Characterization of Lignin Derivatives in Alkaline Polyethylene Glycol-treated Soda Cooking Black Liquor Powder

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To improve the thermal properties of softwood soda lignin, we studied a method of lignin modification using black liquor powder and polyethylene glycol (PEG). In this process, the black liquor powder was directly treated with PEG under alkaline conditions to produce a thermal melting material (alkaline PEG treatment). A model experiment was performed to determine the reaction of the lignin. The lignin in the black liquor powder consisted of 62.16% acid-insoluble lignin (purified lignin) and 37.84% acid-soluble lignin. After alkaline PEG treatment using purified lignin, the samples exhibited weak thermal melting during softening point analysis but did not exhibit appropriate thermal melting during thermal mechanical analysis (TMA). Nuclear magnetic resonance (NMR) data suggest that there was no linkage between lignin and PEG in the alkaline PEG-treated lignin prepared from the purified lignin. On the other hand, when using acid-soluble lignin, NMR data suggest that PEG was introduced to the lignin at its α-carbon position. Acid-soluble lignin PEG derivatives could work as plasticizers to induce the thermal melting of the alkaline PEG-treated lignin prepared from black liquor powder.

Keywords: Alkaline PEG treatment; Dried black liquor powder; Thermal melting; Polyethylene glycol; Softwood soda-AQ lignin

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INTRODUCTION

Lignin is a major component in wood cell walls and can be isolated from wood *via* chemical pulping. Wood can be regarded as a lignin plastic reinforced by cellulose fibers (Hoyt and Goheen 1971). Many million tons of wood are processed annually in the chemical pulping industry to separate lignin from cellulose fibers. Spent liquors (black liquor) from pulping operations such as kraft, soda, and sulfite processes are some of the available sources of lignin. Lignin prepared from the black liquor of industrial pulping processes is called technical lignin. Some types of technical lignin can be used as dispersants, binders, and surfactants (Dizhbite *et al.* 1999; Gargulak and Lebo 2000; Lora and Glasser 2002; Gosselink *et al.* 2004; El Mansouri and Salvadó 2006; Stewart 2008; El Mansouri *et al.* 2011). However, only approximately 2% of the technical lignin produced from industrial pulp manufacturing is utilized for commercial purposes (Gargulak and Lebo 2000). In the industrial pulping process, most of the lignin in black liquor is combusted to generate energy and recover chemicals. To activate the commercial utilization of lignin, the mechanical properties of technical lignin must be improved, a key point in the preparation of these value-added products.

Polymer blending is a simple modification method used to upgrade the thermoplastic properties of lignin (Feldman *et al.* 1995; Feldman 2002). Li *et al.* (1997) reported that lignin-based polymeric materials blended with polyvinyl acetate exhibited improved mechanical and thermoplastic properties. Kadla and Kubo (2004) prepared a blended polymer with a low glass transition temperature (T_g) and thermal softening temperature (T_s) using soda lignin and polyethylene terephthalate.

Chemical derivatization is a direct approach for improving the physical and chemical properties of lignin. Fang *et al.* (2011) reported that dicarboxylic acid prepared by dimerizing unsaturated fatty acids can be reacted with lignin *via* esterification, leading to the formation of lignin derivatives that could remove the rigidity and improve the flexibility of lignin. Although the physical and chemical properties of lignin can be improved *via* chemical derivatization, the cost of commercial-scale treatment is prohibitive.

Carbon fiber (CF) is a high-value added product that can be prepared from lignin (Kubo and Kadla 2004; 2005; Fernandes *et al.* 2006; Shen *et al.* 2011). For efficient lignin-based CF preparation, lignin can be converted into fibers *via* melt-spinning. Lignin-based CF was first prepared from technical lignin blended with polyvinyl alcohol by Otani *et al.* (1969). Sudo *et al.* (1993) developed CF from a hardwood steam-exploded lignin, which was modified to a thermal melting material by phenolation. Uraki *et al.* (1995) produced a lignin fiber that was suitable for CF production *via* melt-spinning using hardwood organosolv lignin obtained from aqueous acetic acid pulping. In the 2000s, Kadla *et al.* (2002) developed a process to prepare hardwood kraft lignin-based CF without chemical modification. They prepared hardwood kraft lignin-based fibers using 5% polyethylene oxide (PEO) as a plasticizer. Recently, Baker *et al.* (2012) developed a method for producing lignin-based CF from purified hardwood lignin. Because the thermal processability of technical hardwood lignin is better than that of technical softwood lignin, the majority of lignin-based CF studies have been performed on hardwood lignin.

