Synthesis of Biodegradable Polyurethane Foams from Condensed Tannin and Bark of Acacia mearnsii

戈, 進杰
九州大学農学部林産学科

https://doi.org/10.15017/10942
Synthesis of Biodegradable Polyurethane Foams from Condensed Tannin and Bark of *Acacia mearnsii*

Jin-jie Ge*****

Abstract

Utilization of wattle tannin (WT) and *Acacia mearnsii* bark (BK) was studied as a partial replacement for synthetic polyols in formulation of polyurethane (PU) preparation. Based on the urethane formation from (+)-catechin, it is suggested that polyhydric condensed tannin can be utilized as a polyol and constitutes hard segments in a PU polymer molecule. Rigid PU foams were prepared from WT and BK and their biodegradability was investigated. Various types of PU foams can be obtained by selecting the appropriate diisocyanates. Hydroxyl groups in B-ring of WT react with isocyanate, and hence WT and BK act as cross-linking agents as well as hard segments in PU foams so as to produce rigid foams at high levels of WT or BK contents. The PU foams derived from WT and BK obviously were degraded by some wood-rotting fungi. The BK moiety was degraded preferentially by fungi and soil microorganisms.

The urethanes derived from catechin and WT were relatively stable under hydrolytic and aminolytic conditions at room temperature. The rates of decomposition of urethanes derived from catechin and WT in both hydrolysis and aminolysis conditions at high temperatures were much faster than those of urethanes derived from phenethyl alcohol and trimethylolpropane.

Key words: *Acacia mearnsii*; polyurethane; wattle tannin; bark; (+)-catechin; condensed tannin; isocyanate; urethane derivatives; rigid polyurethane foam; biodegradability; cross-linking agent; wood-rotting fungi; mechanical strength; soil microorganisms; hydrolysis; aminolysis.

Contents

1. Preface
2. Pheny lurethane Formation from (+)-Catechin as a Model Reaction for Polyurethane Synthesis from Condensed Tannins

---

* Department of Forest Products, Faculty of Agriculture, Kyushu University, Fukuoka 812-8581
** Department of Forest Products, Faculty of Agriculture, Kyushu University, Fukuoka 812-8581
*** Present address: Department of Macromolecular Science, Fudan University, 220 Handan Rd., Shanghai, 200433, P.R. China (現在の所属: 復旦大学 (中国) 高分子科学系)
2.1. Introduction
2.2. Materials and methods
2.2.1. Isolation and identification of reaction products
2.2.2. Determination of product yields
2.3. Results and discussion
2.3.1. Isolation of main reaction products
2.3.2. Identification of main urethanes
2.3.3. Effect of isocyanate/catechin ratio on yields of urethanes
2.3.4. Effect of reaction temperature and a catalyst on urethane yields
2.4. Conclusions
3. Compressive Properties and Biodegradabilities of Polyurethane Foams Derived from Condensed Tannin
3.1. Introduction
3.2. Materials and methods
3.2.1. Preparation of polyester
3.2.2. Preparation of polyurethane foams
3.2.3. Compressive properties measurements
3.2.4. Assay of biodegradability
3.3. Results and discussion
3.3.1. Compressive properties of the tannin-derived polyurethane foams
3.3.2. Biodegradability of the tannin-derived polyurethane foams
3.4. Conclusions
4. Synthesis of Biodegradable Polyurethane Foams from Bark of Acacia mearnsii
4.1. Introduction
4.2. Materials and methods
4.2.1. Materials
4.2.2. Solubility of BK
4.2.3. Preparation and characterization of PU foams
4.2.4. Assay of biodegradability
4.2.5. Infrared (IR) spectral analysis
4.3. Results and discussion
4.3.1. Preparation of bark-derived polyurethane foams
4.3.2. Compressive properties of bark-derived polyurethane foams
4.3.3. Biodegradability of bark-derived polyurethane foams
4.4. Conclusions
5. Decomposition of Polyurethane Foams Derived from Condensed Tannin
Hydrolysis and Aminolysis of Urethanes
5.1 Introduction
5.2. Materials and methods
5.2.1. Synthesis of phenethyl phenylcarbamate (PAU)
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

5.2.2. Hydrolytic treatment of model urethanes
5.2.3. Aminolytic treatment of model urethanes
5.2.4. Isolation and identification of main decomposition products
5.2.5. Hydrolytic treatment of PU foams
5.2.6. Aminolytic treatment of PU foams
5.3. Results and discussion
5.3.1. Identification of main decomposition products
5.3.2. Hydrolytic treatment of CU-I and CU-II
5.3.3. Hydrolytic treatment of PAU
5.3.4. Aminolytic treatment of CU-I and PAU
5.3.5. Hydrolysis of polyurethane foams
5.3.6. Aminolysis of polyurethane foams
5.4. Conclusions
  Abbreviations
  Acknowledgments
  References

1. Preface

There are more than 700 Acacia species in the world, of which Acacia mearnsii De Wild. is in large area of plantation forests in South Africa, East Africa, South America and China because it is one of the fast-growing species. The original seeds were introduced from Australia and A. mearnsii grows naturally on the mainland of south-eastern Australia. The A. mearnsii bark (BK) contains significant amounts of water-soluble component, known as “wattle tannins” (WT). The major components of the aqueous extracts are polyflavanoid tannins (C6-C3-C6 compounds) in nature (Fang et al., 1992; Yazaki et al., 1990; Foo, 1981; Ohara, 1994; Cochanska et al., 1979). Typical structures of different condensed tannins are shown in Fig. 1.

About 500,000 tons of vegetable tannins are produced annually in the world, of which 100,00 tons are WT extracted from the BK of Acacia sp. (Porter et al., 1989). WT have been used for the tanning agents, oil-well drilling, dyestuffs and medicines since the earliest time (Ohara, 1994). The availability of large quantities of tannin provides an impetus for investigating tannin’s potential uses. In recent years, many investigations on their new utilization such as cold-setting adhesives (Calve et al., 1995; Santana et al., 1995; Pizzi et al., 1978; Pizzi et al., 1979; Pizzi, 1980; McGraw et al., 1989; Pizzi et al., 1993a; Pizzi et al., 1993b; Pizzi et al., 1994a; Pizzi et al., 1994b; Pizzi et al., 1994c), adsorbent of heavy metal ions (Yamaguchi et al., 1992a; Yamaguchi et al., 1992b), and precipitation of protein (Kawamoto et al., 1990) have been reported. Biological activities of WT have suggested their potential utilization (Ohara et al., 1994). In spite of extensive
In this study, therefore, utilization of WT and BK as a partial replacement for synthetic polyols in formulation of polyurethane (PU) preparation was studied (Ge et al., 1993; Ge et al., 1996). PUs have been widely used in the fields of fibers, foams, elastomers, and protective coatings (Urquhart et al., 1995). Addition polymerization of diisocyanates (DIs) with polyols is the basic process in their synthesis (Krol et al., 1992; Krol, 1995; Katsuki et al., 1972). Natural polymers are expected to be utilized as polyols for PU preparation (Nakamura et al., 1990). It was thought that WT can also be utilized as a polyol component in PU synthesis, because it has both aliphatic and aromatic hydroxyl groups. However, little is known of the chemical reactions between tannin hydroxyl groups and isocyanates. In the first step of this work, therefore, the reaction of phenyl isocyanate and (+)-catechin as a model reaction between diisocyanate and condensed tannin was studied. Main reaction products were characterized by IR, 1H-NMR, 13C-NMR, 1H-1H NOESY, 13C-1H COSY and FD-MS techniques. Furthermore, yields of the urethanes were determined under different reaction conditions as described in Chapter 2. In the model reaction, phenolic hydroxyl groups of tannin were able to react with isocyanates to form polyurethanes.

In the succeeding chapters, preparation of PUs from WT and WT-containing BK was studied. Thus, in Chapter 3 PU foams were synthesized from non-modified WT, polyester (PES), and DI. The WT content, isocyanate/hydroxyl group (NCO/OH) ratio, and water content were varied to evaluate their effects on the compression properties of the PU foams.

Furthermore, a PU foam containing 25% WT was incubated with three wood-rotting fungi to investigate its potential biodegradability because WT-containing BK can be decayed by wood-rotting fungi in nature.

WT was successfully used for the synthesis of PU foams as described in Chapter 3. However, it is much better if one can obtain PU directly from BK without isolation of the WT, because extraction, concentration, and drying of WT are energy consuming processes. In Chapter 4, therefore, BK was used in PU preparation. The effects of reaction conditions were investigated. Furthermore, biodegradability of the BK-derived PU foams was investigated because the blending of natural polyols, such as tannin into polymer formulation enhances fungal biodegradation as described in Chapter 3.

PU foams from WT and BK have been prepared in Chapters 3 and 4 and it was found that WT and BK components enhanced the biodegradability of the foams. It is not known, however, that the foams derived from WT and BK can be used in the same stability as are usual foams. The possibility of chemical recycling of the WT- and BK-derived foams after use has not been known either. Thus, breakdown of the urethane group was examined by hydrolysis and aminolysis of CU-I, CU-II, and PAU
as the models of PU foams. Furthermore PU foams derived from WT- or TMP-containing polyols were also employed for hydrolysis and aminolysis to learn the difference in the stability.

2. Phenylurethane Formation from (+)-Catechin as a Model Reaction for Polyurethane Synthesis from Condensed Tannins

2.1. Introduction

Condensed tannins, polymeric proanthocyanidins (Fig. 1) are widely distributed in the plant kingdom and have been used for the tanning agents, dyestuffs and medicines since the earliest time. In recent years, many investigations on their new utilization such as cold-setting adhesives, heavy metal ion adsorbents, and adsorbents of protein have been reported as already discussed in Chapter 1. Biological activities of condensed tannins have suggested their potential utilization. Recently, we have found that WT and BK could be successfully incorporated into formulation of PU foams as its other valuable utilization and that WT and BK components enhance biodegradability of the foams by some wood-rotting fungi and soil microorganisms (Ge et al., 1993; Ge et al., 1996) (cf. Chapters 3 and 4).

Addition polymerization of diisocyanates with polyols is the basic process used for synthesis of PU (Fig. 2), which are applied for the production of foams, elastomers, and protective coatings (Urquhart et al., 1995). Aliphatic polyols such as polyethers or polyesters are generally used for synthesis of PUs (Krol et al., 1992; Krol, 1995), probably because alcoholic hydroxyl groups are generally more reactive with isocyanates than phenolic hydroxyl groups (Katsuki et al., 1972).

Recently, polyhydric natural polymers were used as polyols in studies on polyurethane preparation (Nakamura et al., 1990; Yao et al., 1995). However, little is known of the chemical reactions between tannin hydroxyl groups and isocyanates, although Hartman (1977) has reported that bark components of Ponderosa pine (Pinus ponderosa Laws.) and Douglas fir (Pseudotsuga menziesii [Mirb.] Franco) can be used as the major or sole polyol in the reaction with diisocyanate to produce rigid polyurethane foams. He explained and confirmed a series of complex chemical bonds and linkages in the foams prepared using IR and thermogravimetric analyses. However, there was no direct proof if tannin, that is one of the bark components, really reacted with isocyanates to form urethane linkages.

