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Decomposition of polyurethane foams derived from condensed tannin II: Hydrolysis and aminolysis of polyurethane foams

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Abstract To obtain basic information on the stability, decomposition, and recycling of biodegradable polyurethane foam (PUF), we studied hydrolysis and aminolysis of the PUF derived from wattle tannin (WT). The WT-PUF exhibited almost the same stability to a hydrolytic treatment at room temperature as trimethylolpropane (TMP)-PUF, which was prepared by cross-linking with TMP. Weight loss and strength loss of WT-PUF were much larger than those of TMP-PUF during the hydrolytic treatment at an elevated temperature. Hydrolysis was mainly responsible for the cleavage of urethane bonds to form WT and amines at the initial stages of the treatment. At the later stages, however, urethane bonds seemed to be cleaved not only by the hydrolysis but also by aminolysis with the amines formed in the system.

Key words Wattle tannin · Urethane · Hydrolysis · Aminolysis

Introduction

Polyurethane foams (PUFs) prepared from wattle tannin (WT)¹ and the bark of *Acacia mearnsii*^{2,3} and *Cryptomeria japonica*³ have been shown to be biodegradable by some wood-rotting fungi and soil microorganisms. It is not well known, however, whether these foams are as stable as ordinary polyurethane foams under the utilization conditions or if they can be chemically recycled after use.

Hydrolysis, glycolysis, and aminolysis are chemical processes that decompose polyurethane to lower-molecular-weight products.^{4,5} In our previous paper⁶ hydrolysis and aminolysis of low-molecular-weight urethanes derived from catechin were studied as model reactions to learn about the stability of the urethane bonds in PUFs derived from WT. The model catechin urethanes had almost the same stability at room temperature as phenethyl alcohol urethane, which was employed as a model for commercial PUFs. Hydrolysis was the main reaction for the cleavage of the urethane bond during the initial decomposition reaction at relatively low temperatures. Catechin urethanes decomposed much faster at elevated temperatures by aminolysis and by hydrolysis in a continuing reaction without a catalyst.

In the present study we aimed to obtain basic information on the stability of tannin-derived PUFs and on possibility of chemical recycling of their raw materials. PUF was prepared from WT and subjected to mild hydrolytic treatment. Its weight loss and decrease in its elastic modulus by the treatment were evaluated. Yields of selected products on hydrolysis and aminolysis were determined as well.

Materials and methods

Materials

Two PUFs, one containing 25% WT and the other containing 16% trimethylolpropane (TMP), WT-PUF and TMP-PUF respectively, have been chosen for the following decomposition experiment. These PUFs were prepared by mixing WT or TMP with tolylene diisocyanate (TDI) and polyester in the presence of triethylenediamine catalyst, as described in a previous paper.¹

Hydrolytic treatment of PUF blocks

Three PUF blocks (15 × 15 × 15 mm) were placed in water (30 ml) and flooded in vacuo for 10 min at 25°C. Reaction runs were carried out at various temperatures. After a pre-

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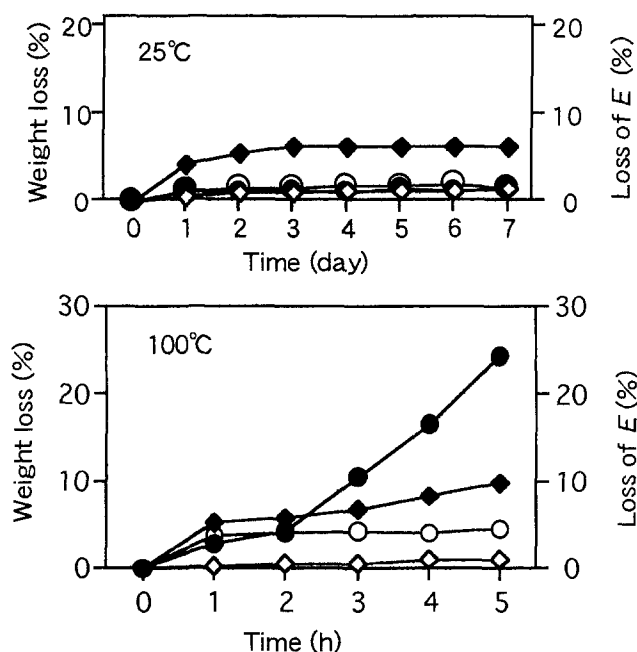


