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Thermal properties of polyurethanes derived from molasses before and after biodegradation

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SUMMARY:
Polyurethane (PU) foams derived from molasses were placed in soil for various periods from 3 to 12 months. Thermal properties of PU's before and after biodegradation were investigated by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition of PU's after 3 month's degradation was separated into two stages indicating that molecular chains of the original and decomposed portions move independently. Based on variation of glass transition temperature (T_g), heat capacity difference at T_g (ΔC_p), thermal degradation temperature and mass loss, the degradation mechanism of PU was establised.

Introdution

Biodegradation mechanism of polymers has been investigated by chemical and enzymatic analysis supported by various kinds of analytical techniques, such as infrared spectroscopy (IR) and gel permeation chromatography (GPC). Mechanical and morphological properties of biodegraded polymers have also been studied by mechanical testing and electron microscopic observation. However, thermal properties of biopolymers during biodegradation have received little attention. In contrast, thermal degradation of biopolymers

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from plant components have been investigated in detail by thermogravimety (TG)[1,2], pyrolysis[3,4] and simultaneous measurement of TG-Fourier transform (FTIR) [5].

We have prepared biourethanes in which biopolymers are introduced in urethane network. The functional groups, such as hydroxyl group and amide groups are used as a reaction site for synthesis of polyols for polyurethane (PU) [6~9]. By changing the amount of biopolymer content, it was found that mechanical and thermal properties of PU can be controlled in a wide range [6~10]. Thermal degradation of polyurethane (PU) samples derived from saccharides and lignin has extensively been studied by TG [6, 8~10] and TG-FTIR [5]. It was shown that PU samples decompose to carbon dioxide and water in the presence of air.

In this study, phase transition behavior of PU samples degraded in soil for various time intervals is investigated by differential scanning calorimetry (DSC) and TG.

Experimental

Chemicals

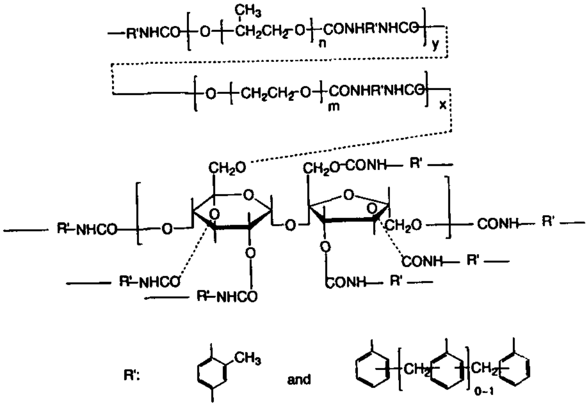
Flexible PU foams were prepared from molasses-polyol, which was a solution of molasses in polyethylene glycol (PEG), by polymerization with polypropylene glycol (PPG), tolylene diisocyanate and diphenylmethane diisocyanate. Molasses was obtained from Syonan Sugar Manufacture Co. Ltd. PEG with average molecular mass 200 and PPG with molecular mass 3,000 were obtained from Daichi Chemical Industry Co. Ltd. Tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) were obtained by Mitsui Toatsu Chemical Co. LTD. Silicon type surfactant was obtained from Nippon Unicar Co. Ltd. Sn type catalyst, Tin octanoate was supplied by Jyohoku

Chemical Industry C. Ltd, and amine catalyst, pentamethyl-diethylnetriamine was obtained from Wako Pure Chemical Industry Co. Ltd.

Preparation of PU foams

Polyol solutions were prepared by mixing molasses and PEG200 at various mixing ratios. Hydroxyl group content of molasses polyol (MP) were determined according to JIS K 1557. In order to prepare PU foams, determin -ed amount of MP was added to PPG 3000. Then surfactant, catalysts and a trace amount of water as a foaming agent were added to MP and PPG mixture under vigorous stirring. Foaming was carried out immediately after removing the stirrer. The obtained foam was cured overnight at room temperature.

Three kinds of model polymers having unit structures composing the above samples were also prepared as reference materials i.e., PU foams from PEG 200, PPG 3000 and molasses (33%) with PPG 3000 were prepared using the same procedure as mentioned above. They are abbreviated as PEG-PU, PPG-PU and Molasses-PU, respectively. A schematic chemical structure of the PU sample is shown in Scheme 1.



