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## Durability of Polyurethane Films from Liquefied Woods

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### Abstract

The resistance of polyurethane (PU) films prepared from liquefied wood (LW) to hydrolysis, and deionized water, acidic solution or basic solution was tested. PU films with different amounts of dissolved woody components (DWC-PU, 0-18.2%), which were prepared from LWs of sugi (*Cryptomeria japonica* D. Don) wood at isocyanate to hydroxyl group ratios (NCO/OH) of 1.0 and 1.2, were aged at 100% relative humidity (RH) and 60°C or 80°C. The chemical resistance of the PU films with a ratio of 1.0 was tested at 20°C for one week. In hydrolytic stability tests, increases in the ageing period significantly increased the weight losses of PU films prepared from LWs at both NCO/OH. This was due to the substances unincorporated into the network structures rather than the degradation of polymer chains. The mechanical properties (tensile strength and maximum elongation) of PU films prepared from LWs were more resistant to hydrolysis than those without woody components since fewer changes were observed in the films (DWC-PU, 12.3%, 16.6%) with a NCO/OH of 1.2 even at 80°C and 100% RH. At a NCO/OH of 1.0, the rigid mechanical properties of the PU film with 18.2% DWC-PU increased after the hydrolytic stability tests at both temperature levels. This was due to the large amounts of substances unincorporated into the network structures. The unincorporated substances acted as a plasticizer. The increase in DWC-PU increased the weight loss after ageing in deionized water, acidic (10% H<sub>2</sub>SO<sub>4</sub>) or basic (10% NaOH) solution because of the unincorporated substances. Especially, the basic solution caused the large weight loss of PU film. This is probably due to the swelling effect of alkali on the woody components in PU film.

*Key words:* wood liquefaction, sugi, *Cryptomeria japonica*, polyurethane, hydrolysis

### Introduction

The liquefaction of wood materials using polyols aims to utilize wood waste as polyurethane (PU) resins (Shiraishi 1993, Kurimoto *et al.* 1992, Yao *et al.* 1993, Yao *et al.* 1995, Yao *et al.* 1996). We have reported procedures to prepare PU films from liquefied wood (LW), and elucidated the role of dissolved woody components in PU network structures. Results of FT-IR analyses showed that co-polymerization of LW and polymeric diphenylmethane diisocyanate (PMDI) contributed to the formation of three-dimensional networks (Kurimoto *et al.* 2000). The mechanical properties (Young's modulus, tensile strength and elongation) and crosslink density of PU films made from LW were controlled by an isocyanate to hydroxyl group ratio (NCO/OH) as in common urethane products (Kurimoto *et al.* 2000, Kurimoto *et al.* 2001). In addition, changing the amount of dissolved woody components in PU film (DWC-PU) is a way to control the factors at a constant NCO/OH. Notably, the increase of DWC-PU enhanced the rigid

mechanical properties of PU films without the extension of isocyanate-charge since the dissolved woody components acted as hard segments. Thermal degradation experiments under a N<sub>2</sub> atmosphere showed that PU films with larger DWC-PU had greater thermal resistance to heat than PU films without the woody components (Kurimoto *et al.* 2001). These results will be adopted to establish effective material formulations for preparing PU products from LW according to desired mechanical properties and conditions in use.

The resistance of PU to hydrolytic or microbial attack is also an important factor that affects its application. The degradation of polymer chains causes a decrease in mechanical properties and leads to failure in use. The degradation process is largely promoted by external factors, such as hot water, saturated steam, warm and moist climates, acidic or basic media, additives, chemicals, etc.

The objective of this paper is to clarify the durability of PU films made from LWs at elevated temperatures (60, 80°C) and a saturated (100%)

humidity. PU films with different DWC-PU were prepared from LWs of sugi (*Cryptomeria japonica* D. Don) wood and PMDI at a NCO/OH of 1.0 and 1.2. The Weight loss and change in mechanical properties of the PU films were measured after aging.

## Materials and Methods

### Materials and chemicals

Sugi wood was ground and passed through a 1 mm screen using a Wiley mill. The fractions passing 1000 $\mu$ m and retained on 106 $\mu$ m mesh screens were used for the liquefaction. Glycerol and PEG400 (polyethylene glycol, average molecular weight, 400) obtained from Wako Pure Chemical Industries (Osaka, Japan) were used as the reaction reagents. Sulfuric acid of extra pure grade was used as the catalyst for liquefaction. MR-100 (Japan Polyurethane Industry Ltd.) with a NCO group content of 7.43 mmol/g was used as the PMDI. All other chemicals used were extra pure grade reagents in accordance with Japanese Industrial Standards and used as received.

