NOTE

Development of lignin as a transparent resin: evaluation of thermal and optical properties of alkoxylated lignophenols

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INTRODUCTION

Worldwide energy consumption has increased rapidly and significantly with technological developments and population growth; reserves of fossil fuels such as coal and petroleum are thus in danger of being exhausted. Therefore, it is essential to discover alternative energy resources.[1,2] Lignocellulose (LC), which exists in plant cells, is a type of biopolymer composite, and it has attracted considerable attention as one such alternative; LC could become an efficient fossil fuel alternative because it is produced from water and carbon dioxide by plant photosynthesis, and is one of the raw materials for biofuels. LC decomposes to cellulose and lignin,[3] where the latter contains phenol derivatives; currently, LC is considered as an industrial waste because of its lack of processability. However, we succeeded in developing a phase-separation system (two-step process II) that can produce processable lignophenol (LP) (Figure 1).[4–6] The structure of LP is similar to that of artificial phenolic resins[7–10] commonly used as plastics; therefore, LP is considered as a natural-polymer-based plastic and an alternative to petroleum-based commodity polymers. It may thus be possible to reduce fossil fuel consumption by producing novel LP-based materials. Further, it may be possible to design its energy cycle. However, LP has lower thermal stability than most plastics because it contains many hydroxyl groups in its side chain. These groups act as reactive functional groups in the presence of epoxy derivatives to produce phenolic-resin-based epoxy resins;[11,12] they also act as metal-ion chelators. However, these groups result in poor chemical resistance, hydrophilicity of the polymer and have poor solubility in organic solvents. Therefore, to develop a high-performance LP, it is necessary to modify these functional groups. Previously, we demonstrated that phenolic resins prepared from phenol derivatives containing protected (alkoxylated) hydroxyl groups[13–16] exhibit higher thermostability; for example, it was demonstrated that 10% loss in weight (T_{d10}) of alkoxylated-naphthalene-based resin occurs at a temperature greater than 400 °C. Further, alkoxylated-phenol-derivative-based phenolic resins exhibited good film-forming abilities and processabilities. Therefore, to develop thermostable, organosoluble, processable and alkaliproof LP-based materials, it is important to protect the hydroxyl groups of LP.

In this study, we synthesized LPs with alkoxylated phenolic and aliphatic hydroxyl groups by Williamson ether synthesis using alkyl halides. The resulting products exhibited good solubility in organic solvents and good film-forming abilities. Furthermore, LPs contain several aromatic moieties from the phenol derivatives. Consequently, modified LP is expected to serve as an optical material (to fabricate polymer-based lenses with high refractive index and low birefringence) similar to polycarbonate (PC).[17]

EXPERIMENTAL PROCEDURE

Materials

Unless otherwise noted, all reagents and chemicals used were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used without further purification. LP was obtained from Japanese cedar (Cryptomeria japonica)-based lignin soaked in p-cresol by means of the phase-separation system (two-step process II) according to the previous report (M_n=2400, M_w/M_n=3.24, eluent: tetrahydrofuran, polystyrene standards).[4] Poly(bisphenol A-carbonate) (PC, M_w=64000) was obtained from Aldrich (St Louis, MO, USA).

Instruments

All the ^{1}H NMR spectra (in CDCl₃ or DMSO-d_6) were recorded by a 400 MHz JEOL (Tokyo, Japan) LNM-EX400 with tetramethylsilane as the internal standard. The Fourier transform infrared spectra were recorded using a JASCO (Tokyo, Japan) Fourier transform infrared 460 plus. Gel permeation chromatography was carried out by a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH (Tokyo, Japan) TSKgel G3000H$_{XL}$ column) using tetrahydrofuran as the eluent after calibration with polystyrene standards, or was carried out by a JASCO UV-1570 detector and a JASCO RI-1530 detector