Kubo *et al.* (1997) reported that softwood lignins, such as soda lignin, prepared by alkaline cooking are infusible. Infusible softwood lignin can be made fusible by removing 30% of the high molecular mass fraction (Kubo *et al*. 1998). Recently, Norberg *et al.* (2013) and Nordström *et al.* (2013) reported the continuous spinning of softwood kraft lignin by adding purified hardwood kraft lignin as a softening agent.

In 2015, we reported a simple softwood lignin modification method using a dried black liquor powder as a starting material. Spray-dried black liquor powder was directly treated with PEG under alkaline conditions (alkaline PEG treatment) (Yoon *et al*. 2015). The alkaline PEG-treated lignin prepared from black liquor powder exhibited its thermal melting property to be a CF precursor. The present study aimed to clarify the reaction of softwood lignin in the alkaline PEG treatment by model experiments using purified and acid-soluble lignin.

EXPERIMENTAL

Materials

Black liquor powder

Black liquor was obtained from Japanese cedar (*Cryptomeria japonica*) wood chips *via* soda-anthraquinone (AQ) cooking. The soda-AQ conditions were as follows: active alkaline charge of 19.5% of wood, AQ charge of 0.1% of wood, cooking time of 2 h, and cooking temperature of 170 °C. Black liquor was dried to a powder using a spray dryer system (Powdering Japan PJMSD-10SY, Japan) operating at a chamber temperature of 90 °C and an inlet air temperature of 180 °C. The dried black liquor powder was then removed from the spray dryer system and kept in a vacuum oven over phosphorus pentoxide for 24 h prior to use (Yoon *et al.* 2015).

Purified lignin (acid-insoluble lignin)

Purified lignin (acid-insoluble lignin) was isolated from black liquor powder. The black liquor powder was dissolved in distilled water until it comprised 40% of the solution's content. The pH of this solution was then adjusted to 2 with 20% sulfuric acid to precipitate the acid-insoluble part. The solution was then centrifuged to recover the precipitate, and the precipitate was washed with water. The centrifuging and washing procedures were repeated eight times. The precipitate was then vacuum-dried for 24 h and used as purified lignin (acid-insoluble lignin).

Acid-soluble lignin fraction

The acid-soluble lignin fraction was extracted from the filtrate of the precipitation solution of the purified lignin preparation. The pH of the filtrate was adjusted to 7 with sodium hydroxide. Water in the filtrate was removed using a rotary evaporator. The remaining material was dried in a vacuum oven for 24 h. After stirring for three days, the dried material was extracted with 1,4-dioxane. The insoluble material in the solution was filtered out, and the dioxane in the filtrate was removed using a rotary evaporator. The remaining material was dried in a vacuum oven for 24 h. The dried material was extracted with chloroform using a shaking apparatus; the chloroform layer was then separated using a separating funnel. Chloroform in the chloroform layer was removed using a rotary evaporator. The remaining material was dried in a vacuum oven for 24 h and used as the acid-soluble lignin fraction.

Methods

Alkaline PEG treatment of black liquor powder

Black liquor powder was directly modified using PEG under alkaline conditions (termed as alkaline PEG treatment) following the method used in our previous study (Yoon *et al.* 2015). The black liquor powder (30 g) was dissolved in PEG 1000 (150 g). The mixture was transferred to a separable flask and heated to 160 °C at atmospheric pressure in an oil bath. After the reaction, the mixture was slowly poured into 500 mL of distilled water and the solution was acidified to pH 2.0 with 3 M HCl to produce a precipitate. The precipitate was filtered and dried in a vacuum oven.

Alkaline PEG treatment of the purified lignin

A model experiment was performed to clarify the reaction of lignin during the alkaline PEG treatment of black liquor powder. The black liquor powder consisted of sodium hydroxide (7.3%), sodium carbonate (66.7%), and lignin (18.0%) (Yoon *et al.* 2015). The purified lignin was used as a model compound. The purified lignin (20 g) was mixed with sodium hydroxide (5 g) and sodium carbonate (50 g). The mixture was dissolved in 375 g of various average molecular weights of PEG (200, 300, 400, 600, 1000, 1500, and 2000), ethylene glycol (EG), or diethylene glycol (DEG). The solution was transferred into a separable flask (500 mL) with mechanical stirring and heated to 160 °C at atmospheric pressure in an oil bath. After the reaction, the reactant was slowly poured into 500 mL of distilled water and the solution was acidified to pH 2.0 with 3 M hydrochloric acid to produce a precipitate. The precipitate was filtered, and the solids were dried in a vacuum oven.