Scheme 1 Chemical structure of PU derived from molasses.

Biodegradation by soil burial method

PU samples were placed in soil at a testing farm in Okinawa Islands which are located in sub-tropical latitudes. The sample size was 5 x 5 x 1 cm). The underneath of the sample (5 x 5 cm) was placed in order to come into contact with the surface of the soil. 50 % of sample surface were covered with a small amount of soil. Samples were buried for 3, 6 and 12 months.

In order to establish reliable sample handling, errors derived from the testing procedure were examined in detail in our previous report [11]. In this experiment, the following procedure established for foam shaped samples was used, i.e. (1) the surface of the sample taken from soil was washed in running water in order to remove contaminants, (2) the sample was rapped with paper towels and pressed, (3) it was dried in air at 60°C for 48 hours, (4) it was placed in a desiccator with P_2O_5 *in vacuo* for 24 hours and (5) it was dried for 36 hours at ordinal pressure.

Thermal analysis (TA)

A Seiko differential scanning calorimeter, DSC 220C and a thermogravimeter/differential thermal analyzer, TG/DTA220 equipped with an Unix analyzing system were used for thermal measurements. In order to pack foam shaped sample into aluminum open type sample vessel with diameter 6 mm, bulky samples were compressed together with a lid using a small rod and the edge of sample vessel was fastened tightly. Sample weight was ca. 6 mg and heating rate 10°C/min. Nitrogen flow rate was 10 ml/min for DSC and 30 ml/min for TG/DTA. Transition temperatures were determined as previously reported [12].

Scanning electron microscopy (SEM)

A Topcon DS-720 scanning electron microscope was used for morphological observation. Samples were coated by gold using an ion spatter.

Results

Figure 1 shows scanning electron micrographs of flexible PU foam with 30% molasses polyol before biodegradation. It is shown that honeycomb structures are well established. Diameter of foam is from 100 to 200 µm. Foams were elastic and appeared in a light yellow.

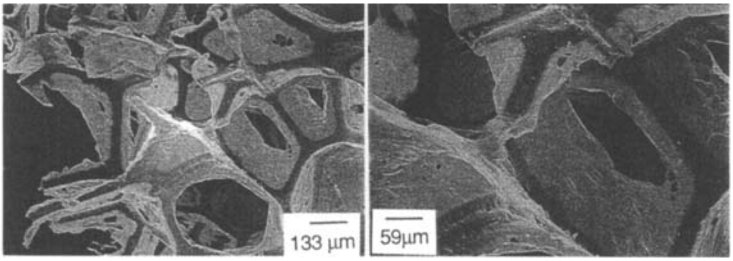


Figure 1 Scanning electron micrographs of original PU.

Flexible PU foams are amorphous and the glass transition temperature (T_g) was observed at ca. -50 °C by DSC. The rubbery state of the sample was thermally stable until ca. 250 °C where the thermal decomposition started. After biodegradation for 3 months in soil, the residual sample was colored and brittle. Figure 2 shows stacked DSC curves of original and biodegraded samples for 3, 6 and 12 months, respectively. In order to confirm whether the sample for TA measurements taken from various parts of buried specimens is homogeneous or not, outer and inner portions of the sample were separated and each portion was measured. For any portion of the samples biodegraded for 3 and 6 months, two T_g's were observed, i.e. the main T_g at ca. -50 °C (T_{g1}) and a new T_g at around -10°C (T_{g2}). After 12 month's biodegradation, T_{g2} disappeared as shown in Figure 2. Figure 3 shows relationships between T_g's and period of biodegradation. As shown in the figure, T_{g1} and T_{g2} are maintained at constant value regardless of period of biodegradation.

