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### Biodegradable Polyurethanes from Plant Components

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## **BIODEGRADABLE POLYURETHANES FROM PLANT COMPONENTS**

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### **ABSTRACT**

Polyurethane (PU) sheets and foams having plant components in their network were prepared by using the following procedure. Polyethylene glycol (PEG) was mixed with one of the following; molasses, lignin, woodmeal, or coffee grounds. The mixture obtained was reacted with diphenylmethane diisocyanate (MDI) at room temperature, and precured PUs were prepared. The precured PUs were heat-pressed and PU sheets were obtained. In order to make PU foam, the above mixture was reacted with MDI after the addition of plasticizer, surfactant (silicone oil), catalyst (di-*n*-butyltin dilaurate), and droplets of water under vigorous stirring. The glass transition temperature, tensile and compres-

sion strengths, and Young's modulus of the PU sheets and foams increased with an increasing amount of plant components. This suggests that saccharide and lignin residues act as hard segments in PUs. It was found that the PUs obtained were biodegradable in soil. The rate of biodegradation of the PUs derived from molasses and coffee grounds was between that of cryptomeria (*Cryptomeria japonica*) and beech (*Fagus sieboldi*).

## INTRODUCTION

Natural polymers are materials which are highly adaptable to their circumstances. They are also materials having appropriate reactivity because of functional groups such as hydroxyl groups. Accordingly, natural polymers having more than two hydroxyl groups per molecule can be used as polyols for polyurethane (PU) synthesis.

Synthetic polymers, which contain natural polymer or their main components such as carbohydrate and lignin residue, are considered to be biodegradable. Therefore, extensive studies have been carried out to synthesize polyurethanes (PUs) which were derived from plant components [1–5]. In these studies, PUs were prepared using polyols such as polyethylene glycol (PEG) and polypropylene glycol (PPG).

The present paper reports our recent studies on the thermal and mechanical properties, and also the biodegradability of PUs prepared from molasses and lignocellulose, such as lignin, woodmeal, and coffee grounds, by polymerization with PEG, PPG, and diphenylmethane diisocyanate (MDI).

## EXPERIMENTAL

### Materials

Molasses (ML) were supplied by Tropical Technology Center Ltd. Lignin (Kraft lignin, KL) was obtained from Holmen Pulping Company. KL was purified by the precipitation method using dilute sulfuric acid. Hardwood solvolysis lignin (SL) was obtained as a by-product in organosolve-pulping of Japanese beech (*Fagus crenata*). The SL was provided by the Japan Pulp and Paper Research Institute Co. Woodmeal from pine was supplied by Miki Sangyo Co. Ltd. The particle size was 60–90 mesh. Coffee grounds were provided by Ueshima Coffee Co. Ltd. PEG, PPG and MDI were commercially obtained. Wood blocks of cryptomeria (*Cryptomeria japonica*) and beech (*Fagus sieboldi*) were obtained from the Experimental Forest Station which belongs to Tokyo University of Agriculture and Technology.

### Preparation of PUs

In order to obtain PUs, it was necessary to dissolve or suspend molasses, lignin, woodmeal, and coffee grounds in polyols such as PEG and PPG. The polyol solutions (in the case of molasses and lignin) or suspensions (in the case of woodmeal and coffee grounds) obtained were mixed with MDI at room temperature, and

precured PUs were prepared. Each of the precured PUs was heat-pressed and a PU sheet was obtained. In order to prepare PU foams, the above polyol solution was mixed with plasticizer, surfactant (silicone oil), and catalyst (di-*n*-butyltin dilaurate), and then MDI was added. The mixture was vigorously stirred with droplets of water which were added as a foaming agent, and a PU foam was obtained.

### Measurements

Thermal properties of PU samples were measured using a differential scanning calorimeter, Seiko DSC 220, and a thermogravimeter, Seiko TG 220, with a workstation 5700. DSC and TG curves were obtained at the scanning rate of 10°C/min.

