



HOKKAIDO UNIVERSITY

Title	Preparation and characterization of softwood lignin-based carbon fibers
Author(s)	Jian, Lin
Degree Grantor	北海道大学
Degree Name	博士(農学)
Dissertation Number	甲第11108号
Issue Date	2013-09-25
DOI	https://doi.org/10.14943/doctoral.k11108
Doc URL	https://hdl.handle.net/2115/56450
Type	doctoral thesis
File Information	Jian_Lin.pdf



**Preparation and characterization of softwood
lignin-based carbon fibers**

Jian Lin

Doctoral Thesis

Supervisor: Professor Yasumitsu URAKI

Laboratory of Forest Chemistry
Division of Environmental Resources
Graduate School of Agriculture
Hokkaido University

Sapporo 2013

TABLE OF CONTENTS

ABBREVIATIONS	1
CHAPTER 1 General Introduction	3
1.1 Lignin.....	3
1.2 CF.....	6
1.3 Lignin-based CFs.....	10
1.4 Research objectives.....	16
CHAPTER 2 Carbon fibers and activated carbon fibers from softwood lignin	18
2.1 Introduction.....	18
2.2 Experimental.....	19
2.2.1 Materials.....	19
2.2.2 Preparation of PEG-lignin.....	19
2.2.3 Melt-spinning.....	21
2.2.4 Oxidative thermostabilization.....	21
2.2.5 Chemical thermostabilization.....	21
2.2.6 Carbonization.....	21
2.2.7 Steam activation.....	22
2.2.8 Characterizations.....	22
2.3 Results and discussion.....	28
2.3.1 Characterization of PEG-lignin.....	28
2.3.2 Preparation of PEG-lignin fibers.....	29
2.3.3 Oxidative thermostabilization.....	31
2.3.4 Chemical thermostabilization.....	33
2.3.5 Carbonization of chemically thermostabilized fibers.....	37
2.3.6 Activation of PEG-lignin based CFs.....	40
2.4 Summary.....	44
CHAPTER 3 Improvement of mechanical properties of softwood lignin-based carbon fibers	45
3.1 Introduction.....	45
3.2 Experimental.....	46
3.2.1 Materials.....	46
3.2.2 Preparation of CFs.....	46
3.2.3 Characterizations.....	47
3.3 Results and discussion.....	47
3.3.1 Blends of PEG-lignin powder and HMTA.....	48
3.3.2 Chemical curing of PEG-fibers with HMTA.....	49
3.3.3 Chemical curing of PEG-fibers with HMTA and HCl aqueous solution.....	52
3.3.4 Oxidative thermostabilization of chemically cured fibers.....	56

3.3.5 Carbonization.....	57
3.4 Summary.....	61
CHAPTER 4 General discussion.....	62
REFERENCES.....	66
ACKNOWLEDGEMENTS.....	76

Abbreviations

ACF/ACFs	Activated carbon fiber/Activated carbon fibers
AL	Alcell lignin
BET	Brunauer, Emmett, and Teller
CF/CFs	Carbon fiber/Carbon fibers
EG	Ethylene glycol
FTIR	Fourier-transform infrared
GPC	Gel permeation chromatography
HMTA	Hexamethylenetetramine
H-SEL	Hydrogenated steam-exploded lignin
HWAL	Hardwood acetic acid lignin
HWKL	Hardwood kraft lignin
HWKL-OP	Hardwood kraft lignin treated by organic purification
$\bar{M}_n$	Number average molecular mass
$\bar{M}_w$	Weight average molecular mass
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PEO	Poly(ethylene oxide)
PEO 100K	Poly(ethylene oxide) with molecular mass of 100,000
PEO 300K	Poly(ethylene oxide) with molecular mass of 300,000
PEO 600K	Poly(ethylene oxide) with molecular mass of 600,000
PET	Polyethylene terephthalate
PL	Pyrolytic lignin
PP	Poly(propylene)

P-SEL	Phenolated steam-exploded lignin
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
SWAL	Softwood acetic acid lignin
SWKL	Softwood kraft lignin
THF	Tetrahydrofuran
TMA	Thermomechanical analysis
T_g	Glass transition temperature
T_f	Thermal-flow starting temperature
UV	Ultraviolet
XRD	X-ray diffraction

CHAPTER 1

General Introduction

1.1 Lignin

Lignin, one of the major cell wall components in higher plants, is the second most abundant biopolymer next to cellulose on the earth (Gosselink *et al.* 2004). In contrast to the cellulose that is a linear polymer and consisted of single monomer and linkage, lignin possesses non-uniform and branched structure, and comprised of several monomers termed as monolignols, coniferyl alcohol, sinapyl alcohol and ρ -coumaryl alcohol, as shown in Fig. 1-2. The monolignols are linked through different types of ether bonds (C—O—C) and carbon-carbon bonds (C—C). Thereby, it has very complex structure (Fig. 1-1) (Ek *et al.* 2009). In addition, hardwood and softwood lignins consist of different monolignol ratios (Table 1-1). Softwood lignin consists of coniferyl alcohol exclusively and only traces of ρ -coumaryl alcohol, while hardwood lignin consists of both coniferyl and sinapyl alcohol with sinapyl/coniferyl ratio from approximately 1 to 3 in addition to trace ρ -coumaryl alcohol.

These monolignols remarkably affect the difference in chemical structure between softwood lignin and hardwood lignin. Softwood lignin is called as guaiacyl lignin, and the guaiacyl unit does not have methoxyl group at C-5 position of aromatic ring. Thereby, guaiacyl lignin is rich in condensed structures (C-C bond), such as β -5 and 5-5 interunitary linkages, involved by C5-carbon in the unit. On the other hand, hardwood lignin is also termed as syringyl-guaiacyl lignin or simply syringyl lignin, and the syringyl units have an extra methoxy group at the C5-position of guaiacyl units. Accordingly, softwood lignin has β -5

and 5-5 types of interunitary linkages in much more frequency than hardwood lignin. The condensed structures would probably limit molecular rotation of softwood lignin at elevated temperature, and show the different thermal behaviors upon the heat-treatment.

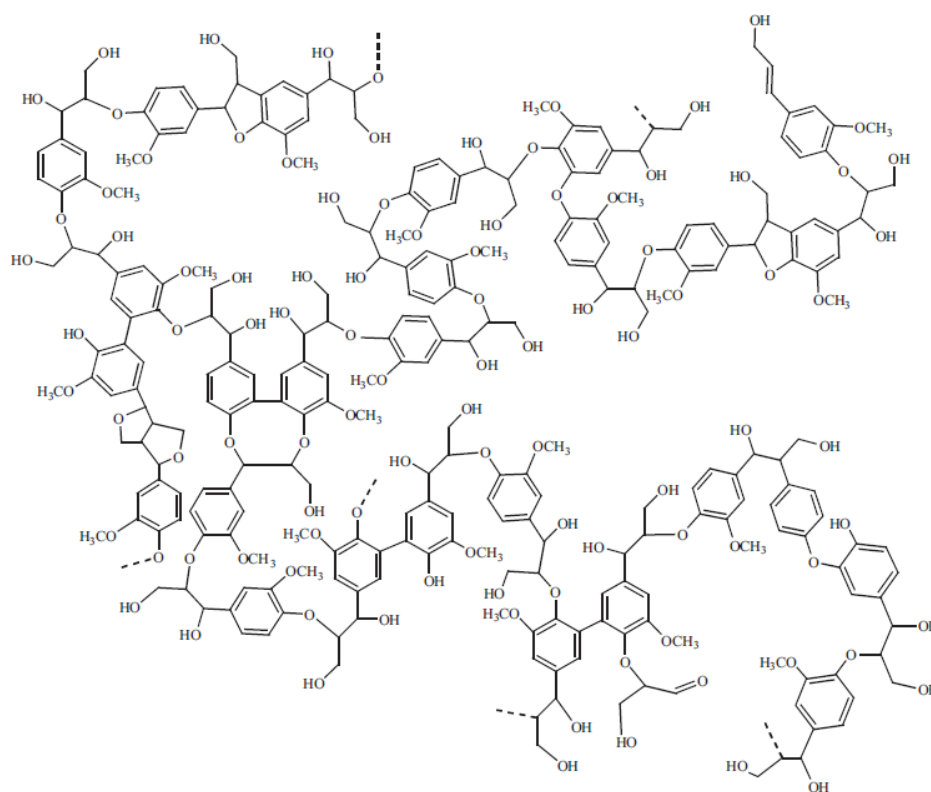


Fig. 1-1. A proposed structure of softwood lignin. The hardwood lignin differs mainly in the content of methoxy groups (—OCH_3). (Ek *et al.* 2009)

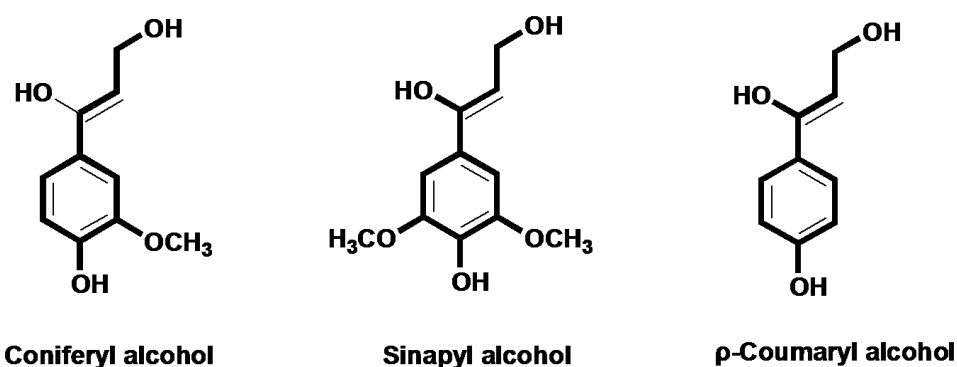


Fig. 1-2. The three main monolignols as precursors of lignin macromolecule. (Ek *et al.* 2009)

Table 1-1. Composition of monolignols in different types of higher plants.

Plant	p-Coumaryl	Coniferyl	Sinapyl
	alcohol	alcohol	alcohol
	(%)	(%)	(%)
Softwood	< 5	>95	None
Hardwood	0-8	25-50	46-75
Grass	5-33	33-80	20-54

(Ek *et al.* 2009)

Annually, a huge amount (around 5×10^6 metric tons) of technical lignins, kraft lignin and lignosulfonate, are produced as a by-product from pulp and paper-manufacturing processes (Mai *et al.* 2000). However, most of them are burnt as a fuel source for energy recovery in pulp and paper mills (Zimovets and Imarov 1996; Mohan *et al.* 2006). However, the technical lignins are utilized as value-added materials in limited aspects: a dispersant in dyestuff and cement (Dilling 1986; Ouyang *et al.* 2009), adhesives (Oiihares *et al.* 1988), and chemicals such as vanillin from lignosulfonates (Pearl 1967). With more and more attention paid to renewable bio-resources, many researchers have been more interested in lignin as raw materials for producing high value-added materials, such as filler (Rozman *et al.* 2011; Shen and Zhong 2007), lignin-based nanofiber (Dallmeyer *et al.* 2010; Gao *et al.* 2012; Ago *et al.* 2012a, 2012b), and lignin-based carbon fiber (CF) (Otani *et al.* 1969; Sudo and Shimizu 1992; Sudo *et al.* 1993; Uraki *et al.* 1995; Kubo *et al.* 1998; Kadla *et al.* 2002; Lin *et al.* 2012; Norberg *et al.* 2013). Especially, the production of CF from technical lignins seems to be a promising utilization due to the fact that a larger amount of CF is used as an alternative light-weight material to iron and metallic materials because

of excellent mechanical properties. Furthermore, CF can further be easily converted to activated carbon fiber (ACF) for an environmental purification.

1.2 CF

CF is a fiber containing carbon content of more than 92 wt%. It can be used in a variety of industries including aerospace, civil engineering, automotive and sport equipments due to its high performance such as high tensile strength, high tensile module, low density, good thermal and electrical conductivities, and excellent creep resistance (Foston *et al.* 2013; Huang 2009). In current CF markets, polyacrylonitrile (PAN)-based CF is predominantly produced as CF with high strength, and pitch-based CF is produced next to PAN-CF as CF with high modulus. As well, a very small amount of CF was also made from rayon. In addition, many other alternatives, such as silk (Majibur *et al.* 2007), chitosan (Bengisu *et al.* 2002), polyacetylene fibers (Sliva and Selley 1975), lignin (Otani *et al.* 1969; Sudo and Shimizu 1992; Sudo *et al.* 1993; Uraki *et al.* 1995; Kubo *et al.* 1998; Kadla *et al.* 2002; Norberg *et al.* 2013), poly(vinylacetylene) (Mavinkurve *et al.* 1995), polyethylene (Horikiri *et al.* 1978), and polybutadiene (Nagasaka *et al.* 1978), have also been investigated as precursors for CF production.

In general, the principal processing steps for preparing CFs typically consist of (1) spinning, (2) thermostabilization, (3) carbonization and sometimes graphitization (4). Of course, the detail CF production process depends on the raw materials.

- (1) Different spinning methods, such as wet-spinning, dry-spinning, and melt-spinning, are used to prepare the precursor fibers, based on the

properties of the raw materials. Wet- and dry-spinning methods require a certain solvent for the dissolution of raw material, which increases the processing cost. In the wet-spinning, spinning solution flows out through the spinneret, and the solute is coagulated by poor solvent in a coagulation bath to form the fiber. In the dry-spinning, the solute is solidified by the evaporation of solvent with hot air or inert gas to yield the precursor fiber. However, melt-spinning does not need any solvent for dissolution, but requires thermally fusible raw material, such as pitch and modified lignin. The fusible material undergoes melt-flow upon heating at the temperature of over thermal-flow starting temperature (T_f), and then is extruded into fiber followed by solidification at a lower temperature than T_f . Thus, melt-spinning is the most inexpensive process.

