Thermal Melting of Lignin Derivatives Prepared from Dried Black Liquor Powder of Softwood Soda-AQ Cooking and Polyethylene Glycol

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Softwood lignin prepared by soda-anthraquinone (AQ) cooking does not have thermal melting characteristics. To improve the properties of softwood soda-AQ lignin, we have invented a new method of lignin modification using dried black liquor powder by a spray dryer system and polyethylene glycol (PEG). In this process, black liquor powder was directly treated with PEG under alkaline conditions to produce PEG-modified lignin (alkaline PEG treatment). Dried black liquor powder prepared by a spray dryer was dissolved into PEG and heated at either 120 or 160 °C at atmospheric pressure. The modified lignin (alkaline PEG-treated lignin) was precipitated with acid and recovered by filtration. The alkaline PEG-treated lignin showed adequate thermal melting characteristics. The treatment temperature and the molecular weights of PEG considerably affected the thermal properties of the alkaline PEG-treated lignin. There was an addition reaction of the PEG to the lignin hydroxyl group at the alpha- (α-) carbon. However, in the acid precipitation step, if the mixture was allowed to set unfiltered for a long time, the PEG bonded with the lignin was hydrolyzed, which yielded the original soda-AQ lignin and PEG polymer.

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

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INTRODUCTION

Technical lignins are divided into two categories (El Mansouri and Salvadó 2006). The first category includes sulfur-containing commercial lignins, such as kraft lignin and lignosulfonate. The second grouping is the non-sulfur lignins obtained from other pulping processes, such as soda, organosolv, steam explosion, and acid hydrolysis. During pulp manufacture, the lignin in black liquor is combusted to generate energy and recover chemicals. It has been reported that only about 2% of the byproduct lignin produced from industrial pulp manufacturing is utilized for purposes other than energy production. Approximately 1,000,000 tons/year of lignosulfonate originating from sulfite pulping, and less than 100,000 tons/year of kraft lignin produced from kraft pulping were utilized commercially (Gargulak and Lebo 2000; Gosselink *et al.* 2004). Technical lignins 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). The existing markets for technical lignins (predominantly lignosulfonates) are confined to low-value products or limited to very narrow market segments (Gosselink *et al.* 2004; Doherty *et al.* 2011). To develop additional applications for technical lignins, it is important to develop modification methods to enhance lignin properties for high-end value-added products.

One of the most important applications of lignin-based high value-added products is carbon fibers (CFs) (Kubo and Kadla 2004; 2005; Fernandes *et al.* 2006). Generally, commercial CFs, such as pitch-based CFs, are produced by a thermal melt spinning method in order to provide precursor fibers. To prepare lignin-based fibers following the industrial melt spinning process, the lignin should melt while being heated and should not be degraded by the heat. Since extensive cross-linking and strong intramolecular interactions of polymeric lignins constrain their utilization in solid material systems (Li *et al.* 1997), hardwood lignins are more easily processed than softwood lignins (Kadla and Kubo 2004). In the 2000s, Kadla *et al.* (2002) developed a process to derive kraft lignin-based CFs from hardwood without chemical modification. They prepared CFs by using hardwood kraft lignin with 5% polyethylene oxide (PEO) as a plasticizer. Polymer blending is a useful technique to improve the physical properties of technical lignins. In polymer blending systems, lignin generally increases the modulus and cold crystallization temperature, but it decreases the melt temperature (Doherty *et al.* 2011). Recently, Baker *et al.* (2012) developed kraft lignin-based CFs by using an organic solvent purification system applied to hardwood kraft lignins.

It is reported that softwood lignins, such as soda lignin, prepared from alkaline cooking are infusible (Kubo *et al.* 1997; 1998). To operate a softwood lignin-based CF production following the industrial melt spinning method, the lignin should have certain thermal melting characteristics. To obtain the desired thermal melting characteristics, the softwood lignin needs chemical modification or blending techniques. Norberg *et al.* (2013) and Nordström *et al.* (2013) reported the continuous spinning of softwood kraft lignin by adding a purified hardwood kraft lignin as a softening agent.