Mechanical properties of PU samples were measured using a tensile test machine, Shimadzu Autograph 500. The strain rate was 5 mm/min for the tensile test and 2 mm/min for the compression test.

### Biodegradation

PU foams derived from molasses and coffee grounds were cut into specimens of 5 cm (width) × 5 cm (length) × 1 cm (thickness). The specimens were pinned on the surface of the ground at the hilly farm that belongs to the Faculty of Agriculture of Tokyo University of Agriculture and Technology, and covered lightly with soil and a net, and they were kept in this state for predetermined periods. Then a certain number of the specimens were taken from the farm, washed, and dried. The average weight loss of five specimens of each kind of sample was calculated according to the following equation: Weight loss (%) =  $(W_s - W_d)/W_s$  (g/g) × 100, where  $W_s$  (g) is the sample weight and  $W_d$  (g) is the sample weight after the sample was kept in the soil for a certain time.

## RESULTS AND DISCUSSION

### Chemical Structure of Prepared PUs

The core structure of prepared PUs consists of saccharide and lignin linked by urethane bonding. Accordingly, it can be assumed that the PUs obtained are essentially copolymers having three-dimensional networks of urethane bonding which have saccharide and lignin components combined with polyol (PEG or PPG). Schematic chemical structures of PUs derived from saccharide and lignin are shown in Fig. 1.

### Thermal Properties of PUs

Figure 2 shows DSC curves of PU sheets with various molasses contents in the PEG-ML system. A marked change in baseline due to glass transition was observed in each DSC curve. Glass transition temperatures ( $T_g$ s) were determined by a method reported previously [6].  $T_g$  increased with increasing content of molasses in polyol, since pyranose and fructose rings from saccharides in molasses act as hard segments in PU networks.

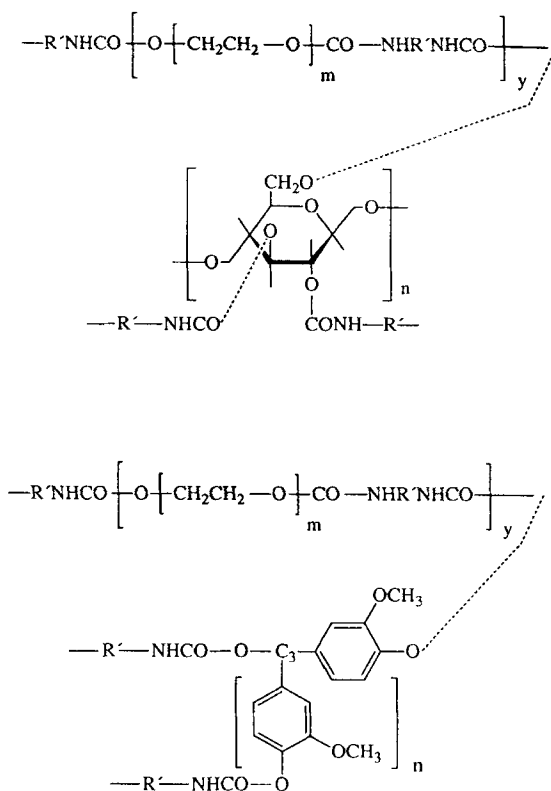


FIG. 1. Schematic chemical structures of PUs from saccharides and lignin.

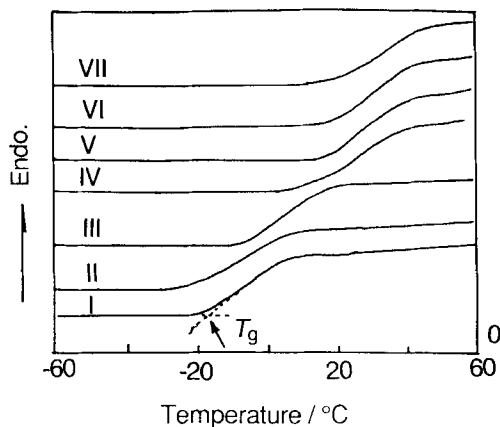


FIG. 2. DSC curves of PU sheets with various molasses contents in PEG-molasses systems. Molasses contents (%): I, 0; II, 5; III, 10; IV, 15; V, 20; VI, 25; VII, 30. Heating rate =  $10^\circ\text{C}/\text{min}$ .

