CHEMICAL THERMOSTABILIZATION FOR THE PREPARATION OF CARBON FIBERS FROM SOFTWOOD LIGNIN

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A thermally fusible softwood lignin was directly isolated by a solvolysis of cedar wood chips with a mixture of polyethylene glycol 400 (PEG 400) and sulfuric acid. Its fusibility was found to be due to a PEG moiety introduced into the lignin by the solvolysis. The lignin was easily formed into fibers by melt-spinning at temperatures ranging from 145 to 172 °C without any modification. The lignin fibers could be converted into infusible fibers as a precursor for carbon fibers (CFs) by conventional oxidative thermal stabilization processing in air or a stream of oxygen for 2 days. We found that the infusible fibers resulted from the partial cleavage of the PEG moiety from the lignin fibers after treatment with 6 M hydrochloric acid at 100 °C for 2 h. The infusible fibers were converted into CFs with a tensile strength of 450 MPa by carbonization at 1000 °C under a N_2 stream.

Keywords: Polyethylene glycol (PEG);Lignin; Chemical thermostabilization; Carbon fibers; Mechanical properties

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INTRODUCTION

Lignin, one of the major cell wall components in higher plants, is the second most abundant renewable bio-resource next to cellulose on Earth. A huge amount of technical lignins are produced as a by-product from pulp and paper-manufacturing processes. However, utilization of technical lignins are usually limited to some applications: a fuel source (Zimovets and Imarov 1996), a dispersant in dyestuff and cement (Dilling 1986; Ouyang *et al*. 2009), adhesives (Oiivares *et al*. 1988), and chemicals (from lignosulfonates) such as vanillin (Pearl 1967). A more valuable application, such as filler, has also been developed (Rozman *et al*. 2011). Preparation of Carbon Fibers (CFs) from technical lignins seems to be a promising process for producing high value-added materials. Furthermore, CFs could be easily converted to activated CFs as an excellent adsorbent.

Lignin-based CFs were first prepared successfully by the end of the 1960's, when an alkaline solution of commercial lignin mixed with polyvinyl alcohol was used (Otani *et al*. 1969). For several decades, various types of lignin, such as steam-exploded lignin (Sudo and Shimizu 1992; Sudo *et al*. 1993), organosolv lignin from atmospheric acetic acid pulping (Kubo *et al*. 1998; Uraki *et al*. 1995), commercial hardwood kraft lignin (Kadla *et al*. 2002), and Alcell lignin (Kadla *et al*. 2002; Ruiz-Rosas *et al*. 2010), have been applied to prepare lignin-based CFs via melt-spinning and electrospinning processes. In such melt-spinning processes, hardwood lignins were almost exclusively used as a raw material because of their thermal fusibility. On the other hand, in the case of softwood it was necessary to modify the lignin or to remove the high molecular mass fraction (Kubo *et al*. 1998) before the spinning process.

The difference in thermal behaviors between hardwood lignin and softwood lignin can be partly explained by the frequency of the presence of condensed structures, such as β-5 and 5-5 in softwood lignin. Hardwood lignin contains both guaiacyl and syringyl units in the range of 25 to 50% and 46 to 75%, respectively, whereas softwood lignin consists of more than 95% of guaiacyl units and less than 5% p-hydroxyphenyl units (Ek *et al*. 2009). Syringyl units have an extra methoxy group at the C5-position of guaiacyl units. Guaiacyl units, thereby, are likely to form condensed structures (C-C bond) at its C5-position. Softwood lignin, therefore, has β-5 and 5-5 types of interunitary linkages much more frequently than hardwood lignin, which would probably limit molecular rotation of softwood lignin at elevated temperature.

In the last century, a solvolysis process, using polyethylene glycol (PEG) on the presence of sulfuric acid as a catalyst, was developed as a liquefaction method of wood (Kurimoto *et al*. 1992 and 1999). In this century, the process was considered again as a candidate for use in a biorefinery for obtaining levulinic acid, which is a potential precursor for synthetic rubbers and plastics (Yamada *et al*. 2007), by minor modification of reaction conditions. As a by-product of the solvolysis, a lignin fraction could be recovered, and it was found to be chemically modified with PEG through ether bonds. We shall refer to this product as PEG-lignin. Besides, lignin grafting with an ethylene glycol (EG) chain was previously reported to be thermally fusible, because the EG moiety in the lignin not only inhibits the formation of intra- and/or intermolecular hydrogen bonding of lignin, but it also acts as an internal plasticizer of the lignin (Kubo *et al*. 2007). We found that this resultant lignin obtained by the solvolysis had high molecular mobility at the elevated temperature; in particular it was found to be thermally fusible.

We succeeded in the preparation of infusible fibers as precursors for CFs by the chemical cleavage of PEG moiety for a 2 h reaction. In this article, we report CFs preparation from PEG-lignin extraction; by this method, mainly fusible fiber can be converted into infusible fiber.