(2) Thermostabilization of the precursory fiber is generally performed to achieve the conversion of fusible fiber into infusible one, of which morphology is not changed by further heating. In the general thermostabilization, the precursor fibers spun by the above processes are oxidatively stabilized by heat treatment at the temperature of 200~400 °C under an oxidizing atmosphere (air or oxygen). The formation of cross-linkages is brought about by the introduction of oxygen into fibers. In the case of PAN, this reaction mainly includes cyclization and dehydrogenation (Huang 2009; Frank *et al.* 2012). While the oxidative thermostabilization of pitch is conducted by accompanying the reactions such as oxidation, dehydrogenation, cyclization, elimination, condensation and cross-linking (Matsumoto and Mochida 1992; Yang and Simms 1993; Drbohlav and Stevenson 1995). Lignin has a complex structure and the

similar reactions with pitch occur during oxidative thermostabilization. Cross-linkages between lignin molecules are formed by introduction of oxygen through a series of elimination, rearrangement, and oxidative reactions of free radicals derived from homolysis of β -O-4 ether bonds in lignin (Braun *et al.* 2005).

The competition of chemical reactions on the surface and deeper layer of fiber with a large diameter often results in the formation of skin-core structure, which prevents oxygen from diffusing into the inside of fiber. Thus, the homogeneous stabilization of fibers cannot be often achieved. To prohibit the appearance of skin-core structure, prolonging holding time and lowering heating rate as well as decreasing the fiber diameter are useful techniques (Lv *et al.* 1998; Brodin *et al.* 2012).

(3) The thermally stabilized fibers without glass transition temperature (T_g) show the infusibility and are subjected to carbonization (1000-2000 °C) in an inert atmosphere (N_2 or Ar). This process is performed to concentrate the carbon by removing the non-carbon elements such as oxygen, hydrogen, and nitrogen, resulting in improvement of mechanical, electrical, thermal properties of the resultant fibers (CFs). Depending upon the precursor fibers and manufacturing conditions, CFs have graphitic structure or turbostratic structure (Fig. 1-3) (Inagaki 2000; Pierson 1995). The plane layers in graphitic crystalline regions (hexagonal network structure) are stacked parallel to each other in a regular fashion (Huang 2009), whereas parallel sheets in turbostratic structure are irregularly stacked or disorderly folded, which is unfavorable for the improvement of mechanical properties of the resultant CFs.

(4) It depends on the final application of CFs whether CFs are further graphitized or not. This process is performed at higher temperature even up to 3000 °C in an inert atmosphere. During the graphitizing process, CFs with higher carbon content of around 100 wt% are obtained. Besides, more or less pre-ordered carbon (turbostratic carbon) is converted into a three-dimensionally ordered graphite structure, and the mechanical properties of CFs are improved, especially for the Young's modulus in the fiber direction (Huang 2009).

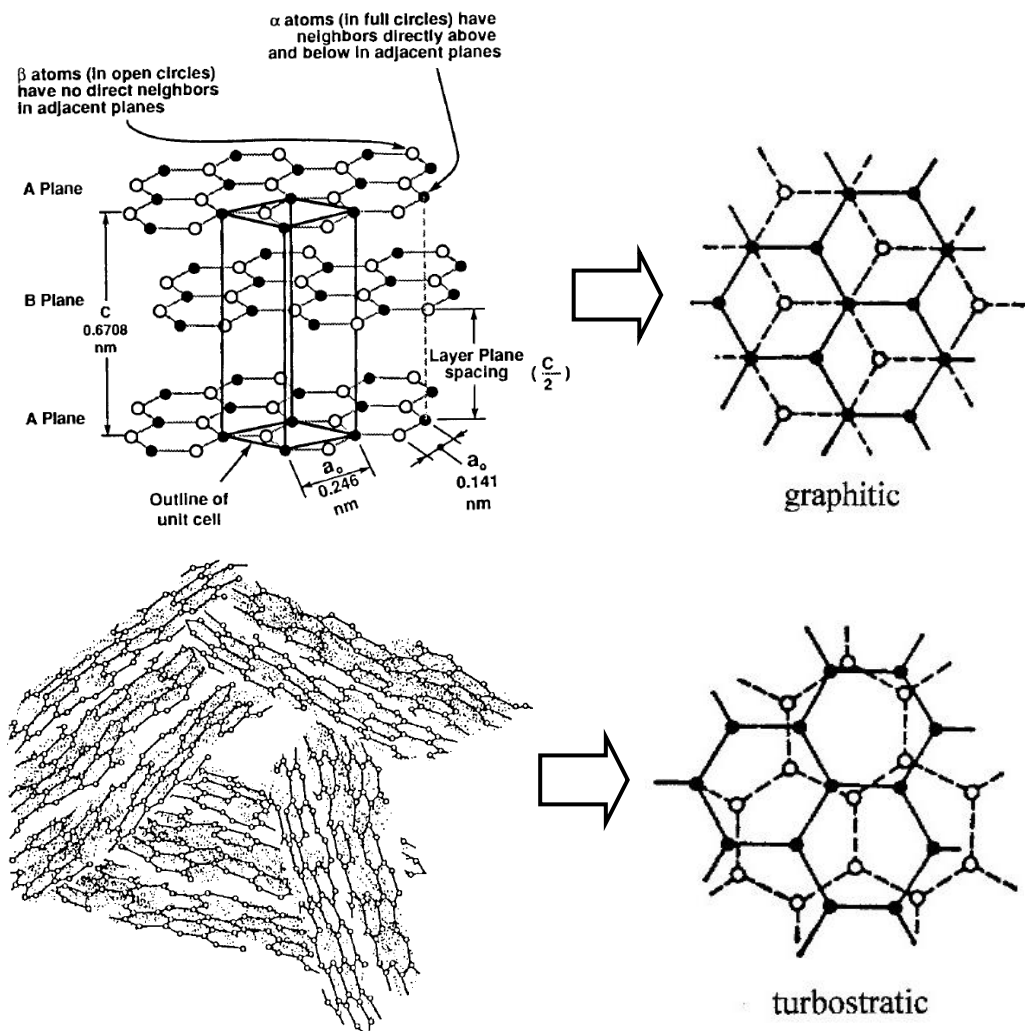


Fig. 1-3. Scheme of graphitic and turbostratic stacking of carbon layers. (Inagaki 2000; Pierson 1995)

1.3 Lignin-based CFs

Due to its polyaromatic macromolecule properties and availability as well as comparative inexpensiveness, lignin can be a candidate to fulfill the requirements as a suitable precursor for CF. Several types of lignin have been used as a feedstock for CF. Lignin-based CF was first successfully prepared by dry-spinning at the end of 1960's; an alkaline solution of commercial lignin (lignosulfonate) was spun by dry-spinning together with poly(vinyl alcohol), and then the obtained fibers were directly converted into CFs (Otani *et al.* 1969). They were produced by Nippon Kayaku Co., Ltd., Japan, but the production was stopped in 1973. After several decades, various types of lignin, such as steam-exploded lignin, organosolv lignin, commercial kraft lignin, recovered lignins from biorefinery processes, and lignin/polymer blends, have been attempted to prepare lignin-based CFs via melt-spinning.

(1) Steam-exploded lignin

Sudo and co-workers developed CFs from steam-exploded lignin, which was obtained from hardwood by steam explosion, and then modified to thermally fusible materials by hydrogenolysis (Sudo and Shimizu 1992) by phenolation. (Sudo *et al.* 1993). By the phenolation, the CFs yield was increased (from 17.4 % to 43.7 %), but decreased the tensile strength of CFs (from 660 MPa to 400 MPa) as compared with those obtained by the hydrogenolysis (Table 1-2).

(2) Organosolv lignin

There were two types of organosolv lignin such as acetic acid lignin and Alcell lignin (AL) used for the production of CFs. Hardwood acetic acid lignin (HWAL) could be processed into CFs without chemical

Table 1-2. Mechanical properties of lignin-based CFs

Samples	Diameter (μm)	Tensile Strength (MPa)	Tensile Modules (GPa)	Elongation (%)	References
H-SEL	7.6 ± 2.7	660 ± 230	40.7 ± 6.3	1.63 ± 0.29	(Sudo <i>et al.</i> 1992)
P-SEL	-----	311 -- 394	-----	1.00 -- 1.22	(Sudo <i>et al.</i> 1993)
HWAL	14.0 ± 1.0	355 ± 53	39.1 ± 13.3	0.98 ± 0.25	(Uraki <i>et al.</i> 1995)
SWAL	35.3 ± 6.3	108 ± 65	-----	-----	(Kubo <i>et al.</i> 1998)
AL	31.0 ± 3.0	388 ± 123	40.0 ± 14.0	1.00 ± 0.23	(Kadla <i>et al.</i> 2002)
HWKL	46.0 ± 8.0	422 ± 80	40.0 ± 11.0	1.12 ± 0.22	(Kadla <i>et al.</i> 2002)
HWKL-OP	9.9 ± 0.8	520 ± 182	28.6 ± 3.2	-----	(Baker <i>et al.</i> 2012)
HWKL/PEO (95/5, w/w)					(Kadla <i>et al.</i> 2002)
(PEO 100K)	46.0 ± 3.0	396 ± 47	38.0 ± 5.0	1.06 ± 0.14	
(PEO 300K)	44.0 ± 4.0	392 ± 89	44.0 ± 12.0	0.91 ± 0.16	
(PEO 600K)	63.0 ± 7.0	339 ± 53	33.0 ± 2.0	1.25 ± 0.26	
HWKL/PET (w/w)					(Kubo and Kadla 2005)
(95/5)	31.0 ± 5.0	669	84.0	1.13	
(87.5/12.5)	45.0 ± 4.0	689	84.0	1.10	
(75/25)	34.0 ± 5.0	703	94.0	1.06	
HWKL/PP (w/w)					(Kubo and Kadla 2005)
(95/5)	47.0 ± 5.0	332	57.0	0.89	
(87.5/12.5)	44.0 ± 5.0	437	54.0	0.85	
(75/25)	76.0 ± 9.0	155	29.0	0.59	
(50/50)	63.0 ± 8.0	167	28.0	0.63	
PL/Cloisite (on PL)					(Qin and Kadla 2011)
0 wt%	49.0 ± 2.0	370 ± 38	36.0 ± 1.0	-----	
1.0 wt% 20A	45.0 ± 1.0	422 ± 24	32.0 ± 1.0	-----	
1.0 wt% 30B	47.0 ± 1.0	438 ± 24	32.0 ± 1.0	-----	

modification by melt-spinning, oxidative thermostabilization (0.5 °C/min of heating rate) and carbonization (Uraki *et al.* 1995). Softwood acetic acid lignin (SWAL) exhibited the spinnability only after the high molecular mass fraction was removed (Kubo *et al.* 1998). The high spinning temperature brought about the decomposition of lignin during melt-spinning, leading to the appearance of defects on fiber surface and then decrease of mechanical strength of the resultant CFs. Besides, lignin fibers were considerably thermostabilized during melt-spinning at elevated temperature, therefore, the oxidative thermostabilization process was not required before carbonization.

AL was easily melt-spun, but the resultant fibers were sensitive to the heating rate for oxidative thermostabilization. The thermostabilization was carried out by the heating at a heating rate of below 0.2 °C/min (Kadla *et al.* 2002). All the mechanical properties of organosolv lignin-based CFs were extremely smaller than those of other lignin-based CFs (Table 1-2).

(3) Kraft lignin

The production of lignin-based CFs from commercial kraft lignin was firstly achieved by using hardwood kraft lignin (HWKL), which did not required any modification (Kadla *et al.* 2002). Melt spinnability of HWKL was further improved by eliminating contaminants present in the original HWKL with organic solvents (Baker *et al.* 2012). Continuous spinning over several hours in a pilot scale was successfully performed, and the mechanical properties were relatively good (Table 1-2). However, the softwood kraft lignin (SWKL) did not show fusibility (Kadla *et al.* 2002). By removing high molecular mass fraction by the ultrafiltration of

softwood black liquors with a 15 kDa ceramic membrane, the lignin preparation isolated from the treated black liquor was able to be melt-spun continuously. It is noteworthy that the resultant fibers could be thermostabilized at a heating rate of 15 °C/min, resulting in to distinctly shorten the processing time (Norberg *et al.* 2013).

(4) Recoverd lignins from biorefinery processes

Pyrolytic lignin (PL) derived from commercial bio-oil production (Qin and Kadla 2011) and the lignin fraction obtained from biorefinery for hemicellulose extraction (Luo *et al.* 2012) have also been applied for the production of CFs. Both recovered lignins showed the low molecular mass and T_g , significantly contributing to the good spinnability. Especially for the PL, lowest spinning temperature was required, in comparison with steam-exploded lignin and organosolv lignin as well as kraft lignin. However, low T_g of lignin resulted in the requirement of small heating rate for the formation of more cross-linkages during oxidative thermostabilization.

(5) Lignin/polymer blends

Various synthetic polymers have been used to blend with lignin for preparing CFs. Poly(ethylene oxide) (PEO) was the first polymer to be used for blending with commercially available HWKL (Kadla *et al.* 2002). It was found that the addition of PEO to HWKL facilitated melt-spinnability, but the good thermostabilization was carried out when PEO content was less than 5 %. The mechanical properties of CFs were not improved by the addition of PEO (Table 1-2). For SWKL, the blends could be spun only with the PEO amount of over 37.5 % (Kubo and Kadla

2005). All the PEO/AL blends showed the excellent spinnability, but the corresponding fibers could not be thermally stabilized even at a heating rate of 0.2 °C/min (Kadla *et al.* 2002; Kubo and Kadla 2004). The good spinnability of PEO-based blends were attributed to intermolecular hydrogen bond between PEO and lignins (Kubo and Kadla 2006).

Polyethylene terephthalate (PET) and poly(propylene) (PP) have also been blended with lignin for the CFs production (Kubo and Kadla 2005). Both lignin blend systems showed a good spinnability. The oxidative thermostabilization can be carried out at the heating rate by the blending, especially PET. However, CFs from both blend systems exhibited a significant difference in mechanical properties (Table 1-2). Lignin/PET (75/25)-based CFs were the strongest among lignin-based CFs reported so far. Its tensile strength was found to be around twice that of lignin/PP-based CFs. The difference may be caused by the difference in miscibility between lignin and polymer. Lignin/PET blends were miscible while the lignin/PP blends were immiscible (Kubo and Kadla 2005; Kadla and Kubo 2004). That was also the reason why lignin/PET-based CFs had smooth surfaces while lignin/PP fibers formed much porous structure (Kubo and Kadla 2005; Kadla *et al.* 2002).

In such fabrication processes of lignin-based CFs, hardwood lignins were almost exclusively used as raw material and directly converted to fibers because of their thermal fusibility. On the other hand, softwood lignins showed thermal infusibility, and were necessary to be modified or remove the high molecular mass fraction (Kubo *et al.* 1998), prior to the spinning process.