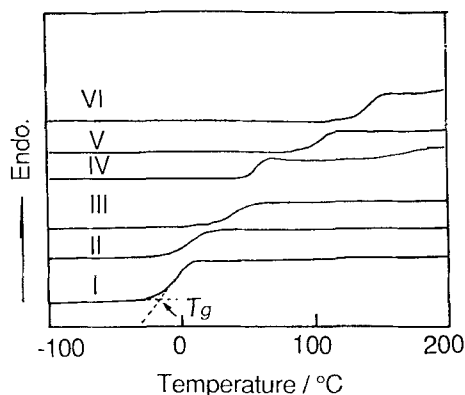


FIG. 3. DSC curves of PU sheets with various lignin (SL) contents in PEG-SL systems. SL contents (%): I, 0; II, 10; III, 20; IV, 30; V, 40; VI, 50. Heating rate = 10°C/min.

Figure 3 shows DSC curves of PU sheets with various lignin (SL) contents in the PEG-SL system.  $T_g$  increases with increasing SL content. It is known that lignin is a crosslinked and highly branched polymer which has rigid phenyl propane structures as repeating units. Lignin also has more than two hydroxyl groups in a molecule. Accordingly, it is considered that lignin reduces the mobility of the main chain of PU molecules.

A similar relationship was observed in the change of  $T_g$ s of PUs with various contents of KL, woodmeal, and coffee grounds. In all cases the increase of plant components in PUs resulted in the increase of  $T_g$ .

### Mechanical Properties of PU Sheets

Figure 4 shows changes of stress ( $\sigma$ , MPa) and elongation ( $\epsilon$ , %) at the breaking points of PU sheets with various molasses contents. As shown in the figure, the  $\sigma$  value increases with increasing molasses content in polyol. The value

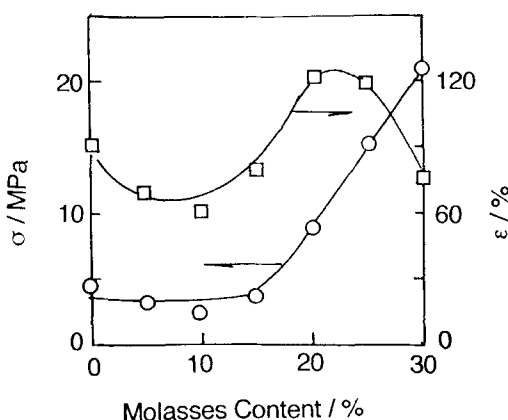


FIG. 4. Relationships between ultimate strength ( $\sigma$ ) and ultimate strain ( $\epsilon$ ) of PU sheets and molasses contents in polyol systems.

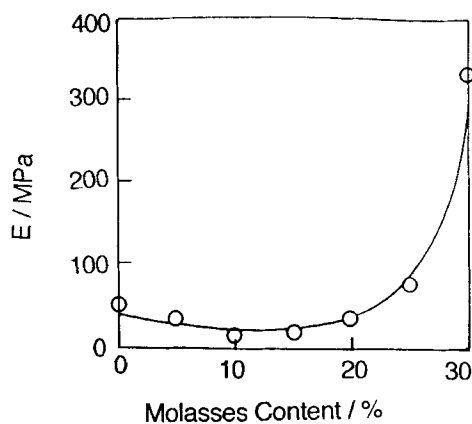


FIG. 5. Relationship between Young's modulus ( $E$ ) and molasses content in polyol systems.

shows a prominent increase when the molasses content exceeds 20% since the  $T_g$  value of the PU sheet becomes higher than room temperature (Fig. 2) and the PU molecules are in the glassy state. The  $\epsilon$  value of the PU sheet derived from molasses shows a maximum at around the molasses content of 20%, since the molecular state of the PU sheet changes from the rubbery state to the glassy state at room temperature when the molasses content exceeds 20%.