EXPERIMENTAL

Preparation of PEG-lignin

A preparation scheme of PEG-lignin is shown in Fig. 1. Sixty grams of air-dried cedar chips were placed in a round bottom flask together with 300 g of polyethylene glycol 400 (PEG 400) and 0.9 g of 95% aqueous sulfuric acid (0.3 wt% on PEG 400). The flask was immersed in an oil bath that was preheated at 160 ^{o}C for 240 min (the 1st cooking). The flask was then cooled to room temperature in an ice water bath, and then 1.2 L of 80% 1,4-dioxane aqueous solution was added to the reaction mixture. The resultant mixture was filtrated through filter paper (No.5C, Advantec) to separate filtrate and residue.

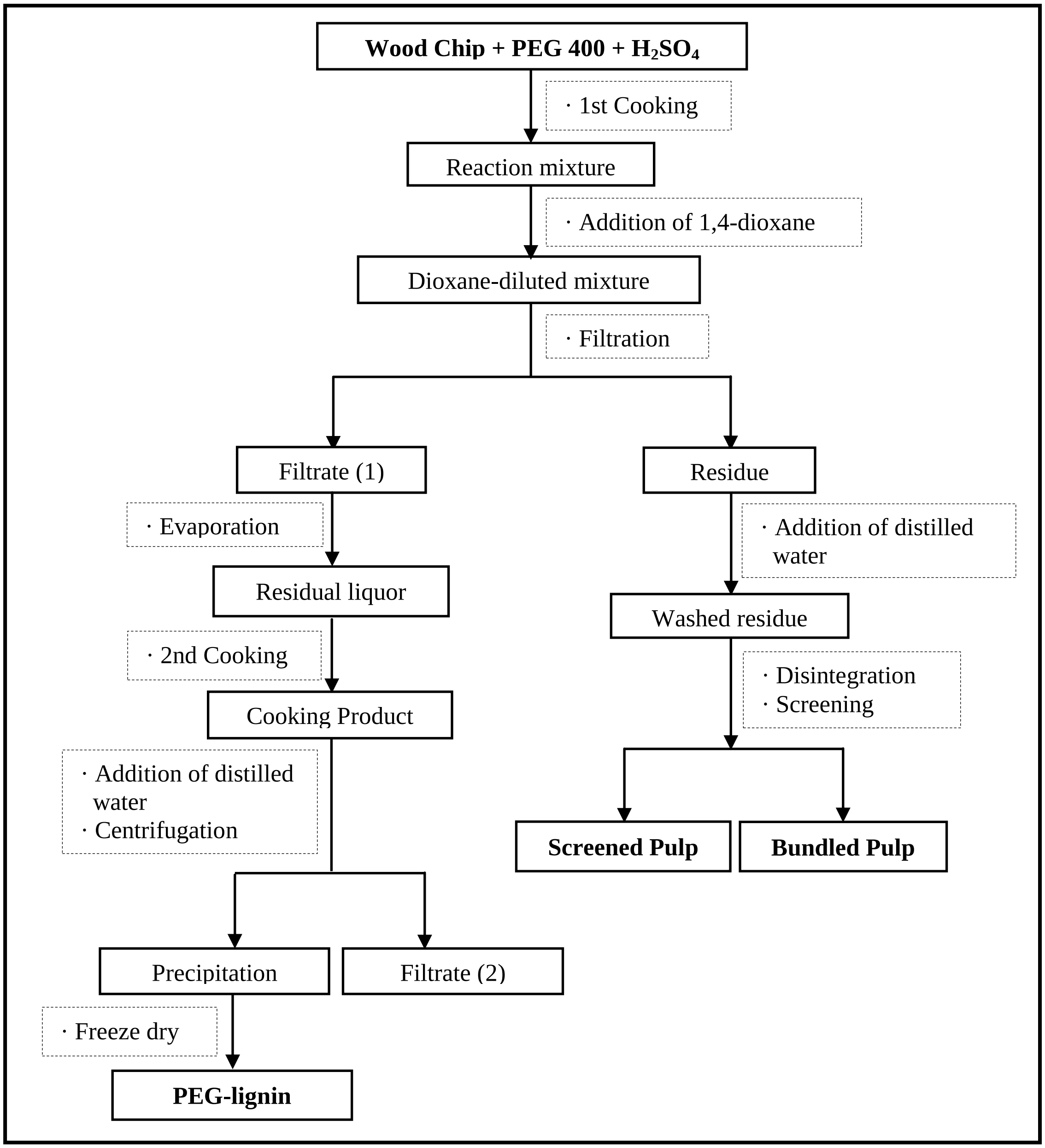

Fig. 1. Preparation scheme of PEG-lignin

The organic solvent (1,4-dioxane) in the filtrate was removed by evaporation under reduced pressure. The resulting residual liquor was transferred into a three-necked flask equipped with a mechanical stirrer and a thermocouple, and the flask was heated at 140 ^{o}C for 150 min as the 2nd cooking. After cooling of the flask, the solution was dropped into 4 L of distilled water with continuous stirring for 30 min. The precipitate was then collected by centrifugation at 11600 G for 15 min. Finally, PEG-lignin powder was obtained by freeze drying.

The insoluble part in the 1st cooking stage was washed three times with 1 L of distilled water, and then it was disintegrated for 10 min. The screened pulp was separated from bundled wood fiber (termed as not or reject) by screening with a 12-cut flat screen. Both weights of screened pulp and bundled fiber were measured after complete drying at 105 °C in an oven overnight.