Evaluation of lignin content

The lignin content of the alkaline PEG-treated lignin was measured using the UV method (Dence 1992; Takahashi *et al.* 2014). Since the composition of the alkaline PEG-treated lignin consists of two components, only one of which (the lignin) absorbs in the UV spectral region, the lignin content measured by the UV method will reflect the amount of lignin in alkaline PEG treated sample. A sample was dissolved in 1,4-dioxane/0.2 M sodium hydroxide (NaOH; v/v = 1/1). The pH of the sample solution was adjusted to 5.0 with acetic acid. UV absorption at 280 nm was determined using a UV spectrophotometer (Shimadzu UV-1800, Japan). The lignin content was calculated from the absorption coefficient of lignin (UV lignin content). The absorption coefficient of the lignin was determined by the following process. The total lignin content of the purified lignin was determined using the Klason lignin method (TAPPI T222 om-02 2006), and the acid-soluble lignin derived from the Klason method was determined using the TAPPI useful method UM 250 um-83 (1991). The absorption coefficient of soda lignin at 280 nm was determined based on the relationship between the concentration based on the total lignin content and UV absorbance of the purified lignin at 280 nm, which was 26.1 $L \bullet g^{-1} \bullet cm^{-1}$.

Thermal melting characteristics

The thermal melting characteristics of the alkaline PEG-treated lignin were evaluated using a softening point system (Mettler Toledo DP 70 Dropping point system, Switzerland). The alkaline PEG-treated lignin powder (200 mg) was poured into a cylinder loaded with a ball of mass 4 g. The thermal melting test was performed by increasing the temperature from 100 to 200 °C at a rate of 2 °C/min. The flow length of the melted sample was monitored by the system.

Thermomechanical analysis (TMA)

TMA was performed using a TMA Q400 (TA Instruments, USA) at temperatures from 20 to 320 °C at a compression loading of 0.05 N under a N_2 stream at 50 mL/min. The values of T_g and T_s were estimated as the first and second transition points in the TMA curves, respectively.

Nuclear magnetic resonance (NMR) analysis

The chemical structures of lignin derivatives were estimated using NMR analysis. Alkaline PEG-treated lignin (200 mg) was dissolved using 600 μL of deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent. The concentration of the lignin solution was 20 to 30 wt.%. The ^{13}C-NMR spectrum of the lignin solution was recorded using a JEOL-500 MHz NMR spectrometer (JEOL, Japan) operating at 125.65 MHz with proton noise decoupling. The spectrum was registered at 28 °C.

RESULTS AND DISCUSSION

Effect of PEG Molecular Weight

The amount of PEG introduced into lignin during treatment was evaluated by determining the UV lignin content of the sample. Figure 1 shows the lignin content of the alkaline PEG-treated lignins using various PEG molecular weights prepared from purified lignin. The lignin content decreased with increasing PEG molecular weight. The decrease in lignin content indicated that increased amounts of PEG were being introduced into the purified lignin.

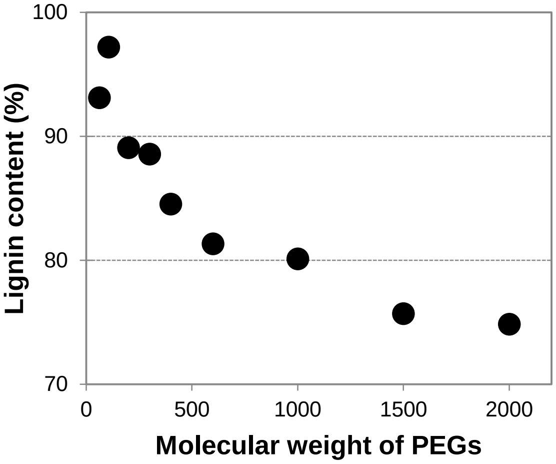

Fig. 1. Effect of PEG molecular weight on the lignin content of alkaline PEG-treated lignin prepared from purified lignin

Thermal Melting Characteristics of Alkaline PEG-treated Lignin

Figure 2 demonstrates the thermal melting behavior of the alkaline PEG-treated lignin prepared from purified lignin (A) and black liquor powder (B) and the softening point that was determined with increasing temperature. As shown in Fig. 2, the alkaline PEG-treated lignin gradually melted with heating.

