Influence of Wood Species on the Properties of Biopolyurethane Prepared from Liquefied Wood with Residue

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ABSTRACT: Biopolyurethane prepared from liquefied wood with the residue of the liquefied wood product was investigated in this article. Previous results indicated that the residue of the liquefaction product was composed mostly of compounds originated from lignin. The chemical structures of lignin in softwood and hardwood are different. The influence of soft- and hardwood species on the chemical structure and mechanical properties of biopolyurethane prepared from liquefied wood with residue was investigated by tensile testing and Fourier transform infrared spectroscopy. The experimental results showed that the liquefaction of softwood occurs within a shorter time than that of hardwood and the biopolyurethane prepared from softwood was harder than that prepared from hardwood, which suggests that the properties of the liquefaction product and biopolyurethane are influenced by the chemical structure of the lignin. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2109–2115, 2010

Key words: biopolyurethane; liquefied wood; wood species; lignin; residue

INTRODUCTION

Recently, global environmental problems have become an important issue. The Biomass-Nippon strategy council reported that the recycle rate of waste wood from tree trimming was ~2%, whereas that from construction and timber milling was ~70 and 95%, respectively. However, in terms of weight, an approximate annual 5 million tons of waste wood remains unused in Japan.[1] It is believed that a contribution to the resolution of global environmental problems would involve the effective utilization of this unused waste wood. In this investigation, powdered waste wood was liquefied with a solvent and an acid catalyst under heating. The principal ingredient of the liquefied wood was polyol. Biopolyurethane was then prepared from liquefied wood and isocyanate as a crosslinking agent.

Recent advances in research on wood have led to wood being converted to various biofuels and various chemical industry feedstocks by chemical methods. Of the studies on polymers prepared from liquefied wood, this investigation is categorized as polymers prepared by solvolysis reaction.[1]

Kurimoto et al.[2–4] studied the mechanical, network structures, and thermal properties of biopolyurethane and the effects of wood species on the properties of biopolyurethane. Wood is composed mostly of lignin, hemicellulose, and cellulose, of which the most difficult to liquefy is lignin, because lignin fragments are easily recondensed in acidic medium to form a residue, as reported Chen and Lu.[5] Therefore, we have considered that the residue of liquefied wood is composed mostly of compounds originated from lignin, and this residue has adverse effects on the mechanical properties of biopolyurethane. Kurimoto et al.[2–4] prepared biopolyurethane after this residue was filtered to remove.

The development of biopolyurethane for use in porous bioconcrete is the goal of this research. Porous bioconcrete consists of wood chips as aggregate and biopolyurethane as a binder.[6] This concrete has continuous internal voids and is therefore used in applications such as vegetation bases, lateral grooves, and drainage pavements for boardwalks. High strength is unnecessary for porous bioconcrete used in these applications; therefore, biopolyurethane prepared with the residue of liquefaction products was investigated in this research. Cost cutting can be achieved without elimination of the residue by simplification of the production process, which will result in a reduction of environmental burden due to a reduction of by-products.

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Various studies on biopolyurethane prepared from liquefied wood with residue have been carried out. Tohmura et al.[7] studied the effect of reaction time on the properties of biopolyurethane using softwood. Lee et al.[8] studied biopolyurethane prepared from various isocyanates with softwood. However, no comparison of biopolyurethane prepared from softwood and hardwood has been carried out. The difference between the chemical structure of lignin in softwood and hardwood is that softwood lignin has guaiacyl propane units and hardwood lignin has both syringyl and guaiacyl propane units. The residue compounds that originate from softwood and hardwood are considered to be different; therefore, the influence of different softwood and hardwood species on the chemical structure and mechanical properties of biopolyurethane prepared from liquefied wood with residue was investigated by tensile testing and Fourier transform infrared (FTIR) spectroscopy.

MATERIALS AND METHODS

Wood species and chemicals

The wood species examined were Sugi (Japanese cedar, *Cryptomeria japonica* D.Don), a softwood, and Shirakaba (Japanese white birch, *Betula platyphylla* var. japonica), a hardwood. Poly(ethylene glycol) (PEG; average molecular weight: 400, Kishida Reagent Chemicals, Osaka, Japan) and glycerol (Junsei Chemical, Tokyo, Japan) were used as the reaction reagents. Sulfuric acid (Nacalai Tesque, Kyoto, Japan) was used as the catalyst for liquefaction. Polymeric diphenylmethane diisocyanate (PMDI; Japan Polyurethane Industry, Tokyo, Japan) was used as the crosslinker, the NCO group content of which was 7.36 mmol g^{-1}.