### Preparation of liquefied wood (LW)

LWs were prepared according to a procedure shown in Fig. 1. Thirty grams of oven-dried wood flour and 61.8 g or 92.7 g of liquefaction solvent were charged into a 500 ml separable flask and heated under reflux for 75 min at 150 $^{\circ}$ C with continuous stirring. The composition of the liquefaction solvent, i. e., glycerol:PEG400:sulfuric acid, was kept constant at 10:90:3. The liquefaction products were then diluted with ten times their weight of a dioxane-water mixture (80/20, v/v) and the unliquefied wood residues in the solution were

filtered using a PTFE membrane-filter (TOYO H050A047A, pore size 0.50 $\mu$ m). The apparent pH of the filtrate after removing the unliquefied wood residues was adjusted to 5.5 with 1 N sodium hydroxide solution (Kurimoto *et al.* 2000). The sodium sulfate formed by the reaction between the sulfuric acid and the sodium hydroxide was removed using the membrane-filter. Finally, dioxane and water in the filtrate were evaporated under reduced pressure until the moisture content was approximately 0.7%. The weight percentage of dissolved woody components (DWC) in LW was defined by the following equation:

$$\text{DWC} = \frac{W_w - W_U}{W_w - W_U + W_G + W_P} \times 100 \quad (1)$$

where  $W_w$ ,  $W_U$ ,  $W_G$  and  $W_P$  are the weights of wood sample before liquefaction, unliquefied wood residue, glycerol and PEG400, respectively (g).

### Characteristics measurements of LWs

Hydroxyl numbers were determined as described in our earlier investigation (Kurimoto *et al.* 1999). One gram of each LW was esterified for 20 min at 110 $^{\circ}$ C with 25 ml of a phthalation reagent, a mixture of 150 g phthalic anhydride, 24.2 g imidazol, and 1000 g dioxane. After that, the excess reagent was titrated with 1 N sodium hydroxide solution. The hydroxyl number was calculated from the difference in titration between the blank and sample solutions.

Acid numbers were determined as follows: eight grams of LW sample was dissolved in a mixture of 80 ml of dioxane and 20 ml of water. The resulting

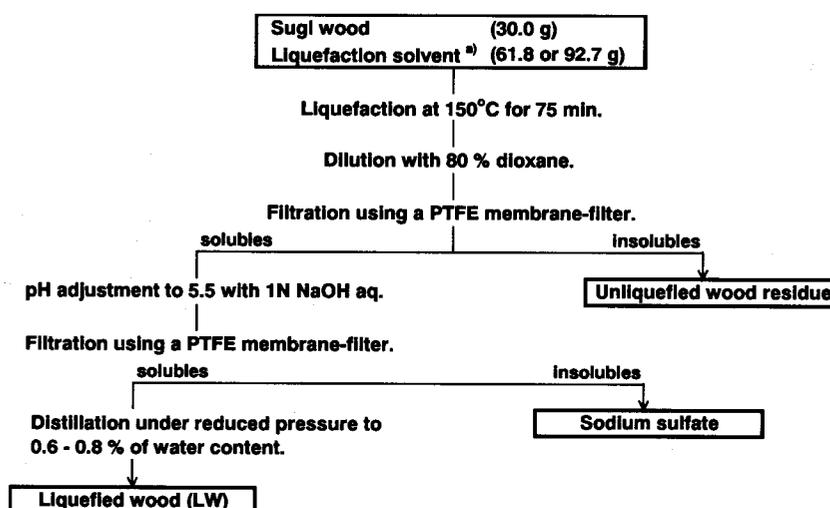


Fig. 1. Procedure used for the preparation of liquefied wood (LW).

<sup>a)</sup> Weight ratio of glycerol:PEG400:sulfuric acid = 10:90:3.

solution was titrated at room temperature with 1 N sodium hydroxide solution. The acid number was calculated from the difference in titration between the blank and sample solutions.

The moisture content was determined by the Karl Fischer method using a moisture content meter (Kyoto Electronics Ltd. MKS-210 model, Kyoto, Japan).

The viscosity at 25 °C was measured using a Brookfield viscometer (Brookfield Engineering Labs. Inc., HAT model, Stoughton, Massachusetts, USA). Optimum spindle and rotational frequency were selected according to JIS K 1557.

### Preparation of PU films

Ten grams of LW dissolved in 10 ml of dichloromethane was mixed with the PMDI in a 100 ml polypropylene cup. The mixture was agitated at 1200 - 1400 rpm for 10 min at room temperature for co-polymerization without a catalyst and/or surfactant. The polymerized mixtures were poured into Petri dishes (diameter, 90mm) for solution-casting to obtain 0.25 mm-thick films. The PU films were gradually dried in a refrigerator below 7 °C for 3 days and were cured for 11 days at 20 °C and 65% relative humidity (RH). Finally, the films were heated at 100 °C for 8 hours in an oven. The NCO to OH ratio and the weight percentage of dissolved woody components in PU film (DWC-PU) are given as follows:

$$\text{NCO/OH} = \frac{M_{\text{MDI}} \times W_{\text{MDI}}}{M_{\text{Poly}} \times W_{\text{Poly}} + W_{\text{Water}} \times 2/18 \times 1000} \quad (2)$$

$$\text{DWC - PU} = \frac{W_{\text{Poly}} \times \text{weight ratio of DWC}}{W_{\text{Poly}} + W_{\text{MDI}}} \quad (3)$$

where  $M_{\text{MDI}}$  is the content of the isocyanate group in PMDI (7.43 mmol/g),  $M_{\text{Poly}}$  is the content of the hydroxyl group in LW (hydroxyl number  $\div$  56.1, mmol/g), and  $W_{\text{MDI}}$ ,  $W_{\text{Poly}}$  and  $W_{\text{Water}}$  are the weights of PMDI, LW, and the water included in LW, respectively (g).

PU films were cut using a steel cutting-die before hydrolytic stability and chemical resistance testing. The shape and dimension of the specimen are shown in Fig. 2.