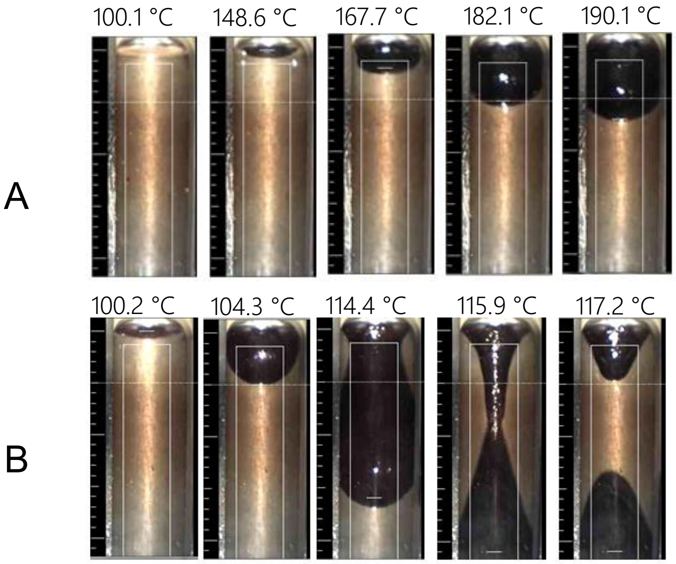

Fig. 2. Thermal softening behavior of alkaline PEG-treated lignin prepared from (A) purified lignin and (B) black liquor powder with increasing temperature to determine softening point

Figure 3(B) shows the melting length of the alkaline PEG-treated lignin prepared from black liquor powder, with the temperature increasing at a rate of 2 °C/min. The alkaline PEG-treated lignin prepared from black liquor powder started melting at 102.2 °C, and the length reached 5 mm at 105.3 °C. At 119.2 ºC, the sample dropped to the bottom of the test cylinder. The thermal melting speed of the alkaline PEG-treated lignin prepared from purified lignin was slower than that of the lignin prepared from black liquor powder. Figure 3(A) shows the melting length of the alkaline PEG-treated lignin prepared from the purified lignin, with the temperature increasing at a rate of 2 °C/min. The thermal melting of the alkaline PEG-treated lignin prepared from the purified lignin started at 151.3 °C. The melting length of the lignin sample steadily increased as the temperature increased, reaching 5 mm at 179.2 °C. The thermal melting characteristics of the alkaline PEG-treated lignin prepared from various molecular weight PEGs (*i.e.*, 200, 300, 400, 600, 1000, 1500, and 2000), EG, and DEG were checked and are shown in Table 1. The melting characteristics of these alkaline PEG-treated lignin types were evaluated by flow length in the softening point system. The "+" in Table 1 indicates that the melting length of the sample was more than 5 mm, whereas the "–" indicates that the sample did not melt or that the melting length was less than 5 mm.

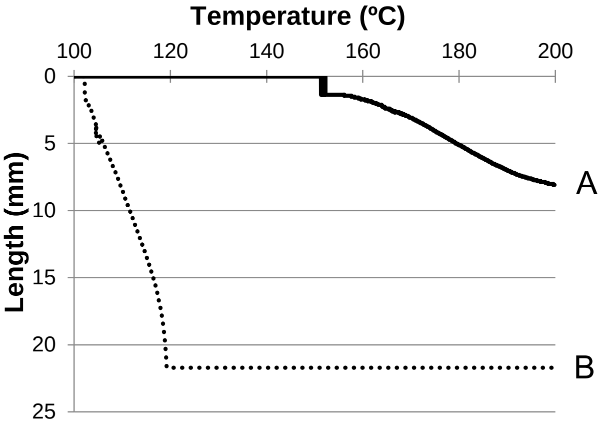

Fig. 3. Thermal softening length of alkaline PEG-treated lignin prepared from (A) purified lignin and (B) black liquor powder

Table 1. Thermal Melting Characteristics of Alkaline PEG-treated Lignin Prepared from Black Liquor Powder and Purified Lignin

	EG	DEG	Molecular Weight of PEGs					Non-treated
			200	400	600	1000	2000	
Black liquor powder	+	+	+	+	+	+	+	−
Purified lignin	−	−	−	−	−	+	+	−