In this work, therefore, we studied the reaction of phenyl isocyanate and (+)-catechin as a model reaction between diisocyanate and condensed tannin, because (+)-catechin has been employed as a model of condensed tannins in some studies (Foo et al., 1983; Mitsunaga et al., 1993; Mitsunaga et al., 1994). The main reaction products were characterized by IR, ¹H- and ¹³C-NMR, ¹H-¹H NOESY, ¹³C-¹H COSY and FD-MS techniques. Furthermore, yields of the urethanes formed were determined under
2.2. Materials and methods

TLC analyses were performed on Merck 60F254 silica-gel precoated plates (solvent: ethyl acetate: benzene: H2O = 1: 1: 0.003 v/v/v). Fluorescent spots were detected UV illumination. FD-MS were recorded on a JEOL JMS-DX300 (JMA 3500). IR spectra were obtained with 2 mg samples in 400 mg KBr pellets using an A102 infrared spectrophotometer (Japan Spectroscopic Co. Ltd.). 1H- and 13C-NMR spectra were recorded in CDCl3 or in acetone-d6 on a JNM-GX 400 spectrometer with tetramethylsilane as an internal standard. 1H·1H NOESY spectra were recorded using a mixing time of 750 ms. The 13C·1H COSY spectra were recorded using a flip angle of 90°.

2.2.1. Isolation and identification of reaction products

Phenyl isocyanate (1.19 g) was added to a solution of catechin (2.90 g) in dry
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

Fig. 2 Reactions for formation of polyurethane foam (Krol et al., 1992).

acetonitrile (30 ml) with stirring and left in a nitrogen atmosphere at 30°C for 24 h.

The reaction mixture was concentrated in vacuo to a small volume; precipitates formed were removed by filtration, and the solvent was evaporated in vacuo to dryness. The residual yellow oil was chromatoographed on a silica gel column (Wakogel C-200) using an ethyl acetate: benzene: H₂O (i: i: 0.003 v/v/v) mixture as an eluent to give two urethane fractions, CD-I and CD-II. Their IR spectra are shown in Fig. 3. However, CD-I, tan-colored crystals, mp.: 93-94°C and Rf=0.18 upon the TLC (Fig. 4), was revealed to be an equimolar mixture of two isomers (CD-IA and CD-IB) by HPLC using a mixture of acetonitrile and water (45:55 v/v) and a column: Develosil ODS-UG-5 C₁₈ column (3.9 mm x 150 mm) (Fig. 5).

The mixture was acetylated at room temperature for 24 h with acetic anhydride and pyridine. Tetraacetates, CU-IA-OAc and CU-IB-OAc were separated each other by means of preparative HPLC using a mixture of acetonitrile and water (50:50 v/v) at a flow rate 9.5 ml/min and serially connected two columns: Waters μ-Bondasphere 5 μ C₁₈-100 A (19×150 mm) and μ-Bondapack C₁₈ (19×150 mm). Eluates were extracted with ethyl acetate, dried over sodium sulfate, and concentrated to dryness prior to subjecting to silica-gel column chromatography (Wakogel C-200) using an ethyl acetate and n-hexane (40:60 v/v) mixture as an eluent to purify both CU-IA-OAc and CU-IB-OAc.

CU-IA-OAc: White crystal, mp.: 72-73°C, mol. wt.: 577 by the FD-MS method (Fig.6). Chemical shifts δ (ppm) for ¹³C-NMR in CDCl₃ (Fig.7): 20.9 (CH₃, Ac), 23.8 (C-4), 68.2
Fig. 3  IR spectra of (+)-catechin (A), CU-I (B) and CU-II (C).

(C-3), 77.5 (C-2), 107.6 (C-8), 108.7 (C-6), 110.1 (C-10), 118.6 (C-2", 6"), 121.9 (C-2'), 123.7 (C-5'), 124.1 (C-4'), 124.2 (C-6'), 129.1 (C-3", 5"), 136.2 (C-1"), 137.0 (C-1'), 141.9 and 142.4 (C-3' and C-4'), 149.3, 149.8 and 154.3 (C-9, C-7 and C-5), 168.3 (C=O, Ac), and 170.1 (C=O, Urethane). δ (ppm) for 'H-NMR in CDCl₃ (Fig.8): 2.01 (3H, s, Alc-OAc), 2.27 (9H, 3s, Ar-OAc×3), 2.67 (1H, dd, J= 6.35, 16.73 Hz, H-4-axial), 2.87 (1H, dd, J= 5.13, 6.35 Hz, H-2), 3.06 (1H, m, 5.13, 6.35, 6.35 Hz, H-3), 6.59 (1H, d, J=2.20 Hz, H-6), 6.67 (1H, d, J=2.20 Hz, H-8), 7.09-7.13 (1H, m, H-4"), 7.20 (1H, d, J=8.7 Hz, H-5' ), 7.25-7.27 (2H, m, H-2', 6'), 7.30-7.35 (2H, m, H-3", 5"), 7.36 (1H, s, H-Urethane), and 7.42-7.44 (2H, m, H-2", 6").
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

Fig. 4 TLC analyses of products from reaction between isocyanate and (+)-catechin.

Fig. 5 An HPLC chart of CU-I (CU-IA + CU-IB).

CU-IB-OAc: White crystal, mp.: 72-73°C, mol. wt.: 577 by the FD-MS method. Chemical shifts δ (ppm) for 13C-NMR in CDCl₃: 20.9 (CH₃, Ac), 23.8 (C-4), 68.2 (C-3), 77.5 (C-2), 107.6 (C-8), 108.7 (C-6), 110.1 (C-10), 118.6 (C-2', 6'), 121.7 (C-2'), 123.8 (C-5'), 124.1...
Fig. 6 FD-MS spectrum of CU-IA-OAc.

Fig. 7 $^{13}$C-NMR spectrum of CU-IA-OAc (CDCl₃).

(C-4\(^{\prime}\)), 124.4 (C-6\(^{\prime}\)), 129.1 (C-3\(^{\prime}\), 5\(^{\prime}\)), 136.0 (C-1\(^{\prime}\)), 137.0 (C-1\(^{\prime}\)), 141.9 and 142.4 (C-3\(^{\prime}\) and C-4\(^{\prime}\)), 149.3, 149.8 and 154.3 (C-9, C-7 and C-5), 168.3 (C=O, Ac), and 170.1 (C=O, Urethane). δ (ppm) for 'H-NMR (Fig.9): 2.01 (3H, S, Alc-OAc), 2.27 (9H, 3s, Ar-OAc\(\times\)3), 2.66 (1H, dd, \(J=6.35, 16.73\) Hz, H-4-axial), 2.87 (1H, dd, \(J=5.13, 16.73\) Hz, H-4-equatorial), 5.16 (1H, d, \(J=6.35\) Hz, H-2), 5.26 (1H, m, \(J=5.13, 6.35, 6.35\) Hz, H-3), 6.59 (1H, d, \(J=2.20\) Hz, H-6), 6.66 (1H, d, \(J=2.20\) Hz, H-8), 7.10-7.14 (1H, m, H-4\(^{\prime}\)), 7.19 (1H, d, \(J=1.7\) Hz, H-2\(^{\prime}\)), 7.25-7.28 (2H, m, H-5\(^{\prime}\), 6\(^{\prime}\)), 7.32-7.35 (2H, m, H-3\(^{\prime}\), 5\(^{\prime}\)), 7.36 (1H, s, H-Urethane), and
Fig. 8 $^1$H-NMR spectrum of CU-IA-OAc (CDCl$_3$).

Fig. 9 $^1$H-NMR spectrum of CU-IB-OAc (CDCl$_3$).
Fig. 10 $^13$C-'H COSY spectrum of CU-IB-OAc ($\text{CDCl}_3$).

Fig. 11 $^13$C-NMR spectrum of CU-II ($\text{CD}_3\text{COCD}_3$).
Polyurethane Foams from Tannin and Bark of Acacia mearnsii 33

INT
1000

Fig. 12  FD-MS spectrum of CU-II-OAc.

Fig. 13  1H-NMR spectrum of CU-II-OAc (CDCl3).

7.42-7.44 (2H, m, H-2", 6") . A 13C-1H COSY spectrum of CU-IB-OAc is shown in Fig. 10.

CU-II: Tan-colored crystals, mp.: 140-141°C, Rf=0.26 upon TLC. 13C-NMR spectra in acetone-d6 (Fig. 11) showed δ (ppm): 29.2 (C-4), 68.3 (C-3), 82.0 (C-2), 95.4 (C-8), 96.4 (C-6), 100.6 (C-10), 119.5 (C-2", 6"), 123.7 (C-2'), 124.1 (C-5'), 124.4 (C-6'), 126.2 (C-4"), 129.7 (C-3", 5"), 139.1 (C-1'), 143.5 and 143.6 (C-3' and C-4'), 151.9 (C-1"), 156.5, 157.2 and 157.8 (C-9, C-7 and C-5) and 170.9 (C=O, Urethane).
CU-II acetate: mp.: 94-95°C, mol. wt.: 654 by the FD-MS method (Fig. 12). δ (ppm) for 'H-NMR in CDCl₃ (Fig. 13): 2.01 (3H, s, Alc-OAc), 2.27 (6H, 2s, Ar-OAc×2), 2.66 (1H, dd, J=6.35, 16.73 Hz, H-4-axial), 2.87 (1H, dd, J=5.13, 16.73 Hz, H-4-equatorial), 5.16 (1H, d, J=6.35 Hz, H-2), 5.27 (1H, m, J=5.13, 6.35, 6.35 Hz, H-3), 6.59 (1H, d, J=2.20 Hz, H-6), 6.67 (1H, d, J=2.20 Hz, H-8), 7.07-7.11 (2H, m, H-4", 4""), 7.28-7.32 (7H, m, H-2', 5', 6', 3", 3"", 5" and 5""); 7.36 (2H, 2s, H-urethane×2), and 7.38-7.40 (4H, m, H-2", 2"", 6", and 6"").

2.2.2. Determination of product yields

Reaction runs were made with different ratios of (+)-catechin to phenyl isocyanate. (+)-Catechin (580 mg) and appropriate amounts of TEDA were dissolved in dry acetonitrile (25 ml) with stirring, and phenyl isocyanate (119, 238, or 357 mg) was added to this solution in a nitrogen atmosphere at 35°C. After a prescribed reaction time, a 0.5 ml aliquot of the reaction mixture was taken and poured into 10 ml of H₂O to give a sample solution for HPLC analysis. Phenyl isocyanate remained in the reaction mixture was almost quantitatively converted to aniline by this procedure. Amounts of main products and starting materials in the reaction mixtures were determined by HPLC conducted with a Waters 208D model using a Develosil ODS-UG-5.
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

C_{18} column (3.9 mm x 150 mm) and detected at 280 nm by the internal standard method with 4-methylguaiacol as a internal standard. The mobile phase was a mixture (45:55 v/v) of acetonitrile / 10 mM phosphate buffer (pH 3.0). An HPLC chart is shown in Fig. 14.