Melt-Spinning

PEG-lignin was spun by using a laboratory spinning apparatus with a single hole nozzle (diameter: 0.8 mm), manufactured at Mechanical Workshop, Technical Division, Faculty of Science, Hokkaido University, at the nozzle temperature ranging from 145 to 172 °C and the winding rates of 45 to 67 m/min under a nitrogen pressure (Uraki *et al*. 1995).

Oxidative Thermostabilization under Air Atmosphere or a Stream of Oxygen (general thermostabilization)

The resultant PEG-lignin fibers were heated from room temperature to 250 °C at the heating rates of 0.1 to 0.5 °C/min, and then the final temperature of 250 °C was maintained for 1 h. This process was conducted under air atmosphere or a stream of oxygen at the flow rate of 0.15 L/min in an electronic muffle furnace (KDF S90/S90G, Denken Co. Ltd., Kyoto, Japan).

Cleavage of PEG Moiety in the Lignin for Preparing Infusible Fibers (chemical thermostabilization)

PEG-lignin fibers were immersed in aqueous hydrochloric acid solution with the concentration of 1 to 6 M at 100 °C for 2 to 6 h. After the chemical treatment, the resultant fibers were washed twice with distilled water, and then roughly dried in an oven at 105 °C for 2 h.

Carbonization

After both the thermostabilization processes, the infusible fibers were carbonized in the same electronic muffle furnace (used in oxidative thermal stabilization step) from room temperature to 1000 °C at a heating rate of 3 °C /min and then held at 1000 °C for 1 h under a N_2 stream at flow rate of 0.15 L/min to yield PEG-lignin based CFs.

Characterizations

Measurement of PEG content (Homma *et al*. 2008; Morgan 1964; Siggia *et al*. 1958)

Approximately 0.2 g of a sample and 5 mL of hydriodic acid were mixed in a branched eggplant flask and then heated at 145 °C for 90 min. All contents in the glass vessel were washed out with about 125 mL of 20% potassium iodide solution after cooling and then subjected to iodometric titration with 0.1 mol/L sodium thiosulfate solution. PEG content in each sample was measured at least twice. PEG content was calculated by following formula,

$$\mathrm{PEG(wt\%)} = [(V_s\text{-}V_b)/1000] \times 0.1 \times (44/2) \times (1/W_s) \qquad (1)$$

where V_s and V_b denote the titration volume of $Na_2S_2O_3$ for a sample and blank, respectively; W_s stands for the sample weight.

Thermomechanical analysis

Thermomechanical analysis (TMA) was performed on a TMA-4000S System (MAC Science System 010, MAC Science, Yokohama, Japan) at temperatures ranging from 30 to 300 ^{o}C under compression loading of 5 g under a N_2 stream at 0.15 L/min. The glass transition temperature (T_g) and thermal-flow starting temperature (T_f) were estimated as a first and a second transition point in TMA profiles (Kubo *et al*. 1996).

Images

Fiber morphology was observed on an optical microscope (Violet laser color 3D profile microscope VK-9500, Keyence Japan, Osaka, Japan) at magnification factors of 10 to 100, and a scanning electronic microscope (SEM; JSM-6301F [FE-SEM], JOEL Ltd., Tokyo, Japan) using gold-coated samples, at magnification factors of 2,000 to 8,000, and at an accelerating voltage of 5 kV, respectively.

Element analysis

Element analysis was measured with a MICRO CORDER JM 10 (MT 6) at the Equipment Management Center in the Creative Research Institution of Hokkaido University. Before measurement, PEG-lignin and other samples were dried at 60 ^{o}C and 80 ^{o}C, respectively, under vacuum overnight.

Mechanical properties

Diameters of a fiber were measured in at least five positions to obtain average values by using the optical microscope described above. Tensile strengths of fibers were measured on a testing apparatus reported previously (Uraki *et al*. 2010). The value was reported as the mean value ± standard deviation based on the measurement results of 40 fibers.

RESULTS AND DISCUSSION

Characterization of PEG-Lignin

PEG-lignin with the molecular mass of 3800 and M_w/M_n of 4.2 was isolated in a powder form from softwood (cedar) chip with PEG 400, as shown in Fig. 1. The yield of PEG-lignin was 50.4% on wood chip. However, its PEG content was 43.8%. Accordingly, the net lignin extracted from the wood chip was estimated to be 28.3%. The lignin content of cedar chip measured by the Klason method (Dence 1992) was 30.6%. Thus, the lignin in cedar chips was considered to be recovered almost quantitatively by this solvolysis process. On the other hand, the sum of the screened pulp yield (30.7 %) and the bundled pulp yield (15.7%) was 46.4%. Thereby, a total yield of lignin and polysaccharide components as the pulps was about 75%. The other components from polysaccharide components in wood might be converted to levulinic acid via 5-hydroxymethyl furfural as an intermediate (Yamada *et al*. 2007; Yamada and Ono 2001).

