RAPID COMMUNICATION

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New method to determine the hydroxyl value in liquefied bark as polyurethane material

Introduction

When preparing polyurethane from a liquefied woody material such as a polyol component, the hydroxyl value in the polyol material is determined using an esterification method with phthalic anhydride or acetic anhydride.[1-6] However, precise hydroxyl values cannot be obtained by the esterification method if aldehyde, sterically hindered hydroxyl, or phenolic hydroxyl groups are present in the polyol material. Other methods using [1]H-nuclear magnetic resonance (NMR) or gas chromatography have been proposed to determine the hydroxyl values in lignin,[7,8] but these methods were not useful when using liquefied woody materials because these materials are complex mixtures of polymers. Therefore, it has been important to develop a new method for determining hydroxyl groups in liquefied woody materials that can react to NCO groups in polymeric methylene diphenylene diisocyanate (PMDI).

To utilize liquefied bark for the preparation of polyurethane, a new method based on consumption of the NCO group in a reaction of phenyl isocyanate with the hydroxyl group in liquefied bark was examined. As standard compounds we used ethylene glycol with primary hydroxyl groups, D-glucose with secondary and primary hydroxyl groups, 3,4-dihydroxytoluene with vic-phenolic hydroxyl groups, and catechin with secondary and vic-phenolic hydroxyl groups. The theoretical and experimental hydroxyl values for these compounds were compared. We showed that the hydroxyl values of liquefied sugi (Cryptomeria japonica) bark samples can be determined more precisely by the method based on consumption of the NCO group than by the conventional esterification method.

Experiments

Materials

Ethylene glycol, D-glucose, and 3,4-dihydroxytoluene were purchased from Wako Pure Chemical Industries (Osaka, Japan) and (+)-catechin from Sigma (St. Louis, MO, USA). These compounds were selected as standard compounds for determining the hydroxyl values.

Liquefied sugi bark was prepared by the bisulfite method described in a previous paper.[9] That is, 2 g of oven-dried sugi inner or outer bark powder, 6 ml of polyethylene glycol (PEG-400, average molecular weight 400), 5 ml of aqueous $NaHSO_3$, and 1 ml of 0.02% sulfuric acid were placed in a 35-ml stainless autoclave and heated to 250°C. The concentration of the aqueous $NaHSO_3$ and the liquefaction time at 250°C were 2% and 90 min for the inner bark and 6% and 30 min for the outer bark. The products were diluted with 80% dioxane aqueous solution and filtered using a glass-fiber filter (TOYO GA-100) after liquefaction. The insoluble residue was washed with a dioxane/water mixture (80:20 v/v) until the filtrate became colorless; it was then dried to a constant weight at 105°C. The dioxane and water in the filtrate were evaporated under reduced pressure to afford a dried liquefied bark sample.

Determination by esterification

The hydroxyl value was determined using esterification, according to the method described by Kurimoto et al.[3,4] A

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mixture of 0.2–0.5 g of a sample and 25 ml of phthalation reagent was heated for 20 min at 110°C. After cooling, 50 ml of a dioxane/water solution (80:20 v/v) was added to the mixture, and the mixture was titrated with 1 N NaOH solution to the equivalence point using a pH meter. The phthalation reagent consisted of a mixture of 30 g phthalic anhydride, 4.84 g imidazol, and 200 ml dioxane. The hydroxyl value based on esterification was calculated as follows.

$$\text{Hydroxyl value (mmol/g)} = (B - A)N/W + \text{acid value}$$

where B is the volume of the NaOH solution required to titrate the blank solution (milliliters); A is the volume of NaOH solution required to titrate the sample solution (milliliters); N is the normality of the NaOH solution; and W is the weight of the sample (grams).

In the case of liquefied bark, the acid value was also determined by titration with 1 N NaOH. A mixture of 1 g of liquefied bark and 100 ml of a dioxane/water solution (80:20 v/v) was titrated with 1 N NaOH to the equivalence point. The acid value was calculated as follows.

$$\text{Acid value} = (C - B)N/W$$

where C is the volume of NaOH solution required to titrate the sample solution (milliliters); and B is the volume of NaOH solution required to titrate the blank (milliliters).