The chemical compositions of the wood species are listed in Table I. The method of Klason lignin isolation from wood powder is described as follows.[9] Wood powders were ground using a mill to pass through a 212-μm screen and were oven-dried at 105°C for 12 h. Soxhlet extraction of wood powder using a benzene-ethanol mixture (2/1 v/v) was carried out for 6 h to prepare delipidated wood powder. After drying, 1 g of delipidated wood powder was charged into a 50-mL beaker to which 15 mL of 72% H_2SO_4 solution was added and stood at room temperature for 4 h with occasional agitation. The mixture was then placed into a 1-L round-bottom flask with 560 mL distillated water, so that the H_2SO_4 concentration became ~3%. This mixture was refluxed with heating for 4 h to hydrolyze carbohydrates. After cooling to room temperature, the black precipitate in the flask was filtered by suction using a glass filter (1GP16). The precipitate (Klason lignin) was washed with hot and cold distilled water and was then oven-dried at 105°C.

TABLE I
Chemical Composition of the Wood Species

Compound	Sugi	Shirakaba
Ethanol-benzene solubles	2.8	4.4
1% NaOH solubles	10.6	17.9
Holocellulose	68.4	70.7
Klason lignin	28.2	22.0
Ash	0.8	0.9

Liquefaction of wood powders

The wood powder was liquefied using a solvent mixture of PEG and glycerol and sulfuric acid as a catalyst. The wood powders were ground using a mill to pass through a 2-mm screen and oven-dried at 105°C for 12 h. Sixty grams of wood powder, 162 g of PEG, 18 g of glycerol, and 5.4 g of sulfuric acid were charged into a 500 mL separation flask and refluxed for 30–240 min at 175°C or 200°C. The characteristics of the liquefied wood products were investigated for various reflux times and temperatures to determine appropriate reaction times for the liquefaction of Sugi and Shirakaba.

Measurement of the hydroxyl number of liquefaction products

The hydroxyl numbers of liquefaction products were determined by the titration method. A mixture of 1 g of liquefaction product and 20 mL phthalation reagent was heated at 110°C for 20 min. This was followed by the addition of 50 mL dioxane and 25 mL distilled water, and the mixture was titrated with a 2*M* NaOH solution to the equivalence point using a pH meter. The phthalation reagent consisted of a mixture of 150 g phthalic anhydride, 24.2 g imidazol, and 1000 g dioxane.[2] The OH number in mg KOH g^{-1} of sample was calculated by the following equation:

$$\text{OH number} = \frac{(B - A)N_N \times 56.1}{W} + \text{acid number}, \quad (1)$$

where A is the volume of the NaOH solution required to obtain the equivalence point (mL), B is the volume of blank solution (mL), N_N is the normality of the NaOH solution, and W is the weight of liquefaction product (g).

A mixture of 2 g liquefaction product, 40 mL dioxane, 10 mL distilled water, and 20 mL of 1*M* NaOH solution was titrated with a 1*M* HCl solution to the equivalence point. The acid number in mg KOH g^{-1} of sample was calculated by the following equation:

$$\text{Acid number} = \frac{(B - C)N_H \times 56.1}{W} \quad (2)$$

where C is the volume of the HCl solution required to obtain the equivalence point (mL), B is the volume of blank solution (mL), N_H is the normality of the HCl solution, and W is the weight of liquefaction product (g).

Measurement of moisture content in the liquefaction products

The moisture content of liquefaction products was determined using a moisture analyzer (A&D, MS-70, Tokyo, Japan). More than 5 g of a liquefaction product was heated at 105°C until the ratio of mass change of the liquefaction product was less than 0.2% min^{-1}.

Preparation of biopolyurethane

Biopolyurethane was prepared from the liquefaction product and PMDI. The [NCO]/[OH] of the biopolyurethane was determined using the following equation:

$$[\text{NCO}]/[\text{OH}]\ \text{ratio} = M_{\text{PMDI}} W_{\text{PMDI}} \Big/ \left(\frac{\text{OH Number}}{56.1} + \frac{2}{18}\frac{C_w}{100} \right) W_{\text{LP}}, \quad (3)$$

where M_{PMDI} is the content of the isocyanate group in PMDI, W_{PMDI} and W_{LP} are the weights of PMDI and the liquefaction product, respectively (g), and C_w is the moisture content of the liquefaction product (%).