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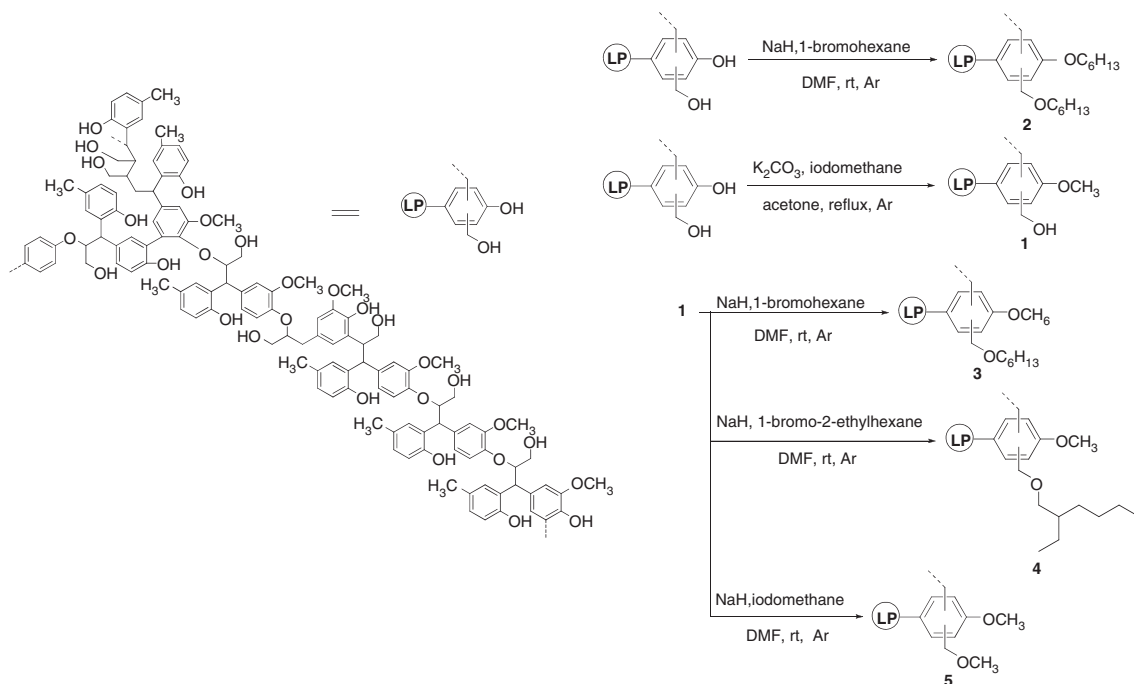
Figure 1 Model polymer structure of lignophenol (LP) and alkoxylation of hydroxyl groups by Williamson ether synthesis.

(TOSOH TSKgel GMH$_{XL}$ and TSKgel G2000H$_{XL}$ columns) using 0.12 mmol l^{-1} LiBr-containing *N,N*-dimethylformamide. High-performance liquid chromatography was carried out by LC-9204 system with a JAI (Tokyo, Japan) UV-3702 detector (JAI JAIGEL 2H-40) using chloroform as an eluent. Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a SII DSC 6220 at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. Ultraviolet visible spectra were recorded on a Beckman Coulter DU800 (Beckman Coulter, Brea, CA, USA). The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of polymer thin films were measured with a prism coupler (Metricon, Pennington, NJ, USA, model PC-2000) equipped with half-waveplates in the light-path and He–Ne/semi-conductor laser sources. The film thickness of the polymers was recorded using a ULVAC Dektak 3 series (ULVAC, Chigasaki, Kanagawa, Japan).

Measurement of refractive indices

Refractive indexes were measured by a prism coupler method according to literature.[18] In this method, the required film thickness is ~ 10 μm. All polymer coating on a synthetic quartz plate (30×30×3 mm) was prepared by spin coating of their concentrated 1,2-dichloroethane solutions. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices were determined by a Metricon model PC-2000 prism coupler, and the birefringence (Δn) was estimated as the difference between n_{TE} and n_{TM}. The average refractive index of the film was calculated using the equation: $n_{av}=[(2n_{TE}^2 + n_{TM}^2)/3)]^{1/2}$. Abbe's number is given by $(n_D-1)/(n_F-n_C)$, where n_D, n_F and n_C are the refractive indices of the materials at the wavelength of sodium *D* (589.3 nm), hydrogen *F* (486.1 nm) and hydrogen *C* (656.3 nm) lines, respectively.[18,19]

RESULTS AND DISCUSSION

Preparation of LPs with alkoxylated hydroxyl groups

LPs, which contain many phenolic and aliphatic hydroxyl groups, exhibit poor solubility in organic solvents, such as chloroform, toluene and hexane; the model polymer structure is shown in Figure 1.[5] By protecting the hydroxyl groups using alkyl halides, the solubility of LPs in organic solvents and their processabilities should improve because of the elimination of hydrogen bonds between each hydroxyl group