Glass transition temperature (T_g) and thermal-flow starting temperature (T_f) of the PEG-lignin were estimated by TMA, which has been reported to be a suitable analytical tool for thermal properties of powdered lignin preparations (Kubo *et al*. 1996). As shown in Fig. 2 (A), the TMA curve of PEG-lignin powder showed two transition points at 78.8 ^oC and 140.7 ^oC, which corresponded to the T_g and T_f, respectively. Thus, this PEG-lignin was completely fusible, and its transition temperatures were considerably lower than those of hardwood acetic acid lignin (T_g = 128 ^oC, T_f = 177 ^oC), as was first found as a thermally fusible isolated lignin (Uraki *et al*. 1995). This thermal fusibility of PEG-lignin would probably be caused by the introduced PEG moiety. The PEG moiety may act as an internal plasticizer, giving the lignin high thermal mobility (Kubo *et al*. 2007).

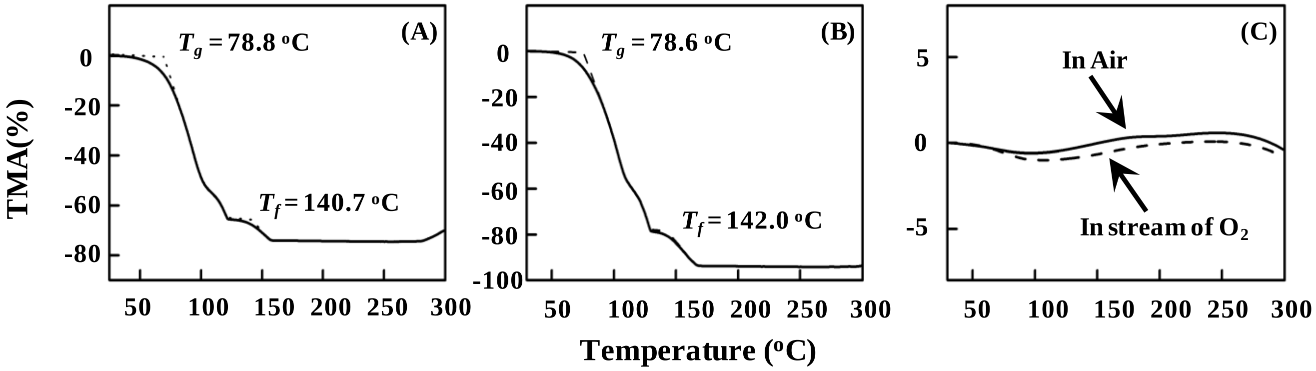

Fig. 2. Thermomechanical analysis (TMA) of PEG-lignin powder (A), PEG-lignin fibers (B), and oxidative thermostabilized PEG-lignin fibers in air and stream of oxygen with heating rate of 0.1 ^oC/min (C), respectively.

Preparation of PEG-Lignin Fibers

The thermally fusible PEG-lignin powder was directly subjected to melt-spinning without further modification. A continuous spinning was successfully carried out at nozzle temperatures ranging from 145 to 172 ^oC. Table 1 shows the relation between nozzle temperature and the winding rates and resultant fiber diameter. This table indicates that an elevated spinning temperature allows a high winding rate of fiber, owing to its lowered molten viscosity, and the higher winding rate, in turn, yields thinner fibers.

Table 1. Spinning Conditions and Tensile Strength of PEG-Lignin Fibers

Entry (^oC)	Spinning Temperature (m/min)	Winding Rate (μm)	Diameter (MPa)	Tensile Strength
1	145-148	45	38.2 ± 5.4	23.1 ± 11.1
2	155-159	47	34.0 ± 4.5	25.5 ± 10.5
3	168-172	67	22.9 ± 3.2	35.5 ± 17.6

Figure 3 (A) and (B) show the morphology of PEG-lignin fibers spun at around 170 ^oC. The fibers had a smooth surface, while several pores existed in the cross-section of a fiber. These pores may be caused by nitrogen gas, which was used for extrusion of

molten lignin under gas pressure. The obtained thinnest PEG fibers with a diameter of around 23 μm were subjected to subsequent processing. The PEG fibers with the smallest diameter showed the greatest tensile strength, as expected (Table 1) (Uraki *et al*. 1995; Kubo *et al*. 1998; Kadla *et al*. 2002; Tagawa and Miyata 1997), which was described as the measured tensile strength divided by cross-sectional area of a fiber.