To change the thermal characteristics of softwood soda lignin, we successfully employed a new lignin modification method which used dried black liquor powder and polyethylene glycol (PEG). Black liquor powder was directly modified using PEG under alkaline conditions (termed as alkaline PEG treatment). This paper presents the alkaline PEG treatment and the chemical and thermal characteristics of the derivatized lignin.

EXPERIMENTAL

Materials

Black liquor was obtained from the bioethanol pilot plant at the Forestry and Forest Product Research Institute (FFPRI; Japan). The bioethanol pilot plant conducts soda-anthraquinone (AQ) cooking of Japanese cedar (*Cryptomeria japonica*), which generates black liquor as a byproduct. The soda-AQ conditions are as follows: active alkaline charge of 19.5% on wood; AQ charge of 0.1% on wood; cooking time of 2 h; and cooking temperature of 170 ºC. The solid content of the black liquor was 28.8%. The black liquor was dried to a powder by 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 (P_2O_5) for 24 h prior to use.

Methods

Chemical analysis of the dried black liquor powder

Dried black liquor powder (10 g) was slowly dissolved in 50 mL of distilled water. The solution was titrated by 1 M hydrochloric acid (HCl) to determine the amount of sodium hydroxide and sodium carbonate (Table 1).

Table 1. Composition of Black Liquor Powder

Composition of black liquor powder		
NaOH %	Na_2CO_3 %	Lignin %
7.3	66.7	18.0

Alkaline PEG treatment

The dried black liquor powder was dissolved in PEG solutions of various average molecular weights (200, 400, 600, 1000, and 2000), ethylene glycol (EG), or diethylene glycol (DEG). The mixture was transferred into a separable flask and heated to either 120 or 160 °C at atmospheric pressure for 2 h 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 by 3 M HCl to produce a precipitate. The precipitate was filtered and the solids dried in a vacuum oven over P_2O_5.

Evaluation of lignin content

The lignin content of the alkaline PEG-treated lignin was measured using the UV method (Lin and Dence 1992), which involved the following steps. 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 pH 5.0 with acetic acid. The UV absorption at 280 nm was measured by a UV spectrophotometer (Shimadzu UV-1800; Japan). The UV lignin content was calculated from the absorption coefficient of lignin of 30.3 $g \bullet L^{-1} \bullet cm^{-1}$ at 280 nm (Takahashi *et al.* 2014).

Thermal melting characteristics

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

Nuclear magnetic resonance (NMR) analysis

The chemical structure of the lignin derivatives was estimated by NMR analysis. Alkaline PEG-treated lignin (200 mg) was dissolved in 600 μL of deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent. The concentration of 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 (Japan) operating at 125.65 MHz with proton noise decoupling. The spectrum was registered at 28 °C.

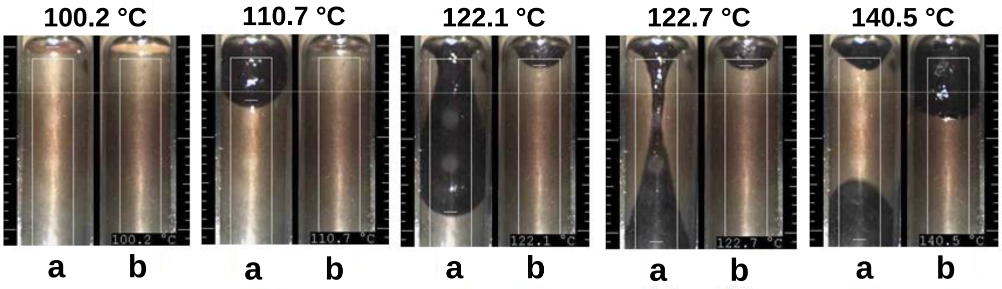

Fig. 1. Thermal softening behavior of the alkaline PEG-treated lignin with elevating temperature to determine softening point. (a) PEG 2000 treated and (b) PEG 1000 treated

Table 2. Thermal Melting Characteristics of the Alkaline PEG-treated Lignins

	Molecular weight of PEGs				
Alkaline PEG-treated lignin	200	400	600	1000	2000
Treated at 120 ºC	-	-	-	+	+
Treated at 160 ºC	+	+	+	+	ND

+ the melting length of sample was greater than 5 mm
- did not melt or the melting length was less than 5 mm
ND not determined