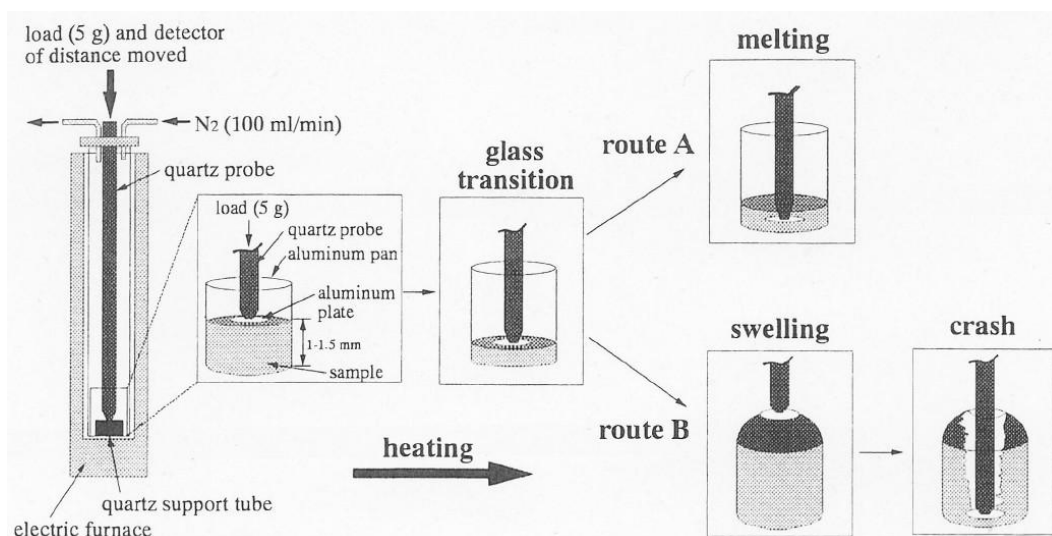


Fig. 1-4. Apparatus for TMA and illustration of the TMA of lignin powder. (Kubo *et al.* 1996)

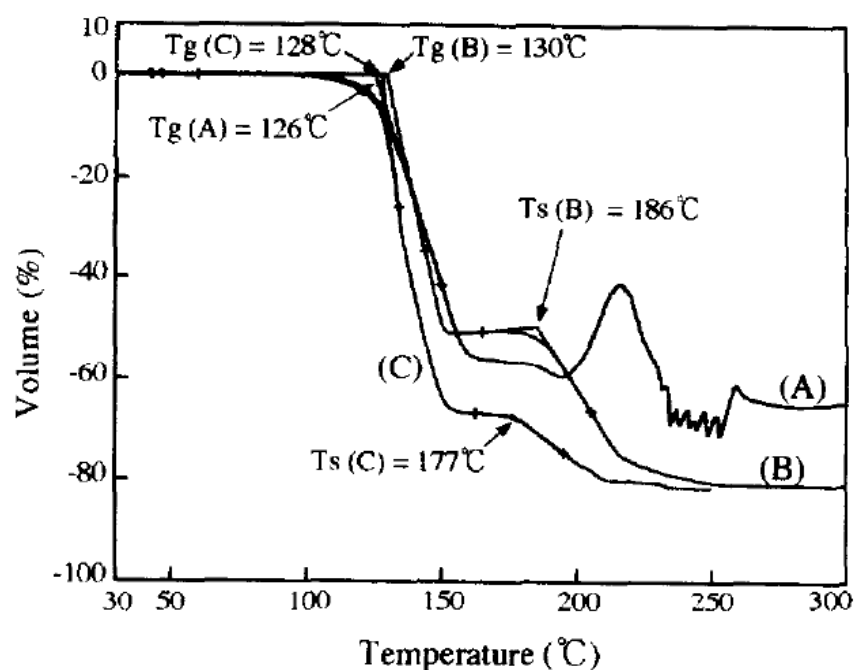


Fig. 1-5. TMA profiles of AL. (A), SWAL; (B), SWAL fusible fraction; (C), HWAL. (Kubo *et al.* 1998)

The different thermal behaviors can be partly explained by the frequency of the presence of condensed structures such as β -5 and 5-5 in softwood lignin.

Thermal behaviors, such as glass transition and thermal flow, of isolated lignins can be characterized by thermomechanical analysis (TMA) (Fig. 1-4) (Kubo *et al.* 1996). In TMA profile, hardwood lignin generally shows two transition points, which corresponded to the T_g at the lower transition point and T_f at the higher point, whereas softwood lignin shows only T_g , but no T_f , suggesting the infusibility (Fig. 1-5) (Kubo *et al.* 1998).

1.4 Research objectives

A large amount of cedar wood can be obtained from plantation in Japan. Especially, timber from forest thinnings cannot be effectively used, sometimes was left in forest. To use it, I intend to develop novel utilization of lignin in cedar wood in my thesis. Therefore, an objective of my thesis is to develop process of CF production from cedar lignin. To achieve this objective, I also attempt to develop novel pulping process to obtain fusible lignin from cedar wood.

When PEO or polyethylene glycol (PEG), which are essentially identical, but the termination depends on molecular mass, is introduced into lignin, the modified lignin must show fusibility, because PEO moiety acts as an internal plasticizer. From this viewpoint, I developed a novel solvolysis pulping of cedar chips with PEG400, and recovered lignin fraction (PEG-lignin) from the black liquor. As expected, this isolated lignin was found to show thermal fusibility. Therefore, I attempted to convert PEG-lignin into CF and ACF with adequate processes. I describe details of researches to obtain such material as follows.

In Chapter 2,

1. To convert the softwood (cedar) lignin into fibers by conventional melt-spinning without any other modification
2. To develop a new viable method of chemical thermostabilization for the

conversion of fusible lignin-based fibers into infusible fibers, and to compare it with tedious oxidative thermostabilization

3. To carbonize the infusible lignin-based fibers into CFs, and further to develop ACFs with large specific surface area

In Chapter 3,

1. To improve the surface morphology of fibers by chemical curing
2. To evaluate the heating rate during oxidative thermostabilization process to decrease the duration of the process
3. To examine the mechanical properties of the resultant CFs and compare them with those of CFs previous reported

Finally, I summarize the spinnability of softwood PEG-lignin, the effect of both chemical thermostabilization and thermal curing processes on the mechanical properties of the resultant CFs in Chapter 4 from the viewpoint of “General Discussion.”

CHAPTER 2

Carbon fibers and activated carbon fibers from softwood lignin

2.1 Introduction

In the last century, a solvolysis process, using 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 terms of biorefinery to obtain levulinic acid from cedar wood (Yamada *et al.* 2007). Besides, levulinic acid was considered to be one of the most valuable materials, because it can be a potential precursor for synthetic rubbers and plastics, as well as for a solvent by minor modification of reaction conditions (Bozell *et al.* 2000; Martin and Jones Prather 2009; Uslu *et al.* 2009).

As a by-product of the solvolysis, a lignin fraction was recovered, and it was found to be modified chemically with PEG through the formation of ether bonds between PEG moiety and lignin. This product was termed as PEG-lignin. Besides, lignin grafted with an ethylene glycol (EG) chain was previously reported to be thermally fusible, because the EG moiety not only inhibits the formation of intra- and/or intermolecular hydrogen bonding of lignin, but also it acts as an internal plasticizer of the lignin (Kubo *et al.* 2007; Kishimoto *et al.* 2006; Uraki *et al.* 2012). I found that this resultant lignin had high molecular mobility at elevated temperature, in particular it was found to be thermally fusible.

In this chapter, I report the preparation of lignin fibers from fusible, modified softwood lignin, and the corresponding infusible fibers as precursors for CFs and ACFs by a new thermostabilization process for the conversion of fusible fiber to infusible fiber.

2.2 Experimental

2.2.1 Materials

Cedar wood chips were obtained from the Department of Biomass Chemistry (Forestry and Forest Products Research Institute, Tsukuba, Ibaraki, Japan). All chemicals used in this study were of analytical grade and used as received without further purification. PEG (400) was purchased from Nakarai tesque. Inc. (Kyoto, Japan); H₂SO₄, HCl, and 1,4-dioxane were purchased from Wako Pure Chemical Industries, Co., Ltd. in Japan.

2.2.2 Preparation of PEG-lignin

A preparation scheme of PEG-lignin is shown in Fig. 2-1. Sixty grams of dried cedar chips were placed in a round bottom flask together with 300 g of PEG 400 and 0.9 g of aqueous H₂SO₄ (0.3 wt% on PEG 400). The flask was immersed in an oil bath with the temperature of 160 °C for 240 min. 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.

The organic solvent (1,4-dioxane) in the filtrate was removed by evaporation under reduced pressure. The resulting liquor was transferred to a three-necked flask equipped with a mechanical stirrer and a thermocouple, and the flask was heated at 140 °C for 150 min. After cooling of the flask, the solution was poured 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.

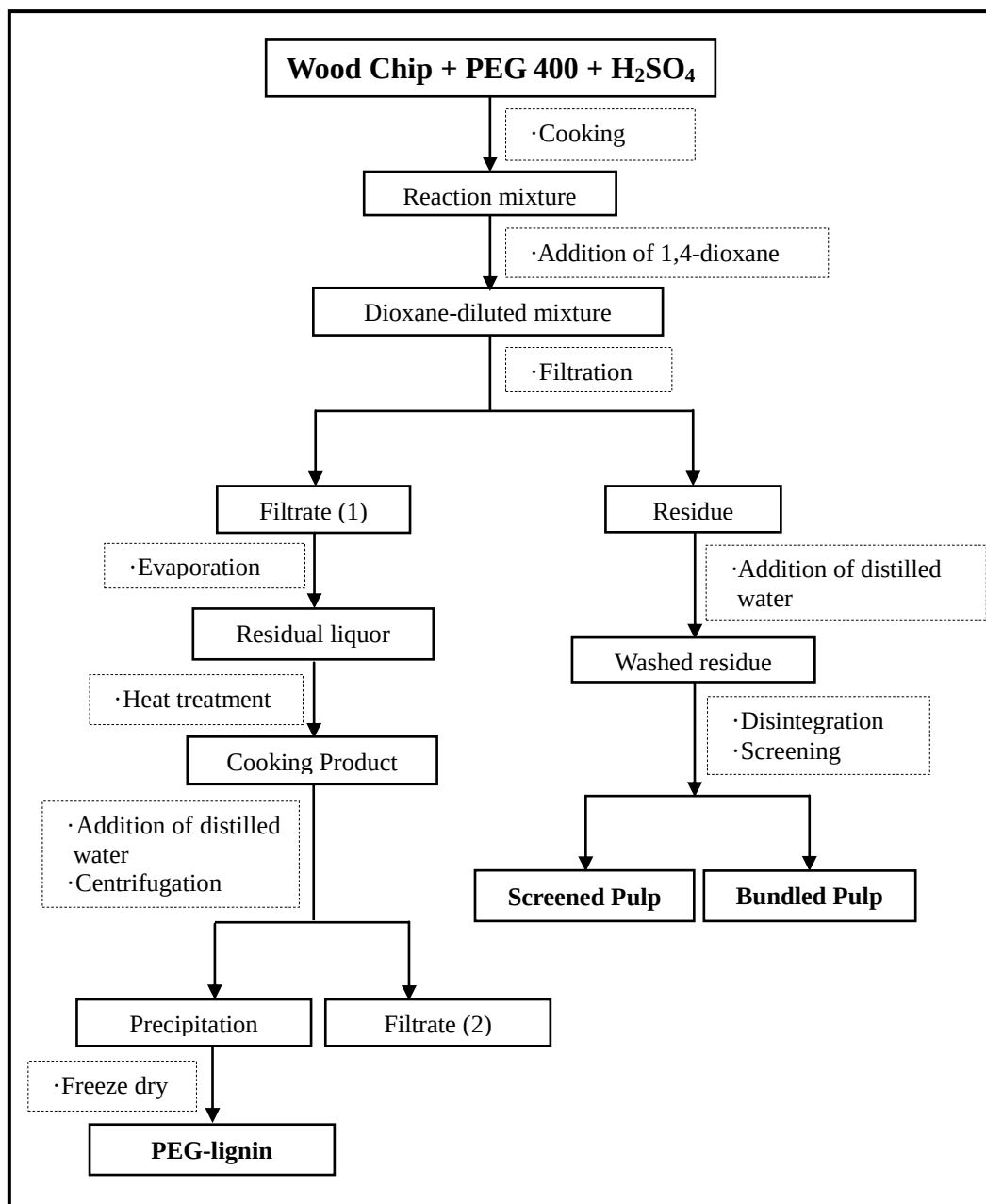


Fig. 2-1. Preparation scheme of PEG-lignin.

The insoluble part in the 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 knot 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.

2.2.3 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 45-67 m/min under a nitrogen pressure (Uraki *et al.* 1995).

2.2.4 Oxidative thermostabilization (general thermostabilization)

The resultant PEG-lignin fibers were heated from room temperature to 250 °C at 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).

2.2.5 Chemical thermostabilization

PEG-lignin fibers were immersed in aqueous HCl solution at concentrations of 1 to 6 M at 100 °C for 2-6 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.

2.2.6 Carbonization

After both the thermostabilization processes, the infusible fibers were carbonized in the same electronic muffle furnace (used in oxidative

thermostabilization 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 N₂ stream at a flow rate of 0.15 L/min to yield PEG-lignin based CFs.

2.2.7 Steam activation

The resultant CFs was subjected to activation to prepare ACFs. The schematic diagram of used instrument for activation with a stream of nitrogen including water was shown in Fig. 2-2. The CFs were heated in the same electronic muffle furnace (used in oxidative thermostabilization step) from room temperature to 900 °C at a heating rate of 10 °C /min under a N₂ stream (flow rate, 0.6 L/min). Subsequently, N₂ was mixed with steam (60.3 RH%) and the mixed gas was introduced for activation at the final temperature of 900 °C for 30 to 90 min.