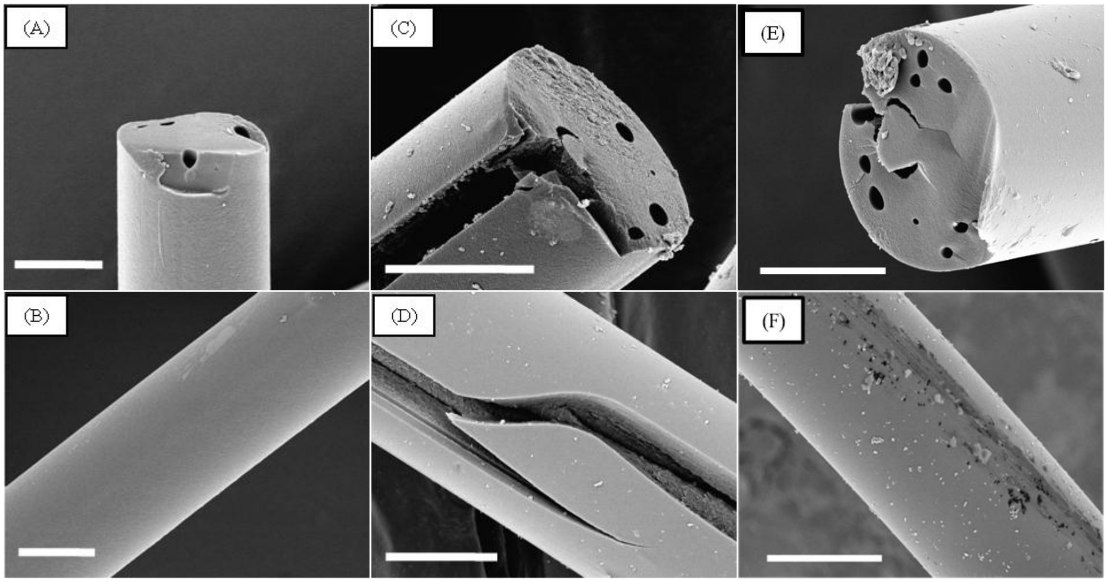

Fig. 3. SEM morphology of various types of fibers. (A) and (B): PEG-lignin fibers spun at 168-172 °C and at a winding rate of 67 m/min; (C) and (D): Chemically thermostabilized PEG-lignin fibers treated with 6 M HCl solution at 100 °C for 4 h; (E) and (F): PEG-lignin based CFs from chemically thermostabilized fibers treated with 6 M HCl solution at 100 °C for 4 h. (White bar =10 μm).

Oxidative Thermostabilization of PEG-Lignin Fibers under Air Atmosphere or a Stream of Oxygen (general thermostabilization)

So far, previous lignin fibers spun by melt-spinning, as well as polyacrylonitrile and pitch fibers as precursors for CFs have been thermostabilized in an oxidative atmosphere, such as air or oxygen, by heating up to around 250 °C to obtain thermally infusible fibers (Uraki *et al*. 1995; Kubo *et al*. 1998; Kadla *et al*. 2002; Morita *et al*. 1981; Lin 1991). In general, during the oxidative thermostabilization process for the lignin fibers, homolysis of β-O-4 ether bonds in lignin generates the free radicals (phenethyl radical and phenoxy radical) by heating at slow heating rate in air or oxygen, resulting in a series of elimination, rearrangement, and oxidative reactions, and then more cross-linkages among lignin molecules (Braun *et al*. 2005). As shown in Fig. 2 (B), PEG-lignin fibers were still fusible. Thereby, we also attempted to thermally stabilize the PEG-lignin fibers upon heating up to 250 °C at several heating rates under air atmosphere or a stream of oxygen.

Unexpectedly, all the oxidative thermostabilized fibers melted and adhered to each other even at the slowest heating rate of 0.1 °C/min (Fig. 4). Nevertheless, in Fig. 2 (C), the TMA profiles of the resultant fibers showed no transition points (T_g and T_f), suggesting the conversion to infusible ones. It is anticipated from these results that if the oxidative thermostabilization is performed at a much slower heating rate (under 0.1

^{o}C/min), infusible fibers without molten adhesion of each fiber might be obtained. However, this process is not viable because it takes a very long time (*i.e*. a couple of days) to get infusible fibers. Therefore, the general oxidative thermostabilization under air atmosphere or oxygen stream is considered to be unsuitable for PEG-lignin fibers, and another method better than oxidative thermostabilization should be explored and applied.

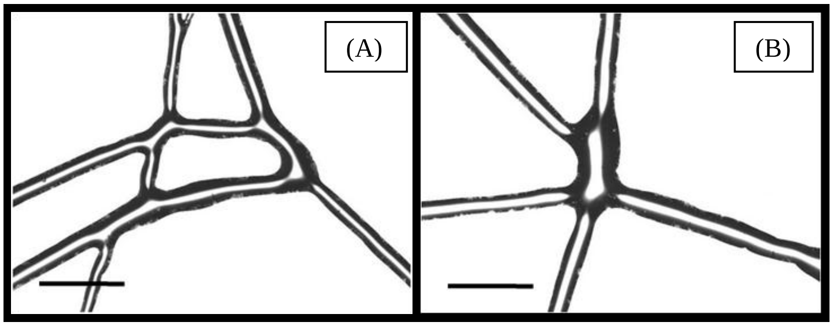

Fig. 4. Microscopic images of oxidative thermostabilized fibers treated under oxygen stream at a flow rate of 0.15 L/min (A) and air atmosphere (B) with the heating rates of 0.1 ^{o}C/min from room temperature to 250 ^{o}C; (bar =300 μm).