The [NCO]/[OH] ratio was set as 1.00 for all biopolyurethane samples. Thirty grams of liquefaction product and the optimum weight of PMDI were mixed in a 500-mL porcelain beaker. The mixture was agitated at ~1200 rpm for 10 min at room temperature. The biopolyurethane was placed in mold at 25°C for 24 h. After demolding the biopolyurethane, it was shaped with a cutter, as shown in Figure 1, and cured at 25°C in a relative humidity of 60% for 6 days.

Fractionation of the liquefaction product

The liquefaction products were diluted to more than 10 times their weight using a dioxane-water mixture (80/20 v/v), and the residue of liquefaction products in the solution was filtered using a polytetrafluoroethylene (PTFE) membrane-filter (TOYOH050A047A, pore size 0.50 μm), washed with distilled water, and then oven-dried at 105°C. The soluble component of the liquefaction products was obtained by evaporation of the dioxane and water from the solution. The

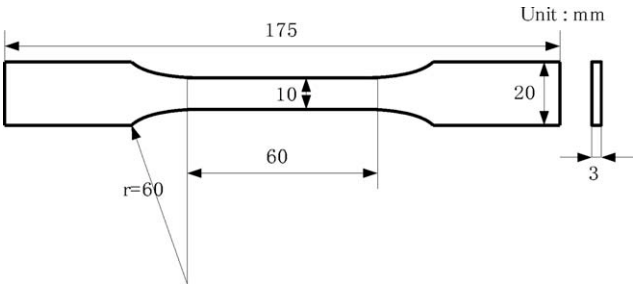

Figure 1 Schematic diagram of a tensile test specimen.

percent of wood residue content was calculated by the following equation:

$$\text{Wood residue content} = w_r/w_l \times 100 \quad (4)$$

where w_r and w_l are the weight of liquefaction product residue and liquefaction product, respectively (g).

Tensile testing of biopolyurethane specimens

Tensile testing of biopolyurethane was based on the JIS K 7113 standard. The tensile test was carried out at room temperature using a tensile-compression testing machine (A&D, RTG-1210, Tokyo, Japan). The tensile test specimen (Fig. 1) was loaded at 2 mm min^{-1}. The initial distance between reference points was ~10 mm. Three replicate specimens were tested under the same conditions. The tensile strength was calculated from the maximum load and the sectional area of the specimen. The maximum elongation was calculated from the distance between reference points at failure and Young's modulus was calculated in the elastic region.

FTIR analysis

The Klason lignin of Sugi and Shirakaba, the soluble component and the residue of the liquefaction products, and the prepared biopolyurethane were analyzed using FTIR (Jasco, FTIR-4100, Tokyo, Japan) spectroscopy. Transmittance measurements of the Klason lignin, liquefaction product residue, and the biopolyurethane were conducted using the KBr pellet method. Transmittance measurements of the liquid soluble component of the liquefaction product was conducted using KBr plates (Jasco, MagHoldIR, Tokyo, Japan).

RESULTS AND DISCUSSION

Investigation of liquefaction time

The liquefaction times for the wood powders at different temperatures are summarized in Table II. The liquefaction time was shorter for higher reaction

TABLE II
Liquefaction Times for the Wood Powders and Reaction Time of Liquefaction Products

Wood	Temperature (°C)	Liquefied time (min)	Reaction time (min)		
Sugi	175	50	60	90	120
	200	20	30	45	60
Shirakaba	175	80	90	120	150
	200	45	50	70	90

temperatures and was shorter for Sugi than that for Shirakaba at the same temperature.

Of the major components of wood, lignin is the most chemically susceptible. Previous reports[3,10,11] have shown that wood powder is liquefied by the degradation of hemicellulose and cellulose after the degradation of lignin. The liquefaction time of softwood was shorter than that of hardwood; therefore, softwood lignin is more chemically susceptible than hardwood lignin.

When the reaction time is too long, the liquefaction product becomes solidified by recondensation. Consequently, the reaction time was set between liquefaction and solidification, as listed in Table II.