### Hydrolytic stability tests

Exposure to humidity was carried out in a 10-liter glass vessel with a stop cock. Twenty five replicates of vacuum-dried PU films and deionized water (100 ml) were separately placed in the glass vessel, and the whole vessel was then heated in an oven at 60 °C or 80 °C. The RH in the vessel reached 100% within 6h. Five replicates were taken out from the vessel after defined periods, i. e., 7, 21, 35, 56 and 84 days. The films taken out were dried in vacuum at 60 °C, and

re-weighed. Weight loss of the film was calculated using the following equation:

$$\text{Weight loss} = \frac{(W_0 - W_D)}{W_0} \times 100 \quad (4)$$

where  $W_0$  and  $W_D$  are the weight of PU film before and after tests (g).

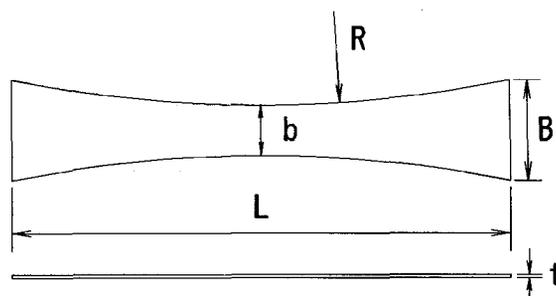


Fig. 2. Shape and dimensions of PU film for mechanical property tests. Note:  $L=40$ ,  $B=8$ ,  $b=4$ ,  $t=0.25$ ,  $R=101$  (unit: mm).

### Tensile tests

Tensile tests were carried out at 20 °C and 65% RH using an universal testing machine, Minebea Co., Ltd. AL-5kN model (Tokyo, Japan). PU films were conditioned for 48 hours before the test.

Films were loaded at 10 mm/min on the movable crosshead. The initial distance between clamps was 30 mm. Five replicates were tested for each condition. Tensile strength ( $TS$ ) was calculated from the tensile ultimate force on the basis of initial sample dimensions (see Fig. 2):

$$TS = \frac{P_{\text{max}}}{b \times t} \quad (5)$$

where  $TS$  is the tensile strength (Pa),  $P_{\text{max}}$  is the maximum force applied to the film (N),  $b$  and  $t$  are the minimum breadth and thickness of the arc-shaped PU film, respectively (mm).

Maximum elongation ( $ME$ ) was taken from the displacement between clamps at failure. Young's modulus could not be evaluated in the present investigation, because the shapes of cross sections of some PU films were changed by the hydrolytic stability test.

### Differential scanning calorimetry (DSC)

Glass transition temperatures ( $T_g$ ) of PU films before and after the hydrolytic stability test were measured using a differential scanning calorimeter (MAC Science Co., Ltd. DSC 3100S model, Tokyo, Japan). A 7 - 10 mg sample was first scanned to 100 °C in order to eliminate the effect of enthalpy

relaxation (Rials and Glasser 1984, Yoshida *et al.* 1990), thereafter cooled to  $-50^{\circ}\text{C}$  and scanned again to  $100^{\circ}\text{C}$ . All scans were carried out under a dry nitrogen flow of 50 ml/min at a heating or cooling rate of  $10^{\circ}\text{C}/\text{min}$ .  $T_g$  in the second scan was defined as one-half the total change in heat capacity ( $C_p$ ) occurring over the transition region.

#### Chemical resistance tests

Deionized water, a 10%  $\text{H}_2\text{SO}_4$  solution and a 10% NaOH solution were used. Five replicates of vacuum-dried PU films were immersed in the deionized water or the chemicals for 7 days at  $20^{\circ}\text{C}$ . The films were then dried in a vacuum at  $60^{\circ}\text{C}$ , and re-weighed. The films exposed to 10%  $\text{H}_2\text{SO}_4$  and 10% NaOH were rinsed with deionized water until the washing solutions changed to neutral. The weight loss of the film was calculated using Eq. (4).

Table 1. Characteristics of LWs and GP

Polyol	DWC <sup>a)</sup> (%)	Hydroxyl number (mg KOH/g)	Moisture Content (%)	Acid number (mg KOH/g)	Viscosity (Pa·s at $25^{\circ}\text{C}$ )
LW-31	31.3	259.9	0.71	19.0	31.1
LW-24	24.2	282.9	0.75	19.7	2.1
GP <sup>b)</sup>	0	435.2	0.21	0	0.18

<sup>a)</sup> weight percentage of dissolved woody components in LW.

<sup>b)</sup> glycerol-PEG400 cosolvent as a control, weight ratio of glycerol:PEG400 was 1:9.

Table 2. Formulations, glass transition temperatures ( $T_g$ ) and mechanical properties of PU films with a NCO/OH of 1.0 and 1.2

PU film	Formulation (%)		DWC-PU <sup>b)</sup> (%)	$T_g$ ( $^{\circ}\text{C}$ )	Tensile strength (MPa)		Maximum elongation (mm)		
	LW <sup>a)</sup>	PMDI			Mean	SD <sup>c)</sup>	Mean	SD <sup>c)</sup>	
NCO/OH = 1.0									
PU1	LW-31	58.1	41.9	18.2	29	29.2	2.5	23.0	2.2
PU2	LW-24	55.4	44.6	14.7	28	39.2	1.7	32.0	1.7
PU3	GP <sup>d)</sup>	47.8	52.2	0	32	38.5	1.9	40.3	2.7
NCO/OH = 1.2									
PU4	LW-31	52.9	47.1	16.6	46	70.1	2.0	1.7	0.1
PU5	LW-24	50.9	49.1	12.3	46	70.0	2.4	1.9	0.2
PU6	GP <sup>d)</sup>	43.3	56.7	0	48	65.8	1.3	2.0	0.3

<sup>a)</sup> see Table 1.