RESULTS AND DISCUSSION

Thermal Melting Characteristics of the Alkaline PEG-treated Lignin

Figure 1 demonstrates the thermal melting behavior of the alkaline PEG-treated lignins (PEG 1000 and PEG 2000 treatments) prepared at 120 ºC. As shown in Fig. 1, the alkaline PEG-treated lignin gradually melted with heating. Figure 2a shows the melting length of the alkaline PEG-treated lignins (PEG 1000 and PEG 2000 treatments), which were made at 120 °C, by increasing the temperature at a rate of 2 °C/min. The thermal melting of the alkaline PEG-treated lignin made with PEG 2000 started at 102.5 °C. The melting length of the lignin sample increased steadily as the temperature rose, reaching 5 mm at 107.8 °C. At 122.5 °C, the sample dropped to the bottom of the test cylinder. The thermal melting speed of the alkaline PEG-treated lignin made from PEG 1000 was slower than that made from PEG 2000. The PEG 1000 lignin sample started melting at 116.2 °C, and the length reached 5 mm at 130.6 °C. At 167.6 °C, the sample dropped to the bottom of the test cylinder. The thermal melting characteristics of alkaline PEG lignin made from various molecular weight PEGs (*i.e.*, 200, 400, 600, 1000, and 2000) were checked and shown in Table 2. The melting characteristics of these derivatized lignins were evaluated by the flow length on the softening point system. The '+' in Table 2 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. In the alkaline PEG treatment at 120 °C, the samples for both PEG 1000 and PEG 2000 had desirable melting characteristics. However, derivatized lignins made with lower molecular weight PEG (*i.e.*, 600, 400, and 200) at 120 °C did not exhibit any of the desired melting characteristics. All derivatized lignin samples showed the desired melting characteristics when the PEG treatments were performed at 160 °C. The melting characteristics of the modified lignins were improved considerably by increasing the reaction temperature of alkaline PEG treatment. Figure 2b shows the melting lengths of the alkaline PEG-treated lignin made at 160 °C by using PEG 400 and PEG 1000. The thermal melting of alkaline PEG-treated lignin made with PEG 1000 started at 102.2 °C. The length reached 5 mm at 106.0 °C, and the sample dropped to the bottom of the test cylinder at 119.2 °C. When compared to the thermal melting temperature at which the length of the sample reached to 5 mm of PEG 1000-lignin treated at 120 °C and 160 °C, the latter was 48.4 degree less than the former. For the PEG 400 treatment, the thermal melting of the derivatized lignin started at 134.1 °C with the length reaching 5 mm at 144.5 °C (Fig. 2b). These data indicate that the higher PEG reaction temperature with the higher PEG molecular weight improved the thermal melting characteristics and physical properties of lignin.

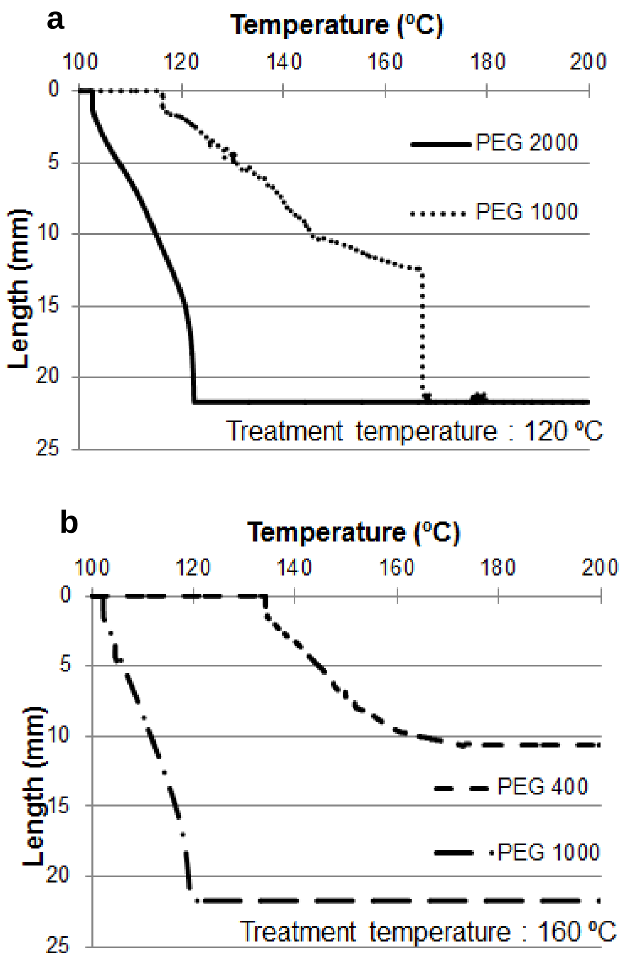

Fig. 2. Thermal softening length of the alkaline PEG-treated lignins. Treatment temperature: (a) 120 °C and (b) 160 °C