Figure 4 shows the TMA curves of various lignin samples. These alkaline PEG-treated lignin types were prepared in the PEG 1000 series (Figs. 4(b) and (c)). Thermal properties such as T_g and T_s were determined using TMA (Kubo *et al.* 1996). As shown in Fig. 4(a), the TMA curve of the purified lignin (a) showed a decrease in dimension change starting at approximately 140 °C. This decrease continued until the temperature reached 220.4 °C, and was followed by a marked increase. During the dimension change-increasing step, the sample swelled and formed a foaming, rigid solid with thermo-setting. This result indicates that these samples were difficult to melt under heat. Because the purified lignin did not exhibit thermal melting characteristics (Table 1), its TMA curve can be regarded as a typical TMA plot of lignin samples that do not show thermal melting.

As shown in Fig. 4(b), the TMA curve of the alkaline PEG-treated lignin prepared from black liquor powder (b) was quite different from that of purified lignin (a). The TMA curve (b) showed T_g at 157.4 °C, and the dimension change decreased rapidly to approximately 190 °C. After this rapid decrease, the decreasing ratio slowed. The TMA curve (b) suggested that the alkaline PEG-treated lignin prepared from black liquor powder exhibited a thermal melting property (Kubo *et al.* 1996).

As shown in Fig. 4(c), the TMA curve of the alkaline PEG-treated lignin prepared from purified lignin showed T_g at 145.4 °C (Fig. 4(c)). The decrease in dimensional change continued until 184.3 °C, followed by a marked increase. This type of TMA curve (c) is similar to that of purified lignin (a) and does not show thermal melting on the softening point analysis system. This suggests that the alkaline PEG-treated lignin prepared from purified lignin did not show appropriate thermal melting performance during TMA analysis. However, the alkaline PEG-treated lignin prepared from purified lignin exhibited a thermal melting property in the softening point analysis system (Table 1). Because the dimensional change of the alkaline PEG-treated lignin prepared from purified lignin dropped at a temperature approximately 30 °C lower than that of purified lignin, the lignin showed more than 5 mm of flow on the softening point analysis system (Fig. 3(a)).

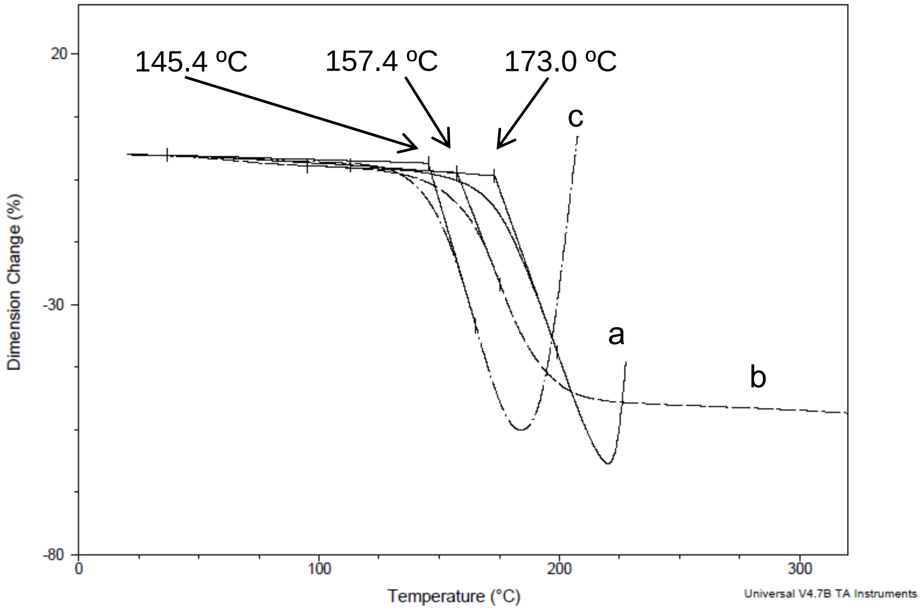

Fig. 4. Thermal mechanical analysis of (a) purified lignin; (b) alkaline PEG-treated lignin prepared from black liquor powder; and (c) alkaline PEG-treated lignin prepared from purified lignin