(Figure 1). However, the yields of alkoxylated LPs were low. In order to protect all of the hydroxyl groups with alkyl groups, it is necessary to use sodium hydrate as a strong base; therefore, condensation reaction between LPs proceeded to form insoluble resins. The molecular weights of alkoxylated LPs (**2–5**) (M_n=3400–7800) were higher than that of the starting LP (M_n=2400). A comparison of the Fourier transform infrared spectra of LP and alkoxylated LPs (**2–5**) revealed that the intensities of peaks attributed to the hydroxyl groups of **2–5** decreased (Figure 2). From the ^{1}H NMR spectra, the peaks of phenolic hydroxy groups of LP (8.8–9.0 p.p.m. in DMSO-d_6) were disappeared in the spectra of alkoxylated LPs (Supplementary Figures S1–S4). On the basis of ^{1}H NMR spectra (Figure 2), the contents of aliphatic hydroxyl groups of LPs (**2** and **3**) are approximately below 3%. (The starting material LP had a small amount of aliphatic hydroxyl groups and exhibited hydrophobic character.) From these results, most hydroxyl groups of **2–5** were alkoxylated. The solubilities of **2–5** in organic solvents such as chloroform, dichloroethane and toluene also increased. In the ^{1}H NMR spectra of **2–5**, peaks attributed to the unprotected hydroxymethyl protons were hardly detected, whereas those of protected aliphatic and aromatic hydroxymethyl protons appeared at around 5.00 p.p.m. (Figure 2). Therefore, we can conclude that the hydroxyl groups were successfully protected.

Thermal properties of LP and 2–5

The thermal properties of alkoxylated LPs (**2–5**) were evaluated by TGA carried out at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. The TGA results are summarized in Table 1 and Figure 3. In the case of **2**, 5 and 10% weight loss (T_{d5} and T_{d10}) were observed at 332 and 359 °C, respectively. The corresponding temperatures of **3**, **4** and **5** were higher than those of **2**; this difference was attributed to the number of aliphatic carbons present in the protective moieties. In the case of **2**, both the hydroxyl groups were alkoxylated by hexyl groups; the aliphatic content was large, and hence, the polymer decomposed at relatively low temperatures. In contrast, in the case of **5**, the protective
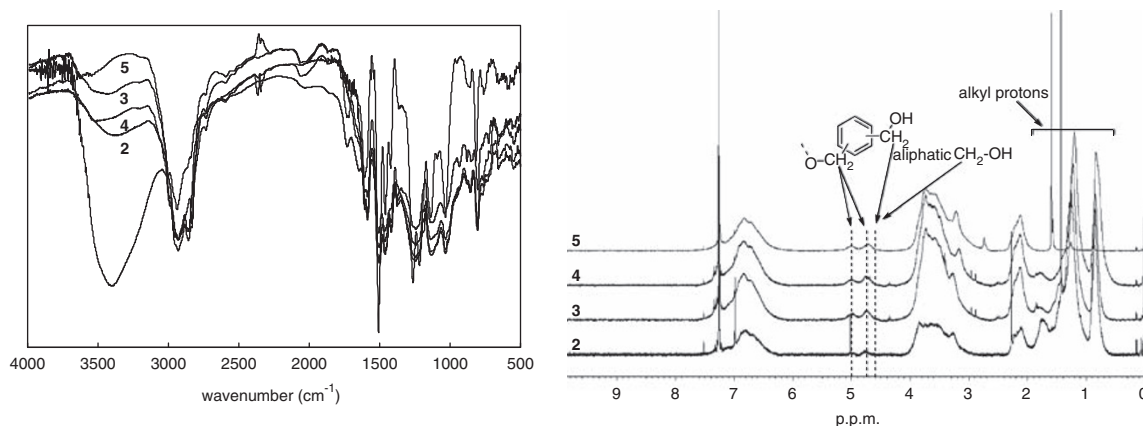
Figure 2 Fourier transform infrared and ^{1}H NMR (CDCl$_3$) spectra of lignophenol (LP) and alkoxylated LPs (**2–5**).

Table 1 Thermal properties of lignophenol (LP) and alkoxylated LPs (2–5)

| Run	T_{d5} (°C)[a]	T_{d10} (°C)[b]	T_g (°C)[c]
LP	171.4	273.9	Not detected
2	332.0	359.1	33.0
3	342.3	362.7	72.3
4	342.4	364.0	67.5
5	346.1	369.0	124.8

[a]Temperature at 5% loss in weight.
[b]Temperature at 10% loss in weight.
[c]Temperature at glass transition point.

group used was only a methyl group, that is, the aliphatic content was low; therefore, it decomposed less readily and exhibited higher thermal stability. These results suggested that the thermal stability of LP can be enhanced by alkoxylation of hydroxyl groups; the TGA result of unprotected LP was as follows: T_{d5}=171 °C and T_{d10}=274 °C. Unprotected LP has a lot of unprotected hydroxyl groups on benzene rings and alkyl chains. These groups were easier to be decomposed by heating than protected hydroxyl groups; therefore, the thermal stability of unprotected LP was less than those of alkoxylated LP (**2–5**). In our previous report,[20] the weight decrease of a conventional phenol novolac (ca. M_n=1500) started below 150 °C due to degradation around the phenolic hydroxy groups. Alkoxylation of hydroxy group can add good thermal stability to phenolic polymers.