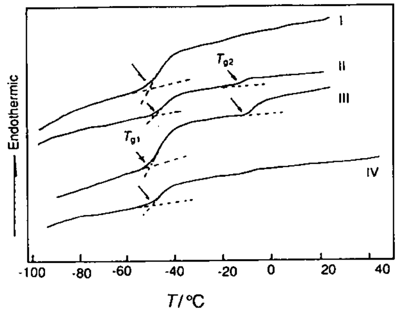


Fig. 2. Stacked DSC curves of PU samples placed in soil for various time intervals. I;0, II; 3 months, III; 6 months, IV 12 months

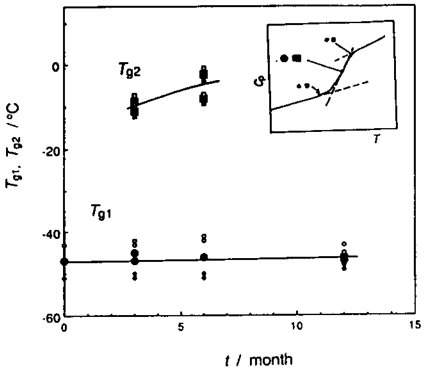


Fig. 3. Relationship between glass transition temperatures T_{g1} and T_{g2}) and period of biodegradation (t).

Figure 4 shows the heat capacity difference (ΔC_p) at the T_g. When two T_g's were observed, two ΔC_p's were also calculated. ΔC_p at T_{g1} decreased by ca. 30 percent when the sample was biodegraded for 3 months. With increasing treating period, total ΔC_p value increased and showed maximum at 3 months and then decreased, indicating that molecular motion of the main chain is enhanced after biodegradation for 3 months.

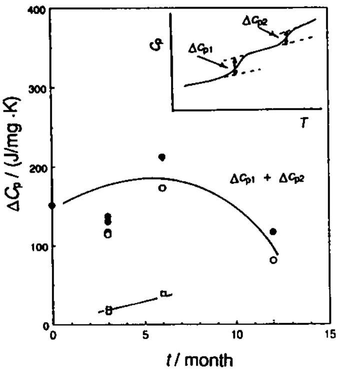


Fig. 4. Relationship between heat capacity difference (ΔC_p) and biodegraded period (t).

Figure 5 shows DSC curves of reference samples of PU foam, i.e. PEG-PU, PPG-PU and Molasses-PU, respectively. T_g of PPG-PU is observed at -46°C, in contrast T_g's of PEG-PU and Molasses-PU are observed at 64 and 87 °C, respectively. This indicates that PPG long chains act as a flexible component and enhance the molecular motion of PU. PEG short chain and molasses increase the rigidity of PU network.

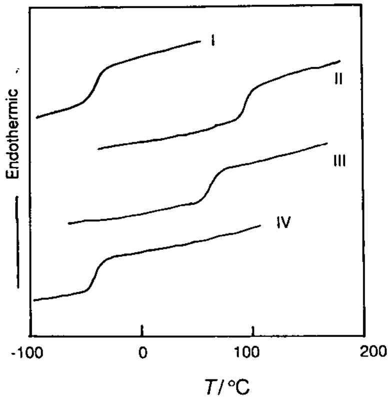


Fig. 5. DSC curves of PU sample (original) and reference polym- I;original, II; Molasses-PU, III; PEG-PU, IV; PPG-PU

Figures 6 shows TG curves of PU samples biodegraded for various time intervals. TG curves indicate that thermal degradation occurs in two stages, at around 250 °C and 370°C. Decomposition temperatures (T_{d1} and T_{d2}) are defined as indicating by arrows in the figure. Both T_d's (at around

250 and 370 °C) are maintained at a constant value, regardless of treating period in soil. However, the amount of mass loss varied as a function of period of biodegradation as shown in Figure 7. Figure 7 shows relationships between mass loss (%) and period of biodegradation of PU samples. The mass loss at the first stage is defined as Δm_1 and that of the second stage Δm_2. Δm_1 increases at 3 month biodegradation and levels off. Δm_2 decreases gradually with increasing treating period.