OH number and moisture content of liquefaction products

The properties of liquefaction products are summarized in Table III. There was no obvious difference between the OH number and moisture content of Sugi and Shirakaba. The amount of residue in Shirakaba had a greater tendency to increase than that of Sugi. It seems that the reason for this is the different chemical structure of lignin. The amounts of residues from treatment of Sugi for 120 min at 175°C, Sugi for 60 min at 200°C, and Shirakaba for 90 min at 200°C were large. Longer reaction times resulted in an increase of residue produced by recondensation.

Mechanical properties of biopolyurethane

The mechanical properties of the biopolyurethanes are shown in Figure 2(a–c). The mechanical properties of all the biopolyurethanes were different. In particular, the wood species and reaction time had a significant effect on the mechanical properties. Comparison under conditions of same reaction time was difficult, because the liquefaction times listed in Table II were different for the different wood species and temperatures. Experimental results indicated that the appropriate reaction times for the maximum tensile strength and maximum elongation were different for Shirakaba. Therefore, the maximum tensile strength or maximum elongation for the same wood species and/or the same temperature were compared. In addition, for the same wood species and temperature, when the tensile strength was a maximum value, the Young's modulus was also a maximum value.

The influence of wood species was first investigated under the condition of the same reaction temperature. The maximum tensile strength and the maximum Young's modulus of Sugi biopolyurethane were larger than that of Shirakaba biopolyurethane. The maximum elongation of Shirakaba biopolyurethane was larger than that of Sugi biopolyurethane, which indicated that Sugi biopolyurethane was harder than Shirakaba biopolyurethane.

The influence of reaction time was next investigated under the condition of the same reaction temperature. In the case of Sugi, longer liquefaction times resulted in an decrease of tensile strength and maximum elongation. For Sugi, the appropriate reaction times for maximum tensile strength and elongation was 60 min at 175°C and 30 min at 200°C. In the case of Shirakaba, there was no relationship between the maximum tensile strength and the reaction time, although longer reaction times resulted in a decrease in maximum elongation. For Shirakaba, the appropriate reaction time for maximum tensile

TABLE III
Characterization of Liquefaction Products and Properties of the Liquefaction Product and PMDI Mixture

Wood	Temperature (°C)	Time (min)	OH number (mg KOH g^{-1})	Moisture content (%)	Residue (%)	Ratio of liquefied product and PMDI
Sugi	175	60	213	3.6	1.17	1.00 : 1.07
		90	221	3.2	0.761	1.00 : 1.02
		120	201	3.9	37.8	1.00 : 1.08
	200	30	204	3.0	1.04	1.00 : 0.95
		45	213	3.3	0.903	1.00 : 1.02
		60	171	3.4	28.9	1.00 : 0.92
Shirakaba	175	90	208	2.9	2.34	1.00 : 0.94
		120	198	3.5	2.63	1.00 : 1.01
		150	220	3.5	2.15	1.00 : 1.06
	200	50	174	2.7	1.65	1.00 : 0.83
		70	189	2.6	2.83	1.00 : 0.85
		90	200	1.4	41.6	1.00 : 0.70