Table 1 also lists the temperature values corresponding to the glass transition points (T_g) of hydroxyl-group-alkoxylated LPs along with their alkyl chain lengths (types of alkyl groups). To accurately evaluate T_gs, DSC measurements were carried out on **2–5** (Figure 3, T_gs of **2**: 33.0 °C, **3**: 72.3 °C, **4**: 67.5 °C, **5**: 124.8 °C). The DSC measurement results suggested that the hydroxyl-group-alkoxylated LPs (**2–5**) behaved in a manner similar to conventional amorphous polymers (Figure 3).[19] The DSC profile of **5** (with C$_1$ (methyl) chain) exhibited a relatively distinct T_g, whereas those of **2** (with C$_6$ (hexyl) chain), **3** (with C$_1$ (methyl) and C$_6$ (hexyl) chains) and **4** (C$_1$ (methyl) and C$_8$ (2-ethylhexyl) chains) were broad over a wide range of temperatures, and their T_gs appeared at lower temperatures than that of **5**. These results clearly indicate that T_gs of alkoxylated LPs depend on the number of carbon atoms or the length of alkyl chains in the protective groups. In the case of unprotected LP, DSC measurement could not be carried out because it decomposed early at a low temperature. We have therefore succeeded in enhancing the thermal stability of LP by
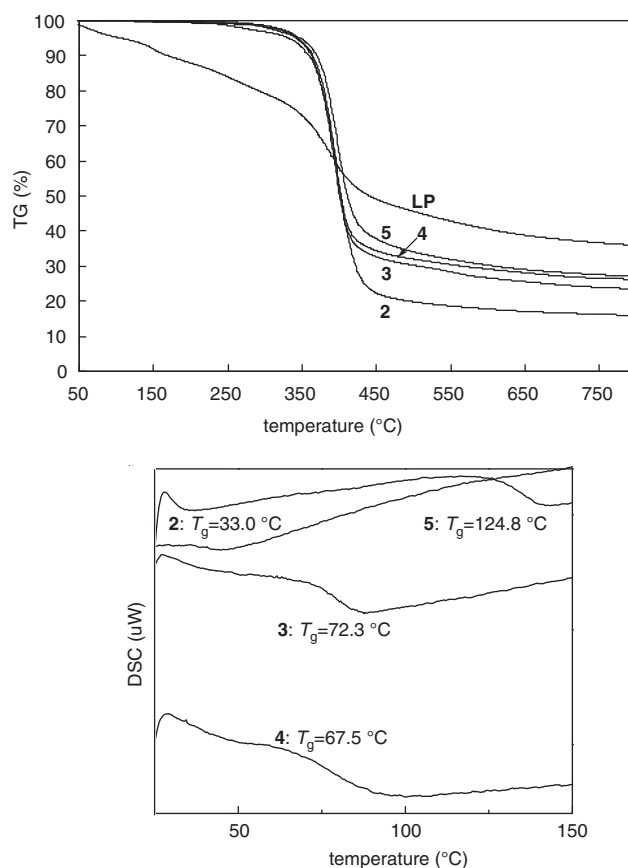
Figure 3 Thermogravimetric (TG) charts of lignophenol (LP) and **2–5** under nitrogen atmosphere and differential scanning calorimetry (DSC) analyses of alkoxylated LPs (**2–5**).

alkoxylation of the phenolic and aliphatic hydroxyl groups using alkyl groups. The T_gs of hexyloxylated (**2**) and methoxylated LPs (**5**) appeared at a slightly low and high temperature, respectively; however, these values were smaller than that of PC ($T_g \sim 150$ °C). From this result, it is possible to use **2–5** as commodity polymers.

Optical properties
Alkoxylated LPs (**2–5**) contained aromatic moieties, alkyl chains in their protective groups and oxygen; therefore, they could be qualified