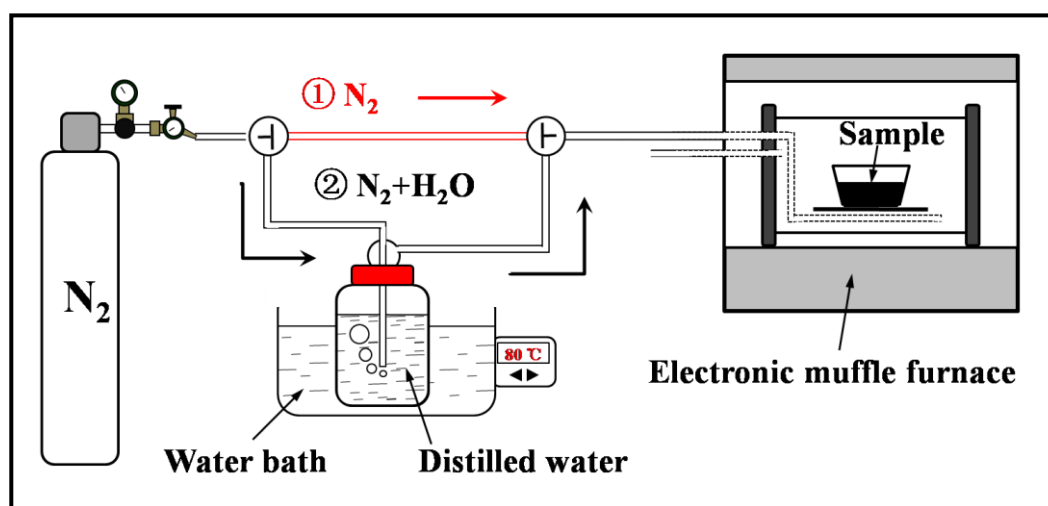


Fig. 2-2. The schematic diagram of instrument for water stream activation.

2.2.8 Characterizations

Measurement of PEG content (Morgan 1946; Homma *et al.* 2008)

The apparatus to measure the PEG content was schematically shown in Fig. 2-3. Approximately a mixture of 0.2 g sample and 5 mL hydroiodic acid solution was added in a branched eggplant flask connected with a pipette to introduced a small amount of nitrogen flow and another eggplant flask to collect iodine with about 25 mL 20% potassium iodide solution. After the mixture heated at 145 °C for 90 min and then cooled, all contents in the glass vessels were washed out with about 125 mL 20% potassium iodide solution and then added with about 5 mL 1% starch solution for iodometric titration with 0.1 mol/L sodium thiosulfate solution. The titration volume of sodium thiosulfate solution was measured until the color of the solution was clear. Each sample including blank was measured at least 2 times. PEG content was calculated by following formula,

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

where: V_s —— Titration volume of $\text{Na}_2\text{S}_2\text{O}_3$ for a sample;

V_b —— Titration volume of $\text{Na}_2\text{S}_2\text{O}_3$ for blank;

W_s —— Sample weight;

Elemental analysis

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

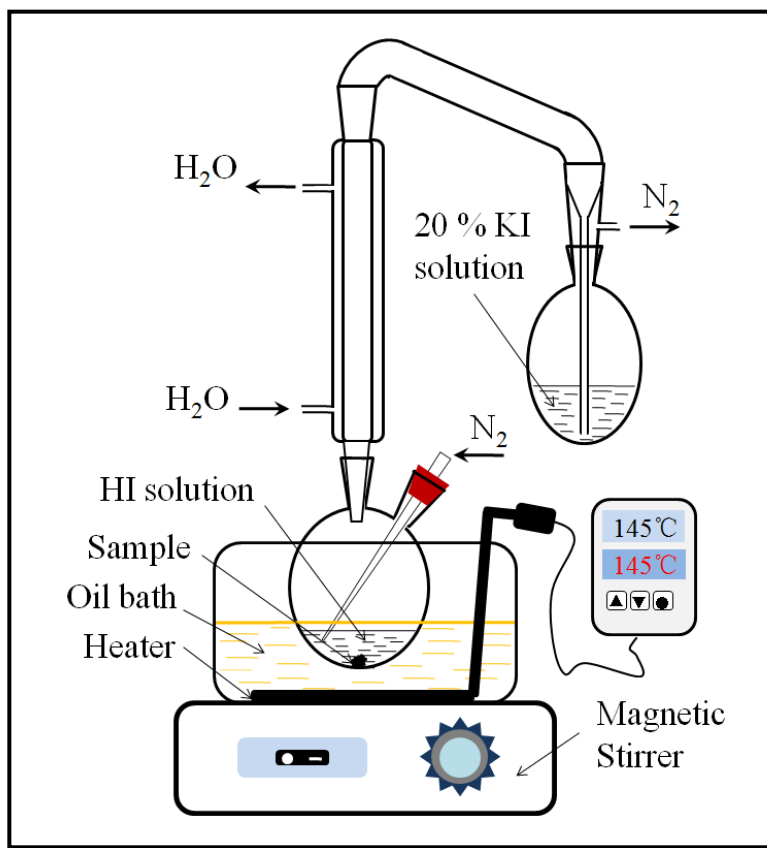


Fig. 2-3. The apparatus to measure the PEG content.

Molecular mass

The weight average molecular mass ($\bar{M}_w$) and number average molecular mass ($\bar{M}_n$) of the PEG-lignin were determined by Size exclusion chromatography (SEC) with Shimadzu GPC system (Class VP for GPC) equipped with a column of Shodex KF-803L at 40 °C. Tetrahydrofuran (THF) was used as the eluent (0.5 mL/min) and the wavelength of ultraviolet (UV) detection was 280 nm. The PEG-lignin concentration in THF was 5 mg/mL, and the injection volume was 20 μ L. Polystyrene standards were used for the calibration.

Determination of Klason lignin

The lignin content (acid-insoluble lignin) of cedar wood was determined by the Klason method (Dence 1992). Prior to the determination, wood meal (40-60 mesh) was extracted with a benzene/ethanol (2/1, v/v) mixture to remove the extractives. Subsequently, to 500 mg of extractive-free wood meal, 7.5 mL of 72 % H₂SO₄ was added and completely mixed in a 500 mL conical flask, and kept at 25 °C for 4 h with occasional mixing with a glass rod. Then, 208 mL of distilled water was added to the mixture in a conical flask to decrease the concentration of H₂SO₄ to 4 %. The conical flask with the mixture was covered and placed in an autoclave at 121 °C for 1 h. After cooled off, the mixture was filtered using a glass filter (1G4). Insoluble lignin was washed each with 500 mL of hot distilled water (70 °C) until its pH becomes neutral, and then dried in an oven at 105 °C until it reached to a constant weight. Three replications were performed for one sample. The lignin content was calculated by the following formula:

$$\text{Lignin content (wt\%)} = [(W_2 - W_1) / 500 \text{ mg}] \times 100 \% \quad (2-2)$$

where: W_1 —oven-dry weight of glass filter;

W_2 —oven-dry weight of glass filter and acid-insoluble lignin;

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 °C under compression loading of 5 g under a N₂ stream at 0.15 L/min. T_g and T_f were estimated as the first and the second transition point in TMA profiles, respectively (Kubo *et al.* 1996).

Images

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

Mechanical properties

Diameters of a fiber were measured at 5 positions at least to obtain the 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 $\pm$ standard deviation, based on the results of 40 fibers.

Porous measurement

N₂ adsorption–desorption isotherms were determined at -196 °C by a surface area analyzer (Quantachrome, Autosorb-1). Prior to measurement, the samples were preheated at 300 °C for 3 h under vacuum to remove any moisture or volatiles within the existing pores of the materials. The Brunauer, Emmett, and Teller (BET) model was used to calculate the surface area of the samples from N₂ adsorption isotherms in the range of the relative pressure (P / P_0) from 0.05 to 0.30 (11 points) (Okada *et al.* 2003). The adsorption volumes at relative pressures of 0.1 and 0.96 are equal to the volume of micropores, and the total volume of micropores and mesopores, respectively (Azargohar and Dalai 2008; Shimada *et al.* 2000; Rodriguez-Reinoso *et al.* 1982).

Methylene blue adsorption capacity

Liquid-phase adsorption tests for CFs and ACFs were conducted, using methylene blue as the adsorbate. Firstly, methylene blue solution with four different concentrations (0.24 mg/L, 0.48 mg/L, 1.2 mg/L, and 2.4 mg/L) were prepared, and the adsorption values of each methylene blue solution were taken at 630 nm from UV spectrometer (UV-1800, Shimadzu). These results were measured for drawing the standard calibration curve.

Subsequently, samples were mixed with 25 mL of methylene blue solution (1200 mg/L) in a 100 mL of conical flask. The mixture was shaken for 30 min in a water bath (20~30 °C) with a shaking rate of 150 rpm. After shaking, the mixture was filtered and the filtrate was scanned by UV spectrometer. The adsorption values at 665 nm were compared with the standard calibration curve to obtain the final concentration of methylene blue after adsorption. The adsorption capacity was estimated by the following formula:

$$Q = [(1200 - C) \times 25 / 1000] / S \quad (2-3)$$

where: Q——Adsorption capacity, mg/g;

C——Final concentration of methylene blue after adsorption, mg/L;

S——Sample weight, g;

Finally, at least two replications were carried out for each sample to obtain the different methylene blue solution concentrations which were higher and lower 0.24 mg/L, respectively. Calibration line of the adsorption capacity as a function of the methylene blue concentration was obtained to calculate the methylene blue

adsorption capacity of the corresponding sample when at the concentration of 0.24 mg/L (Christina *et al.* 2012; Shimada *et al.* 1999).

2.3 Results and discussion

2.3.1 Characterization of PEG-lignin

PEG-lignin with the $\bar{M}_w$ of 3800 and $\bar{M}_w / \bar{M}_n$ of 4.2 was isolated in a powder form from softwood (cedar) chip treated with PEG 400, as shown in Fig. 2-1. The yield of PEG-lignin was 50.4% on wood chip. Its PEG content was 43.8%. Accordingly, the net lignin extracted from the wood chip was estimated to be 28.3%. Since lignin content of cedar chip measured by the Klason method (Dence 1992) was 30.6%, the lignin in cedar chips was 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-hydroxy-methyl furfural as an intermediate (Yamada *et al.* 2007; Yamada and Ono 2001).

T_g and T_f of the PEG-lignin were estimated by TMA, which had been reported to be a suitable analytical tool for thermal properties of powdered lignin preparations (Kubo *et al.* 1996). As shown in Fig. 2-4 (A), the TMA curve of PEG-lignin powder showed two transition points at 78.8 °C and 140.7 °C, 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 ($T_g = 128$ °C, $T_f = 177$ °C), which was first found as a thermally fusible isolated lignin (Uraki *et al.* 1995).

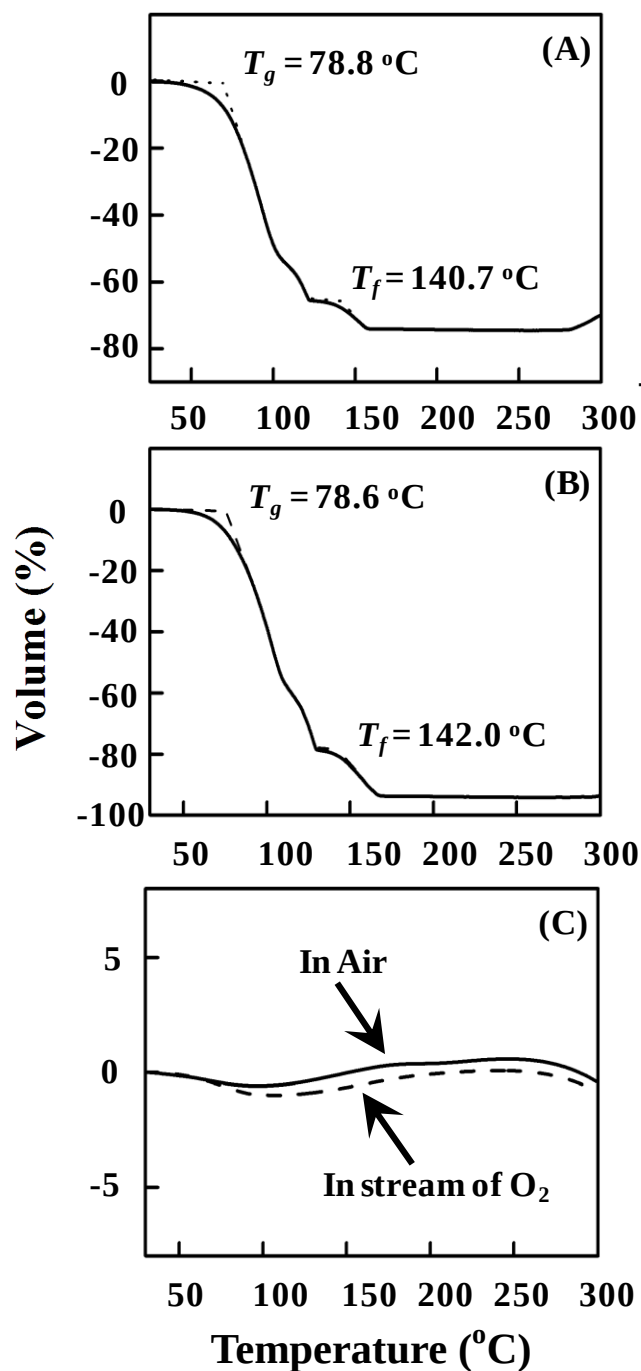


Fig. 2-4. TMA profiles of PEG-lignin powder (A), PEG-lignin fibers (B), and oxidative thermostabilized PEG-lignin fibers in air and stream of oxygen with heating rate of 0.1 °C/min (C), respectively.

2.3.2 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 °C. Table 2-1 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 2-1. Spinning Conditions and Tensile Strength of PEG-Lignin Fibers.

Entry	Spinning temperature (°C)	Winding rate (m/min)	Diameter (μm)	Tensile strength (MPa)
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

Fig. 2-5 shows the morphology of PEG-lignin fibers spun at various temperatures. All the fibers had a smooth surface, while several pores existed in the cross-section of a fiber. These pores may be caused by the introduction of nitrogen gas, which was used for extrusion of molten lignin under pressure. The thinnest PEG-lignin fibers with a diameter of around 23 μm were obtained with a spinning temperature of around 170 °C, which were subjected to the subsequent processing. The PEG-lignin fibers with the smallest diameter showed the greatest tensile strength, as expected (Table 2-1) (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.