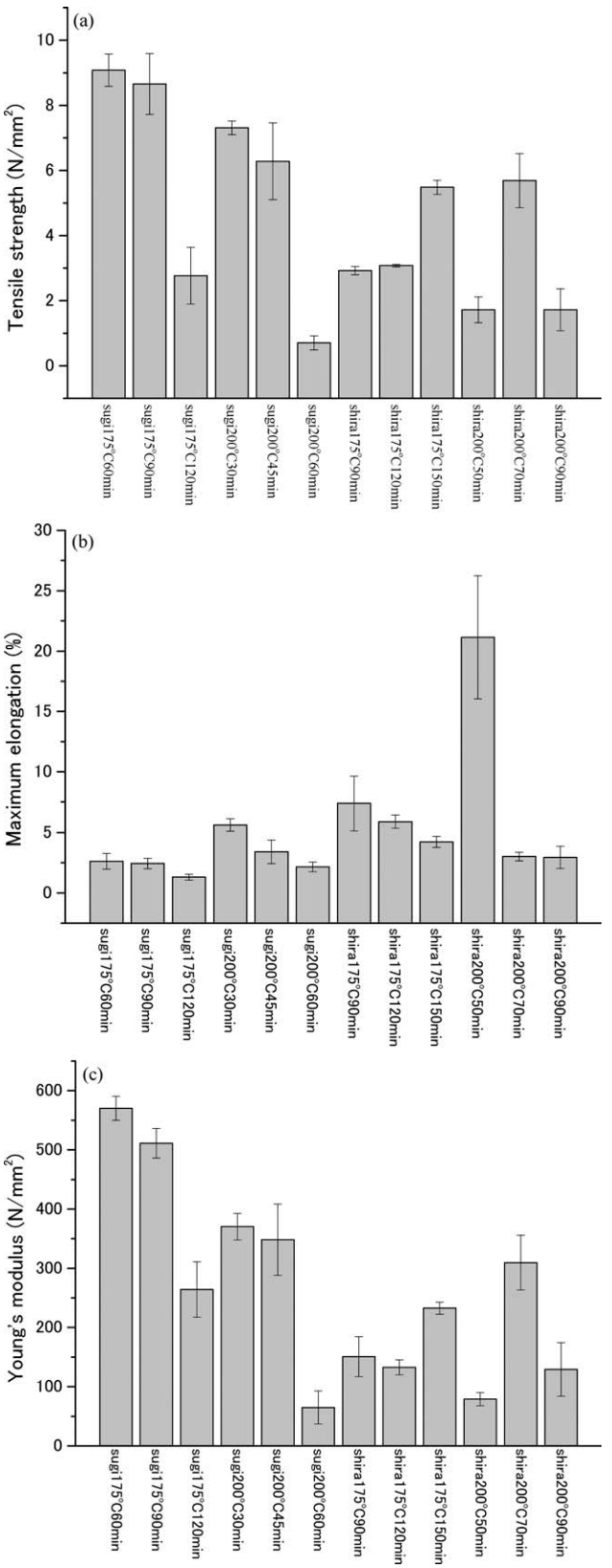

Figure 2 Mechanical properties of biopolyurethanes. (a) Tensile strength, (b) maximum elongation, and (c) Young's modulus.

strength was 150 min at 175°C and 70 min at 200°C. The appropriate reaction times for maximum elongation was 90 min at 175°C and 50 min at 200°C.

When the amount of liquefaction product residue was large, the tensile strength and maximum elongation were small. Thus, recondensation has an adverse influence on the mechanical properties of the resulting biopolyurethane.

FTIR analysis

The FTIR spectra of Klason lignins are shown in Figure 3. FTIR analysis of the Klason lignins spectra in this investigation was based on the assignments given by Boeriu et al.[12] and Xiaoa et al.[13] The FTIR spectra of Sugi and Shirakaba lignin show a weak bond signal at 1716 cm^{-1}, which is the unconjugated carbonyl/carboxyl stretching. Sugi lignin shows aromatic skeleton vibrations at 1605, 1508, and 1423 cm^{-1} and C—H deformation combined with aromatic ring vibration at 1462 cm^{-1}. Shirakaba lignin shows aromatic skeleton vibrations at 1605, 1506, and 1418 cm^{-1} and C—H deformation combined with aromatic ring vibration at 1456 cm^{-1}. The aromatic skeleton vibration of Sugi lignin at 1508 cm^{-1} has stronger intensity than the C—H deformation combined with aromatic ring vibration at 1462 cm^{-1}, but the band at 1506 cm^{-1} of Shirakaba lignin is weaker than the band at 1456 cm^{-1}. C=O stretching at 1267 cm^{-1}, CH in-plane deformation at 1140 cm^{-1}, and C—H out-of-plane vibrations in 2, 5, and 6 positions of guaiacyl propane units at 865 and 819 cm^{-1} are due to the guaiacyl propane units of Sugi lignin. The spectra of Shirakaba lignin shows a band at 1322 cm^{-1}, which is characteristic for syringyl and guaiacyl propane units. It is thought that the guaiacyl propane unit is more chemically susceptible than the syringyl propane unit, due to the shorter