Fig. 1. Effect of hydrolytic treatment in water at 25°C (top) and 100°C (bottom) on weight loss and the loss of elastic modulus (E) of PUF blocks. Filled diamonds, weight loss of WT-PUF; open diamonds, weight loss of TMP-PUF; filled circles, loss of E in WT-PUF; open circles, loss of E in TMP-PUF

scribed reaction time, the blocks were cooled in cold water and removed from the water to measure their weights and elastic modulus (E) values after successive drying in vacuo at room temperature for 24h and at 60°C for 2h. E values were determined as described in a previous paper.¹ The weight losses and the losses of E were calculated from the weights and E values before and after the hydrolytic treatment of each block.

Hydrolytic treatment of PUF particles

The PUFs were chopped into 3- to 5-mm particles, and about 0.1g of these particles was suspended in a solution of water (55mM) in acetonitrile (30 ml) to give a sample for hydrolysis. Other handlings were the same as those for PUF blocks except for determining E .

The amounts of tannin and aromatic amines (calibrated as tolylene-2,4-diamine) produced in the reaction mixture were determined using the acidified vanillin method⁷ and a colorimetric method of Matsui et al.,⁸ respectively. Their contents were calculated based on the compositions of raw materials for PUF preparation.

Aminolytic treatment of PUFs

The chopped PUF particles (ca. 0.1g each) were added to acetonitrile solutions (30 ml) containing water (55mM) and aniline (10mM) to give samples for aminolysis. The aniline remaining after the treatment was determined by high-performance liquid chromatography (HPLC) as described

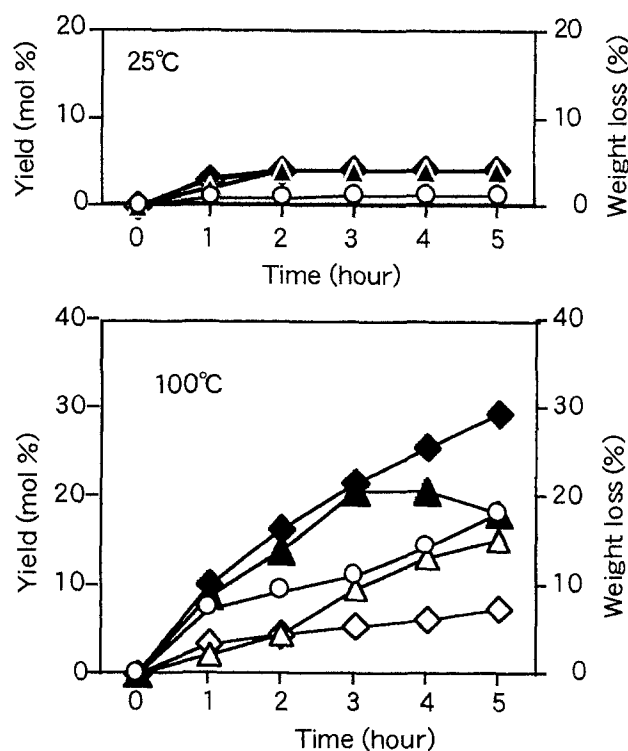


Fig. 2. Weight loss and products yields from hydrolytic treatment of the PUF particles in aqueous acetonitrile at 25°C (top) and 100°C (bottom). Filled diamonds, weight loss of WT-PUF; open diamonds, weight loss of TMP-PUF; filled triangles, aromatic amines from WT-PUF; open triangles, aromatic amines from TMP-PUF; open circles, tannin from WT-PUF. Tannin and aromatic amines are shown as the percent of the tannin and tolylene diisocyanate used for the PUF preparation, respectively

in a previous paper.⁶ Other handlings were the same as those for hydrolysis.