2.3. Results and discussion

2.3.1. Isolation of main reaction products

On a TLC of products from the reaction of catechin with phenyl isocyanate (Fig. 4) observed were three main spots having Rf values of 0.61 (diphenylurea), 0.26 (CU-II), and 0.18 (CU-I), respectively, besides starting materials.

CU-II was isolated by silica gel column chromatography. However, CU-I fraction was composed of two compounds, CU-IA and CU-IB, as revealed by HPLC (Fig. 5). Trials to separate CU-IA and CU-IB by preparative HPLC failed because each fraction very easily recurred as an equimolar mixture of the two compounds, even though each fraction consisting of a single peak was collected. This phenomenon suggests that CU-IA and CU-IB are in equilibrium with each other, and hence they are tautomeric isomers. We assumed that a free hydroxyl group might be involved in the tautomerism. Therefore, the two isomers were separated after acetylation of the mixture by means of preparative HPLC. Further purification of each of the acetates, CU-IA-OAc and CU-IB-OAc, was made on a silica gel column.

2.3.2. Identification of main urethanes

IR spectra of the main products, CU-I (a mixture of CU-IA and CU-IB) and CU-II in Fig. 3 exhibited a strong band at 1,710 cm^{-1} that is characteristic of a urethane linkage (Hartman, 1977; Wu et al., 1992; Urquhart et al., 1995). FD-MS results of their acetates (Figs. 6 and 11) indicate that one and two isocyanate groups were introduced to a catechin molecule to form CU-I (m/z: 577) and CU-II (m/z: 654), respectively.

Chemical shifts of all of the hydrogens and carbons in ^1H- and ^13C-NMR spectra of compounds CU-IA, CU-IB, and CU-II were assigned as listed in the section 2.2.1. by means of ^13C-^1H COSY (Fig. 10). A signal of aliphatic OAc was observed near 2.01 ppm for each ^1H-NMR spectrum of the three compounds (Figs. 8, 9 and 13).

All carbons in the A- and C-rings of CU-II exhibited almost the same chemical shifts in a ^13C-NMR spectrum as the corresponding carbons in catechin did. However, chemical shifts of carbons in its B-ring were different by -2 to 8 ppm from those of the corresponding carbons of catechin (Table 1). These results indicate that CU-II is a disubstituted urethane at the 3’- and 4’-positions of catechin as shown in Fig. 15. ^1H-NMR data supported this structure. Thus, signals of protons at the 2’ and 5’ positions (H-2’ and H-5’, respectively) of CU-II-OAc shifted from those of catechin acetate to lower magnetic fields at about 7.3 ppm as shown in Fig. 16(I).

In ^1H-NMR spectrum of the acetate CU-IA-OAc, a signal of H-2’ was observed in a
Table 1 Change of chemical shifts and signal assignments for $^{13}$C-NMR of CU-II.

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Δδ (ppm)</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>157.833</td>
<td>0.132</td>
<td>C-5</td>
</tr>
<tr>
<td>96.445</td>
<td>0.321</td>
<td>C-6</td>
</tr>
<tr>
<td>157.234</td>
<td>0.029</td>
<td>C-7</td>
</tr>
<tr>
<td>95.482</td>
<td>0.102</td>
<td>C-8</td>
</tr>
<tr>
<td>156.519</td>
<td>-0.336</td>
<td>C-9</td>
</tr>
<tr>
<td>100.649</td>
<td>0.073</td>
<td>C-10</td>
</tr>
<tr>
<td>82.011</td>
<td>-0.656</td>
<td>C-2</td>
</tr>
<tr>
<td>68.291</td>
<td>-0.044</td>
<td>C-3</td>
</tr>
<tr>
<td>29.278</td>
<td>0.452</td>
<td>C-4</td>
</tr>
<tr>
<td>143.515</td>
<td>-2.116</td>
<td>C-3' or C-4'</td>
</tr>
<tr>
<td>143.632</td>
<td>-2.058</td>
<td>C-4' or C-3'</td>
</tr>
<tr>
<td>126.190</td>
<td>-5.897</td>
<td>C-1'</td>
</tr>
<tr>
<td>124.059</td>
<td>8.377</td>
<td>C-2'</td>
</tr>
<tr>
<td>123.753</td>
<td>8.538</td>
<td>C-5'</td>
</tr>
<tr>
<td>124.410</td>
<td>4.379</td>
<td>C-6'</td>
</tr>
<tr>
<td>170.998</td>
<td></td>
<td>C-7</td>
</tr>
<tr>
<td>151.936</td>
<td></td>
<td>C-8</td>
</tr>
<tr>
<td>139.151</td>
<td></td>
<td>C-9</td>
</tr>
<tr>
<td>129.708</td>
<td></td>
<td>C-10</td>
</tr>
<tr>
<td>119.520</td>
<td></td>
<td>C-11</td>
</tr>
</tbody>
</table>

Δδ: Difference of chemical shifts of carbons between the CU II and catechin.

Fig. 15 Reaction of (+)-catechin with phenyl isocyanate as a model reaction of tannin and disocyanates.

relatively low magnetic field near 7.3 ppm, whereas a H-5’ signal appeared in a higher magnetic field at 7.2 ppm as a doublet (J=8.7 Hz) as shown in Fig. 16(II). On the contrary, the spectrum of CU-IB-OAc exhibited the H-2’ signal in a relatively high magnetic field (7.18 ppm, d, J=1.7 Hz), and the H-5’ signal in a lower field (7.28 ppm) as shown in Fig. 16(III).

These results clearly indicate that an urethane group is located at the 3’-position in CU-IA-OAc and at the 4’-position in CU-IB-OAc as shown in Fig. 17. Furthermore, NOESY spectra shown in Figs. 18 and 19 confirm positions of acetyl groups in compounds CU-1A-OAc and CU-IB-OAc. The H-5’, H-6, and H-8 signals of CU-IA-OAc
showed correlations with aromatic acetyl signals (Fig. 18), which indicates that the 4', 5', and 7-hydroxyl groups in catechin are acetylated, and consequently, only the 3'-position is bonded through an urethane linkage. In a similar manner, an urethane bond at the 4'-position in CU-IB-OAc was confirmed from the correlations of the
H-2', H-6, and H-8 signals with aromatic acetyl signals (Fig. 19). Therefore, CU-IA and CU-IB were identified as 3'-O-(phenylcarbamoyl)catechin and 4'-O-(phenylcarbamoyl)catechin, respectively.

As mentioned above, CU-IA and CU-IB were interconvertible or came to equilibrium at room temperature. We therefore propose here a tautomerism in which an urethane bond or a phenylcarbamoyl group can migrate reversibly between two phenolic hydroxyl groups in a catechol ring as shown in Scheme 1. To our knowledge no reversible migration of an urethane bond of this type has been discovered so far.

It is worth noting that the alcoholic hydroxyl group in catechin did not react with isocyanate as seen from the structures of CU-IA, CU-IB, and CU-II, although alcoholic...
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

Hydroxyl groups generally are more reactive with isocyanates than phenolic ones (Katsuki et al., 1972). We did not detect 3-O-(phenylcarbamoyl) catechin (CU-X in Fig. 17) which is the hypothetical product from the alcoholic hydroxyl group of catechin. The product CU-X, even if formed, should be much less stable than the products CU-IA, CU-IB, and CU-II because of its steric hindrance between the carbonyl oxygen atom in the urethane group and the B-ring carbons of catechin as illustrated in Fig. 17. On the other hand, phenolic hydroxyl groups in the A-ring also did not react with isocyanate. This may be attributed to lower electron densities at the oxygen atoms in the A-ring than those in the B-ring. From these results, it is suggested that phenolic hydroxyl groups in the B-ring of a condensed tannin molecule participated in its reaction with disocyanate molecules when polyurethane foams were prepared from WT or tree bark. An alcoholic hydroxyl group and phenolic hydroxyl groups in the A-ring in a catechin unit are not likely to be important for tannin-isocyanate reactions.

2.3.3. Effect of isocyanate/catechin molar ratio on yields of urethanes

Reaction runs were conducted by using three different molar ratios of phenyl isocyanate/catechin (1:1, 2:1, and 3:1) at 35°C. No catalyst was added. Yields of major
products are plotted against reaction time in Figs. 20-22, where yields of CU-IA and CU-IB are combined and expressed as a yield of CU-1 because they are easily interconvertible as described above.

Combined yield of CU-1 and CU-II always accounted for more than 90% of catechin consumed, which indicates that the phenolic urethane formation is the major reaction of catechin with isocyanate. Both the initial formation of CU-1 and the retarded production of CU-II were significantly accelerated with increasing ratio of phenyl isocyanate to catechin. Consequently, yields of CU-1 declined in the later phases of the reaction runs at the ratios 2:1 and 3:1 (Figs. 21 and 22). This simultaneous decrease in CU-1 and increase in CU-II indicate that CU-II can be produced quite easily from CU-1 if phenyl isocyanate is in enough amounts. However, rate of the reaction was slow at room temperature without catalyst.

2.3.4. Effect of reaction temperature and a catalyst on urethane yields

In the preparation of WT- or BK-derived polyurethane foams with TEDA as a catalyst, temperatures were elevated to about 60°C in one min even if the runs began at room temperature. We therefore examined the influences of reaction temperature
Fig. 20 Yield of products from reaction between phenyl isocyanate and (+)-catechin. Notes: phenyl isocyanate: (+)-catechin = 1 : 1 (mol/mol), reaction temperature: 35°C.

Fig. 21 Yield of products from reaction between phenyl isocyanate and (+)-catechin. Notes: phenyl isocyanate: (+)-catechin = 2:1 (mol/mol), reaction temperature: 35°C.
Fig. 22 Yield of products from reaction between phenyl isocyanate and (+)-catechin. Notes: phenyl isocyanate: (+)-catechin = 3:1 (mol/mol), reaction temperature: 35°C.

Fig. 23 Yield of products from reaction between phenyl isocyanate and (+)-catechin. Notes: phenyl isocyanate: (+)-catechin = 1:1 (mol/mol), reaction temperature: 60°C.
and a catalyst, TEDA, on the production rate of urethanes, CU-I and CU-II. As generally expected reaction of (+)-catechin with isocyanate was accelerated by elevating reaction temperature up to 60°C (Fig. 23). No discernible side reactions were observed even at the elevated temperature. This might be favorable for the preparation of polyurethane foams from WT or BK, because reaction of diisocyanates with polyols containing WT or BK were considerably exothermic.

In the presence of 0.5% TEDA as a catalyst both catechin and phenyl isocyanate were rapidly consumed and, at the same time, urethanes were quickly formed as exemplified in Fig. 24. As shown in Fig. 25, total yield of CU-I and CU-II increased with increasing TEDA dose up to 1.5% both after 1 h and 24 h reaction runs, whereas the total yield leveled off at the TEDA dose more than 1.5%. This result suggests that the optimum TEDA dose should be 1.5% which has been employed for the synthesis of rigid foams from WT and BK as described in Chapters 3 and 4.