<sup>b)</sup> weight percentages of dissolved woody components in PU film.

<sup>c)</sup> standard deviation.

<sup>d)</sup> glycerol-PEG400 cosolvent as a control.

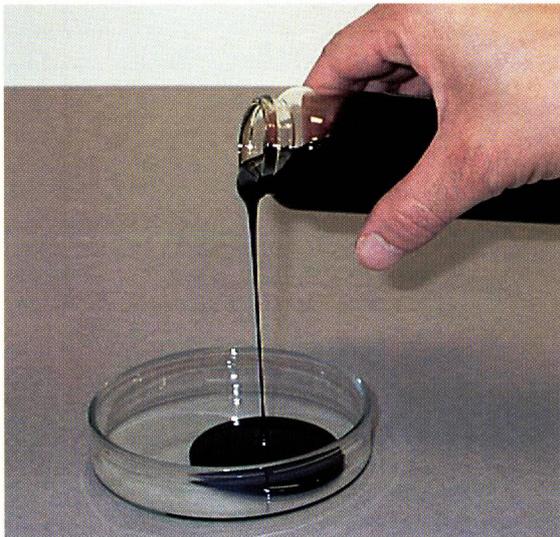


Fig. 3. Appearance of LW-24 DWC=24.2%).

## Results and Discussion

### Characteristics of PU films before the tests

Polyols of widely different types were used for the production of PU films. The characteristics of LWs and GP (glycerol-PEG400 co-solvent as a control) are summarized in Table 1. The appearance of LW-24 is shown in Fig. 3. LW-31 and LW-24 contained 31.3% and 24.2% DWC, respectively, whereas GP had no woody components. The hydroxyl number of LWs decreased from 435.2 mg KOH/g to 259.9 mg KOH/g with the increase in DWC from 0% to 31.3%. The viscosity at 25°C markedly increased from 0.18 Pa·s to 31.1 Pa·s. The reason for this is the increase in the amount of LW fragments having partially degraded woody components (Kurimoto *et al.* 2000).

The characteristics of PU films (PU1 ~ PU6) prepared from the above mentioned LWs and GP with a NCO/OH of 1.0 and 1.2 are shown in Table 2. Fig. 4 shows the appearance of PU films with the ratio of 1.0. All the PU films obtained were transparent and appeared to be homogeneous. No gel particles or bubble formations were observed in the films.

The mechanical properties and  $T_g$  of PU films (PU1, PU2 and PU3) at a NCO/OH of 1.0 varied depending on the DWC-PU. When the DWC-PU increased from 0% to 18.2%, the maximum elongation largely decreased from 40.3 mm to 23.0 mm. In addition, the tensile strength of PU1 was less than that of the others (PU2 and PU3). These results could be attributed to the dissolved woody components in PU film. They acted as a hardener in PU-networks (Kurimoto *et al.* 2000). No significant differences were observed in the mechanical properties and  $T_g$  of PU films (PU4, PU5 and PU6) with a NCO/OH of 1.2.

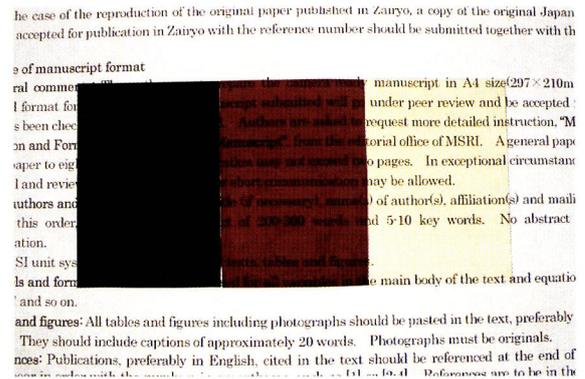


Fig. 4. Appearance of PU films with different amounts of dissolved woody components (DWC-PU) at a NCO/OH of 1.0. left: PU1, 18.2%; center: PU2, 14.7%; right: PU3, 0%.

### Weight loss of PU films after the hydrolytic stability tests

Weight losses of PU films with a NCO/OH of 1.0 after the hydrolytic stability test at 60°C and 100% RH are shown in Fig. 5. No significant weight loss of PU3 (0% DWC-PU, control) was observed. In contrast, increases in the aging time increased the weight losses of PU1 (18.2% DWC-PU) and PU2 (14.7% DWC-PU), reaching 6.6% and 3.0% after 84 days, respectively. The increase in weight loss of PU1 was larger than that of PU2 all through the aging experiment. This was probably due to the higher DWC-PU of PU1 compared to PU2. At 18.2% DWC-PU, the weight losses of PU1 were largely increased as shown in Fig. 6.