Effect of the Reaction Temperature of Alkaline PEG Treatment on Grafting PEG onto Lignin

The PEG content grafted into the soda lignin during the treatment was evaluated by determining the lignin content analysis of the samples. Figure 3 shows the lignin content of the alkaline PEG-treated lignins for various PEG molecular weights prepared at 120 °C (circle) and 160 °C (square). The lignin content of the alkaline PEG-treated lignin prepared at 120 °C decreased linearly with increasing molecular weight of PEG used in the reaction.

The decrease in the lignin content indicated the increased amounts PEG being grafted onto the soda lignin. The lignin content of derivatives prepared at 160 °C was much lower than that of derivatives prepared at 120 °C. This indicated that a higher amount of PEG was introduced into the lignin when the grafting reaction temperature was performed at 160 °C. It should be noted that the better thermal melting characteristics of the lignin treated at 160 °C was attributable to the introduction of higher amounts of PEG.

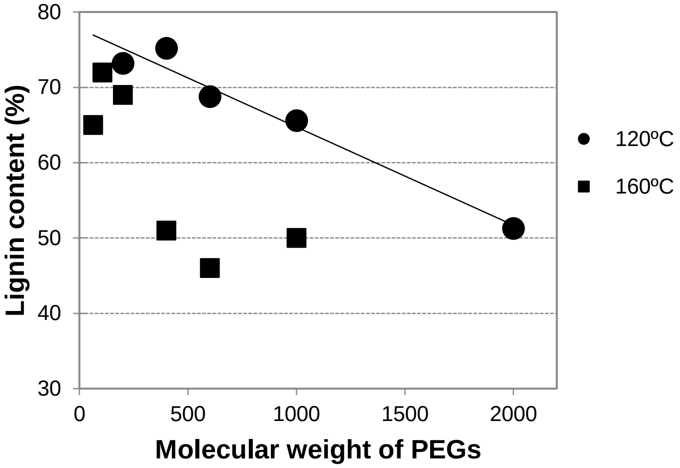

Fig. 3. Effect of the PEG molecular weight on the lignin content of the alkaline PEG-treated lignin at 120 °C (●) and 160 °C (■)

Reaction Mechanism of the Alkaline PEG Treatment of Lignin

In the alkaline PEG treatment, since excess amount of PEG exists around lignin molecules, possible reaction site on the lignin will be wholly reacted with PEG. If the number of possible reaction site did not increase in the reaction, then the relationship between the amount of introduced PEG and the size of PEG would be linear. Figure 3 showed a linear correlation between the lignin content in alkaline PEG-treated lignin prepared at 120 °C and the molecular weight of PEG. This suggested that the number of possible reaction sites on the lignin was limited and did not increase in the treatment at 120 °C. The alkaline PEG-treated lignin was analyzed using ^{13}C-NMR to clarify the bonded position of the PEG to the lignin. Figure 4 shows the ^{13}C-NMR spectrum of the alkaline PEG-treated lignin that was prepared using PEG 400 at 160 °C. The signal at 55.6 ppm was assigned to the carbon atoms of the methoxy groups of lignin. The strong signal at 69.8 ppm (Fig. 4b) was primarily assigned to the methylene carbons of the repeating unit of the PEG polymer. The signals at 72.3 ppm (Fig. 4a) and 60.2 ppm (Fig. 4d) were assigned to the methylene carbons of the alcoholic end groups of the 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 at 66.3 ppm (Fig. 4c) was assigned to methylene carbons bonded to the alpha carbon on the lignin side chain *via* an ether linkage (Kishimoto *et al.* 2004). This data strongly suggested that PEG is grafted to the lignin with an ether bond at the α-carbon of the lignin, as shown in Fig. 4.