Chemical Structure of Alkaline PEG-treated Lignin

The alkaline PEG-treated lignin was analyzed using ^{13}C-NMR to clarify the bonded position of the PEG to the lignin. Figure 5 shows the ^{13}C-NMR spectra of the purified lignin (A), the alkaline PEG-treated lignin prepared from the purified lignin in PEG 1000 (B), PEG 400 (C), and PEG 200 (D), and the alkaline PEG-treated lignin prepared from black liquor powder in PEG 400 (E). Signal assignment was reported in our previous study (Yoon *et al.* 2015). The signal at 55.6 ppm was assigned to the carbon atoms of the methoxy groups of lignin. The strong signal (b) at 69.8 ppm was primarily assigned to the methylene carbons of the repeating unit of a PEG polymer. The signals at 72.3 ppm (a) and 60.2 ppm (d) were assigned to the methylene carbons of the alcohol end-groups of PEG. These three signals (a, b, and d) could be detected even if unreacted PEG remained in the sample. In addition to these three signals, a small signal (c) at 66.3 ppm was assigned to the methylene carbons bonded to alpha (α-) carbon on the lignin side-chain *via* an ether linkage (Kishimoto *et al.* 2004). These data strongly suggest that PEG was grafted to the lignin with an ether bond at the α-carbon of lignin. As shown in Fig. 5(E), the alkaline PEG-treated lignin prepared from black liquor powder showed the signal (c). However, this signal was not detected in the spectra of the alkaline PEG-treated lignin prepared from purified lignin (Fig. 5(B–D)). These data suggest that there was no linkage between lignin and PEG on the alkaline PEG-treated lignin prepared from purified lignin. This suggested that the data shown in Fig. 1 of increasing amount of introduced PEG with increasing molecular weight of PEG might due to the unreacted PEGs in the sample. Generally, a higher molecular weight of PEG will result in stronger interaction between PEG and the other polymeric materials (Pillin *et al.* 2006). Removing of the unreacted higher molecular weight fraction of PEG would be difficult.

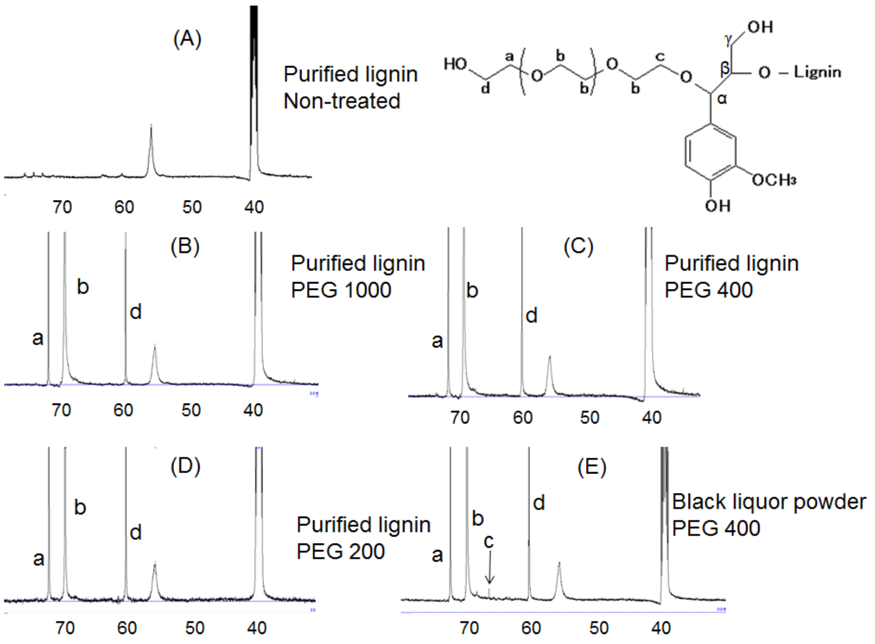

Fig. 5. ^{13}C-NMR spectra of (A) purified lignin, alkaline PEG-treated lignin prepared from (B) purified lignin with PEG 1000, (C) purified lignin with PEG 400, (D) purified lignin with PEG 200, and (E) black liquor powder with PEG 400

Reaction of Acid-soluble Lignin

The alkaline PEG-treated lignin prepared from black liquor powder exhibited thermal melting properties. However, the alkaline PEG-treated lignin prepared from purified lignin showed weak thermal melting during softening point analysis and did not show appropriate thermal melting performance during TMA analysis. Black liquor powder includes a considerable amount of lignin and consists of acid-insoluble lignin (62.16%) and acid-soluble lignin (37.84%), as shown in Fig. 6. As the lignin in black liquor powder includes both acid-insoluble lignin (purified lignin) and acid-soluble lignin, alkaline PEG treatment was performed using the acid-soluble lignin as a model compound.