Results and discussion

Hydrolysis of PUFs

Weight loss of about 5% was observed when the WT-PUF blocks were kept in water for 2 days at 25°C; the TMP-PUF blocks exhibited almost no weight loss under the same conditions as shown in Fig. 1. About 4% weight loss was observed for WT-PUF particles after 2h of hydrolytic treatment in aqueous acetonitrile at 25°C. A similar weight loss curve was obtained for TMP-PUF particles at 25°C (Fig. 2). Almost no change was observed in the E of WT-PUF after the same treatment. The initial weight losses are likely to result from the leaching of low-molecular-weight components contained in the PUFs. It is therefore suggested that urethane bonds in WT-PUF and TMP-PUF have almost the same stability to hydrolysis at room temperature.

On the other hand, the weight losses in both WT-PUF blocks and particles occurred much faster than those of

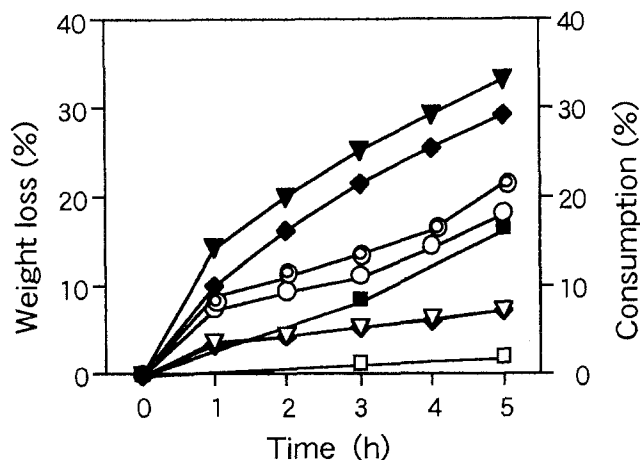


Fig. 3. Effect of aniline on weight loss of WT-PUFs and TMP-PUFs in aminolytic treatment at 100°C. *Inverted filled and open triangles*, weight loss of WT-PUF with aniline and TMP-PUF with aniline, respectively; *filled and open diamonds*, weight loss of WT-PUF without aniline and TMP-PUF without aniline, respectively; *filled and open squares*, consumption of aniline in WT-PUF and in TMP-PUF, respectively; *double open circles*, tannin yield from WT-PUF with aniline; *open circles*, tannin yield from WT-PUF without aniline. Aniline is shown as the percent of aniline added

TMP-PUF at a high temperature (100°C) as shown in Figs. 1 and 2, respectively. Urethane bonds between tannin phenolic hydroxyl groups and isocyanate groups are likely to be cleaved during the hydrolytic treatment, as it was observed in a previous study⁶ that phenolic urethanes derived from catechin were hydrolyzed more easily than an alcoholic urethane derived from phenethyl alcohol. Matsui et al.⁸ observed that aliphatic urethane bonds were not hydrolyzed in water-containing dimethylacetamide at 100°C for 60 min. In addition, the large decreases in *E*, compared with the small weight losses for the WT-PUF after the reaction for 5 h at 100°C (Fig. 1), suggests that the tannin moiety, which act as cross-linking points and hard segments in the urethane polymer molecule, was hydrolyzed. In fact, tannin was liberated by hydrolysis of WT-PUF particles at 100°C (Fig. 2). However, the yield of aromatic amines showed maxima located at 4 h. This result suggests that the aromatic amines produced from hydrolysis were probably involved in aminolysis of WT-PUF providing urea bonds and simultaneously liberating tannin moieties in a continuing treatment process.

Aminolysis of PUFs

The aminolytic treatments of the WT-PUF and TMP-PUF particles were undertaken by adding small amounts of aniline to their hydrolytic treatment systems at 100°C. Decomposition of WT-PUF was accelerated to a small extent by adding aniline, whereas dissolution of TMP-PUF was not influenced by the aniline addition (Fig. 3). Tannin as a decomposition product increased, and simultaneously aniline was consumed during the aminolytic treatment. The result indicates that aminolysis of WT-PUF occurred during the aminolytic treatment, which suggests that the aromatic amines formed by hydrolysis should also cause its aminolysis under the hydrolytic condition mentioned above. The ease of hydrolysis and aminolysis of WT-PUF may result in its ease of natural decomposition when buried under ground or left in the aquatic environment for a long time. This property of WT-PUF may also assist its chemical recycling by decomposing it into the raw materials tannin and aromatic diamines.

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