Figure 5 shows a proposed reaction mechanism between the soda lignin and the PEG polymer under alkaline treatment conditions. In general, there are few alcoholic hydroxyl groups on the benzyl position (α-carbon position) of soda or kraft lignin (Adler and Hernestam 1955). However, the NMR spectrum in Fig. 4 shows the chemical structure of the lignin with the PEG bonded at its α-carbon position.

Under the alkaline condition, lignin containing free phenolic hydroxyl groups were deprotonated and released the hydroxyl groups at the α-carbon position to form the quinone methides. The terminal hydroxyl group in PEG should react with the quinone methides in the lignin at α-carbon position.

The higher amounts of PEG introduced onto the lignin at 160 °C suggested that the number of reaction sites in the soda lignin increased with increasing reaction temperatures. The vanillin yields from the alkaline nitrobenzene oxidation of soda-AQ lignin was 9% based on lignin content (Takahashi *et al.* 2014). This indicated that the soda-AQ lignin has possible reaction sites at α-carbon position. Thus, the alkaline PEG-treated lignin prepared at 160 °C had higher amounts of PEG than that prepared at 120 °C.

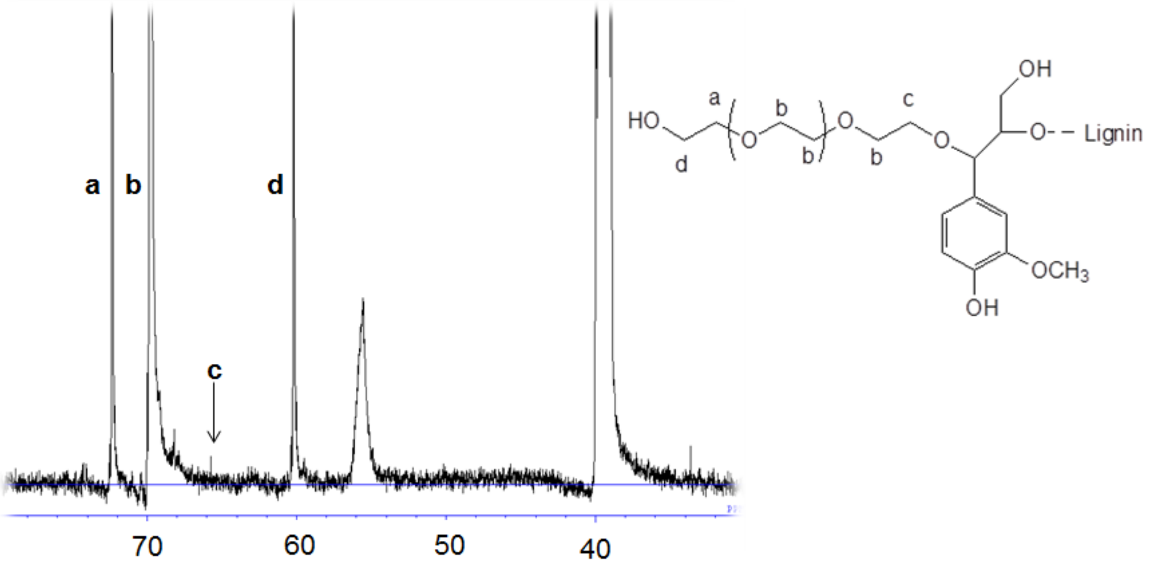

Fig. 4. ^{13}C-NMR spectrum of alkaline PEG-treated lignin

Stability of Alkaline PEG-Treated Lignin at Acidic Condition

After the alkaline PEG treatment, the mixture was acidified with 3 M HCl to precipitate the derivatized lignin. Figure 6 shows the effect of time between acidification and filtration on the lignin content of soda lignin derivatized with PEG 1000 at 120 °C. As shown in Fig. 6, the lignin content increased as the time between acidification and filtration increased.