The above-mentioned behaviors of catechin suggest that polyhydric condensed tannins can be utilized as a polyol and play a role of cross-linking agents in a polyurethane polymer molecule. Thus, several phenolic hydroxyl groups in a tannin molecule might react to form urethane linkages when condensed tannins in bark were subjected to the reaction with diisocyanates as ingredients of the polyurethane synthesis catalyzed with TEDA. Therefore, tannin moieties in the polyurethane
molecule may constitute hard segments and contribute to the rigidity of polyurethane molecules.

2.4. Conclusions

(+) -Catechin easily reacted with phenyl isocyanate, to produce three major urethane derivatives, CU-IA, CU-IB and CU-II. The CU-IA and CU-IB are tautomeric isomers in which the free hydroxyl group might be involved. An alcoholic hydroxyl group and phenolic hydroxyl groups in A-ring of a catechin unit are not likely to be important for tannin-isocyanate reaction. CU-II became the main product if phenyl isocyanate is in enough amounts. It is suggested that polyhydric condensed tannins can be utilized as a polyol and constitute hard segments in a polyurethane polymer molecule.
3. Compressive Properties and Biodegradibilities of Polyurethane Foams Derived from Condensed Tannin

3.1. Introduction

About 500,000 tons of vegetable tannins are produced annually in the world, of which 100,000 tons is wattle tannin (WT) extracted from the bark of *Acacia* sp (Porter et al., 1989). A major use of tannins has been for leather manufacture, oil-well drilling, water treatment, agricultural trace metal treatments, and so forth (Hergart, 1989). The availability of large quantities of tannin provides an impetus for investigating tannin's potential uses. Recently, investigators have examined tannins as a component in adhesives, absorbent of protein and heavy metal ions, and wood preservatives (Chung et al., 1989; Yamaguchi et al., 1991a; Yamaguchi et al., 1991b; Laks et al., 1988). In spite of extensive research, attempts to expand the use of tannins into other areas have not been very successful.

PU foams commonly are prepared by reacting isocyanates and polyols, and are used widely in various fields. Success with the incorporation of plant components into PU formulations has been reported. Thus, lignin, lignocellulose, and cornstarch have been added to PU foam formulations as replacements for synthetic polyols (Hsu et al., 1975; Saraf et al., 1984; Saraf et al., 1985a; Saraf et al., 1985b; Yoshida et al., 1987; Hirose et al., 1989; Nakamura et al., 1988; Nakamura et al., 1989; Yoshida et al., 1990; Reimann et al., 1990; Nakamura et al., 1990; Yano et al., 1989; Cunningham et al., 1991; Cunningham et al., 1992).

In this study, WT was utilized as a polyol component in polyurethane synthesis, because it has both aliphatic and aromatic hydroxyl groups. In a model reaction (Chapter 2) phenolic hydroxyl groups of catechin reacted with isocyanate to form urethane. To give the best performance, polyol and isocyanate should be reacted without the use of solvents so as to avoid the heterogeneous cell structure which can be formed in PU by solvent vaporization. Therefore, in this study, PU foams were synthesized from non-modified WT, PES, and DI. Carbon dioxide generated from the reaction between water and DI was used as a foaming agent. The WT content, NCO/OH ratio, and water content were varied to evaluate their effects on the compression properties of the PU foams.

Condensed tannins were reported to be natural wood preservatives in the bark and wood of some species (Laks et al., 1988). However, tannin-containing bark can be decayed by wood-rotting fungi in nature. This fact suggests that tannin-derived PU foams may be biodegradable. Therefore, a PU foam containing 25% WT was incubated with three wood-rotting fungi to investigate its potential biodegradability.

3.2. Materials and method

WT, sebacic acid, PEG 400, TDI, MDI, HDI, and other reagents were obtained
Table 2 Properties of polyester.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl groups (mmol/g)</td>
<td>1.35</td>
</tr>
<tr>
<td>Carboxyl group (mmol/g)</td>
<td>0.14</td>
</tr>
<tr>
<td>Viscosity (cP at 25°C)</td>
<td>3800</td>
</tr>
</tbody>
</table>

3.2.1. Preparation of polyester

Sebacic acid (145 g), PEG 400 (320 g), trimethylolethane (9.8 g), and xylene (14 g) were heated to 250°C within 2 h and maintained at this temperature with stirring in a nitrogen atmosphere. The reaction was conducted until the amount of water distilled off from the condensation reached 95% of the theoretical amount. Properties of the PES synthesized are shown in Table 2. Hydroxyl and carboxyl groups in the PES and WT were determined according to Abe and Matsumoto (1958). Viscosity was measured using a Brookfield viscometer.

3.2.2. Preparation of polyurethane foams

WT was dissolved in PES by stirring at 80°C for 5.5 h. It was assumed that this mixing procedure would not cause any changes of hydroxyl group contents in WT and PES. A surfactant (silicone oil WF30), catalyst (TEDA or DBTL), TMP as a cross-linking agent and water were added to this solution with stirring after cooling to room temperature. Then the DI was added, and the mixture was stirred at 700 rpm to yield PU foam. The NCO/OH ratio, WT content, and water content were defined as follows:

\[
\frac{\text{NCO/OH}}{100\%} = \frac{w_{\text{DI}} \times I_{\text{DI}}}{w_{\text{WT}} \times H_{\text{WT}} + w_{\text{PES}} \times H_{\text{PES}} + w_{\text{TMP}} \times H_{\text{TMP}}}
\]

\[
\text{WT (\%)} = \frac{100w_{\text{WT}}}{w_{\text{WT}} + w_{\text{PES}} + w_{\text{TMP}} + w_{\text{DI}}}
\]

water content (\%) = \frac{100w_{\text{H}_{2}\text{O}}}{w_{\text{WT}} + w_{\text{PES}} + w_{\text{TMP}} + w_{\text{DI}}}

where \( I_{\text{DI}} \) is the content of the isocyanate group in the diisocyanate, and \( H_{\text{WT}} \) is the content of total (phenolic and aliphatic) hydroxyl groups in WT (7.1 mmol/g). \( H_{\text{PES}} \) and \( H_{\text{TMP}} \) are the contents of hydroxyl groups in PES and TMP, respectively, and \( w_{\text{H}_{2}\text{O}} \), \( w_{\text{DI}} \), \( w_{\text{WT}} \), \( w_{\text{PES}} \), and \( w_{\text{TMP}} \) denote the weights of water, DI, WT, PES, and TMP, respectively.

3.2.3. Compressive properties measurements

Compressive strength (\( \sigma \)) of the foams were measured according to ASTM D 1621 using a Tensilon testing machine after curing at room temperature for a week. The \( \sigma \) value was the strength in the case of a sample having a yield point below
10% strain. If the sample showed no yield point below 10% strain, $\sigma$ was defined as the stress at 10% strain. Compressive modulus of elasticity ($E$) was defined as follows:

$$E = \frac{W}{AS}$$

where $W =$ load (N), $A =$ initial cross-sectional area ($m^2$), and $S =$ strain.

### 3.2.4. Assay of biodegradability

The standard method of the wood decay test, Japanese Industrial Standard (JIS-) Z 2119-1977, was modified to apply to assays of the biodegradabilities of PU foams. Tests were performed on two different categories of PU foams, one containing 25% WT and the other containing 16% TMP. From each category, 36 rectangular parallelepiped blocks ($20 \times 20 \times 15$ mm) were cut out and dried at 60°C for 2 h prior to measurements of their weights and $E$ values. Three groups of 9 blocks each were incubated at 30°C with the following fungi: *Coriolus versicolor* (L. ex Fr.) Quel., *Phanerochaete chrysosporium* Burds., and *Tyromyces palustris* (Berk. and Curt.) Murr., and the remaining group of 9 blocks was incubated without fungi as the control after sterilization with propylene oxide gas for 10 h. After 1, 2, and 3 months of incubation, 3 blocks were taken from each group incubated with and without each fungus for measuring their weights and $E$ values after drying at 60°C. The weight losses and the losses of modulus of elasticity were calculated from respective differences of weights and $E$ values before and after the incubation of each block.

Incubation conditions, except for temperature, were in accordance with JIS-Z 2119-1977.

### 3.3. Results and discussion

#### 3.3.1. Compressive properties

In a preliminary experiment we tried to prepare PU foams from WT by reaction with either MDI or TDI as a DI, and either PEG 400 or PEG 1000 as a polyol under catalysis of an organotin compound, because Nakamura *et al.* (1989) had prepared PU foams from kraft lignin by using similar formulations. However, WT did not give any good PU foams by this method.

In this study, therefore, PES shown in Table 2 was prepared by condensation between sebacic acid and PEG 400 and used as a polyol instead of PEG 400 or PEG 1000 for the synthesis of PU foams containing WT. A combination of TDI and TEDA was more suitable rather than was the MDI-DBTL system for synthesis of PU foams from a polyol mixture consisting of PES and WT. Cross linking agents such as TMP were not essential for preparing the WT-containing PU foams. When no WT was included, however, the produced PU was a very viscous oil if no cross-linking agent was included in the formulation. This indicates that WT plays the role of a cross-linking agent in PU foam synthesis.

The $\sigma$ and densities ($\rho$) of the PU foams derived from WT are plotted against
NCO/OH ratios in Fig. 26. The $\sigma$ increased with increasing NCO/OH whereas $\sigma/\rho$ showed a maximum located at 1.0 of the NCO/OH. With a small NCO/OH ratio (0.8), foaming was unsatisfactory because of the incomplete reaction of water, and hence, the obtained PU had a relatively large $\rho$ value and a "rubber" like texture. At a greater NCO/OH ratio, the PU became harder and at extremely large ratio (for example, NCO/OH = 1.6) the PU was brittle. Isocyanates are capable of forming three types of bonds in relationship to NCO/OH ratios. In addition to normal urethane bonds, biuret linkages may be created by moisture, and allophanate linkages may result from the reaction of excess diisocyanate and urethane groups. Thus, increasing NCO/OH ratios should result in more frequent allophanate cross-linkages which have predominant effects on $\sigma$ and $\rho$. The above results suggest that a NCO/OH ratio of 1.0 should be the optimum in the WT-PES-TDI system.

As shown in Fig. 27, WT contents influenced both $\sigma$ and $\rho$ of the PU foams. Thus, $\sigma$ exponentially increased, and $\rho$ linearly increased with increasing WT contents within a range of 10-20%. The values of $\sigma$ and $E$ were divided by $\rho$ to normalize the effects of $\rho$ values. Thus, specific compressive strength and specific modulus of elasticity are represented by $\sigma/\rho$ and $E/\rho$, respectively. Both $\sigma/\rho$ and $E/\rho$ of PU foams were found to exponentially increase with increasing WT contents. This indicates that WT gives rise to a reaction between isocyanate and hydroxyl and hence acts as a cross-linking agent and also a hard segment in PU foams so as to produce rigid PU foams at high levels of WT contents because phenolic hydroxyl groups of catechin can react with isocyanate to form urethane bonds as described in Chapter 2.