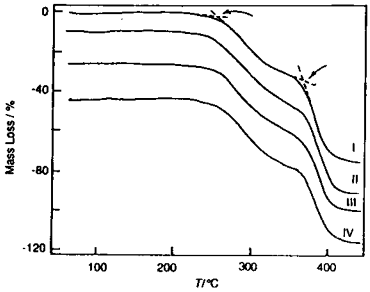


Fig. 6. Stacked TG curves of PU's placed in soil for various time
intervals. I;0, II; 3 months, III; 6 months, IV; 12 months

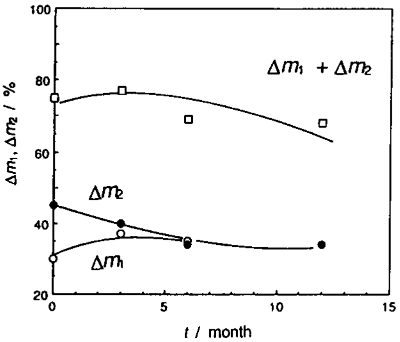


Fig. 7. Relationship between mass loss (Δm_1 and Δm_2) and period of biodegradation in soil (t).

Figures 8 shows TG curves of reference PU's. The mass loss of Molasses-PU (curve I) and PEG -PU (curve II) are observed at the first stage. In constrast, the mass loss of PPG-PU occurs in two stages.

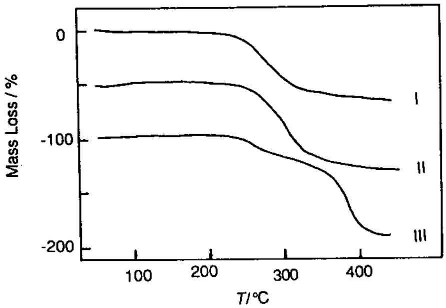


Figure 8 Stacked TG curves of reference PU's.
I; Molasses-PU, II; PEG-PU, III; PPG-PU

Figure 9 shows electron micrographs of PU foams biodegraded for 3 months in various magnifications. It is clearly seen that thin films covering each cell disappear after biodegradation. Degradation proceeds not only on the surface but also within the framework structure of the sample.

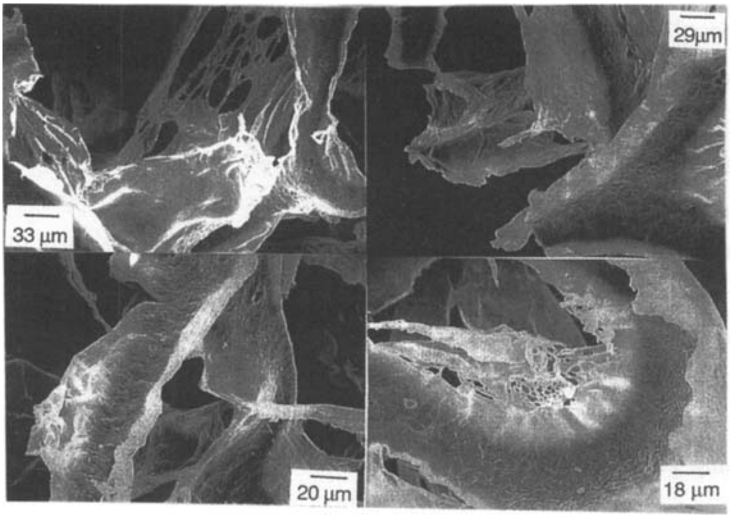


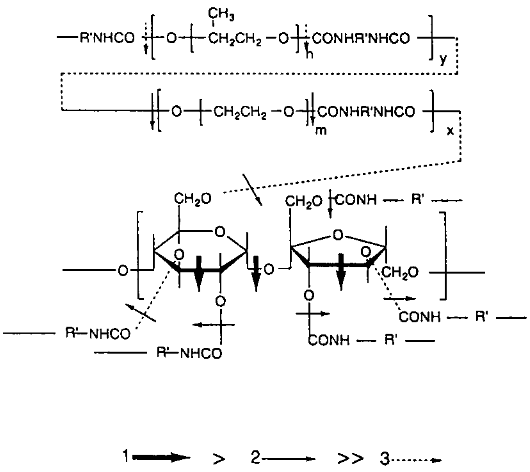
Fig.9. Scanning electron micrographs of biodegraded PU foams for 3 months in various magnifications.