The weight losses of PU1, PU2 and PU3 during the hydrolytic stability test at 80°C and 100% RH are shown in Fig. 7. The elevated temperature accelerated the weight losses of PU films. For PU3, the loss began to increase after 35 days, and reached 2.5% after 84 days, being 13 times greater than that at 60°C and 100% RH. The weight losses of PU1 and PU2 were approximately twice than those at 60°C and 100% RH in any aging period (Fig. 5 vs Fig. 7). The weight losses of PU1 and PU2 after 84 days reached 11.8% and 7.2%, respectively.

The effect of the NCO to OH ratio on the weight losses of PU films was examined at 80°C and 100% RH. The amount of hard segments improves the material's performance even at an elevated temperature. The time courses of weight loss of PU films with a NCO/OH of 1.2 are shown in Fig. 8. No significant weight loss was found in PU6 (0% DWC-PU, control) even after 84 days. The weight losses of PU4 (16.6% DWC-PU) and PU5 (12.3% DWC-PU) increased gradually, and reached 6.2% and

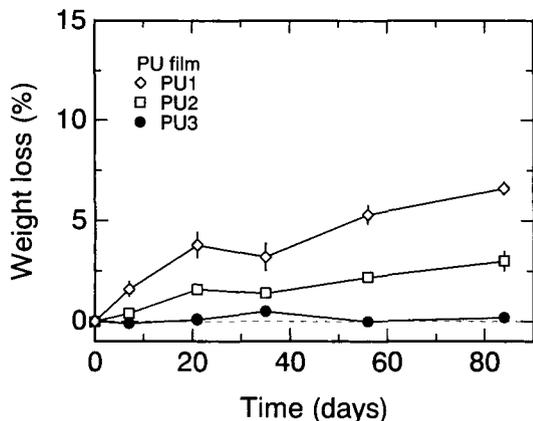


Fig. 5. Weight losses of PU films with a NCO/OH of 1.0 during the hydrolytic stability test at 60°C and 100% RH.  
Note: The plotted values in the figure are means of five replicates and the error bars indicate ranges of standard deviations.

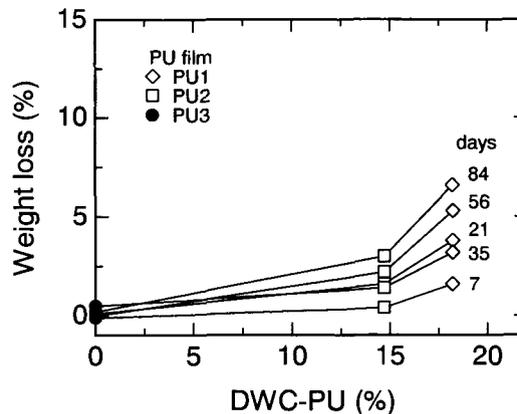


Fig. 6. Effects of the amount of dissolved woody components (DWC-PU) on the weight losses of PU films during the hydrolytic stability test at 60°C and 100% RH.  
Note: The plotted numbers in the figure indicate the aging period in days.

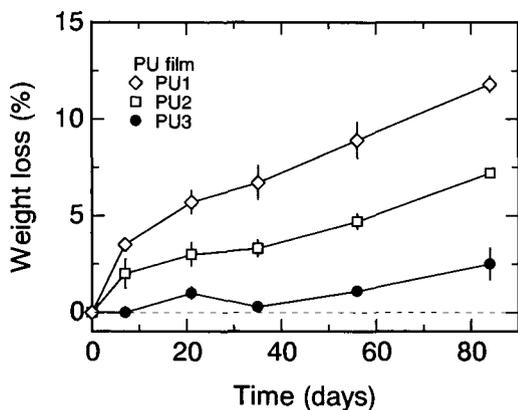


Fig. 7. Weight losses of PU films with a NCO/OH of 1.0 during the hydrolytic stability test at 80°C and 100% RH.  
Note: The plotted values in the figure are means of five replicates and the error bars indicate ranges of standard deviations.

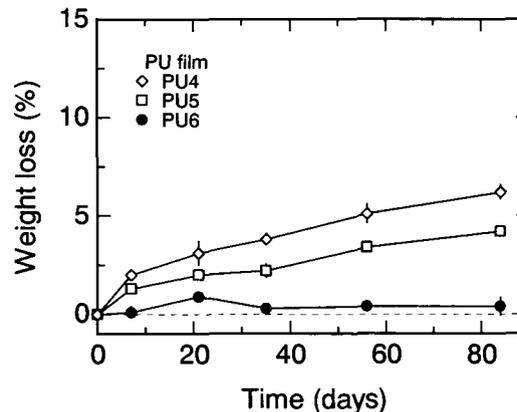


Fig. 8. Weight losses of PU films with a NCO/OH of 1.2 during the hydrolytic stability test at 80°C and 100% RH.  
Note: The plotted values in the figure are means of five replicates and the error bars indicate ranges of standard deviations.

4.2% after 84 days, respectively. These results are obviously lower than the weight losses of PU films with a NCO/OH of 1.0 (see Fig. 7) under the same conditions of temperature and relative humidity. This may be attributed to the increase in the crosslink density and/or the amount of hard segments.