Three different DI's, that is HDI, MDI, and TDI were employed to examine the effects of WT contents on $\rho$ and the mechanical properties ($\sigma$ and $E$) of PU foams. Again $\rho$ increased linearly and mechanical properties increased exponentially for all DI systems with the increase of WT content as can be seen in Fig. 28. The $\rho$ values of PU foams from TDI and MDI systems were slightly less than those of a HDI system at given WT contents. However, the PU foams from TDI, and MDI had larger $\sigma$ values than those from HDI. This can be ascribed to the presence of rigid aromatic rings in TDI and MDI molecules. This result suggests that various types of PU foams can be obtained by selecting the appropriate DI.

Fig. 29 shows the $\sigma/\rho$ of PU foams prepared by using varying amounts of water. The $\sigma/\rho$ value steeply decreased when the water content was increased to more than 2.5%. An increase in water content may result in a decrease in cross-linkages between the WT and the DI because the NCO/OH ratio is constant. These results suggest that the optimum water content should be about 2.5% or less in this system.

### 3.3.2. Biodegradability

Two categories of PU, one containing 25% WT and the other containing 16% TMP as a cross-linking agent were treated with three wood rotting fungi, *C. versicolor*, *P.*
chrysosporium, and T. palustris. Formulations and properties of these PU foams are shown in Table 3. Their weight losses and losses of $E$ during the treatments are shown in Fig. 30.

For the PU foam containing WT, both the weight loss and the loss of $E$ increased with increasing periods of fungal treatment, whereas they were very small for the PU containing TMP. Average weight losses for the WT-containing PU foam were 1.9%, 4.4%, and 3.9% within one, two, and three months, respectively, while no weight losses greater than 0.5% were observed for the controls treated only with incubation medium for the same periods of time. Average losses of $E$ for the WT-containing PU were 13%, 23%, and 24% within the same periods, respectively. However, the controls and the TMP-containing PU exhibited losses in $E$ of less than 5%.

The large decreases in $E$ as compared with the very small weight losses for the
WT-derived PU foam suggest that the fungi selectively degraded the tannin moiety which probably acts as cross-linking points and hard segments in a PU polymer molecule as discussed above. Thus, blending of natural polyols such as WT into PU-foam formulations enhances biodegradation by fungi, although PU foams prepared from only synthetic materials are not degraded easily by micro-organisms. As can be seen from Fig. 30, both the weight and $E$ of the PU derived from WT moderately
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

![Graph showing the effects of TDI, MDI, and HDI on \( \sigma \), \( E \), and \( \rho \) of PU foams. Notes: NCO/OH: 1.0, TMP: 0%, H₂O: 2.5%, silicon oil: 1.0%. For TDI-PES-WT, TEDA 0.5%; for MDI-PES-WT, DBTL 3.0%; for HDI-PES-WT, DBTL 3.0%.]

Decreased within the first month, then continually decreased for the succeeding two months. This result suggests that the penetration of the fungi into the interior of PU
Fig. 29 Effects of water contents on the $\sigma / \rho$ of PU foams.
Notes: NCO/OH: 1.0, TMP: 0.5%, TEDA: 0.5%, silicon oil: 1.0%.

Table 3 Formulations and properties of PU foams containing 25% WT and 16% TMP.

<table>
<thead>
<tr>
<th></th>
<th>PU foam (WT 25%)</th>
<th>PU foam (TMP 16%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES (%)</td>
<td>51.6</td>
<td>47.6</td>
</tr>
<tr>
<td>WT (%)</td>
<td>25.0</td>
<td>0</td>
</tr>
<tr>
<td>TMP (%)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>TDI (%)</td>
<td>22.9</td>
<td>36.4</td>
</tr>
<tr>
<td>Water (%)</td>
<td>2.5</td>
<td>1.0</td>
</tr>
<tr>
<td>TEDA (%)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Silicone oil WF30 (%)</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>NCO/OH</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Densities (g/cm$^3$)</td>
<td>0.193</td>
<td>0.078</td>
</tr>
<tr>
<td>Compressive strengths (kPa)</td>
<td>69.5</td>
<td>36.5</td>
</tr>
<tr>
<td>Compressive elasticities (kPa)</td>
<td>822</td>
<td>426</td>
</tr>
</tbody>
</table>

Foams needs time. Therefore, it is expected that the weight loss and loss of $E$ will be satisfactorily large if the period of fungal treatment is prolonged.

Laks et al. (1988) have reported that copper complexed, condensed tannin-containing bark extracts have efficacy as wood preservatives. In our study, however, the PU foams derived from WT obviously were degraded by some wood-rotting fungi. Those PU foams are really expected to be biodegraded under natural circumstances and incorporated into mass cyclic process in the ecological system of the earth if the
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

3.4. Conclusion

WT can be utilized as a polyol component in PU synthesis. WT gives rise to a reaction between isocyanate and hydroxyl groups and hence acts as a cross-linking agent and also a hard segment in PU foams so as to produce rigid PU foams at high levels of WT contents. Various types of PU foams can be obtained by selecting the appropriate DI. The PU foams derived from WT obviously were degraded by some wood-rotting fungi. These results indicate that WT components play a role of cross-linking agents and hard segment in PU polymer molecule. WT serves also as a contributing material for maintaining biodegradable properties of PU foams.
4. Synthesis of Biodegradable Polyurethane Foams from the Bark of *Acacia mearnsii*

4.1. Introduction

PUs have been finding increasing applications in the field of fibers, foams, elastomers, and protective coatings. Addition polymerization of DIs with polyols is the basic process in their synthesis (Krol et al., 1992). Natural polymers containing more than two hydroxyl groups in the main chain are expected to be utilized as polyols for PU preparation (Nakamura et al., 1990). In Chapter 3, we described that WT was used successfully for the synthesis of PU foams, which were biodegradable with some wood-rotting fungi. However it is much better if one can obtain PU directly from bark without isolation of tannins, because extraction, concentration, and drying of tannins are energy consuming processes.

There are more than 700 *Acacia* species in the world, of which *Acacia mearnsii* De Wild. is in large area of plantation forests in South Africa, East Africa, South America and China because it is one of the fast-growing species. The largest area in South Africa covers 160,000 ha (Yazaki et al., 1990). There are about 10,000 ha of *Acacia* plantations in China which are increasing by approximately 3,300 ha per year (Zheng et al., 1988). Most of BK is usually burnt off although a major use of BK has been for tannin production. The protein-adsorbing polyphenols can be extracted from BK (Ohara et al., 1995), and its wood also is useful for pulp production (Fang et al., 1992).

In this study, therefore, we tried to utilize BK as a partial replacement for synthetic polyols in formulations of PU preparations, because it contains approximately 50% tannin that is extractable with hot water (Table 4). The effects of reaction conditions such as BK content, NCO/OH ratio, and water content on the compression properties of the PU foams were investigated. Furthermore, biodegradabilities of the BK-derived PU foams were investigated by incubating them with wood-rotting fungi and soil microorganisms, because the blending of natural polyols, such as tannin and lignin, into polymer formulations enhances fungal biodegradation (Ge et al., 1993).

4.2. Materials and method

4.2.1. Materials

Bark of *A. mearnsii* obtained from the Kasuya Experiment Forest of Kyushu University was ground into powder (80 mesh pass). Chemical components and hydroxyl group content in BK (Table 4) were determined by standard methods (Yasuda, 1985) and the method of Abe and Matsumoto (1958), respectively. Sebacic acid, PEG 400, TMP, TDI, MDI, HDI and other reagents were commercially obtained. PES was synthesized as described in Chapter 3. Hydroxyl and carboxyl groups in the PES were 1.35 and 0.14 mmol/g, respectively. Its viscosity was 3,800 cP at 25°C.
Table 4 Chemical composition and hydroxyl group contents of A. mearnsii Bark.

<table>
<thead>
<tr>
<th></th>
<th>Benzene extract (%)</th>
<th>Hot water extract (%)</th>
<th>Hot alkali extract (%)</th>
<th>Holocellulose (%)</th>
<th>Lignin (%)</th>
<th>Hydroxyl group content (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.2</td>
<td>48.7</td>
<td>23.7</td>
<td>16.4</td>
<td>7.5</td>
<td>5.3</td>
</tr>
</tbody>
</table>

4.2.2. Solubility of BK

Three grams of BK were mixed with 10 ml of PES or PEG 400 and stirred (250 rpm) at 80°C for 5.5 h. The mixture was filtrated with a sintered glass filter (1G1) after centrifugation. The insoluble residue was washed repeatedly with a mixture of PES (or PEG) : dioxane (10:1) at 80°C, and finally was washed with dioxane. Then the residue was weighed after being dried at 105°C.

4.2.3. Preparation and characterization of PU foams

As described in Chapter 3 with WT-based PU foams, BK was suspended in PES and stirred at 80°C for 5.5 h. After cooling to room temperature, surfactant, catalyst, cross-linking agent, if necessary, and water were added to the suspension in which BK was mostly dissolved with stirring. Then DI was added, and the mixture was stirred at 700 rpm to afford PU foams.

The NCO/OH ratio and the BK content are defined as the following equations:

\[
\text{NCO/OH} = \frac{W_{\text{DI}} \times I_{\text{DI}}}{W_{\text{BK}} \times H_{\text{BK}} + W_{\text{PES}} \times H_{\text{PES}} + W_{\text{TMP}} \times H_{\text{TMP}}} \\
\text{BK (\%)} = \frac{100 W_{\text{BK}}}{W_{\text{BK}} + W_{\text{PES}} + W_{\text{TMP}} + W_{\text{DI}}}
\]

Here, \( W_{\text{DI}}, W_{\text{BK}}, W_{\text{PES}}, \) and \( W_{\text{TMP}} \) are the weights of DI, BK, PES, and TMP, respectively. \( I_{\text{DI}} \) denotes the isocyanate group content in the diisocyanate, and \( H_{\text{BK}}, H_{\text{PES}}, \) and \( H_{\text{TMP}} \) refer to the hydroxyl group contents in BK, PES, and TMP, respectively.

Definition of water content and measurements of compressive strength (\( \sigma \)) and compressive modulus of elasticity (\( E \)) of the foams have been described in Chapter 3.

4.2.4. Assay of biodegradability

Two assay methods were employed to evaluate the biodegradabilities of the PU foams. One (method A) is the modified method of the standard wood decay test, JIS-Z 2119-1977, and the other (method B) is a modification of a soil microorganisms decay test (Laks et al. 1988). For both the tests used were three different categories of PU foams, two of them containing 15% BK and 30% BK, respectively, and the other one containing 16% TMP but no BK.

For the method A, the PU foam blocks were incubated at 30°C with one of the
following fungi: *C. versicolor*, *P. chrysosporium*, and *T. palustris* as previously described in Chapter 3. 