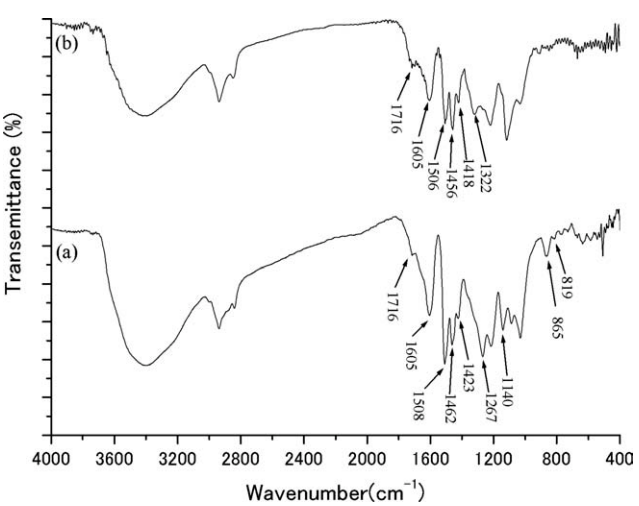

Figure 3 FTIR spectra of (a) Sugi and (b) Shirakaba lignins.

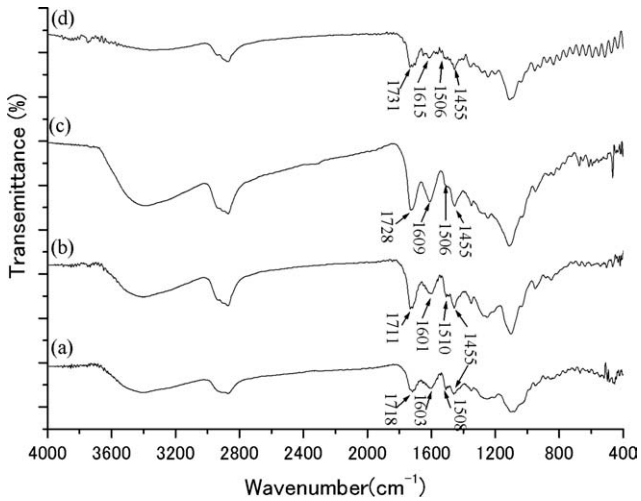

Figure 4 FTIR spectra of liquefaction product residues from treatment of (a) Sugi at 175°C for 90 min, (b) Sugi at 200°C for 45 min, (c) Shirakaba at 175°C for 120 min, and (d) Shirakaba at 200°C for 70 min.

liquefaction time of Sugi compared with that of Shirakaba.

The FTIR spectra of the liquefaction product residues are shown in Figure 4. Aromatic skeleton vibrations around 1602 and 1508 cm^{-1} and the C—H deformation combined with aromatic ring vibration at 1455 cm^{-1} are common for the residue of Sugi. The aromatic skeleton vibrations around 1610 and 1506 cm^{-1} and the C—H deformation combined with aromatic ring vibration at 1455 cm^{-1} is common for the Shirakaba residue. The aromatic rings originate from lignin; therefore, the residue contains compounds originated from lignin. The differences in the FTIR spectra of the residues were reflected in the different mechanical properties of the resultant biopolyurethanes.

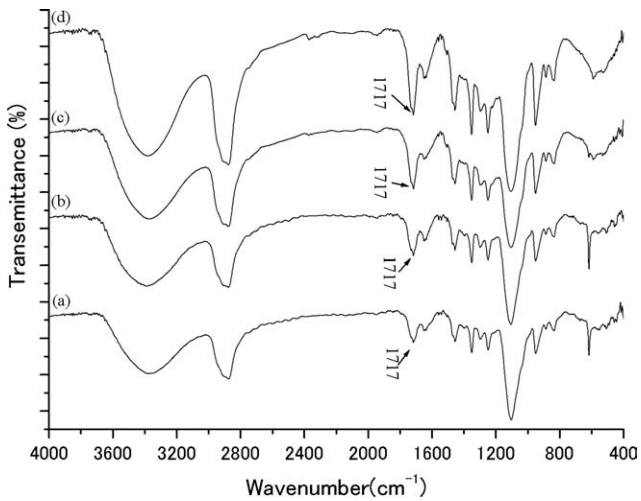

Figure 5 FTIR spectra of soluble components of liquefaction products from the treatment of (a) Sugi at 175°C for 90 min, (b) Sugi at 200°C for 45 min, (c) Shirakaba at 175°C for 120 min, and (d) Shirakaba at 200°C for 70 min.