Determination by NCO method

The prepolymer test of polyurethane (JIS K7301) was applied to develop the NCO method for hydroxyl value determination. That is, 0.2–0.5 g of a sample and 0.05 mmol of catalyst were dissolved in 5 ml of 1,4-dioxane in a flask. 1,4-Diazabicyclo-[2.2.2]-octane (DABCO) (Wako, Osaka, Japan) and di-n-butyltindilaulate (DBTDL) (Wako) were used as catalysts. Phenylisocyanate 9 mmol (Aldrich Chemical Company, Milwaukee, WI, USA) were added to the solution, and the solution was then stirred at room temperature for 2 h. Dry toluene (25 ml) and acetone (10 ml) were added to the flask followed by 10 ml of 13%-di-n-butylamine toluene solution. The mixture was stirred for

15 min before 60 ml of 2-propanol was added. The mixture was then titrated with 0.5 N HCl using a pH meter.

Two blanks were prepared. The first $(BL1)$ included all the reagents listed above but omitted the sample; second $(BL2)$ omitted the sample and phenyl isocyanate. The hydroxyl value based on the reaction of the hydroxyl and NCO group was calculated as follows.

$$\text{Hydroxyl value (mmol/g)} = (A - D)/W = (S - B1)N/W$$

$$A = (B2 - B1)N$$

$$D = (B2 - S)N$$

where A is the NCO group added before the reaction (millimoles); D is the NCO group that remains after the reaction (millimoles); W is the weight of the sample (grams); $B1$ is the volume of HCl required to titrate $BL1$ (milliliters); $B2$ is the volume of HCl required to titrate $BL2$ (milliliters); S is the volume of HCl required to titrate the sample (milliliters); and N is the normality of HCl.

Results and discussion

Hydroxyl values of standard compounds

Table 1 shows the hydroxyl values determined by the NCO and esterification methods for standard compounds. An experimental value close to the theoretical one was obtained only for ethylene glycol using the esterification method. The experimental values for the other compounds were considerably less than the theoretical ones. Therefore, it is suggested that the esterification method is not suitable for determining hydroxyl values of materials containing phenolic hydroxyl groups or for alcoholic materials with high steric hindrance.

The values determined by the NCO method varied depending on the kind and amount of catalyst. When only DBTDL was used as a catalyst, the hydroxyl values for D-glucose and 3,4-dihydroxytoluene were considerably less than the theoretical values. In particular, in the case of (+)-catechin, gel formation was observed in the DBTDL-

Table 1. Hydroxyl values of standard compounds determined by esterification and NCO methods

Compound	Theoretical value	Esterification method with phtharic anhydride	NCO method, by the catalyst(s) used			
			DBTDL	DABCO	DABCO/DBTDL (molar ratio 1:1)	DABCO/DBTDL (molar ratio 2:1)
Ethylene glycol	32.2	31.5 (±0.51)	31.50 (±0.51)	27.70 (±0.24)	29.70 (±0.22)	29.00 (±0.34)
D-Glucose	27.7	5.86 (±1.63)	5.86 (±1.63)	7.65 (±0.68)	17.20 (±1.52)	25.40 (±0.14)
3,4-Dihydroxytoluene	16.1	1.35 (±0.20)	1.10 (±1.21)	9.26 (±1.82)	7.54 (±0.90)	9.96 (±1.06)
(+)-Catechin	17.2	4.73 (±0.89)	–	13.40 (±0.64)	11.40 (±0.61)	13.20 (±0.45)
Deviation (%) from theoretical value						
Mean	–	61.3	–	37.7	33.1	19.9
Maximum	–	91.6	–	72.4	53.2	38.1

Results are in millimoles per gram: mean (±SD)
DBTDL, di-n-butyltindilaulate; DABCO, 1,4-diazabicyclo-[2.2.2]-octane

catalyzed reaction system, and consequently titration could not be performed after the reaction. We reported that a sparingly soluble reactant, organotin complex, was formed when DBTDL and a reactant with catechol-type hydroxyl groups were mixed in acetonitrile (M. Oyadomari, K. Ueno, T. Ashitani, K. Sakai, submitted). It was therefore thought that the polymer complex of catechin and DBTDL was also formed during the hydroxyl value determination by the NCO method using the DBTDL catalyst. It is known that DBTDL mainly catalyzes the reaction of the aliphatic hydroxyl groups with isocyanate.[10] Therefore, the hydroxyl values determined by the NCO method using only the DBTDL catalyst were similar to those obtained by the esterification method. When DABCO was used as the sole catalyst for determining the hydroxyl value of glucose, 3,4-dihydroxytoluene, or catechin, deviations from the theoretical values were much less than those observed with the esterification method or the DBTDL-catalyzed NCO method. However, the experimental value for ethylene glycol using the DABCO catalyst was quite a bit lower than the theoretical value. DABCO mainly catalyzed urethane formation from phenols with isocyanate.[10] The results shown above, except for those of glucose, are in agreement with results obtained in previous studies. The experimental value for glucose with the DBTDL catalyst was quite a bit lower than the theoretical value. It is thought that this low experimental value for glucose with the DBTDL catalyst was caused by high steric hindrance of its secondary hydroxyl groups.