For the method B, one group of nine blocks (2×2×1.5 cm) of PU foams was buried in 200 g of a mixture of culture soil and leaf mould (1:1) and then incubated at 30°C. Water content of the culture was maintained at 60% by the occasional addition of water. The other group of nine blocks was sterilized with propylene oxide gas for 10 h, and incubated with the soil mixture that was previously sterilized with an autoclave (121°C, 30 min) as the control. After one, three, and six months of incubation, three blocks were taken from each group for measuring their weights and E values after drying at 60°C. The weight losses and the losses of E were calculated from differences of weights and E values before and after the incubation of each block.

4.2.5. Infrared (IR) spectral analysis

Surfaces of PU blocks were filed into powder to give PU foam samples. IR spectra were obtained with 2 mg of BK or PU foam sample in 400 mg KBr pellets using an A 102 Infrared Spectrophotometer (Japan Spectroscopic Co. Ltd.).

4.3. Results and discussion

4.3.1. Preparation of bark-derived polyurethane foams

BK meal was slightly less soluble than WT in PES and PEG 400 probably because BK consists of complex components as shown in Table 4. Solubility of BK meal was only 56.5% in PEG 400 whereas it was 88.3% in PES that had been prepared by condensation between sebacic acid and PEG 400, and successfully used for the synthesis of PU foams containing WT (Chapter 3). Therefore, we used the BK suspension in PES, where most of the BK components were dissolved, as a polyol mixture for synthesis of BK-derived PU. A combination of TDI and TEDA was suitable for the synthesis of PU foams from a polyol mixture consisting of PES and BK.

Hartman (1977) reported that the bark of Ponderosa pine (*P. ponderosa*) and Douglas fir (*P. menziesii*) can be used as a the major or sole polyol in the reaction with DI to produce rigid PU foams. A series of complex chemical bonds and linkages in the prepared foams have been explained and confirmed by IR and thermogravimetric analyses, although density and compressive properties of the foams have not been reported. Initial attempts, therefore, were made to prepare PU foams containing BK by mixing the BK with the isocyanates. However, it did not yield any good PU foams by this method probably because of the differences in tree species and hence differences in the chemical natures of their bark components.

4.3.2. Compressive properties

Compressive strength (σ) and elastic modulus (E) increased almost exponentially and density (ρ) increased linearly with increasing BK contents of the PU foams (Fig.
With increasing BK contents, the specific strengths ($\sigma/\rho$) of PU foams were found to increase rapidly at any given NCO/OH ratio, and thousands times more rigid foams can be obtained by increasing the BK contents as shown in Fig. 32. This indicates that BK components act as cross-linking agents and also as hard segments in PU molecules so as to produce rigid PU foams at high levels of BK content. Large numbers of cross-linking can be produced by addition polymerization of isocyanate with hydroxyl groups in BK components. Similar effects of WT were observed for WT-derived PU foams as described in Chapter 3.

The specific modulus of elasticity ($E/\rho$) of the PU foams derived from BK are plotted against NCO/OH ratios in Fig. 33. Increasing NCO/OH ratios should result in
more frequent aliphaneate cross-linkages which have predominant effects on compressive strengths of PU foams as already discussed. However, at BK contents higher than 25%, the $E/\rho$ values of PU foams began to level off or decline. Thus, the $E/\rho$ of PU foams containing 25, 30, and 35% BK showed maxima located at NCO/OH ratios of 1.6, 1.4, and 1.2, respectively. As the cross-linking densities still could be increasing over these points, this phenomenon suggests that the quantitative balance of soft and hard segments has a significant influence on the mechanical properties of PU foams.

PU foams were prepared by using three different DIs, that is HDI, MDI, and TDI to evaluate the effects of DIs on their mechanical properties. Similarly to WT-PU foams in Chapter 3, $\rho$ increased linearly, and mechanical properties increased almost exponentially with increasing BK contents for all DI systems as shown in Fig. 34. The PU foams prepared from an HDI system possessed smaller $\sigma$ and $E$ values and larger $\rho$ values than those from TDI and MDI systems at given BK contents, because of the presence of rigid aromatic rings in TDI and MDI molecules.

When PU foams were prepared by adding varying amounts of water, the $\sigma/\rho$ linearly decreased with increasing water dose regardless of their BK contents as shown in Fig. 35. Water reacts with isocyanate groups to produce carbon dioxide and amine which reacts in turn with additional isocyanate to form an urea bond. Therefore,
increases of water contents should decrease actual NCO/OH ratios in the PU formulations and, consequently, diminish the cross-linking densities and compressive strengths of the PU foams, because we did not take into account the water dose in the calculation of the NCO/OH ratio as described in Section 4.2.3. However, slopes of the lines in Fig. 35 decline with increasing contents of BK. This may be ascribed to larger numbers of cross-linking points in PU molecules produced by increasing the BK content. Water content may not affect compressive strength of PU foams severely at high levels of cross-linking points even if water may decrease linkages between the BK components and DI molecules to a certain extent.

4.3.3 Biodegradability

Three categories of PU, two of them containing 15 and 30% BK, respectively, and
the other containing 16% TMP as a cross-linking agent, were treated with three wood-rotting fungi, *T. palustris*, *C. versicolor*, and *P. chrysosporium* (Method A), and with soil microorganisms (Method B). Formulations and properties of these PU foams are shown in Table 5.
Both the weight losses and the losses of $E$ increased with increasing periods of microbial treatments of the BK-derived PU foams as shown in Figs. 36-39. On the other hand, almost no change was observed in the weight and $E$ of the PU containing TMP (data not shown). This tendency is consistent with the results with WT-derived PU foams described in Chapter 3. Weight losses after the six month treatments were 4-10 % for the 15% BK-PU foam, and 7-13 % for the 30% BK-PU foam. Losses of $E$ were 22-28 % for the 15% BK-PU, and 25-35 % for the 30% BK-PU within the same treatment periods.

The above-mentioned results indicate that microorganisms can degrade the PU foams at a rate which increases with increasing BK contents in the foams. The results are not explained by the simple leaching of BK components from the PU foams because the controls which were incubated under sterile conditions exhibited very small losses in weight and $E$ values. Thus, biodegradable PU foams can be synthesized by blending...
Table 5  Formulation and properties of PU foams that were employed for biodegradability tests.

<table>
<thead>
<tr>
<th>PU foams</th>
<th>15% BK-PU (%)</th>
<th>30% BK-PU (%)</th>
<th>16% TMP-PU (%)</th>
<th>PES (%)</th>
<th>BK (%)</th>
<th>TMP (%)</th>
<th>TDI (%)</th>
<th>Water (%)</th>
<th>TEDA (%)</th>
<th>Silicone oil WF30 (%)</th>
<th>NCO/OH</th>
<th>Density (g/cm³)</th>
<th>Compressive strength (kPa)</th>
<th>Compressive elasticity (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% BK-PU</td>
<td>59.5</td>
<td>45.2</td>
<td>47.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.098</td>
<td>3.12</td>
<td>33.9</td>
</tr>
<tr>
<td>30% BK-PU</td>
<td>15.0</td>
<td>30</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.164</td>
<td>171</td>
<td>2115</td>
</tr>
<tr>
<td>16% TMP-PU</td>
<td>2.6</td>
<td>0.5</td>
<td>16.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.078</td>
<td>35.5</td>
<td>426</td>
</tr>
</tbody>
</table>

Fig. 36  Effects of periods of microbial treatments on weight losses of 15% BK-PU foams.

BK into PU-foam formulations. Treatment with *T. palustris* resulted in larger decreases in both weight and $E$ values of BK-derived PU foams than treatments with the other fungi whereas this was not the case for the WT-derived foams as described in Chapter 3. This difference may be ascribed to the fact that BK contains holocellulose components (Table 4).
Fig. 37 Effects of periods of microbial treatments on losses of $E$ of 15% BK-PU foams.

Fig. 38 Effects of periods of microbial treatments on weight losses of 30% BK-PU foams.
Fig. 39 Effects of periods of microbial treatments on losses of $E$ of 30% BK-PU foams.

An infrared spectrum of a BK-derived PU foams (Curve C) is compared in Fig. 40 with those of a PU foam prepared with TMP (Curve B) and BK powder (Curve A). The absorption band at 1730 cm$^{-1}$ (a) is assigned to the C=O of ester and urethane groups (Hartman, 1977) and the band at 1610 cm$^{-1}$ (b) is assigned to the aromatic C=C of tannin and lignin components in BK and that of TDI. The absorption ratio (b/a) that may be regarded as a relative abundance of BK components decreased linearly with increasing losses of $E$ during the decay of the BK-derived PU foams as shown in Fig. 41. However, almost no change was observed in the infrared spectra of TMP-PU after the decay test. It is indicated that wood-rotting fungi and soil microorganisms preferentially degraded the BK components, which act as cross-linking points and hard segments in PU polymer molecules because losses of $E$ increased with increasing periods of microbial treatments as discussed above.

Simple leaching of BK components should not be responsible for the decrease of $E$ because both the absorbances at 1610 and 1730 cm$^{-1}$ decreased with increasing periods of microbial treatments of BK-derived PU, indicating that a part of the urethane bond was lost during the decay while the same bond in the BK-derived PU was stable in the TMP-PU molecule.

4.4. Conclusion

Rigid PU foams prepared from BK generally showed similar mechanical properties as those of the WT-derived PU prepared in Chapter 3. BK effectively contributed to
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

Fig. 40 IR spectra of BK (A), 16% TMP-PU (B), and a PU foam (C) derived from BK. Notes: a: 1730 cm⁻¹, C=O of ester and urethane groups, b: 1610 cm⁻¹, C=C in BK and TDI.

Fig. 41 The relationships between losses of E and b/a during treatments with soil microorganisms (△), T. palustris (○), and C. versicolor (■). Notes: b/a: absorption ratios of 1,610 cm⁻¹ (b) to 1,730 cm⁻¹ (a).
increases in the mechanical strengths of PU foams. At large BK contents, the obtained PU foams were hard, regardless of the NCO/OH ratio within the range of the present experiment. These results indicate that BK components play a role as cross-linking agents and hard segments in PU polymer molecules. BK is likely to serve also as a contributing material for maintaining biodegradable properties of PU foams, because the BK moiety was degraded preferentially by fungi and soil microorganisms in biodegradation tests.

5. Decomposition of Polyurethane Foams Derived from Condensed Tannin Hydrolysis and Aminolysis of Urethanes

5.1. Introduction

As described in Chapter 3 and 4, PU foams have been prepared from WT and BK, respectively. WT and BK components enhanced the biodegradation of the foams by some wood-rotting fungi and soil microorganisms. It is not well known, however, that the foams derived from WT and BK can be used in the stability of ordinary foams and the possibility of chemical recycling after use.

Hydrolysis, glycolysis and aminolysis are chemical processes for the decomposition of polyurethane to lower molecular products (Campbell et al.; 1977; Kanaya et al., 1994). In order to examine the breakdown of the urethane group and to learn the stability of polyurethane foams, PU foam derived from WT was employed for hydrolysis and aminolysis. For comparison, PU foam containing 16%TMP was synthesized and also used in hydrolytic and aminolytic treatments.