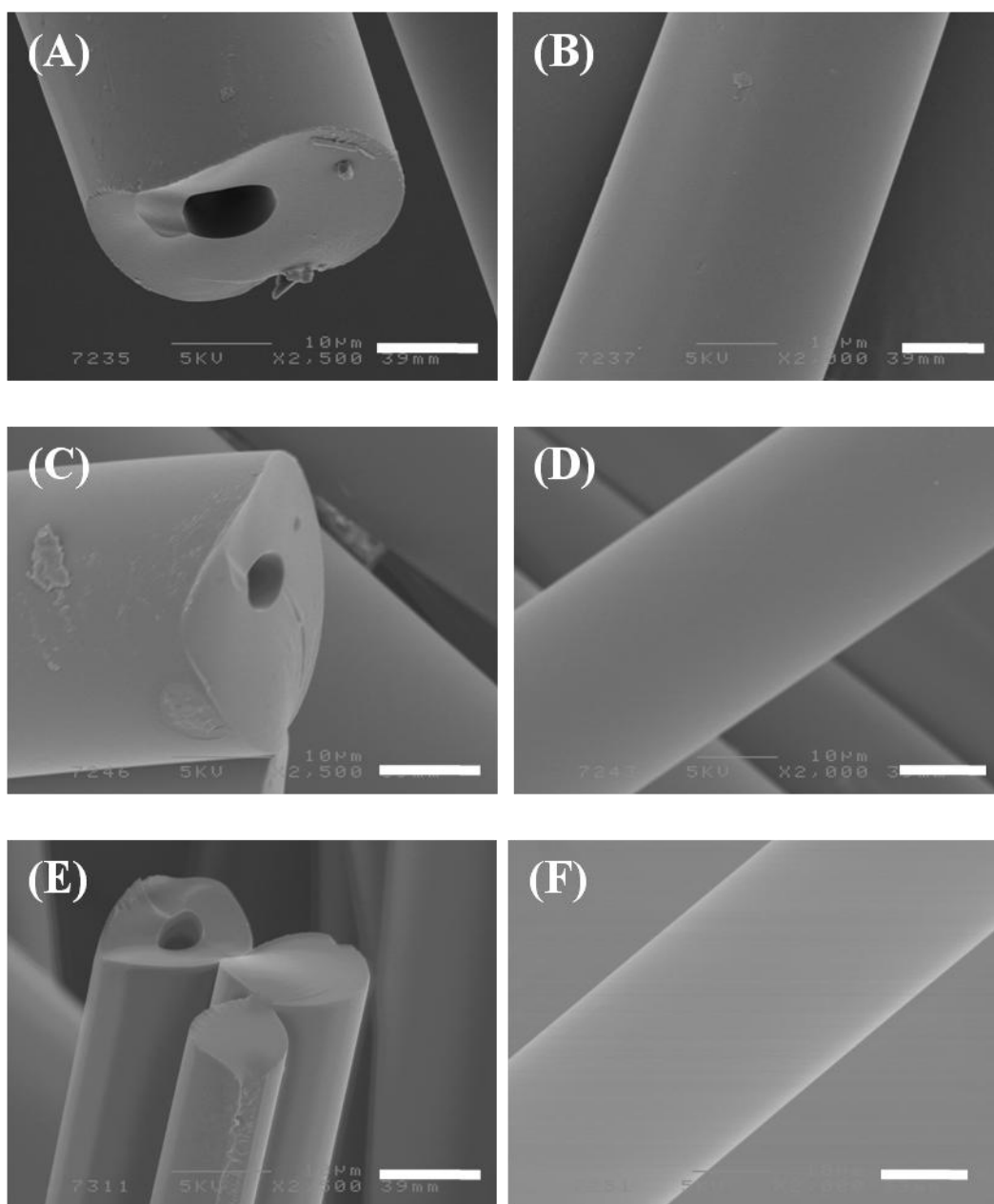


Fig. 2-5. SEM morphology of PEG-lignin fibers spun at various temperatures. (A) and (B), 145-148 °C; (C) and (D), 155-159 °C ; (E) and (F), 168-172 °C. (White bar =10 μm).

2.3.3 Oxidative thermostabilization

So far previous lignin fibers spun by melt-spinning as well as polyacrylonitrile and pitch fibers as precursors for CF have been thermostabilized

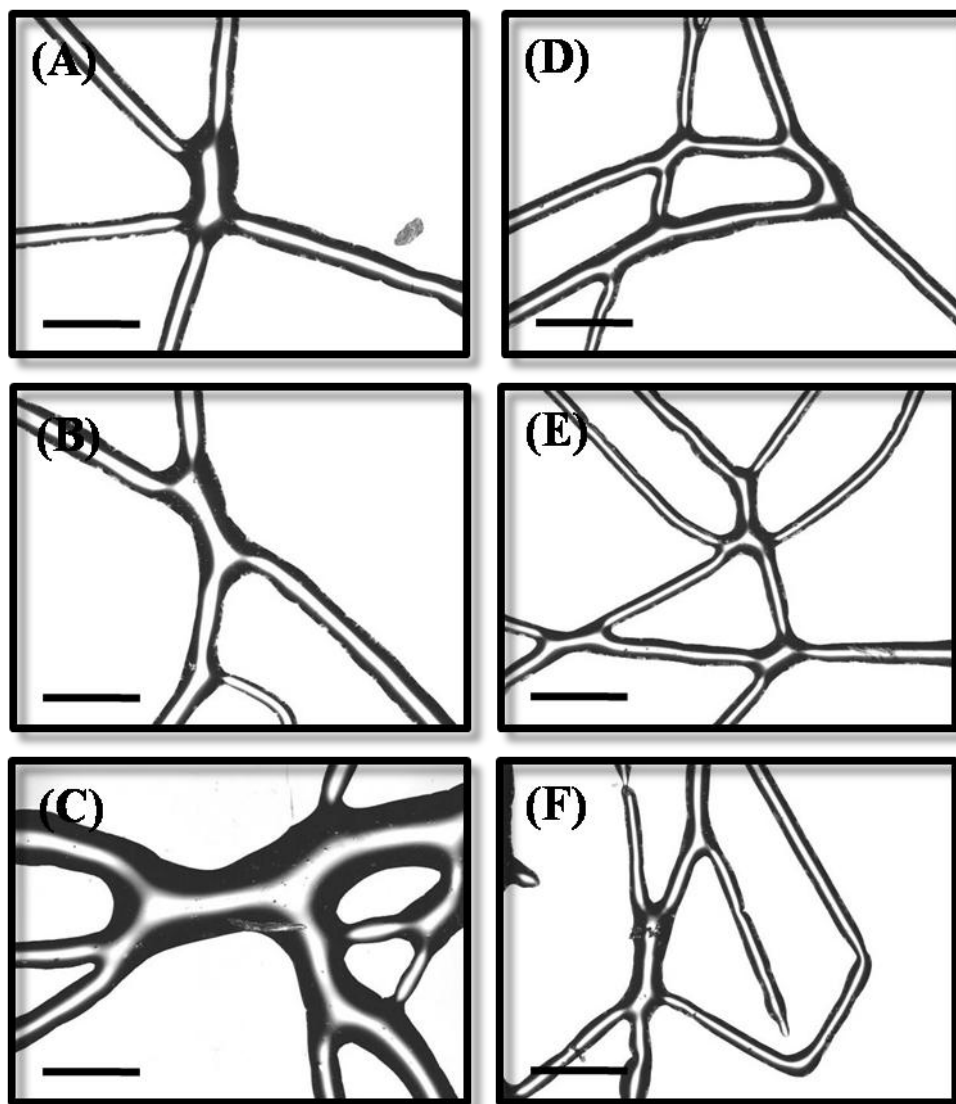


Fig. 2-6. Microscopic images of oxidatively thermostabilized fibers treated on heating from room temperature to 250 °C under air atmosphere and oxygen stream at a flow rate of 0.15 L/min at different heating rates. (A), Air, 0.1 °C/min; (B), Air, 0.3 °C/min; (C), Air, 0.5 °C/min; (D), O₂, 0.1 °C/min; (E), O₂, 0.3 °C/min; (F), O₂, 0.3 °C/min. (Black bar =300 μm).

by heating them up to around 250 °C under an oxidative atmosphere, such as air and oxygen, 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) on heating at a slow heating rate under air or oxygen, resulting in a series of elimination, rearrangement, and oxidative reactions, and then more cross-linkages formed among lignin molecules (Braun *et al.* 2005). As shown in Fig. 2-4 (B), PEG-lignin fibers were still fusible. Thereby, I 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. 2-6). Nevertheless, in Fig. 2-4 (C), the TMA profiles of the resultant fibers showed no transition points (T_g and T_f), suggesting the conversion to infusible fibers. It is anticipated from these results that if the oxidative thermostabilization is performed at a much slower heating rate (under 0.1 °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, another method better than oxidative thermostabilization should be explored and applied.

2.3.4 Chemical thermostabilization

Since the thermal mobility and fusibility of PEG-lignin fibers were attributed to the introduction of PEG into the lignin, it was considered necessary to reduce PEG content in the lignin in order to convert PEG-lignin fiber to an infusible form. After several trials, I 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 °C for 2 to 6 h, the fibers were still fusible, as shown in Fig. 2-7. By increasing HCl concentration to 3 M, the fibers showed only T_g , suggesting the PEG-lignin fibers were converted to an infusible form.

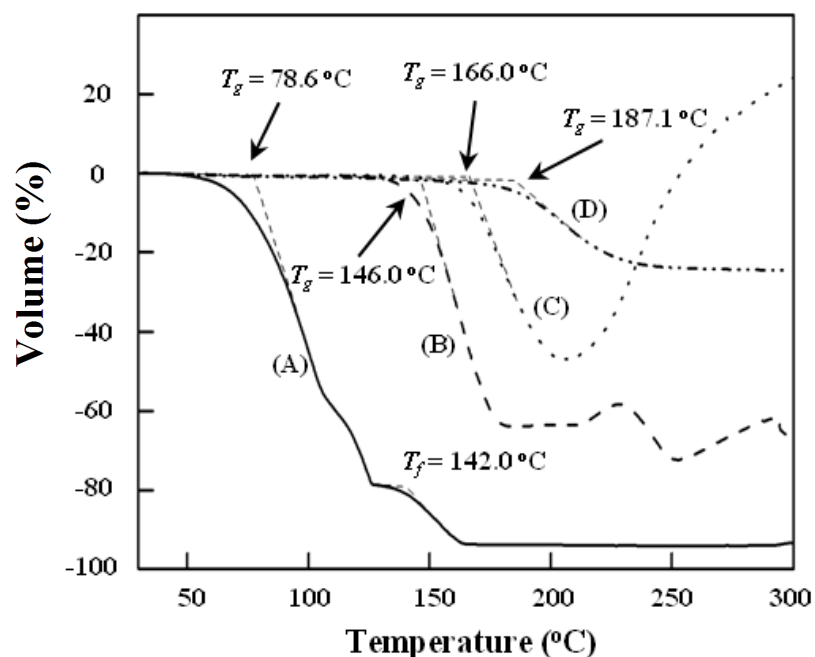


Fig. 2-7. TMA profiles for PEG-lignin fibers (A) and chemically thermostabilized PEG-lignin fibers treated with HCl solution at the concentrations of 1 M (B), 3 M (C) and 6 M (D) at 100 °C for 2 h, respectively.

However, the resultant fibers unexpectedly expanded over 200 °C, just 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 on heating. I next found that the PEG-lignin fibers were converted to an infusible form by immersing them in 6 M HCl aqueous solution for 6 h at 100 °C. Finally, the conversion was found to be complete by

immersion only for 2 h. Although the resultant fibers showed T_g , no expansion was observed at a higher temperature than T_g , as shown in Fig. 2-7. Thus, the short-time thermostabilization for the PEG-lignin fibers was achieved by the chemical treatment with 6 M HCl aqueous solution.

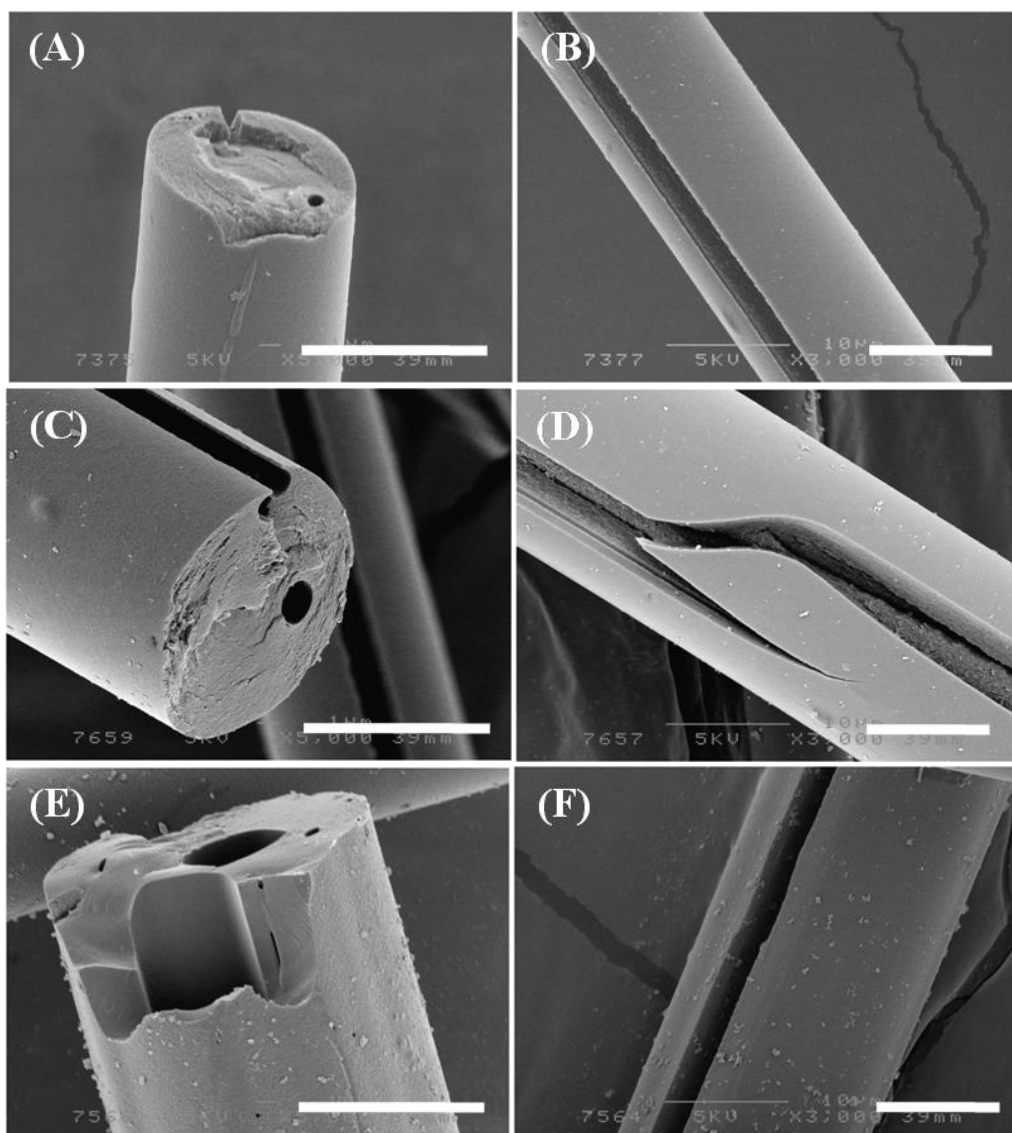


Fig. 2-8. SEM morphology of chemically thermostabilized PEG-lignin fibers treated with 6 M HCl solution at 100 °C for 2 h (A) and (B), 4 h (C) and (D), 6 h (E) and (F). (white bar =10 μm).