Cleavage of PEG Moiety from Lignin (chemical thermostabilization)

Since the thermal mobility and fusibility of PEG-lignin fibers were attributed to the introduction of PEG into the lignin, the conversion of them to an infusible form was expected by reduction of PEG content in the lignin. After several trials to cleave the PEG moiety from lignin, we found a facile method for the conversion; partial cleavage of PEG moiety was carried out by chemical reaction with concentrated HCl solution. When the PEG-lignin fibers were immersed in 1 M HCl aqueous solution at 100 ^{o}C for 2 to 6 h, the fibers were still fusible, as shown in Fig. 5. By increasing the HCl concentration to 3 M, the fibers showed only T_g, suggesting the conversion of them into an infusible form.

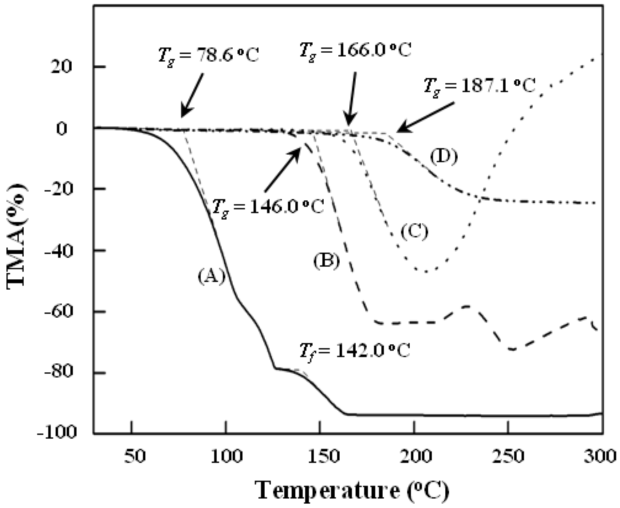

Fig. 5. TMA profiles for PEG-lignin fibers (A) and chemically thermostabilized PEG-lignin fibers treated with HCl solution at the concentrations of 1 M (B), 3 M (C) and 6 M (D) at 100 ^{o}C for 2 h, respectively

However, the resultant fibers expanded over 200 °C, as well as softwood acetic acid lignin (Kubo *et al*. 1996). This phenomenon implies that thermal decomposition of the fibers occurred at that temperature, and that the fiber morphology was changed by heating. We found that the PEG-lignin fibers were converted into fusible ones by immersing in 6 M HCl aqueous solution for 6 h at 100 °C. Finally, the conversion was found to be completed by the 2 h immersion. Although the resultant fibers showed T_g, no expansion was observed at a higher temperature than T_g, as shown in Fig. 5. Thus the short-time thermostabilization for the PEG-lignin fibers was performed by the chemical treatment with 6 M HCl aqueous solution.

Figures 3 (C) and (D) show the morphology of chemically thermostabilized lignin fibers treated with 6 M HCl solution at 100 °C for 4 h. Splits on the fiber surface were observed. In addition, pores existing in the cross-section still remained. These defects would have appeared during the chemical thermostabilization process, wherein ether bonding between lignin and PEG was promoted by protonizing action of HCl, followed by the cleavage of the ether bonding, which resulted in a significantly more flabby structure occurring in the interior of lignin fibers. To confirm the cleavage of the PEG moiety, the PEG content was measured. The PEG content of chemically thermostabilized lignin fibers was decreased with prolonged reaction time (Fig. 6). Accordingly, the conversion of thermally infusibility was dependent on the degree of cleavage by PEG moiety from PEG-lignin fibers, but the treatment also led to defects.

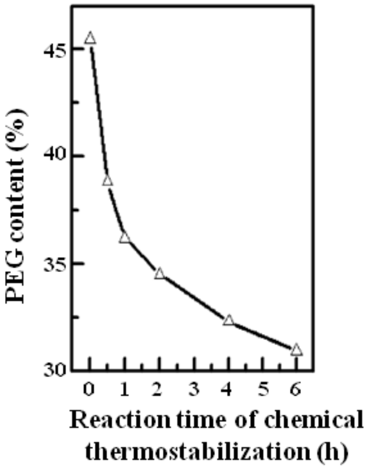

Fig. 6. Changes in PEG contents of PEG-lignin fibers with increasing time of chemical thermostabilization at 100 °C, using 6 M HCl solution

Carbonization of Chemically Thermostabilized PEG-lignin Fibers

The resulting infusible lignin fibers were subjected to carbonization at temperatures ranging from room temperature to 1000 °C and at a heating rate of 3 °C/min under a nitrogen stream. The CFs yield of 35.3% was calculated based on PEG-lignin powder, which was higher than that of CFs prepared from acetic acid hardwood and softwood lignin (Uraki *et al*. 1995; Kubo *et al.* 1998) but lower than that of hardwood kraft lignin based CFs (Kadla *et al*. 2002). CFs with a carbon content of 91.9 % were obtained (Table

2). The morphology of CFs derived from the chemically thermostabilized lignin fibers treated with 6 M HCl solution at 100 °C for 4 h was observed with SEM [Fig. 3 (E) and (F)]. There are still big size pores existing in the cross-section, as well as lots of small size pores occurring on the surface of CFs.