Discussion

The results indicate that the saccharide component and the urethane bonding, connecting long flexible PPG chains and short PEG chains with saccharide structures are broken in the initial stage of degradation. In our previous studies using a model low molecular weighg compounds, we have confirmed that the urethane linkage decomposes by microorganisms, i. e. a *Bacterium* and two kinds of *Acrynomiyces* which are isolated from soil [11 . The high T_{g2} observed in DSC curves of PU's after 3 and 6 month's degradation (Figure 2, curves II and III) is attributable to the molecular motion of short PU chains with saccharide structure and/or with saccharide fragments. The low T_{g1} (Figure 2, curves I ~ IV) is attributable to the main chain motion of PPG component. This can be confirmed by the fact that T_g of PU derived from PPG (PPG-PU) was observed at a similar temperature (Figure 5, curve IV). After 12 month's degradation in soil, saccharides are preferentially decomposed, and the high T_{g2} was hardly observed (Figure 2, curve IV)). Variation of DC_p indicates that firstly the molecular mobility is enhanced (Figure 4) and then is reduced after prolonged degradation in soil.

Thermal decomposition of PU's takes place in two stages, mass loss occurring at the low temperature is attributed to thermal decomposition of saccharide and PEG components and that of high temperature side can mainly be attributed to the decomposition of PPG components (Figure 8). The difference in thermal decomposition of PU's before and after biodegradation is not prominent in TG results (Figure 6), when they are compared with DSC results (Figure 2), however, total mass loss gradually decreases with increasing period of biodegradation. At the same time, mass loss at low decomposition temperature (Δm_1) slightly increased after 3 month's biodegradation (Figure 7) indicating that the saccharide-PEG component is large at this stage.

It is thought that thermal analysis is a useful technique in order to analyze the degradation process of polymers. Based on the thermal analytical results, the degradation process of PU's derived from molasses is shown in the following scheme where degradation proceeds accompanying with the increasse in the size of the arrow.



Scheme 2 Degradation scheme suggested by thermal analysis.

Acknowledgments

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References

[1] T. Nguyen, E. Zavarin , E.M. Barrall II, *J. Macromol Sci. Rev. Macromol Chem.* **C20**, 1 (1981)

2)T. Nguyen, E. Zavarin, E.M. Barrall II, *J. Macromol Sci., Rev. Macromol Chem.* **C21**, 1 (1981)

3)M. Wada, S. Fujishige, S. Uchino, N. Oguri, *Kobunshi Ronbunsyu (J. Polym. Chem., Japan)* **53**, 20 (1996)

4)M. Wada, S. Fujishige, S. Uchino, N. Oguri, *Kobunshi Ronbunsyu (J. Polym. Chem., Japan)* **53**, 201(1996)

5) K. Nakamura , Y. Nishimura, P. Zetterlund, T. Hatakeyama, H.Hatakeyama, *Thermochimica Acta* **282/283**, 433 (1996).

6) H. Hatakeyama, S. Hirose, K. Nakamura, T. Hatakeyama, New Types of Polyurethanes Derived from Lignocellulose and Sacchrides, in Cellulosics; Chemical, Biochemical and Material Aspects, J. F. Kennedy, G. O. Phillips, and P. A.Williams, Eds., Ellis Horwood, 1993, p. 389.

7) K. Nakamura , Y. Nishimura, T. Hatakeyama, H. Hatakeyama, *Sen-i Gakkaishi (J. Fiber Sci. Technol. Japan)* **51**, 111 (1995)

8)8K. Nakamura, R. Morck, A. Reimann, K. P. Kringstad, H. Hatakeyama, *Polym. Adv. Technol.* **2**, 41 (1991)

9) P. Zetterlund, S. Hirose, T. Hatakeyma, H. Hatakeyama, A-CAlbersson, *Polymer Internatianal* **42**, 1 (1997)

10) K. Nakamura, T. Hatakeyama, H. Hatakeyama, *Polym. Adv. Tecnol.* **2**, 151 (1992)

11) N. Morohoshi, S. Hirose, H. Hatakeyama, T. Tokashiki, K. Teruya, *Sen-i Gakkaishi* 51, 143 (1995)

12) T. Hatakeyama, F. X. Quinn, Thermal Analysis, John Wiley &Sons, Chichester (1994)