Fig. 2-8 show the morphology of chemically thermostabilized PEG-lignin fibers treated with 6 M HCl solution at 100 °C for 2-6 h. Splits on the fiber surface were observed obviously; 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 (Fig. 2-9). 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. 2-10).

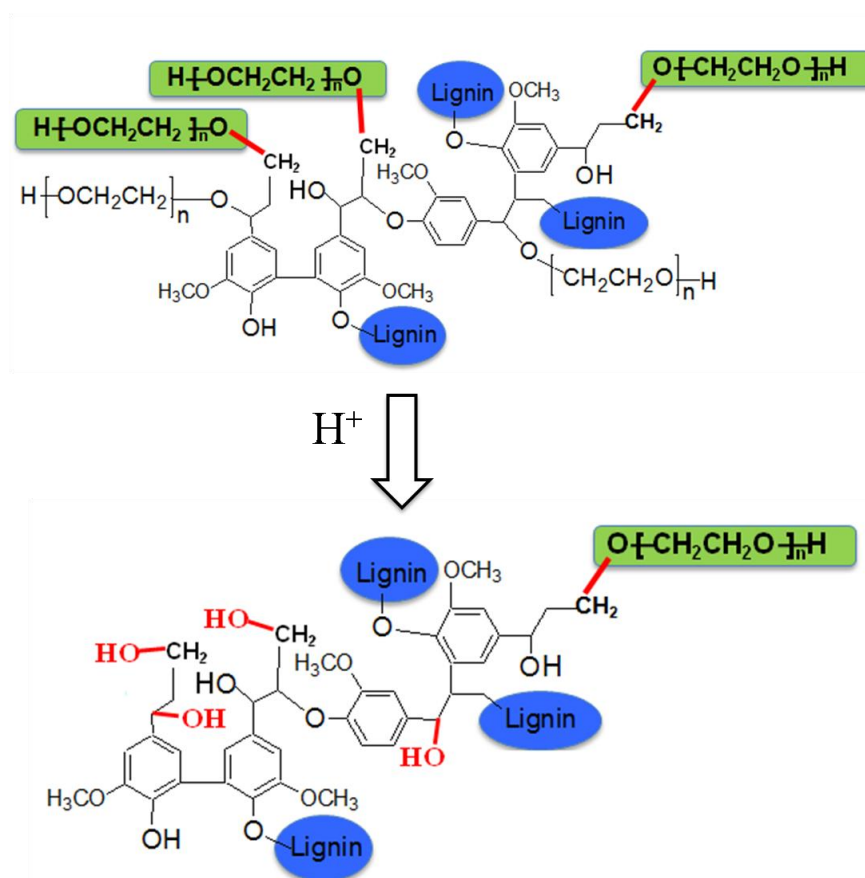


Fig. 2-9. The cleavage behavior of ether bonding between lignin and PEG moiety.

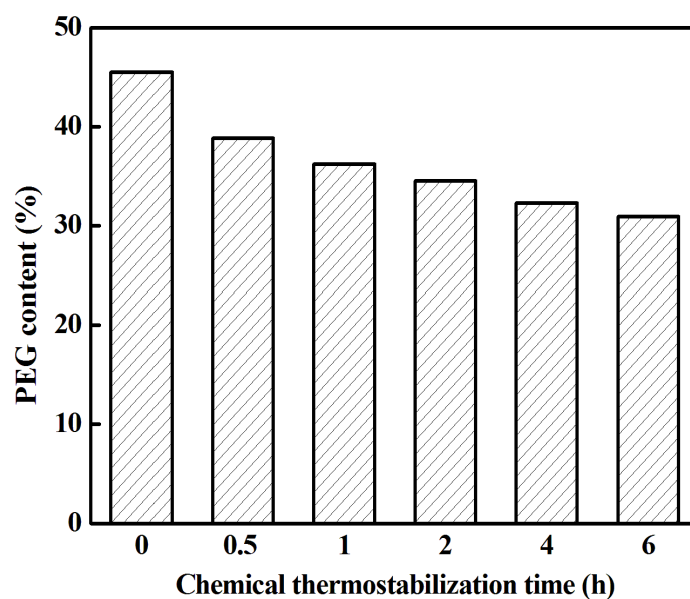


Fig. 2-10. Changes in PEG contents of PEG-lignin fibers with increasing time of chemical thermostabilization at 100 °C, using 6 M HCl aqueous solution.

2.3.5 Carbonization of chemically thermostabilized 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 yield of CFs was calculated to be 35.3% based on PEG-lignin powder, which was higher than those of CFs prepared from acetic acid hardwood and softwood lignin [32.7 % and 23.3 %, respectively] (Uraki *et al.* 1995; Kubo *et al.* 1998) but lower than that of hardwood kraft lignin based CFs [45.7 %] (Kadla *et al.* 2002). CFs with a carbon content of 91.9 % were obtained (Table 2-2). The morphology of CFs derived from the chemically thermostabilized lignin fibers treated with 6 M HCl solution at 100 °C for 2 h, 4 h, and 6 h was observed with SEM (Fig. 2-11). There are still big-sized pores [$< 3 \mu\text{m}$] existing in cross-section as well as lots of small-sized pores occurring on the surface of CFs.

Table 2-2. Elemental Analysis of PEG-lignin, and its corresponding CFs, and

Samples ¹	ACFs			
	Content (%) ²			
	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

¹ 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;

² Ash content was found to be below detection limit for CFs and ACFs.

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, were measured as shown in Table 2-3. Only a slight difference was observed among them, indicating that the duration of chemical thermostabilization did not affect the mechanical properties of CFs. Furthermore, the average tensile strength of CFs in this study was found to be approximately 450 MPa, which was 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 commercially available

[422 Mpa] (Kadla *et al.* 2002).

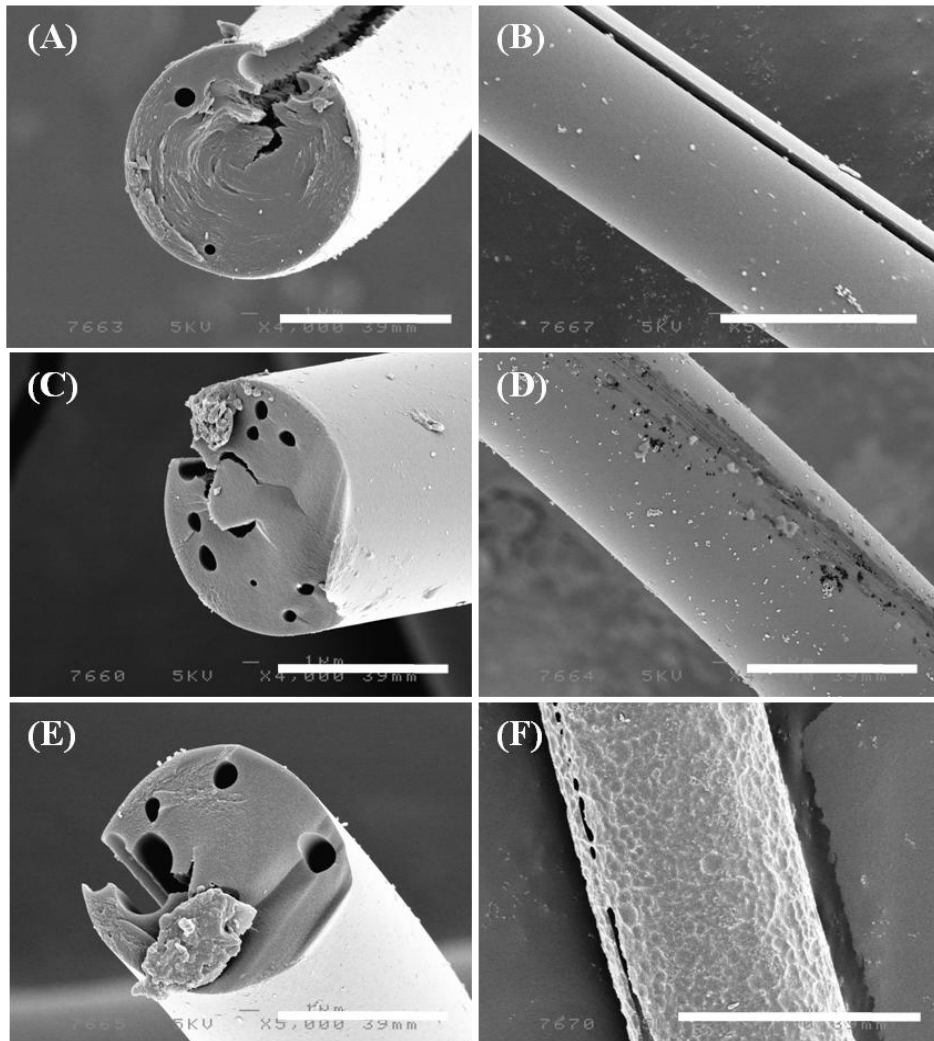


Fig. 2-11. SEM morphology of CFs derived from chemically thermostabilized PEG-lignin fibers treated with 6 M HCl solution at 100 °C for (A) and (B), 2 h; (C) and (D), 4 h; (E) and (F), 6 h. (white bar = 10 μ m).

However, tensile strength of the PEG-lignin based CFs was not necessarily stronger than that of the lignin-based CFs previously reported, 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 (10-12 μm in Table 2-3) 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 probably 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 2-3] compared with other types of lignin-based CFs [*e.g.* 1.1 % for CFs from hardwood kraft lignin] (Kadla *et al.* 2002).

Table 2-3. Mechanical Properties of PEG-Lignin Based CFs.

Samples ¹	Diameter (μm)	Tensile strength (MPa)	Tensile modules (GPa)	Elongation (%)
CF-2	11.5 $\pm$ 2.0	441 $\pm$ 100	23.0 $\pm$ 5.4	2.0 $\pm$ 0.5
CF-4	10.4 $\pm$ 1.3	457 $\pm$ 188	26.2 $\pm$ 13.3	2.1 $\pm$ 1.1
CF-6	10.2 $\pm$ 1.2	451 $\pm$ 156	24.7 $\pm$ 7.2	1.6 $\pm$ 0.8

¹ CF-2, -4 and -6 denote the CFs from chemically thermostabilized fibers treated with 6 M HCl aqueous solution at 100 °C for 2 h, 4 h and 6 h, respectively.

2.3.6 Activation of PEG-lignin based CFs

PEG-lignin based CFs with porous and flabby structure were activated on heating from room temperature to 900 °C at a constant heating rate of 10 °C/min

under a N₂ atmosphere, and then the temperature was maintained at 900 °C under a stream of a mixed N₂ and steam for 30, 60, and 90 min, respectively. The morphology of resultant ACFs were presented in Fig. 2-12. With an increase in the activation time, more pores seemed to develop on the surface of ACFs, which was quantitatively proved by nitrogen adsorption-desorption measurement.

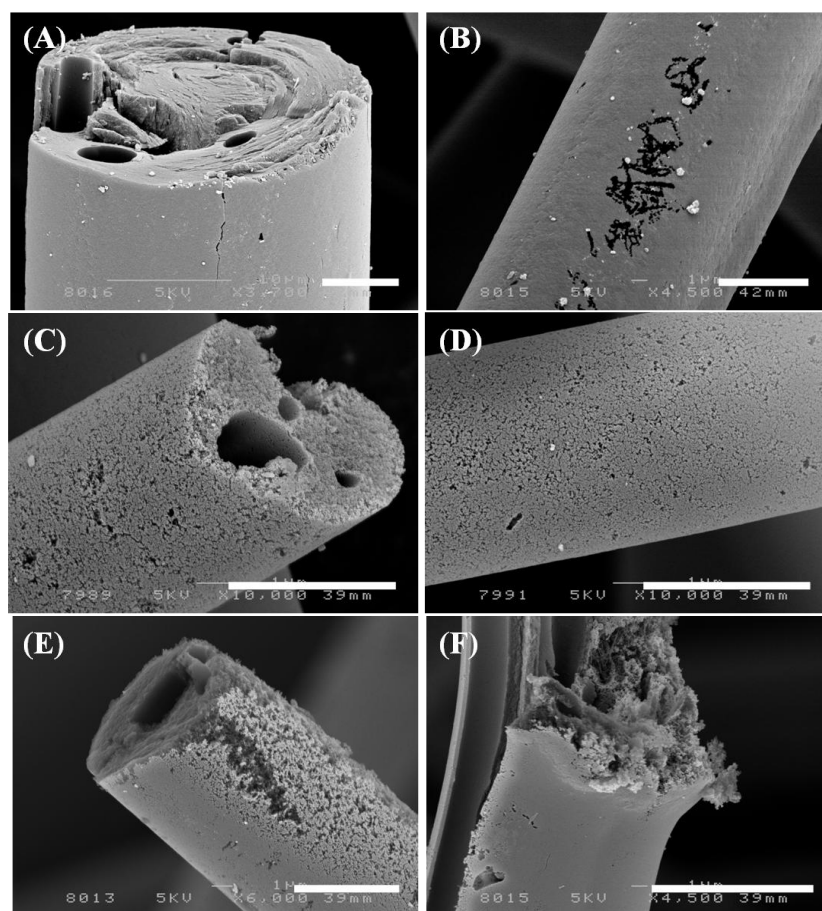


Fig. 2-12. SEM morphology of ACFs obtained from CFs activated at 900 °C for (A) and (B), 30 min; (C) and (D), 60 min; (E) and (F), 90 min. (white bar =5 μm).