Table 2. Elemental Analysis of PEG-lignin, Corresponding CFs, & Activated CFs

Samples*	Content (%)**			
	C	H	O	N
PEG-lignin	65.0	6.43	28.6	0
CFs	91.9	0.96	7.12	0
ACF-30	93.7	0.98	5.35	0
ACF-60	95.0	0.97	4.06	0
ACF-90	94.8	0.94	4.28	0

* CFs were prepared from chemically thermostabilized fibers treated with 6 M HCl solution at 100 °C for 2 h; ACF-30, 60, and 90 denote that the CFs were activated with water steam at 900 °C for 30 min, 60 min, and 90 min, respectively;
** No ash was detected for CFs and ACF.

Mechanical properties of CFs, derived from chemically thermostabilized fibers treated by 6 M HCl solution at 100 °C for 2 h, 4 h, and 6 h, respectively, were measured as shown in Table 3. Only a slight difference was observed among them, indicating that the duration of chemical thermostabilization did not affect mechanical properties of CFs. Furthermore, the average tensile strength of CFs in this study was found to be approx-imately 450 MPa, which is comparable or even superior to those of previously reported CFs prepared from phenolated steam-exploded lignin (around 400 MPa) (Sudo *et al*. 1993), hardwood lignin (355 MPa) (Uraki *et al*. 1995), and softwood lignin (108 MPa) (Kubo *et al.* 1998) from acetic acid pulping, as well as hardwood kraft lignin commer-cially available (422 MPa) (Kadla *et al*. 2002).

Table 3. Mechanical Properties of PEG-Lignin-based CFs

Samples*	Diameter (μm)	Tensile strength (MPa)	Tensile modules (GPa)	Elongation (%)
CF-2	11.5 ± 2.0	441 ± 100	23.0 ± 5.4	2.0 ± 0.5
CF-4	10.4 ± 1.3	457 ± 188	26.2 ± 13.3	2.1 ± 1.1
CF-6	10.2 ± 1.2	451 ± 156	24.7 ± 7.2	1.6 ± 0.8

* CF-2, -4 and -6 denotes the CFs from chemically thermostabilized fibers treated with 6 M HCl solution at 100 °C for 2 h, 4 h and 6 h, respectively.

However, tensile strength of the PEG-lignin based CFs was not necessarily stronger than previous lignin-based CFs, taking the relation between fiber diameter and fiber tensile strength into consideration. It was reported that the tensile strength of fiber is dependent on their size (Tagawa and Miyata 1997). The diameters of the PEG-lignin-based CFs (10 to 12 μm in Table 3) in this study were about one fourth of those of CFs prepared from the hardwood kraft lignin (46 μm), as previously reported (Kadla *et al*. 2002). It is not surprising that tensile strength of the PEG-lignin-based CFs is calculated to be quite lower than that of the hardwood kraft lignin-based CFs, when they are compared at the same diameter. This drawback in relatively low tensile strength of the

PEG-lignin-based CFs can be attributed to their porous, flabby structure. Additional evidence is given from the fact that relatively higher elongation was observed (1.6 to 2.1% in Table 3) compared with other types of lignin-based CFs (*e.g.* 1.1 % for CFs from hardwood kraft lignin) (Kadla *et al*. 2002). Furthermore, the PEG-lignin based CFs with porous and flabby structure in this study were further activated with a stream of water steam at 900 ^{o}C for 30, 60, and 90 min. The corresponding specific surface areas of activated CFs measured by nitrogen adsorption were 2038 m^2/g, 2442 m^2/g, and 3060 m^2/g, respectively, indicating that the PEG-lignin based CFs can be a promising precursor of activated CFs.

CONCLUSIONS

Thermally fusible PEG-lignin was prepared from softwood (cedar) chips by solvolysis, using PEG 400 and sulfuric acid, and was found to show good spinnability to form PEG-lignin fibers with a diameter of 23 μm without further modification. The PEG-lignin fibers were converted into infusible fibers by chemical thermostabilization with concentrated HCl aqueous solution for a very short period (2 h), as compared with that by general oxidative thermostabilization (2 days). The infusible fibers were, in turn, transformed into CFs. The resultant CFs showed comparable or slightly superior tensile strength to those of CFs previously produced from other types of lignin preparation. Hence, it can be concluded that the PEG-lignin based CFs are applicable to raw material for activated CFs rather than general purpose use in terms of mechanical properties (Prauchner *et al*. 2005).

REFERENCES CITED

Braun, J. L., Holtman, K. M., and Kadla, J. F. (2005). “Lignin-based CF: Oxidative thermostabilization of kraft lignin,” *Carbon* 43(2), 385-394.

Dence, C. W. (1992). “*Methods in Lignin Chemistry*,” S. Y. Lin and C. W. Dence (eds.), Springer-Verlag, Berlin.

Dilling, P. (1986). “Low electrolyte sodium lignosulphonate(s) are used as dispersants in dyestuffs and additives in printing gels,” *US Patent* 4590262-A.

Ek, M., Gellerstedt, G., and Henriksson, G. (2009). “Lignin,” In: *Pulp and Paper Chemistry and Technology, Volume 1: Wood Chemistry and Biotechnology*, Henriksson, G. (ed.), Walter de Gruyter GmbH & Co. KG., 121-124.

Homma, H., Kubo, S., Yamada, T., Matsushita, Y., and Uraki Y. (2008). “Preparation and characterization of amphiphilic lignin derivatives as surfactants,” *J. Wood Chemistry and Technology* 28(4), 270-282.