When the mixture was filtered immediately after acid precipitation (0 min), the lignin content of the precipitate, that is the alkaline PEG-treated lignin, was 52.3%. When the mixture was left undisturbed for 240 min before filtration, the lignin content of the alkaline PEG-treated lignin increased to 66.1%. The data from Fig. 6 suggested that the precipitate should be separated within 30 min in order to preserve the grafted PEG content in the alkaline PEG-treated lignin. Under acidic aqueous conditions, the PEG bonded at lignin's α-carbon position would be hydrolyzed. At the acid precipitation step, when the acid solution was kept undisturbed for a long time prior to filtration, the lignin with the PEG bonded at its α-carbon position became hydrolyzed, as shown by the dotted lines in Fig. 5.

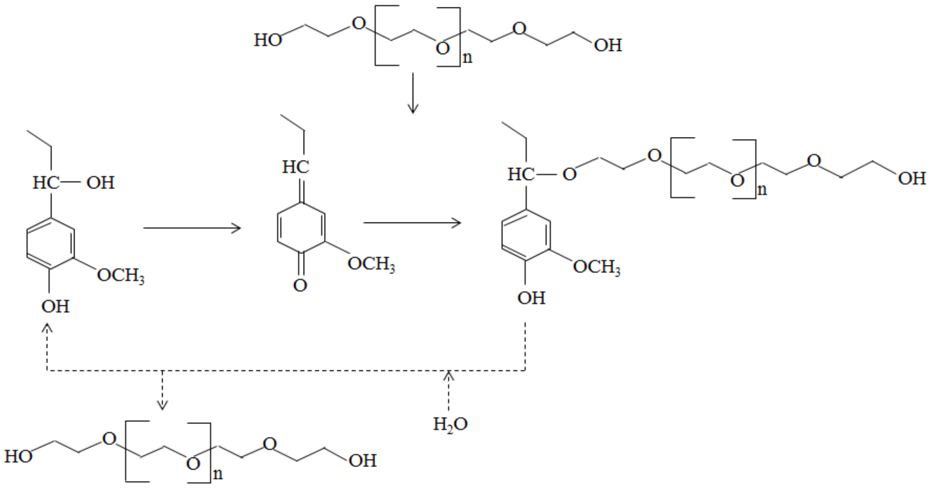

Fig. 5. A reaction mechanism between soda-AQ lignin and PEG in the alkaline PEG treatment

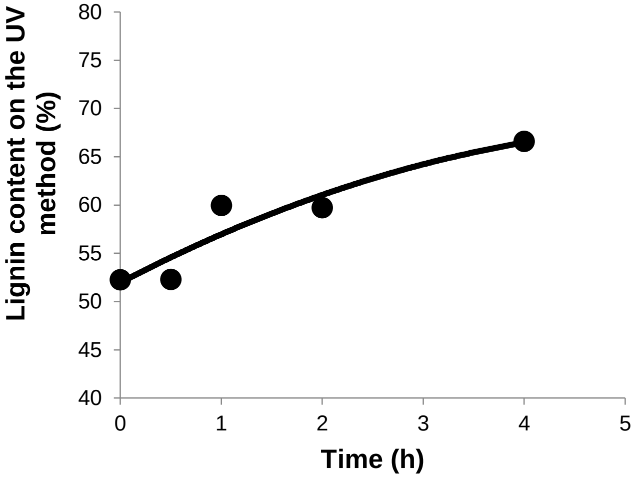

Fig. 6. Effect of the time between precipitation and filtration on the lignin content of the alkaline PEG-treated lignin (120 °C)

CONCLUSIONS

1. The alkaline PEG-treated lignin from a softwood soda-AQ black liquor powder showed thermal melting characteristics with heating.
2. At the 120 °C alkaline PEG treatment, the samples made from PEG 1000 and PEG 2000 showed thermal melting; however, the samples using lower PEG molecular weights (*i.e.*, 600, 400, and 200) did not exhibit significant thermal melting. On the other hand, for the 160 °C alkaline PEG treatment, all samples showed thermal melting.
3. The treatment temperature and molecular weight of PEG had considerable effects on the physical properties of the alkaline PEG-treated lignin. The better melting characteristics of the 160 °C-treated lignin could be due to the higher amount of PEG grafted onto the soda-AQ lignin.

4. The NMR data suggested that the PEG grafted to α-carbon of lignin *via* an ether linkage. Under acidic aqueous conditions, the lignin with grafted PEG was hydrolyzed, which yielded the original soda-AQ lignin and PEG polymer.

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