On the other hand, from the reaction of phenyl isocyanate and (+)-catechin as a model reaction between diisocyanate and condensed tannin, three urethane products, CU-I (a mixture of 3'-O-(phenylcarbamoyl)catechin and 4'-O-(phenylcarbamoyl)catechin), and CU-II (3',4'-di-O-(phenylcarbamoyl)catechin) were obtained as described in Chapter 2. CU-I and CU-II were also studied as models of PU foams derived from WT or BK, and employed for hydrolysis and aminolysis. In order to learn the difference in rate of decomposition between the urethanes derived from catechin and alcoholic hydroxyl, PAU (phenethyl alcohol urethane) was synthesized and also used in hydrolysis and aminolysis.

5.2. Materials and methods

TLC analyses were performed on Merck 60F, silica-gel precoated plates (solvent: ethyl acetate: n-hexane = 40:60). Fluorescent spots were detected under UV illumination. FD-MS were recorded on a JEOL JMS-DX300 (JMA 3500). GC-MS analyses were conducted with a Shimazu GC-17A and a QP-5000 equipped with a NB-5 column (0.25 mm by 30 m; 0.4-µm film thickness). Helium was used as a carrier gas. The column temperature was programmed from 150 to 280°C (4°C/min). Electron ionization (70
was applied.

5.2.1. Synthesis of phenethyl phenylcarbamate (PAU)

Phenyl isocyanate (1.19 g) and DBTL (5 mg) was added to a solution of phenethyl alcohol (PA) (1.22 g) in dry acetonitrile (20 ml) with stirring and left in a nitrogen atmosphere at 30°C for 8 h. The solvent was evaporated \textit{in vacuo} to dryness. The residual yellow solid was chromatographed on a silica gel column (Wakogel C-200) using an ethyl acetate: hexane (40:60) mixture as an eluent to give PAU as white crystal. Yield: 91%, mp.: 80-81°C, Rf = 0.85 on the TLC, and mol. wt.: 241 by the FD-MS method.

5.2.2. Hydrolytic treatment of model urethanes

CU-I, CU-II and PAU have been chosen as model urethanes for the decomposition experiment. Their synthesis, isolation and identification have been disclosed in Chapter 2.

Urethanes (10 \mu mol) were dissolved in 1.0 ml of acetonitrile containing water (55 mM) in ampules for hydrolytic treatments. Oxygen was purged with nitrogen. The sealed ampules were enclosed in a mini autoclave. Reaction runs were made at different temperatures. After a prescribed reaction time, the ampules were taken from the autoclave and cooled in cold water. The amounts of the decomposition products and starting material in the reaction mixtures were determined by HPLC (high performance liquid chromatography) conducted with a Waters 208D model using a Develosil ODS-UG-5 C$_{18}$ column (3.9 mm × 150 mm) and a UV detector, Tosoh UV8011 at 280 nm. The mobile phase was a mixture (45:55) of acetonitrile/10 mM phosphate buffer (pH 3.0). 4-Methylguaiacol was used as an internal standard.

5.2.3. Aminolytic treatment of model urethanes

Urethanes (10 \mu mol) and aniline (10 \mu mol) were dissolved in 10 ml of acetonitrile for aminolytic reatments in ampules. Other handling was the same as that of a hydrolytic treatment.

5.2.4. Isolation and identification of main decomposition products

The main decomposition products were characterized by the GC-MS technique. Some products were isolated by means of preparative HPLC equipped with a column: Waters μ-Bondasphere 5 μ C$_{18}$-100A (19 × 150 mm) using a mixture of acetonitrile: water (45:55) at a flow rate of 8.0 ml/min. Eluates were extracted with ethyl acetate, dried over sodium sulfate, and the fractions were concentrated to dryness and acetylated at room temperature for 24 h with acetic anhydride and pyridine to give the samples for GC-MS analyses.
5.2.5. Hydrolytic treatment of PU foams

Two different PU foams, one containing 25% WT and the other containing 16% trimethylolpropane (TMP), WT-PU and TMP-PU respectively, have been chosen for the following decomposition experiment. Preparation of these PU foams has been described in Chapter 3. The formulations are given in Table 3.

A) Three PU foam blocks (15 × 15 × 15 mm) were put into water (30 ml) and flooded *in vacuo* for 10 min at 25°C. Reaction runs were carried out at different temperatures. After a prescribed reaction time, the blocks were cooled in cold water and taken from the water for measuring their weights and elastic modulus ($E$) values after successive drying *in vacuo* at room temperature for 24 h and at 60°C for 2 h. $E$ values were determined as described in Chapter 3. 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.

B) The PU foams were chopped into 3-5 mm particles and *ca.* 0.1 g of them was suspended in a solution of water (55 mM) in acetonitrile (30 ml) to give a sample for hydrolysis. Other handleings were the same as those for PU blocks except determination of $E$.

The amounts of tannin and aromatic amines (calibrated as tolylene-2,4-diamine) produced in the reaction mixture were determined by using the acidified vanillin method (Broadhurst *et al.*, 1978) and a colorimetric method of Matsui *et al.* (1993), respectively. Calculation of their contents were based on the compositions of raw materials for PU foam preparation.

5.2.6. Aminolytic treatment of PU foams

The chopped PU foam particles (*ca.*, 0.1 g each) were added to acetonitrile solutions (30 ml) containing water (55 mM) and aniline (10 mM) to give samples for aminolysis. Aniline remained after the treatment was determined by the HPLC method as described above. Other handleings were the same as those for hydrolysis.

5.3. Results and discussion

5.3.1. Identification of main decomposition products

HPLC charts of decomposition products of CU-I and CU-II in hydrolysis are shown in Fig. 42 and Fig. 43, respectively. The decomposition products were identified based on retention times in HPLC and fragmentation patterns in GC-MS analyses.

5.3.2. Hydrolysis of CU-I and CU-II

CU-I was not easily hydrolyzed at 40°C, but was decomposed at 60°C. The amount of catechin produced was almost equal to the consumption of CU-I (Fig. 44). The yield of aniline produced corresponded to the consumption of CU-I at low temperatures and
short reaction times. However, the aniline yield produced was reduced at high temperatures or long reaction times. Aniline could almost not be detected at 100°C after 3 h, but quite large amounts of diphenylurea were detected (Fig. 45). From this result, it is suggested that hydrolysis is the main reaction in the beginning stage of the decomposition of CU-I, and retarded aminolysis can occur by aniline produced from hydrolysis as illustrated in Fig. 46. It also is suggested that the temperature dependence of the aminolysis rate is larger than that of the hydrolysis rate.

In the hydrolytic treatment of CU-II, the yield of diphenylurea always was higher than that of aniline (Figs. 47 and 48). It was thought that aminolysis would occur much easier in the case of CU-II than in that of CU-I even at such a moderate temperature as 60°C. The yield of CU-I at 100°C showed maxima after nearly 3 h of reaction, while the amount of catechin increased at any given time of the reaction. These simultaneous decrease in CU-I and increase in catechin indicate that catechin can be produced via CU-I that was formed from CU-II.

From these results, it is suggested that not only hydrolysis but also aminolysis can be involved in the breakdown of the urethane bonds if polyurethane foams derived from condensed tannin are exposed to hydrolytic conditions at high temperatures.
1. Catechin
2. Aniline
3, 4. CU-I
5. Methylguaiacol (I.S.)
6. Diphenylurea
7. CU-II

Fig. 43 Products from hydrolysis of urethane of catechin (CU-II).

Fig. 44 Consumption of CU-I (●) and yield of aniline (◇), catechin (□), and diphenylurea (▲) during hydrolytic treatment of CU-I at 40°C and 60°C.
5.3.3. Hydrolytic treatment of PAU

In order to compare it with the decomposition rate of CU-I, the hydrolytic treatment of PAU as a model of ordinary polyurethanes also was conducted at 40 and 100°C (Fig. 49). Both urethanes, CU-I and PAU, were very difficult to decompose at 40 °C. It was made clear, however, that the rate of breakdown of the urethane group in CU-I is much faster than that of PAU at high temperatures. In the hydrolytic treatment of PAU, hydrolysis reaction preferentially occurred as indicated by almost the same
yields of PA and aniline. Diphenylurea, that implies aminolysis, was formed hardly even at a temperature as high as 100°C. Consequently, it is suggested that polyurethane derived from WT has almost the same stability as ordinary polyurethane derived from polyester or polyether at room temperature, but that the WT-derived polyurethanes can be decomposed more easily than the ordinary polyurethanes at high temperatures.

5.3.4. Aminolytic treatment of CU-I and PAU

Kanaya et al. (1994) prepared MDI-aminoethanol (MEA) urethane adduct as a model of usual polyurethane foams and reported that the decomposition process of polyurethane foam by alkanolamines was not aminolysis but glycolysis, and MDI-MEA urethane adduct was decomposed in the presence of excess alkanolamines. Almost no aminolysis was observed, however, during the decomposition reaction, although the aminolysis of urethane was surmised.

In this study, aminolysis of CU-I was carried out because aminolysis was observed in hydrolytic treatments of CU-I and CU-II. Nearly 70% of CU-I can be decomposed in the presence of aniline at 100°C for 7 h (Fig. 50). In order to compare the decomposition rate of CU-I with that of PAU, the aminolysis of PAU was also carried out at 40°C (Fig. 51) and at 100°C (Fig. 52). Compared with CU-I, the rate of decomposition of PAU was slightly slower at 40°C. However, at 100°C, the difference between the decomposition rates of CU-I and PAU became significantly large (Fig. 52). This result indicates that decomposition of CU-I was significantly accelerated with increasing temperature of reaction, whereas decomposition of PAU was quite difficult even at the high
Fig. 48 Consumption of CU-II (●) and yield of CU-I
(○), aniline (◇), catechin (□), and
diphenylurea (△) during hydrolytic treatment of CU-II at 100°C.

Fig. 49 Consumption of PAU (■) and yield of aniline (◇), PA (○), and
diphenylurea (△) during hydrolytic treatment of PAU at 40°C and 100°C. Consumption of CU-I (●) is shown for comparison.
temperature.

Both rates of the hydrolysis and aminolysis of CU-I were much faster than those of PAU at high temperatures. The difference between the two urethanes in hydrolysis and aminolysis seems to be due to the difference between the structures of CU-I and PAU.

On the other hand, the rate of decomposition of PAU in hydrolysis is almost the same as in aminolysis. However, the rate of decomposition of CU-I in aminolysis is faster than that in hydrolysis. It was indicated that the temperature dependence of CU-I in aminolysis is higher than that in hydrolysis. From these results, it is suggested that the rate of decomposition of polyurethane derived from WT both in hydrolysis and aminolysis is faster than that of ordinary polyurethane at high temperatures.

5.3.5. Hydrolysis of polyurethane foams

Weight loss of about 6% was observed for the blocks after 7 days and that of about 4% was observed for the chopped WT-PU foam after 5 h of hydrolytic treatments at 25°C as shown in Figs. 53 and 54, respectively. Almost no change was observed in $E$ of WT-PU foams at 25°C. The results are explained as the result of the leaching of low molecule components contained in WT-PU foams. From this result, it is suggested that WT-PU has almost the same stability as TMP-PU at room temperature. On the other hand, the weight losses in both WT-PU foam blocks and the chopped foams are much faster than that of TMP-PU foams at a high temperature (100°C) as shown in Figs. 55 and 56, respectively, though the chopped foams lost weights faster due to their smaller particle size as generally expected.