Kadla, J. F., Kubo, S., Venditti, R. A., Gilbert, R. D., Compere, A. L., and Griffith, W. (2002). “Lignin-based carbon fiber for composite fiber applications,” *Carbon* 40(15), 2913-2920.

Kubo, S., Uraki, Y., and Sano, Y. (1996). “Thermomechanical analysis of isolated lignins,” *Holzforschung* 50(2), 144-150.

Kubo, S., Uraki, Y., and Sano, Y. (1998). "Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping," *Carbon* 36(7-8), 1119-1124.

Kubo, S., Yamada, T., Hashida, K., and Ono, H. (2007). "Grafting of ethylene glycol chains in lignin during the solvolysis for biomass conversion using ethylene carbonate/ethylene glycol system," *Chemistry Letters* 36(4), 502-503.

Kurimoto, Y., Doi, S., and Tamura, Y. (1999). "Species effects on wood-liquefaction in polyhydric alcohols," *Holzforschung* 53(6), 617-622.

Kurimoto, Y., Shirakawa, K., Yoshioka, M., and Shiraishi N. (1992). "Liquefaction of untreated wood with polyhydric alcohols and its application to polyurethane forms," *FRI (New Zealand) Bull* 176, 163-172.

Lin, S. S. (1991). "Oxidative stabilization in production of pitch based carbon-fiber," *Sampe J.* 27(1), 9-14.

Morgan, PW. (1964). "Determination of ethers and esters of ethylene glycol: A modified alkoxyl analysis," *Industrial and Engineering Chemistry, Analytical Edition* 18, 500-504.

Morita, K., Miyachi, H., and Hiramatsu, T. (1981). "Stabilization of acrylic fibers by sulfur atoms mechanism of stabilization," *Carbon* 19(1), 11-18.

Oiivares, M., Guzmfin, J. A., Natho, A., and Saavedra, A. (1988). "Kraft lignin utilization in adhesives," *Wood Science and Technology* 22, 157-165.

Otani, S., Fukuoka, Y., Igarashi, B., and Sasaki, K. (1969). "Method for producing carbonized lignin fiber," *US Patent* 3461082.

Ouyang, X. P., Ke, L. X., Qiu, X. Q., Guo, Y. X., and Pang, Y. X. (2009). "Sulfonation of alkali lignin and its potential use in dispersant for cement," *J. Dispersion Science and Technology* 30(1), 1-6.

Pearl, I. A. (1967). "*The Chemistry of Lignin*," New York: Marcel Dekker, 298-307.

Prauchner, M. J., Pasa, V. M. D., Otani, S., and Otani, C. (2005). "Biopitch-based general purpose carbon fibers: Processing and properties," *Carbon* 43(3), 591-597.

Rozman, H. D., Koay, E. L., and Tay, G. S. (2011). "Preliminary study on the utilization of lignin as filler in ultra-violet (UV) curable system," *J. Applied Polymer Science* 120(5), 2527-2533.

Ruiz-Rosas, R., Bedia, J., Lallave, M., Loscertales, I. G., Barrero, A., Rodríguez-Mirasol, J., and Cordero, T. (2010). "The production of submicron diameter carbon fibers by the electrospinning of lignin," *Carbon* 48(3), 696-705.

Siggia, S., Starke, A. C., and Garis, J. J. (1958). "Determination of oxyalkylene groups: In glycols and glycol and polyglycol ethers and esters," *Analytical Chemistry* 30(1), 115-116.

Sudo, K., and Shimizu K. (1992). "A new carbon fiber from lignin," *J. Applied Polymer Science* 44(1), 127-134.

Sudo, K., Shimizu, K., Nakashima, N., and Yokoyama, A. (1993). "A new modification method of exploded lignin for the preparation of a carbon fiber precursor," *J. Applied Polymer Science* 48(8), 1485-1491.

Tagawa, T., and Miyata T. (1997). "Size effect on tensile strength of carbon fibers," *Materials Science and Engineering A: Structural Materials Properties Microstructure and Processing* 238(2), 336-342.

Uraki, Y., Kubo, S., Nigo, N., Sano, Y., and Sasaya, T. (1995). "Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping," *Holzforschung* 49(4), 343-350.

Uraki, Y., Matsumoto, C., Hirai, T., Tamai, Y., Enoki, M., Yabu, H., *et al*. (2010). "Mechanical effect of acetic acid lignin adsorption on honeycomb-patterned cellulosic films," *J. Wood Chemistry and Technology* 30(4), 348-359.

Yamada, T., Aratani, M., and Kubo S. (2007). "Chemical analysis of the product in acid-catalyzed solvolysis of cellulose using polyethylene glycol and ethylene carbonate," *J. Wood Science* 53(6), 487-493.

Yamada, T, and Ono H. (2001). "Characterization of the products resulting from ethylene glycol liquefaction of cellulose," *J. Wood Science* 47(6), 458-464.

Zimovets, I. P., and Imarov, A. K. (1996). "Production and utilization of generator gas from lignin," *Chemistry and Technology of Fuels and Oils* 32(6), 288-289.

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