#### Weight loss of PU films after the chemical resistance tests

The weight losses of PU1, PU2 and PU3 after immersion in deionized water, acidic solution or basic solution for 7 days at 20°C are shown in Fig. 9. The difference in DWC-PU produced a large variation in weight loss among the PU films. In deionized water, there was slight weight loss (0.4%) in PU3. In contrast, increases in DWC-PU increased the weight loss of PU1 and PU2 to 4.1% and 2.5%,

respectively. The greater weight loss compared to PU3 could be attributed to the substances unincorporated into the network structures of both PU films. Based on our earlier investigation (Kurimoto *et al.* 2001), it can be concluded that both LW-31 and LW-24 contain small amounts of low molecular weight substances having less than one -OH group per molecule.

When the 10% H<sub>2</sub>SO<sub>4</sub> solution was used, the weight losses of PU1, PU2 and PU3 were the same as in deionized water. Immersion in the 10% NaOH solution significantly increased the weight loss of PU1 and PU2 to 12.0% and 8.1%, respectively, but did not increase the weight loss (0.6%) of PU3. The difference in effect between the H<sub>2</sub>SO<sub>4</sub> and NaOH solutions on the weight losses of PU1 and PU2 is probably due to the swelling effect of alkali on the

woody components (Fengel 1980). Swelling permits easier entry of the NaOH solution into the networks of PU1 and PU2, and promotes the release of the unincorporated substances from the network structures better than in the  $H_2SO_4$  solution.

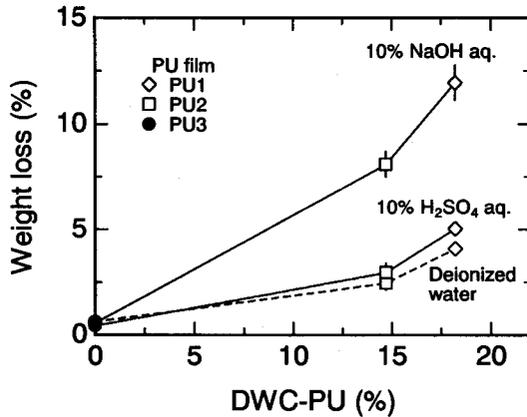


Fig. 9. Effects of the amount of dissolved woody components (DWC-PU) on the weight losses of PU films during the chemical resistance tests at 20°C for 7 days.

Note: The plotted values in the figure are means of five replicates and the error bars indicate ranges of standard deviations.

### Factors affecting the weight loss of PU films

The comparison of weight loss between the hydrolytic stability tests and the chemical resistance tests shows that two factors are acting on the PU films. One is the presence of substances unincorporated into the network structures of the films. The other is the degradation of polymer chains by hydrolysis. The ether linkage of polyether polyurethanes is degraded by hydrolysis, although polyether polyurethanes are more hydrolytically stable than polyesters (Schollonberger and Stewart 1971, Singh and Saxon 1975). Urea linkages show less hydrolytic stability than urethane linkages.

In the hydrolytic stability test at 60°C and 100% RH, it was considered that the PU films with a NCO/OH of 1.0 underwent no significant degradation by hydrolysis. The existence of the substances unincorporated into the network structures of PU films promoted the weight loss. Therefore, PU3 without woody components showed no weight loss even after 84 days (see Fig. 5). When the temperature increased from 60°C to 80°C, the effect of the degradation by hydrolysis on the weight loss of PU films became apparent. Especially the increases in weight loss of PU3 with aging (see Fig. 7) strongly suggested that the hydrolysis is the dominant factor behind the weight loss. In the case of PU1 and PU2, both factors are acting together to promote weight loss.

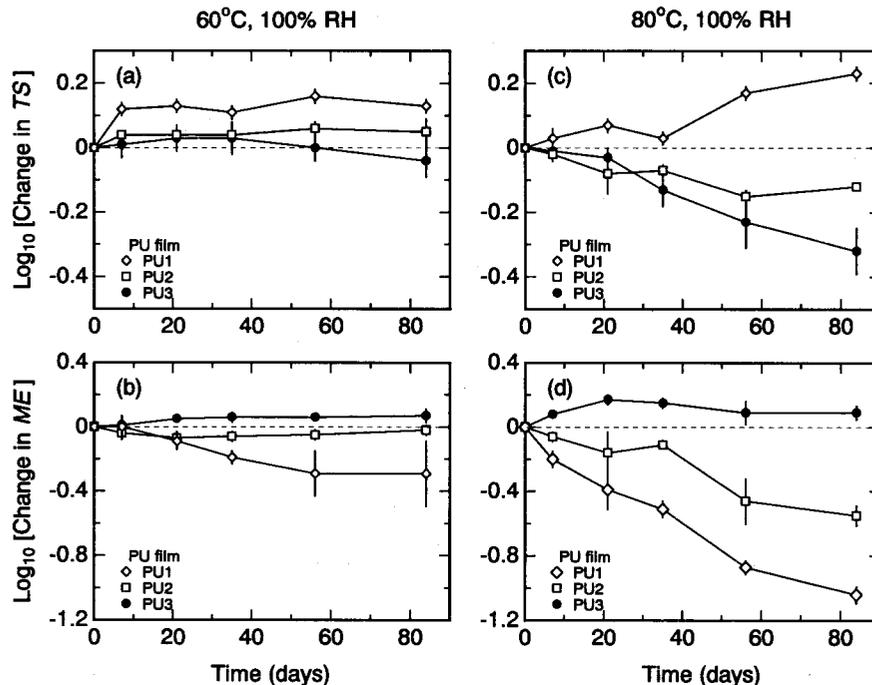


Fig. 10. Changes in tensile strength (*TS*) and maximum elongation (*ME*) of PU films with a NCO/OH of 1.0 during the hydrolytic stability test. a,b: 60°C and 100% RH; c,d: 80°C and 100% RH.