As shown in Table 2-4, the corresponding specific surface areas of activated CFs obtained from the N₂ adsorption isotherms (Fig. 2-13) were 2038 m²/g, 2442 m²/g, and 3060 m²/g, respectively, which were much larger than those

of other types of ACFs prepared from hardwood acetic acid lignin [1250 m²/g] (Uraki *et al.* 1997), softwood acetic acid lignin [1930 m²/g] (Uraki *et al.* 2001), rayon [1635 m²/g] (Rong *et al.* 2002), PAN [1320 m²/g] (Tavanai *et al.* 2009), petrium-pitch [2400 m²/g] (Alcaniz-monge, *et al.* 1997) and phenolic resin [~2500 m²/g] (Shimada *et al.* 1993). The total pore volume of ACFs also showed the same increasing trend with the prolonged activation time, and was much greater than that of CFs and activated charcoal (Table 2-4). Besides, methylene blue adsorption capacity of ACFs derived from 90 min-activation was around 9 times greater than those of CFs (Fig. 2-14).

Table 2-4. Nitrogen adsorption properties of carbonized and activated materials.

Samples ¹	Activation time (min)	Yield ² (%)	BET (m ² /g)	Surface area		Total pore volume (mL/g)	Average pore size (nm)
				Internal ³ (m ² /g)	External ³ (m ² /g)		
Charcoal	0	-----	323	263	60	0.1958	2.42
A-Charcoal	60	77.0	549	475	74	0.3516	2.56
CFs	0	-----	775	741	34	0.4095	2.12
ACFs	30	54.4	2038	1911	127	1.029	2.31
	60	19.5	2442	2196	246	1.153	2.39
	90	12.9	3060	2829	231	1.472	2.29

¹ A-Charcoal was prepared from charcoal by water steam activation; CFs was PEG-lignin based carbon fiber and ACFs was activated CFs;

² The yield of ACF was based on CF.

³ The values were calculated from the T-plot method on the bases of specific surface area.

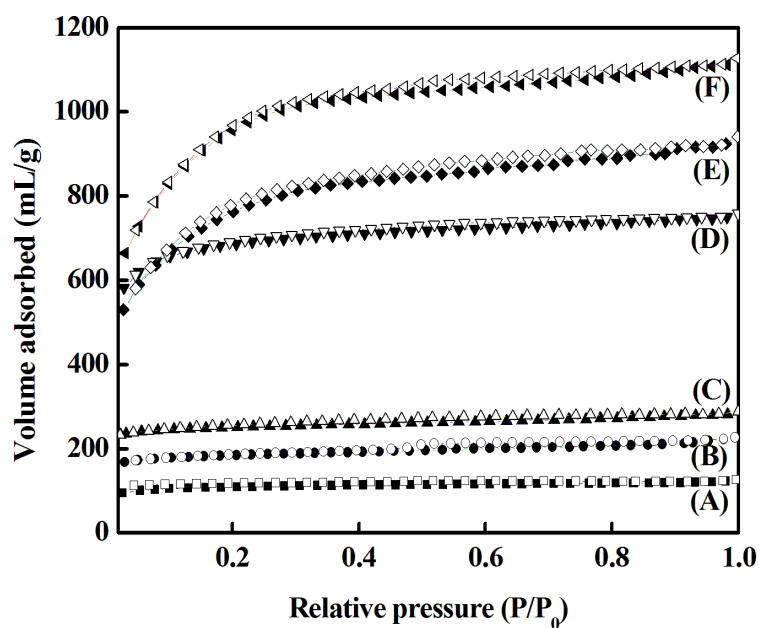


Fig. 2-13. N₂ adsorption isotherms at 77K of various carbon materials. (A), Charcoal; (B), Activated charcoal; (C), PEG-lignin based CFs; (D), ACFs treated with 30 min activation; (E), ACFs treated with 60 min activation; (F), ACFs treated with 90 min activation.

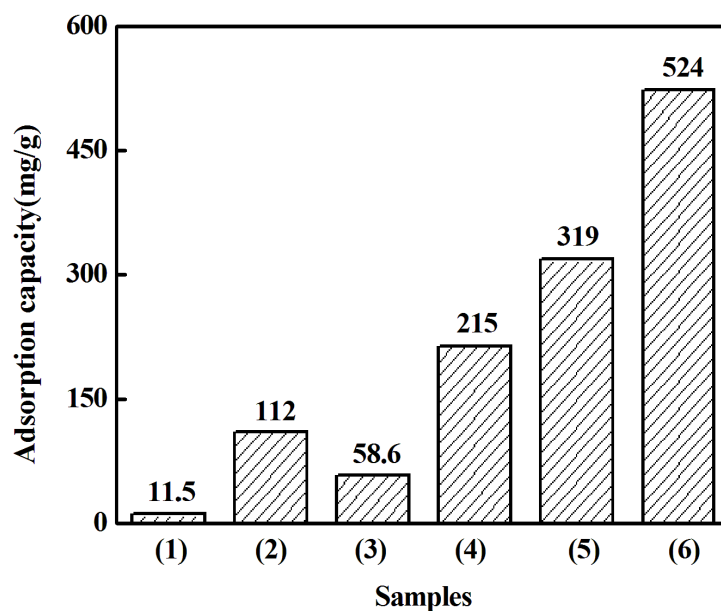


Fig. 2-14. Methylene blue adsorption capacity of various carbon materials. (1), Charcoal; (2), Activated charcoal; (3), PEG-lignin based CFs; (4), (5), and (6), ACFs treated with 30 min, 60 min, and 90 min activation, respectively.

2.4 Summary

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).

CHAPTER 3

Improvement of mechanical properties of softwood lignin-based carbon fibers

3.1 Introduction

To prepare thermostabilized fibers as precursory fibers for CFs from PEG-lignin fibers, an oxidative thermostabilization was firstly attempted. As a result, this attempt was found unsuccessful even at a relatively low heating rate of 0.1 °C/min, because the obtained fibers melted and adhered to each other. Next, alternative thermostabilization process, namely, “chemical thermostabilization,” was developed to obtain infusible fibers. This process was achieved by removing some of PEG moiety from PEG-lignin. However, the chemically thermostabilized fibers had some defects such as splits and flabby structures by the release of PEG moiety during this process. The defects also remained in the corresponding CFs, which was a disadvantage for preparing CFs with high mechanical properties (Chapter 2). If defects-free thermostabilized fibers can be prepared, the mechanical strength would be improved.

A curing reaction is considered as one of the effective techniques to generate a large amount of cross-linkages. As a common cross-linking reagent, hexamethylenetetramine (HMTA) is generally used for curing to prepare thermosetting products (Wang et al. 2010; Alma and Kelley 2000; Choi et al. 2000), such as phenolic resin. When HMTA is applied to softwood lignin, HMTA can crosslink aromatic carbons at unsubstituted position of aromatic ring thorough methylene bridge, because softwood lignin consists of more than 95 % of guaiacyl

units and less than 5 % p-hydroxyphenyl units (Ek *et al.* 2009), and neither of them has methoxy group at the C2, C5, and C6-position.

Accordingly, I investigated how chemical cross-linking of PEG-lignin powder and PEG-lignin fibers works by HMTA treatment. By a combination of this curing reaction and oxidative thermostabilization, defect-free, infusible fibers with a smooth surface fibers were obtained. In this chapter, the mechanical properties of CFs prepared from the infusible fibers are also discussed.

3.2 Experimental

3.2.1 Materials

PEG-lignin powder was isolated from cedar wood chips, and then spun to the corresponding fibers under the same conditions as mentioned in chapter 2 (2.2.2 preparation of PEG-lignin and 2.2.3 melt-spinning). Other all chemicals used were of analytical grade and used as received.

3.2.2 Preparation of CFs

Chemical curing was performed with HMTA in the form of powder and liquid. PEG-lignin powder was manually mixed with HMTA powder by using mortar and pestle, prior to melt-spinning. The HMTA content was 1, 2, and 5 wt%, based on the weight of PEG-lignin powder. PEG-lignin fibers were immersed in HMTA aqueous solution at concentrations of 5 to 60 g/L, containing 0.1 to 3 M HCl. The mixture systems were then heated at the temperature of 60, 80, and 100 °C for 1 h, respectively. The resultant fibers were washed twice with distilled water, and then roughly dried *in vacuo* at 40 °C for 2 h.

Subsequently, the cured PEG-lignin fibers were subjected to

heat-treatment. Oxidative thermostabilization was first performed on heating from room temperature to 250 °C at heating rates of 0.5 to 2 °C/min, and then the temperature was maintained at 250 °C for 1 h. This process was conducted under air atmosphere in an electronic muffle furnace (KDF S90/S90G, Denken Co. Ltd., Kyoto, Japan). Afterwards, the resultant oxidatively thermostabilized fibers were carbonized in the same electronic muffle furnace 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 N₂ stream at a flow rate of 0.15 L/min to yield CFs.

3.2.3 Characterizations

TMA measurement, determination of mechanical properties of CFs, PEG content measurement, and observation of fiber morphology were performed, according to the method as described in chapter 2 (2.2.8 Characterization).

Fourier-transform infrared (FTIR) analysis of the PEG-lignin fibers and chemically cured fibers were conducted to determine the changes in functional groups, using the diffuse reflectance FTIR (BIO-RAD FTS-50A FTIR) method. The dried samples were mixed with fine powder of KBr at the ratios of 5~10 %. Numbers of scan was 128, with a spectral resolution of 2 cm⁻¹.

X-ray diffraction (XRD) of PEG-lignin based CFs and chemically cured CFs were carried out on a Rigaku RINT2000 X-ray diffractometer (Tokyo, Japan), after pulverization of CFs. Data were collected with a scan speed of 0.5 degree/min and a scan step of 0.02 degree at 40kV and 200 mA in the 2 theta (θ) range from 5 to 60 degrees, using Cu-Kα radiation.

3.3 Results and discussion

3.3.1 Blends of PEG-lignin powder and HMTA

PEG-lignin was isolated from cedar wood chips, and milled into fine powder. After mixing this powder manually with varying amounts of HMTA, the blends were subjected to melt-spinning to obtain partially cross-linked fibers. However, no fiber was obtained even at the smallest addition (1 % on PEG-lignin) of HMTA. PEG-lignin seemed to have already converted to an infusible material by crosslinking reaction on the heating for melt-spinning. This conversion was also confirmed by TMA measurement of the blends, by which the thermal properties of powdered lignin can be analyzed (Kubo *et al.* 1996).

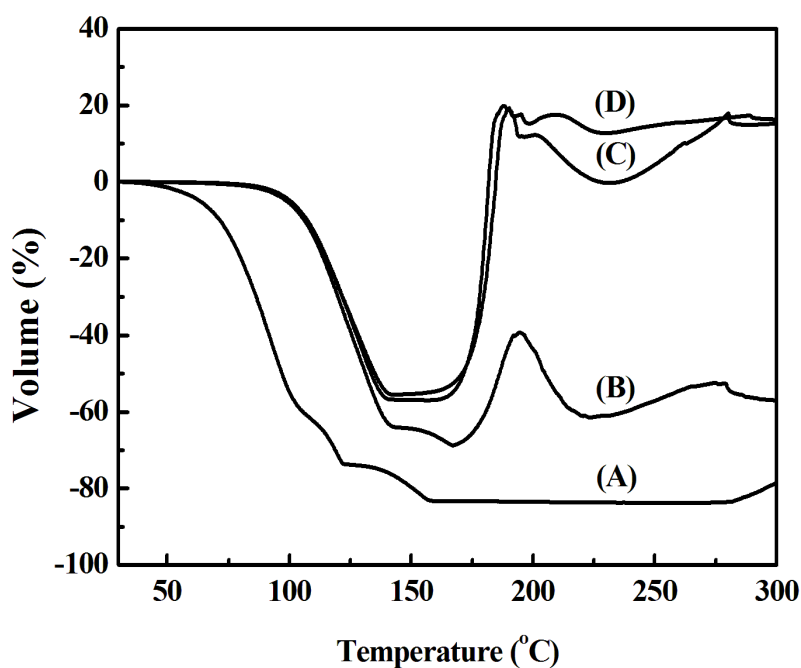


Fig. 3-1. TMA of PEG-lignin powder blended with HMTA of various contents. (A), 0 %, (B), 1 %, (C), 2 %, (D), 5 %, respectively.

As shown in Fig. 3-1 (A), the TMA curve of PEG-lignin powder without HMTA showed two transition points at 79 °C and 141 °C, corresponding to its T_g

and T_f , respectively. By the addition of 1% HMTA to PEG-lignin (Fig. 3-1 (B)), T_g was shifted to 102 °C, and the blend still showed the second transition point (T_f), indicating it exhibits thermal fusibility. However, this lignin expanded at the spinning temperature of about 170 °C, probably due to the thermal decomposition, as observed in softwood kraft lignin (Kubo *et al.* 1996). This result indicated that melt-spinning was practically impossible. Even with further increase in HMTA charge (Figs. 3-1 (C) and (D)), T_g was almost identical to that at 1 % charge of HMTA, but no T_f was observed in their TMA profiles. These results suggested that PEG-lignin was cross-linked easily by using HMTA to be converted to infusible material.

3.3.2 Chemical curing of PEG-fibers with HMTA

To obtain infusible fibers, PEG-lignin fibers prepared by melt-spinning without HMTA addition were immersed in an aqueous HMTA solution at the concentrations ranging from 5 g/L to 60 g/L, and then heated at the temperature of 60, 80, and 100 °C for 1 h. The resulting fibers were observed to have almost the same morphology as the original fibers, except for the fibers treated at 100 °C (Fig. 3-2). The fibrous morphology was changed at the treatment temperature of 100 °C, because the temperature was about 20 °C higher than the T_g of PEG-lignin fibers. The treated fibers were, in turn, subjected to oxidative thermostabilization. Unfortunately, all the oxidatively thermostabilized fibers melted and adhered to each other at a heating rate of 0.5 °C/min (Fig. 3-3), indicating that the curing reaction was insufficient. These results may be caused by the limited amount of cross-linkages among lignin molecules with formaldehyde released from HMTA (Blazzevic *et al.* 1979; Wang *et al.* 2007).