The FTIR spectra of the soluble components of the liquefaction products are shown in Figure 5. Although the intensity of the bands may differ, the FTIR spectra were very similar. C=O stretching of esters at 1717 cm^{-1} is common for all soluble components of liquefaction products. The bond signals around 1716 cm^{-1} in Figure 3 are carbonyl/carboxyl stretching of lignins; however, because no bond signals of aromatic skeleton vibrations were observed around 1605, 1508, and 1423 cm^{-1}, which indicated that the soluble component of the liquefaction products did not contain compounds originated from lignin. Yamada and Ono[10,14] reported that an ethylene glycol (EG)-levulinic acid ester was formed by reaction of cellulose and EG. Therefore, it is thought that the band at 1717 cm^{-1} indicates the presence of levulinic acid ester. Generally, because the FTIR spectra were very similar, the soluble component of the liquefaction products was thought to have no influence on the mechanical properties of the biopolyurethane.

The mechanical properties of polyurethane is generally influenced by [NCO]/[OH]. When the mechanical properties are the same for the same [NCO]/[OH], it is thought that the properties of the liquefaction products are almost the same. Kurimoto et al.[3] reported that there was no significant difference in the mechanical properties of biopolyurethanes produced from various wood species with the same [NCO]/[OH]. However, the results in this study were not the same as that reported by Kurimoto et al.[3]; the various liquefaction products in the study by Kurimoto et al.[3] had almost the same properties, but the various liquefaction products in this study had different properties. This difference is due to the residue component in the biopolyurethane. The residue in the liquefaction products is composed mostly of compounds originated from lignin;

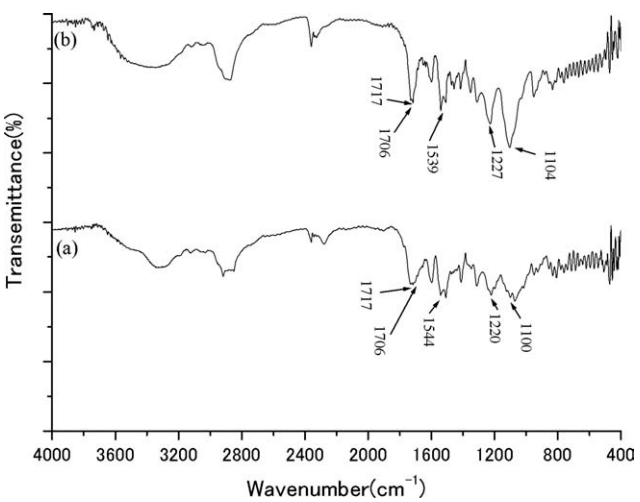

Figure 6 FTIR spectra of biopolyurethanes prepared from Sugi liquefaction products obtained from treatment at (a) 175°C for 60 min and (b) 175°C for 120 min.

therefore, the lignin species have a significant influence on the mechanical properties of biopolyurethanes.

The FTIR spectra of the Sugi biopolyurethane prepared from liquefaction products obtained by treatment at 175°C for 60 and 120 min are shown in Figure 6. FTIR analysis of the spectra recorded for the biopolyurethane produced in this study is based on the assignments given by Kurimoto et al.[4] The band signals around 1717, 1706, 1540, and 1220 cm^{-1} are assigned to the urethane linkages of biopolyurethane. The C—O—C stretch vibration around 1100 cm^{-1} is common for Sugi biopolyurethanes. The intensity of this band signal was stronger for Sugi biopolyurethane produced from liquefaction products obtained by treatment at 175°C for 120 min than that at 175°C for 60 min. Therefore, longer reaction times increases the amount of recondensation products produced, which have an adverse influence on the mechanical properties of the resulting biopolyurethanes.

CONCLUSIONS

The following conclusions were obtained from this investigation:

- The liquefaction of the softwood Sugi required a shorter time than that of the hardwood Shirakaba, because the guaiacyl propane units found in Sugi are more chemically susceptible than the syringyl propane units found in Shirakaba.
- Biopolyurethane prepared from Sugi was harder than that prepared from Shirakaba.
- The residue of the liquefaction products contained compounds that originated from lignin.

Therefore, the properties of liquefaction products and the resulting biopolyurethane were influenced by the chemical structure of lignin. In addition, the following findings were obtained:

- Appropriate liquefaction times for optimization of the tensile strength and elongation of the resulting biopolyurethanes were identified. In the case of Shirakaba, the appropriate reaction times for optimization of the tensile strength and elongation were different.
- The increase of recondensation reactions during liquefaction had an adverse influence on the mechanical properties of the resulting biopolyurethanes.

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