Note: The plotted values in the figures are means of five replicates and the error bars indicate the standard deviations.

### Mechanical properties of PU films after the hydrolytic stability tests

Changes in tensile strength and maximum elongation of PU films with a NCO/OH of 1.0 during the hydrolytic stability tests are graphed logarithmically in Fig. 10. There were no significant changes in tensile strength and maximum elongation of PU3 (0% DWC-PU) with increases in the aging time at 60°C and 100% RH. When the DWC-PU was increased to 14.7% (PU2), the tensile strength after 7 days was 1.1 times the initial (unexposed) tensile strength and remained constant even after 84 days. At 18.2% DWC-PU (PU1), the tensile strength after 7 days was 1.3 times the initial tensile strength and also remained constant. An inverse relationship was observed between maximum elongation and the aging of PU1. The maximum elongation decreased to 2/3 of initial elongation within 56 days, then remained constant until 84 days. No significant change in maximum elongation was observed in PU2 with aging. The large DWC-PU gave PU1 the rigid mechanical properties during the hydrolytic stability test at 60°C and 100% RH.

When the temperature increased from 60°C to 80°C, PU3 underwent a more rapid hydrolytic attack than PU1 and PU2. The tensile strength of PU3 significantly decreased with aging. The tensile strength remaining after 84 days was 1/2 of the initial strength. In contrast, the maximum elongation after 21 days increased to 1.5 times the initial value and was kept constant even after 84 days. The decrease in tensile strength and the increase in maximum elongation can be explained by the degradation of polymer chains of PU3.

The increase of DWC-PU markedly improved the tensile strength of PU1 and PU2 at 80°C and 100% RH. The remaining tensile strength of PU2 (with 14.7% DWC-PU) after 84 days was twice that of PU3. A further increase in DWC-PU from 14.7% to 18.2% increased the tensile strength of PU1 and reached 1.7-fold the initial value after 84 days. The maximum elongations of PU1 and PU2 after 84 days were 1/10 and 1/2 of the initial elongation, respectively. In the case of PU1 and PU2, two factors, i. e., the substances unincorporated into the network structures and the degradation by hydrolysis, acting together caused the weight loss during the hydrolytic stability test at 80°C and 100% RH. The rigid mechanical properties of PU1 and PU2 indicate that less polymer degradation occurred during the tests compared to PU3.

It is interesting that the rigid mechanical properties of PU1 increased during the hydrolytic stability tests. This is quite different from the trend for the mechanical properties of PU3 at 80°C and 100% RH (see Fig. 10-c,d). The  $T_g$  of PU1 and PU3 during the hydrolytic stability test at 80°C and 100% RH was therefore examined. DSC scans of the PU films are shown in Fig. 11. The  $T_g$  of PU1 shifted to higher temperatures from 29°C to 48°C with aging while the

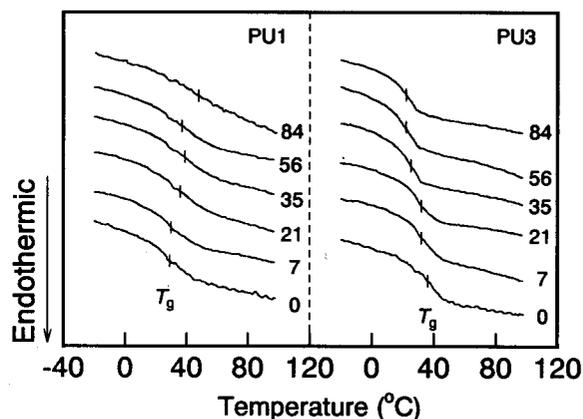


Fig. 11. DSC scans of PU1 and PU3 after the hydrolytic stability test at 80°C and 100% RH.

Note: The numbers in the figure represent the aging period in days.

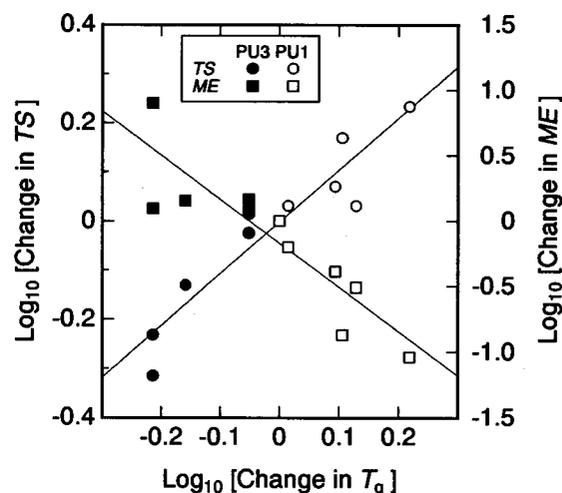


Fig. 12. Relationships between the changes in glass transition temperature ( $T_g$ ) and the changes in tensile strength (TS) and maximum elongation (ME) of PU1 and PU3 during the hydrolytic stability test at 80°C and 100% RH.

$T_g$  of PU3 occurred at lower temperatures from 36°C to 22°C. The increases in  $T_g$  of PU1 and the decreases in  $T_g$  of PU3 agreed well with the changes in the mechanical properties of PU1 and PU3 (Fig. 12).