The large decreases in the modulus of elasticity as compared with the small weight losses for the WT-PU foams after 5 h reaction (Fig. 55) suggests that tannin moiety which acts as cross-linking points and hard segments in the PU polymer molecule was hydrolyzed. In fact, tannin was formed by hydrolysis of chopped WT-PU foams at 100°C (Fig. 56). However, the yield of aromatic amines (as TDA) showed maxima located at 4 h. This result suggests that aminolysis of WT-PU foams probably occurred by aromatic amines produced from hydrolysis.

5.3.6. Aminolysis of polyurethane foams

The aminolytic treatments of the chopped WT-PU and TMP-PU foams were made by adding a small amount of aniline to their hydrolytic treatment systems at 100°C. Decomposition of WT-PU was accelerated by the addition of aniline whereas dissolution of TMP-PU was not influenced by the aniline addition. During the aminolytic treatment tannin as a decomposition product increased, and simultaneously aniline was consumed (Fig. 57). The result clearly indicates that aminolysis of WT-PU with aniline occurred during the aminolytic treatment, and hence, suggests that its aminolysis with the aromatic amines formed by the hydrolysis should also occur in the
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

hydrolytic treatments. The ease of hydrolysis and aminolysis of WT-PU may result in its ease of natural decomposition when buried under ground or left in the aquatic environment. This property of WT-PU may also assist its recycle by decomposing it into raw material tannin and aromatic diamines.
Fig. 52 Consumption of PAU (■) and aniline (◇), and yield of PA (○) and diphenylurea (△) during aminolytic treatment of PAU at 100°C. Aminolytic consumption of CU-I (●) is shown for comparison.

Fig. 53 Effect of hydrolysis on weight loss and loss of E of PU foam blocks at 25°C. Legend: ◆: Weight loss of WT-PU, ○: Weight loss of TMP-PU, ●: Loss of E in WT-PU, ◇: Loss of E in TMP-PU.

5.4. Conclusions

Hydrolysis of the urethane group was the main reaction in the initial decomposition step of CU-I in the presence of water. Aniline generated by the hydrolysis in turn caused aminolysis of urethanes especially at high temperatures. The rates of both hydrolysis and aminolysis of CU-I are much faster than those of PAU at high temperatures. The temperature-dependence of aminolysis of CU-I seems larger than
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

WT-PU has almost the same stability as that of TMP-PU at room temperature. The weight losses of both WT-PU foam blocks and the chopped foams were much larger than that of TMP-PU foams in hydrolytic treatments at a high temperature. Thus, urethane linkages with tannin moiety in WT-PU foams might be more easily
Fig. 56 Yield of products from hydrolysis of the chopped PU foams at 100°C.
Legend: ◆: Weight loss of WT·PU, ◇: Weight loss of TMP·PU, ○: Tannins formed from WT·PU, ▲: Aromatic amines from WT·PU, △: Aromatic amines from TMP·PU.
Note: Tannin and aromatic amines are shown as % of tannin and urethane bond in PU foam, respectively.

Fig. 57 Effect of aniline on weight loss of WT- and TMP-PU foams in hydrolytic treatment at 100°C.
Legend: ▼: Weight loss of WT-PU with aniline, ◆: Weight loss of WT-PU without aniline, ▼: Weight loss of TMP-PU with aniline, ◇: Weight loss of TMP-PU without aniline, ■: Consumption of aniline in WT-PU, □: Consumption of aniline in TMP-PU.
Note: Aniline is shown as % of aniline added.
Polyurethane Foams from Tannin and Bark of Acacia mearnsii

hydrolyzed than those in TMP-PU foams. The decomposition of WT-PU was accelerated by addition of aniline to the hydrolytic treatment system. Aminolysis reaction was confirmed as the aniline added was consumed during the treatment.

In conclusion, the urethanes derived from catechin and WT showed a nearly similar stability as urethanes derived from phenethyl alcohol and TMP in the presence of water at room temperature. However, the former were less stable than the latter at high temperature in moist conditions.

Abbreviations

\begin{itemize}
  \item \textbf{Ac} \quad \text{Acetyl}
  \item \textbf{BK} \quad \textit{Acacia mearnsii} bark
  \item \textbf{COSY} \quad \text{Correlation spectroscopy (NMR)}
  \item \textbf{d} \quad \text{Doublet (NMR)}
  \item \textbf{DBTL} \quad \text{DIBUTYLTIN DILAURATE}
  \item \textbf{DI} \quad \text{Diisocyanate}
  \item \textbf{E} \quad \text{Compressive modulus of elasticity}
  \item \textbf{FD-MS} \quad \text{Field desorption mass spectra}
  \item \textbf{GC-MS} \quad \text{Gas chromatography-mass spectrometry}
  \item \textbf{HDI} \quad \text{Hexamethylene diisocyanate}
  \item \textbf{HPLC} \quad \text{High performance liquid chromatography}
  \item \textbf{Hz} \quad \text{Hertz}
  \item \textbf{IR} \quad \text{Infrared}
  \item \textbf{J} \quad \text{Coupling constant (NMR)}
  \item \textbf{JIS} \quad \text{Japanese Industrial Standard}
  \item \textbf{m} \quad \text{Multiplet (NMR)}
  \item \textbf{MDI} \quad \text{DIPHENYL METHANE DIISOCYANATE}
  \item \textbf{mp.} \quad \text{Melting point}
  \item \textbf{m/z} \quad \text{Mass/charge ratio}
  \item \textbf{n} \quad \text{Normal (e.g. } n\text{-hexane)}
  \item \textbf{NCO/OH} \quad \text{Isocyanate/hydroxyl group ratio}
  \item \textbf{NMR} \quad \text{Nuclear magnetic resonance}
  \item \textbf{NOESY} \quad \text{Nuclear Overhauser effect and exchange spectroscopy (NMR)}
  \item \textbf{PA} \quad \text{Phenethyl alcohol}
  \item \textbf{PAU} \quad \text{Phenethyl alcohol urethane (=Phenethyl phenylcarbamate)}
  \item \textbf{PEG} \quad \text{Polyethylene glycol}
  \item \textbf{PES} \quad \text{Polyethylene glycol sebacate}
  \item \textbf{PU} \quad \text{Polyurethane}
  \item \textbf{s} \quad \text{Singlet (NMR)}
  \item \textbf{t} \quad \text{Triplet (NMR)}
\end{itemize}
Acknowledgments

I would like to take this opportunity to express my deep sense of gratitude and appreciation to Professor Kokki Sakai, Faculty of Agriculture, Kyushu University for his supervision, encouragement and patience during the whole course of the work. I am extremely grateful to Associate Professor Ryuichiro Kondo in the same Faculty for his guidance in the course of this study and critical advice.

I am also sincerely grateful to Mr. K. Fujita and Dr. H. Yamaguchi, Faculty of Agriculture, Kyushu University, for their instructive suggestions and valuable opinions in the work described in Chapter 2 and 3, respectively. I thank Mr. T. Moroiwa for BK analysis and Mrs. K. Mori and all the colleagues in Wood Chemistry Lab. for providing a helpful and congenial atmosphere where this work was achieved.

The financial assistance from the Association of International Education of Japan during my stay in the Department of Forest Products, Kyushu University is gratefully acknowledged. This work was supported in part by the Bio Renaissance Program of the Japanese Ministry of Agriculture, Forestry, and Fisheries; and also by the Scientific Research Fund (No. 07306008) of the Japanese Ministry of Education, Science, and Culture.

References


Polyurethane Foams from Tannin and Bark of Acacia mearnsii

cord to rubber. Chemistry and Significance of Condensed Tannins, HEMINGWAY, R. W. and KARCHESY, J. J. (eds.), Plenum Press, pp. 479-492


HARTMAN, S. (1977) : Polyurethane foams from reaction of bark and diisocyanate. ACS Symp. Ser., 43 : 257-269


Polyurethane Foams from Tannin and Bark of Acacia mearnsii

II, Rowe, J. W. (eds.). Springer-Verlag, pp.993-994


(Received 22 June 1998; Accepted 4 September 1998)
ポリウレタンフォームの合成

要約

モリシマアカシアのタンニン及び樹皮からの生分解性ポリウレタンフォームの合成

モリシマアカシア（Acacia mearnsii De Wild.）は温暖地で良好に生育し、その樹皮には抽出成分として著量のワットルタンニン（WT）が含まれる。一方、プラスチック廃棄物による環境汚染は年々ひどくなり、使用後に微生物によって分解されるポリマーの開発が要望されている。ここでは、モリシマアカシアの樹皮及びWTの新用途開拓を意識してポリウレタン（PU）フォームの合成法を開発し、さらにその物性及び生分解の可能性について研究した。

まず、WTのモデル化合物として(+)-カテキンを選び、これを芳香族単官能性のフェニルイソシアナートとを、トリエチレンジアミン触媒存在下に反応させた。単離した生成物の化学構造から、カテキンのA環に存在するアルコール性水酸基、A環のレゾルシンノール型水酸基及びB環のカテコール型水酸基のうち後者が選択的に反応することが知られた。さらに、イソシアナートとカテキンのモル比が1を越える条件では互いに隣接するカテコール型水酸基の両方が反応したジウレタンも生成することから、WTを原料とするPUは架橋密度の大きい高分子になると予想した。

次に、ポリエチレングリコールとセバシン酸からジオール型のポリエステルを合成し、これにWTを溶解してポリオール混合物とした後、イソシアナートと反応させてPUフォームを合成する方法を開発した。得られたフォームの強度的性質を測定した結果、圧縮強度及び圧縮ヤング率はWT配合量の増加とともに著しく増加し、WTがPU分子内で架橋剤及びハードセグメントの働きをするという結果を得た。また、WTを単離することなくモリシマアカシアの樹皮そのものを配合しても硬質のPUフォームが生成したことから、同様に樹皮成分が架橋点及びハードセグメントとして機能すると推測される。

さらに、樹皮及びWTを原料とするPUフォームの生分解性について検討し、これらのフォームは白色腐朽菌、褐色腐朽菌及び土壌微生物によって徐々に分解されることやタンニン成分が優先的に分解されることを明らかにし、タンニン及び樹皮由来のフォームは使用後に自然の物質循環系に組み込まれると推測した。また、水分存在下でPUとそのモデル化合物の安定性について検討し、WT由来のウレタン結合は低温ではアルコール型のポリオール由来のウレタンと同様に安定であるが、高温では加水分解及びアミノリシスにより開裂され易く、使用後に分解して原料回収を行ううる可能性を示唆した。

キーワード：モリシマアカシア、ワットルタンニン、硬質ポリウレタンフォーム、樹皮、カテキン、総合型タンニン、イソシアナート、ウレタン誘導体、生分解性、架橋剤、木材腐朽菌、強度、土壌微生物、加水分解、アミノリシス