as carbon-rich aromatic polymer materials. PC based on bisphenol A, whose structure is similar to that of phenolic resins such as LPs, has been used as an engineering plastic, highly thermostable material and so on. Recently, PC has been used as an optical material having high refractive index; however, its birefringence is high because of the orientation of its main chains. Considering that their structures are comparable, alkoxylated LPs could serve as optical materials not only with high refractive indices similar to that of PC but also with lower birefrigence than that of PC due to the complicated structures of the main chains, as shown in Figure 1. The refractive indices, birefringences, Abbe's numbers and thickness of polymer coating on the quartz glass (2–5) are listed in Table 2. Film samples for the refractive index measurement were prepared from their 1,2-dichloroethane solutions (30% w/v) by the spin-coating method (Figure 4). The average refractive index (n_{av}) and the birefringence (Δn) of PC were found to be 1.582 and 0.011, respectively. In contrast, n_{av} values of 2 and 3 (1.5496 and 1.5694, respectively) were found to be smaller than that of PC; however, Δn values and Abbe's numbers of 2 and 3 were sufficient for optical materials (<0.001 and >30, respectively). Δn may be small in the cases of 2 and 3 as compared with that of PC because of steric hindrance imposed by the long alkyl chains in the

protecting groups; this steric hindrance may interfere with the formation of π–π aromatic interactions between the benzene rings of the main chains. The Abbe's numbers of 2 and 3 are higher than that of PC, despite the comparable refractive indices and lower Δn values. The wavelengths at which polymer coatings of 2 and 3 exhibited transmittance of over 90% were found to be 381 and 464 nm, respectively (Figure 4) (The origin of the color of alkoxylated LPs (2–5) may be impurities (by-products) or CT absorption between remaining bromine or iodine moieties with benzene ring or alkoxy group. In the case of alkoxylated LPs 4 and 5, partial transparent and colored coatings were obtained. Therefore, the aggregation of polymers occurred by π-stacking or other interaction.). The transparency of these coatings was attributed to the phenolic resin-like structure of the main chain with long alkoxyl groups. However, in the cases of 4 and 5, the optical measurements could not be carried out because their coatings cracked. The film-forming abilities of LPs probably depend on the length or type of protective alkyl chain. This result revealed that hydroxyl-group-alkoxylated LPs (2 and 3) can also be used as optical materials such as PC.
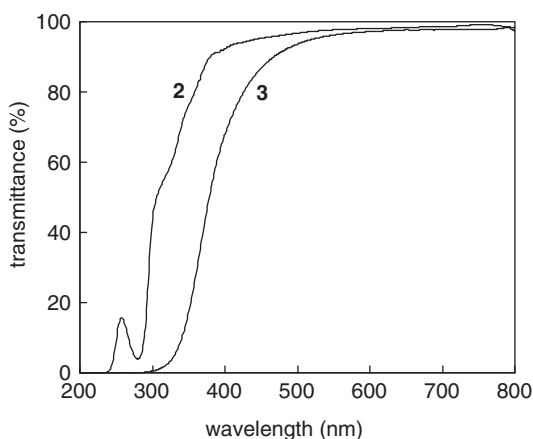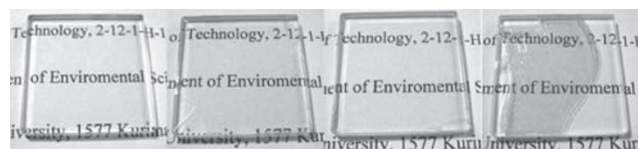
Table 2 Optical properties of alkoxylated LPs (2–5) and PC

Run	d (μm)[a]	n_{TE}[b]	n_{TM}[b]	n_{av}[b]	Δn[b]	Abbe's number[b]
2	10.3	1.5496	1.5495	1.5496	<0.001	34.4
3	17.7	1.5696	1.5690	1.5694	<0.001	31.4
4	17.1	—	—	—	—	—
5	17.3	—	—	—	—	—
PC	7.0	1.5895	1.5708	1.5820	0.011	30.0

Abbreviations: LP, lignophenol; PC, polycarbonate.
[a]Film thickness.
[b]Measured at 632.8 nm.

CONCLUSION

We successfully prepared LPs (2–5) having hydroxyl groups alkoxylated with different types of alkyl halides by Williamson ether synthesis. TGA results suggested that 2–5 had enhanced thermal stability as compared with LP because of alkoxylation of hydroxyl groups. Further, we found that hydroxyl-group-alkoxylated LPs can be used as optical materials, such as bisphenol A-based PC, because the refractive indices and birefringences of these LPs are comparable with those of PC. In particular, 2 and 3 exhibited good film-forming abilities with transparency; further, 3 had an approximate T_g as a commodity polymer. These results suggest that natural polymer LPs are highly advantageous in that they have very good material properties and they can be produced from biomass.[21] We are now investigating the optimization of the properties of functionalized LPs as an optical material and an engineering plastic.

Procedures and spectral data of 2–5 are provided in Supplementary information.

Figure 4 Polymer coatings on the quartz glass 2–5 prepared by the spin-coating method, and transparency of thin polymer coating of 2 and 3.

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