The decreases in  $T_g$  of PU3 were caused by the degradation of polymer chains during the hydrolytic stability test. It is clear that a defect in the network structures lowers the temperature at which the chain movements occur. Whereas, the elevation in  $T_g$  of PU1 suggests that the substances unincorporated into the network structures acted as a plasticizer. The plasticizing agent is a lubricant in the molecular system which enhances the mobility of chains (Rials and Glasser 1984). When the substances unincorporated into the network structures are lost

from PU1, the thermal energy required to initiate the chain movements becomes larger and the  $T_g$  can occur at higher temperatures. Subsequently, this resulted in the improved rigidity of PU1 during the hydrolytic stability test.

Changes in tensile strength and maximum elongation of PU4 (16.6% DWC-PU), PU5 (12.3% DWC-PU) and PU6 (0% DWC-PU) during the hydrolytic stability test at 80°C and 100% RH are shown in Fig. 13. The increase in the NCO to OH ratio from 1.0 to 1.2 stabilized the mechanical properties of PU4 and PU5, that is, the changes in tensile strength and maximum elongation were less. The percentage decreases in the tensile strength of both films were about 10% after 21 days and remained constant even after 84 days. There were no significant changes in maximum elongation of PU4 and PU5 all through the aging period.

The remaining tensile strength of PU6 was also improved by the increase in NCO/OH. The tensile strength after 84 days was about 3/4 of the initial value. However, the maximum elongation after the same period was 3.7 times the initial elongation. The significant increases in maximum elongation of PU6 were considered to be due to the degradation of polymer chains, although the weight loss of PU6 after the hydrolytic stability test was only 0.4%.

### Conclusion

PU films with different DWC-PU (0-18.2%), which were prepared from LWs of sugi wood at NCO to OH ratios of 1.0 and 1.2, were aged at 100% relative humidity at 60°C or 80°C. The chemical resistance of the films with the NCO/OH of 1.0 was also tested at 20°C for one week.

In the hydrolytic stability tests, increases in the aging period significantly increased the weight loss of PU films made from LWs at both NCO/OH. High temperature (80°C) promoted weight loss faster than low temperature (60°C), although the increase in a NCO/OH could reduce the loss. The presence of substances unincorporated into the network structures of the PU film rather than the degradation of polymer chains was the major reason for the weight losses.

Less change in mechanical properties (tensile strength and maximum elongation) was observed in the PU films (12.3%, 16.6% DWC-PU) with a NCO/OH of 1.2 even at 80°C and 100% RH. The PU films without woody components showed large changes in mechanical properties, that is, decreases in tensile strength and increases in maximum elongation with increases in the testing period. Therefore, it can be concluded that the PU films made from LWs were more resistant to hydrolysis than the PU films without woody components. If a high fixing content of woody components is required for the network, then fractionation of LW will be necessary.

At a NCO/OH of 1.0, the PU film with large DWC-PU (18.2%) increased rigid mechanical properties after the hydrolytic stability tests. This was

due to the large amounts of substances unincorporated into the network structures. The unincorporated substances acted as a plasticizer.

The increase in DWC-PU increased the weight loss after immersion in deionized water, acidic (10%  $H_2SO_4$ ) or basic (10% NaOH) solution because of the unincorporated substances. The basic solution particularly reduced the weight loss of PU film. This is probably due to the swelling effect of alkali on the woody components in PU film.

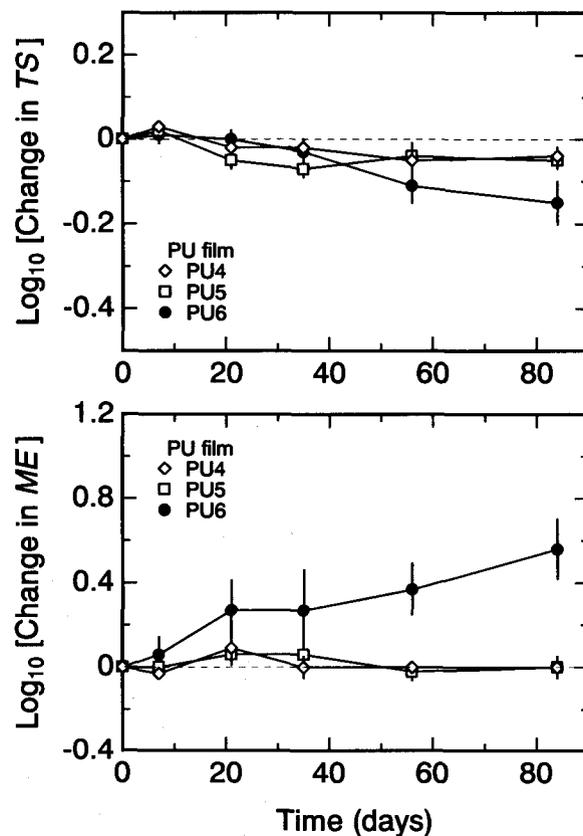


Fig. 13. Changes in tensile strength ( $TS$ ) and maximum elongation ( $ME$ ) of PU films with a NCO/OH of 1.2 during the hydrolytic stability test at 80°C and 100% RH.

Note: The plotted values in the figure are means of five replicates and the error bars indicate ranges of standard deviations.

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