Therefore, a mixture of the two catalysts was applied for determining hydroxyl values of the standard compounds. The effect of different DABCO/DBTDL molar ratios on the hydroxyl values determined by the NCO method is also shown in Table 1. At a DABCO/DBTDL molar ratio of 1:1, the experimental values were still lower than the theoretical values for glucose, 3,4-dihydroxytoluene, and catechin. As shown in Table 1, determining the phenolic hydroxyl groups or the alcoholic groups with high steric hindrances gave values near the theoretical values when the catalysts were used at a DABCO/DBTDL molar ratio of 2:1.

Hydroxyl values of liquefied products

The residues after liquefaction of sugi inner and outer bark amounted to 14% and 30%, respectively. Liquefied barks are supposed to be complex mixtures of aliphatic alcohol (e.g., polyethylene glycol), alcohols derived from carbohy-

drates, and phenolics derived from lignin and suberin. The hydroxyl values for liquefied sugi bark determined by the esterification and NCO methods using different catalysts are shown in Table 2. The values obtained by the NCO method were larger than those obtained by the esterification method. When DBTDL was used as the sole catalyst, there was little difference between the values for the liquefied inner and outer barks. However, when DABCO or a mixture of DABCO and DBTDL was used as a catalyst, the difference increased. The liquefied inner bark has more decomposed cellulose components than the liquefied outer bark.[9] Therefore, the larger hydroxyl values observed by the NCO method for liquefied inner bark than for the liquefied outer bark might originate from decomposed cellulose components, which are supposed to have secondary hydroxyl groups. During liquefaction of lignocellulosic materials, it is known that cellulose is converted to glycosides or decomposed to levulinic acid.[11] Based on the high hydroxyl value of liquefied inner bark, it is thought that cellulose in the bark is converted to glycosides during the liquefaction process.

The outer bark contains more phenolic components than the inner bark because it has a higher Klason lignin value than the inner bark.[9] Therefore, when determining the hydroxyl value for liquefied outer bark, a high hydroxyl value was predicted when using the DABCO catalyst, which mainly catalyzes the reaction of the phenolic hydroxyl group with the NCO group. However, the hydroxyl value of the liquefied outer bark did not markedly increase when DABCO was used as the catalyst compared to the DBTDL catalyst when using the NCO method. The Klason lignin value may include the amount of suberin, which is contained in the outer bark of sugi in quite large amounts.[12] Lignin and suberin have fewer hydroxyl groups than does cellulose. In addition, it is thought that the condensed tannin may not be abundant in sugi outer bark and, if present, is modified to other polymeric compounds during liquefaction.[12,13] For the above reasons, it is thought that the hydroxyl value of the liquefied outer bark did not increase when DABCO, rather than DBTDL, was used as catalyst.

Conclusions

When the hydroxyl values of materials containing phenolic or sterically hindered hydroxyl groups were determined by the esterification method, the values were considerably smaller than the theoretical values. In contrast, the NCO

Table 2. Hydroxyl values of liquefied sugi bark estimated by the esterification and NCO methods

Liquefied sugi bark	Esterification method with phtharic anhydride	NCO method, by the catalyst used		
		DBTDL	DABCO	DABCO /DBTDL = 2
Inner bark	4.580 ($\pm$0.006)	7.84 ($\pm$0.18)	16.70 ($\pm$0.57)	20.30 ($\pm$0.11)
Outer bark	4.690 ($\pm$0.181)	6.99 ($\pm$0.04)	8.57 ($\pm$0.55)	9.57 ($\pm$0.67)

Results are in millimoles per gram: mean ($\pm$SD)

method provided hydroxyl values much closer to the theoretical values for such materials, though the values varied depending on the kinds and amounts of catalysts.

The quantity of hydroxyl groups reacting with the NCO group could be directly determined by the NCO method using a catalyst mixture consisting of DABCO and DBTDL in a molar ratio of 2:1. Therefore, this method can be considered useful for determining the hydroxyl value before preparing polyurethane from liquefied wood or bark.

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