As shown in Fig. 5, Young's modulus ( $E$ , MPa) of a PU sheet derived from molasses increases with increasing molasses content, since pyranose and fructose rings from the saccharides in molasses act as hard segments in PU networks.

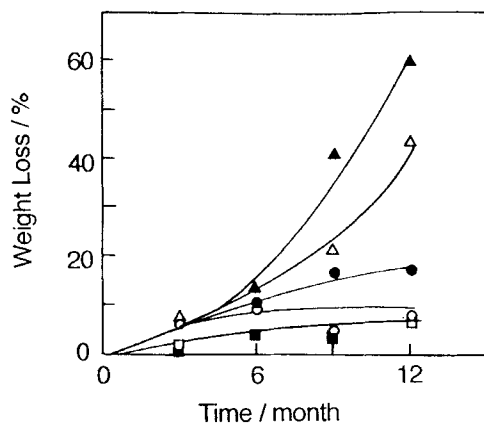


FIG. 6. Relationship between weight loss and degradation time. ( $\Delta$ ,  $\blacktriangle$ ) Buna; ( $\circ$ ,  $\bullet$ ) PU derived from molasses (33%); ( $\square$ ,  $\blacksquare$ ) Sugi; ( $\Delta$ ,  $\circ$ ,  $\square$ ) degraded at a hilly open farm; ( $\blacktriangle$ ,  $\bullet$ ,  $\blacksquare$ ) degraded at a farm in a forest.

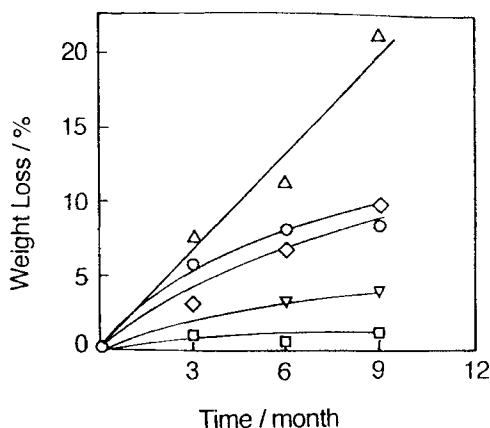


FIG. 7. Relationship between weight loss and degradation time at a hilly open farm. (△) Buna; (○) PU derived from coffee grounds (20%); (◇) PU (30%); (▽) PU (40%); (□) Sugi.

### Biodegradation of PU Foams

Figure 6 shows the weight loss (%) of PU foams derived from molasses which were kept in soil for a certain period up to 12 months according to our experimental plans. Figure 7 shows weight loss (%) of PU foams derived from coffee grounds which were kept in soil for a certain period up to 9 months. In the above figures, SUGI represents the weight loss of cryptomeria samples, BUNA that of beech sample, MO 33% and MO 50%, those of PU foams prepared from polyols containing 33% and 50% molasses. A group of the specimen was biodegraded at a hilly open farm, and the other group of specimens was biodegraded at a farm in a forest, both of which belong to the Tokyo University of Agriculture and Technology. As seen from the above figures, weight losses of PU foams derived from molasses are lower than those of beech blocks but higher than those of cryptomeria. This suggests that the PUs prepared in this study have good biodegradability, comparable with natural wood.

### CONCLUSION

The following conclusions are obtained from the above experimental results.

1. PU films and foams having a variety of thermal and mechanical characteristics were derived from molasses, lignin, woodmeal, and coffee grounds.
2. The glass transition temperature and the breaking strength of PU increased with increasing amounts of plant components in PU, since saccharide and lignin residues act as hard segments in the PU molecular networks.
3. The above PUs were biodegraded by microorganisms in soil, showing biodegradability between that of beech and cryptomeria.



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