
- Yao, Y.; Yoshioka, M.; Shiraishi, N.; Mokuzai Gakkaishi 1993, 39, 930.
- Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. Holzforschung 1996, 50, 85.
- Maldas, M.; Shiraishi, N. Int J Polym Mater 1996, 33, 61.
- Lee, S. H.; Yoshioka, M.; Shiraishi, N. J Appl Polym Sci 2000, 78, 311.
- Lee, S. H.; Yoshioka, M.; Shiraishi, N. J Appl Polym Sci 2000, 78, 319.
- Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. J Appl Polym Sci 1994, 52, 1629.
- Yao, Y.; Yoshioka, M.; Shiraishi, N. Mokuzai Gakkaishi 1995, 41, 659.
- Kurimoto, Y.; Doi, S.; Tamura, Y. Holzforschung 1999, 53, 617.
- Lee, S. H.; Teramoto, Y.; Shiraishi, N. J Appl Polym Sci 2001, 82.
- Yamada, T.; Ohara, S.; Kato, A.; Ono, H. The 40th Anniversary Conference of the JWRS; Springer: Germany, 1995; p 289 (in Japanese).
- Wieweg, R.; Hchtlen, A. Polyurethane in Kunststoff-Handbuch; Carl Hanser Verlag: Munchen, Germany, 1966; band VII.
- Wirpsza, Z. Polyurethanes, Chemistry, Technology and Application; Horwood: New York, 1993.
- Oda, Y.; Nakamura, S.; Oki, I.; Kato, T.; Shinagawa, H. Mutat Res 1985, 147, 219.
- Reifferscheid, G.; Heil, J.; Oda, Y.; Zahn, R. K. Mutat Res 1991, 253, 215.
- Hans, H. V.; Karbe, L.; Westendorf, J. Mutat Res 1997, 394, 81.
- Oda, Y.; Nakamura, S.; Oki, J.; Kato, T. Mutat Res 1985, 147, 219.