Figure 7 shows the ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from the acid-soluble lignin fraction. This alkaline PEG-treated lignin was prepared in the PEG 1000 series. The signal at 55.4 ppm was assigned to the carbon atoms of lignin methoxy groups. The strong signal at 69.8 ppm (Fig. 7(b)) was assigned to the methylene carbons of the repeating unit of the PEG polymer. The signals at 72.4 ppm (Fig. 7(a)) and 60.3 ppm (Fig. 7(d)) were assigned to the methylene carbons of the alcohol end-groups of PEG. In addition, a strong signal at 66.4 ppm (Fig. 7(c)) was detected. The signal was assigned to methylene carbons bonded to the α-carbon on the lignin side chain *via* an ether linkage (Kishimoto *et al.* 2004). This spectrum strongly suggests that PEG was introduced to acid-soluble lignin at its α-carbon position. In the spectrum of the alkaline PEG-treated lignin prepared from black liquor powder (Fig. 5(E)), the small signal (c) might be caused by the reaction of the acid-soluble lignin in the black liquor powder. The alkaline PEG-treated lignin prepared from black liquor powder exhibited good thermal melting properties. However, the alkaline PEG-treated lignin prepared from purified lignin exhibited weak thermal melting properties and did not exhibit appropriate thermal melting performance during TMA analysis. The acid-soluble lignin in black liquor powder could provide thermal melting characteristics to the alkaline PEG-treated lignin prepared from black liquor powder. The data shown in Fig. 7 suggest that the acid-soluble lignin reacted with PEG to produce PEG-lignin derivatives. These derivatives may work as a plasticizer to induce the thermal melting of alkaline PEG-treated lignin prepared from black liquor powder.

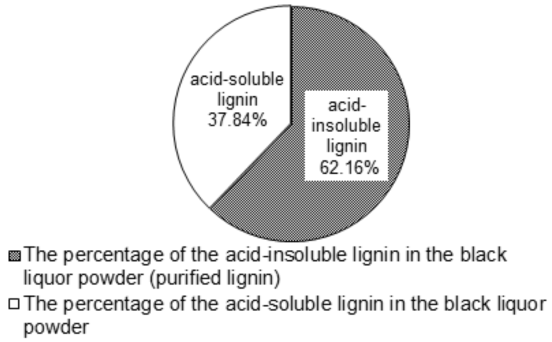

Fig. 6. Percentage of acid-soluble and acid-insoluble lignin in black liquor powder

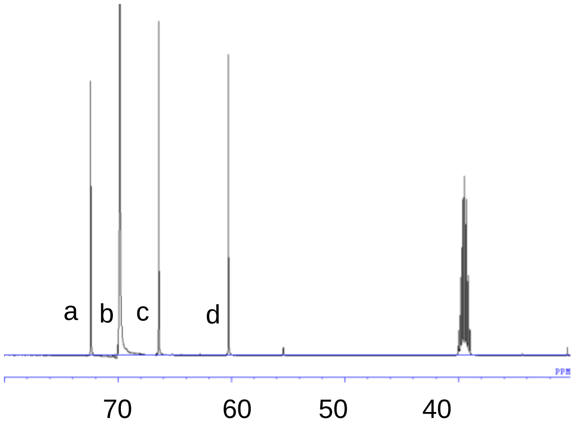

Fig. 7. ^{13}C-NMR spectrum of alkaline PEG-treated lignin prepared from the acid-soluble lignin fraction

CONCLUSIONS

1. Alkaline PEG-treated lignin prepared from black liquor powder exhibited good thermal melting properties; on the other hand, that prepared from purified lignin exhibited weak thermal melting during softening point analysis and did not exhibit appropriate thermal melting during TMA analysis.

2. The lignin in black liquor powder includes both acid-insoluble lignin (purified lignin) and acid-soluble lignin. The NMR data of the alkaline PEG-treated lignin prepared from purified lignin suggest that there was no linkage between lignin and PEG in the

samples. On the other hand, the NMR data of samples prepared from the acid-soluble lignin fraction suggest that PEG was grafted onto the lignin, thus producing PEG-lignin derivatives. PEG-lignin derivatives may work as a plasticizer to induce the thermal melting of alkaline PEG-treated lignin prepared from black liquor powder.

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