The decomposition of HMTA to generate formaldehyde and ammonia is strongly dependent on the pH in the reaction medium (Swift *et al.* 2003); the lower the pH is, the more formaldehyde is generated. Therefore, the chemical curing of PEG-lignin fibers with several amounts of HMTA was attempted in aqueous HCl solutions at various concentrations of 0.1 to 3 M, because defects would probably appear at much stronger acid concentration, just like chemically thermostabilized fibers reported previously (Chapter 2).

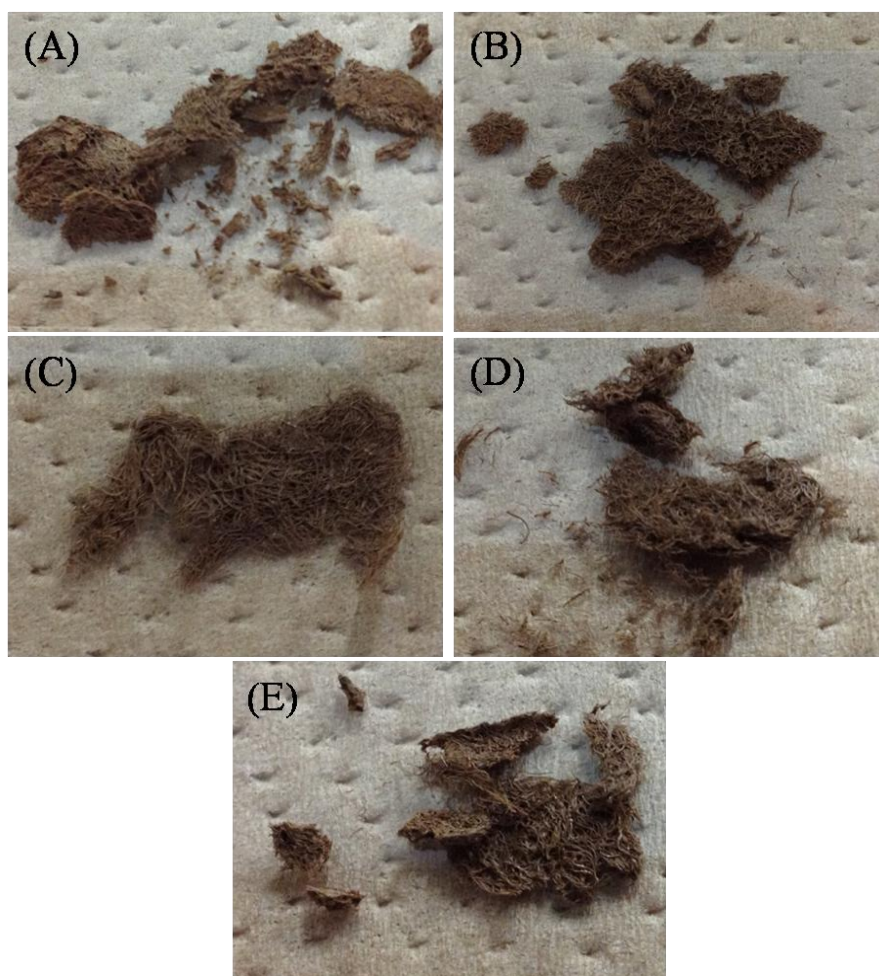


Fig. 3-2. Chemically cured fibers treated with HMTA aqueous solution of (A), 5 g/L; (B), 10 g/L; (C), 20 g/L; (D), 40 g/L; and (E), 60 g/L at 100 °C for 1 h, respectively.

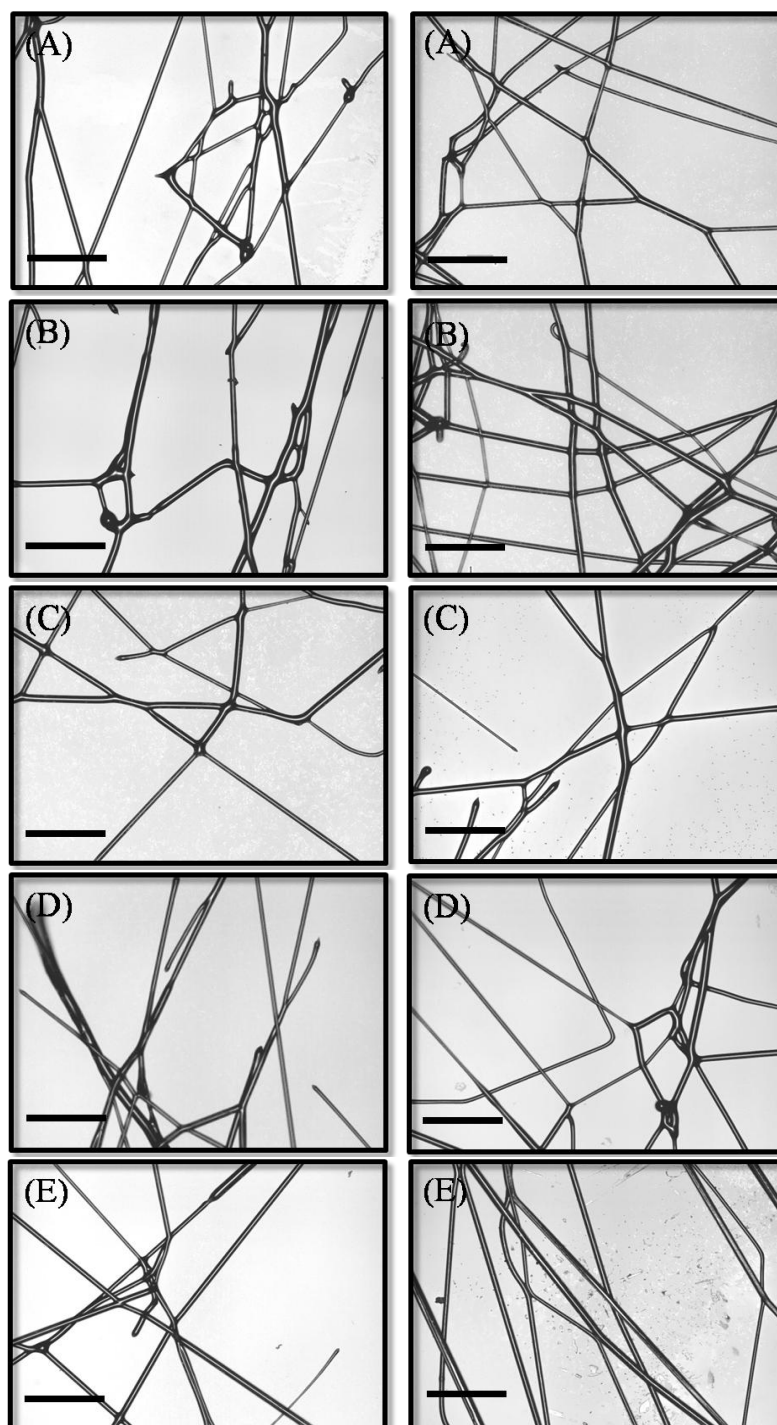


Fig. 3-3. Microscopic images of chemically cured fibers after oxidative thermostabilization with the heating rates of 0.5 °C/min. Chemically cured fibers were derived from PEG-lignin fibers treated with HMTA aqueous solution of (A), 5 g/L; (B), 10 g/L; (C), 20 g/L; (D), 40 g/L; and (E), 60 g/L at 60 °C (Left) and 80 °C (Right) for 1 h, respectively. (Black bar =300 μ m).

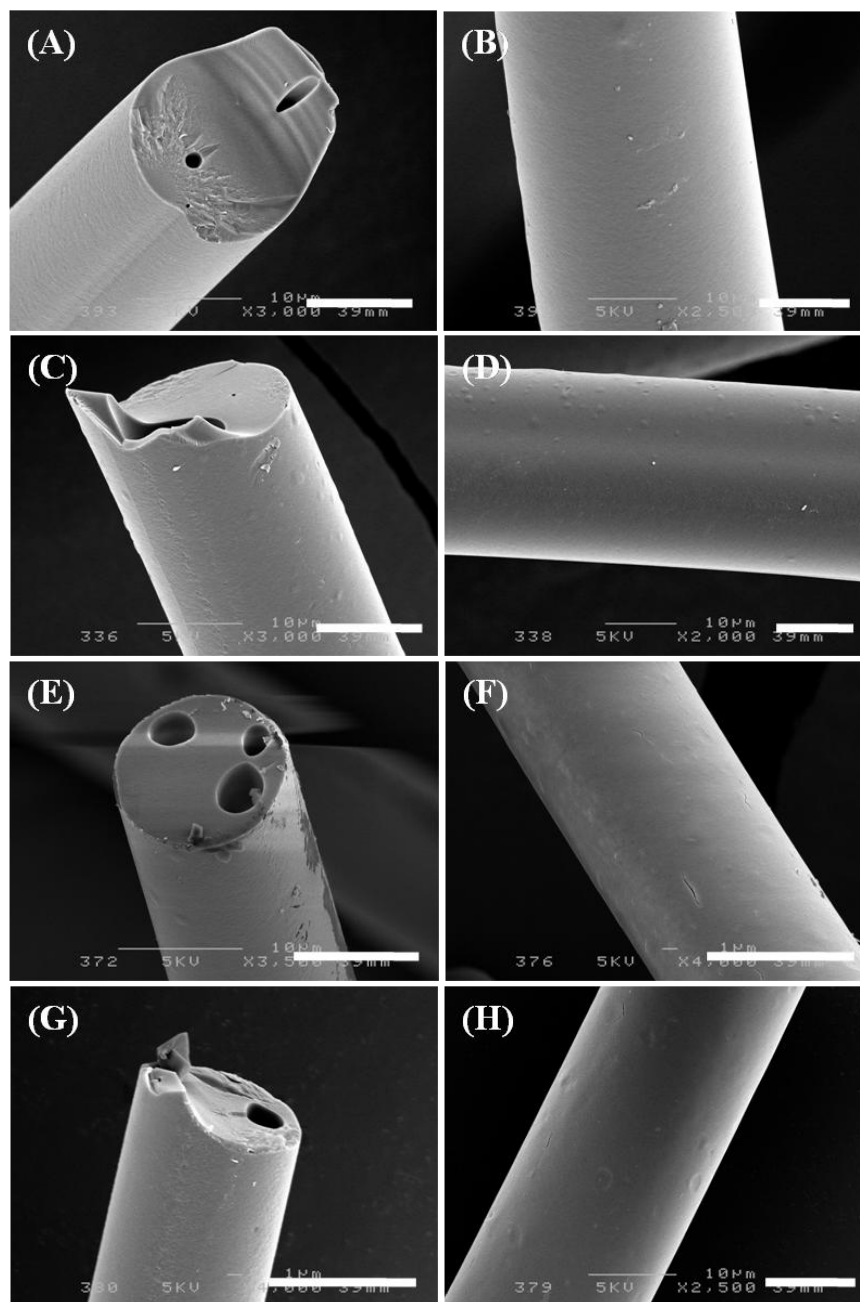


Fig. 3-4. SEM morphology of chemically cured fibers treated with the mixture system containing HCl and HMTA of (A) and (B), 0.1 M and 20 g/L; (C) and (D), 2 M and 40 g/L; (E) and (F), 3 M and 40 g/L; (G) and (H), 3 M and 60 g/L at 85 °C for 1 h, respectively. (White bar = 10 μ m).

3.3.3 Chemical curing of PEG-fibers with HMTA and HCl aqueous solution

The chemical curing reactions for PEG-fibers were performed with the

mixed solution of HCl and HMTA at the concentrations of 0.1 M and 20 g/L (the abbreviated name of condition; 0.1, 20), 2 M and 40 g/L (2, 40), 3 M and 40 g/L (3, 40), 3 M and 60 g/L (3, 60), respectively. All the resultant fibers kept the fibrous shape and a smooth surface, as shown in Fig. 3-4. They still showed T_g , but did not expand over 200 °C from the TMA profiles of these cured fibers (Fig. 3-5), indicating that the fiber morphology would not be changed upon heating. These results implied that PEG-fibers were converted into relatively thermally stable fibers through the curing reaction, probably due the formation of cross-linkage between lignin macromolecules by HMTA treatment. Existing of such cross-linking structure through methylene bridges can be confirmed by FTIR measurement (Ma and Zhao 2008).

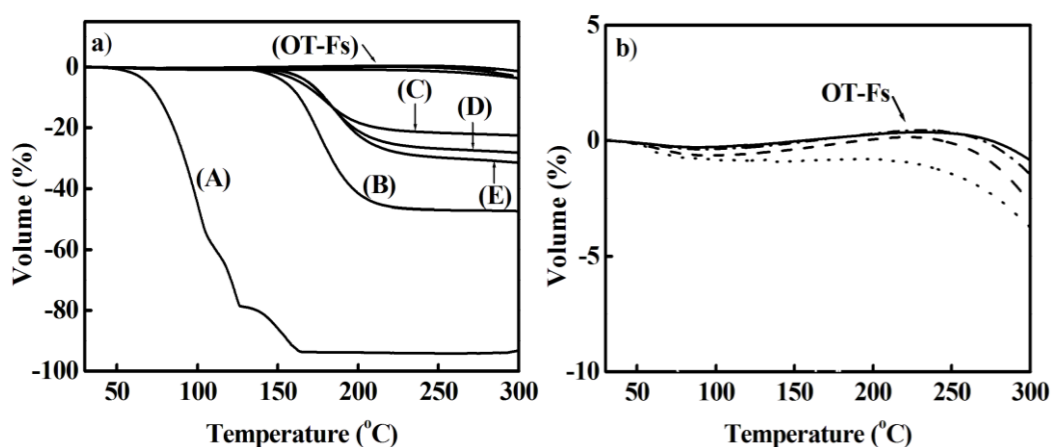


Fig. 3-5. a) TMA profiles for PEG-lignin fibers and their thermostabilized fibers. (A), PEG-lignin fibers; (B), chemically cured fibers with (0.1, 20); (C), with (2, 40); (D), with (3, 40); (E), with (3, 60); (OT-Fs), oxidatively thermostabilized fibers derived from chemically cured fibers (B), (C), (D), and (E), respectively. b) Expanded TMA of OT-Fs derived from chemically cured fibers (B), (—); (C), (·····); (D), (---); and (E), (- · - · -), respectively.

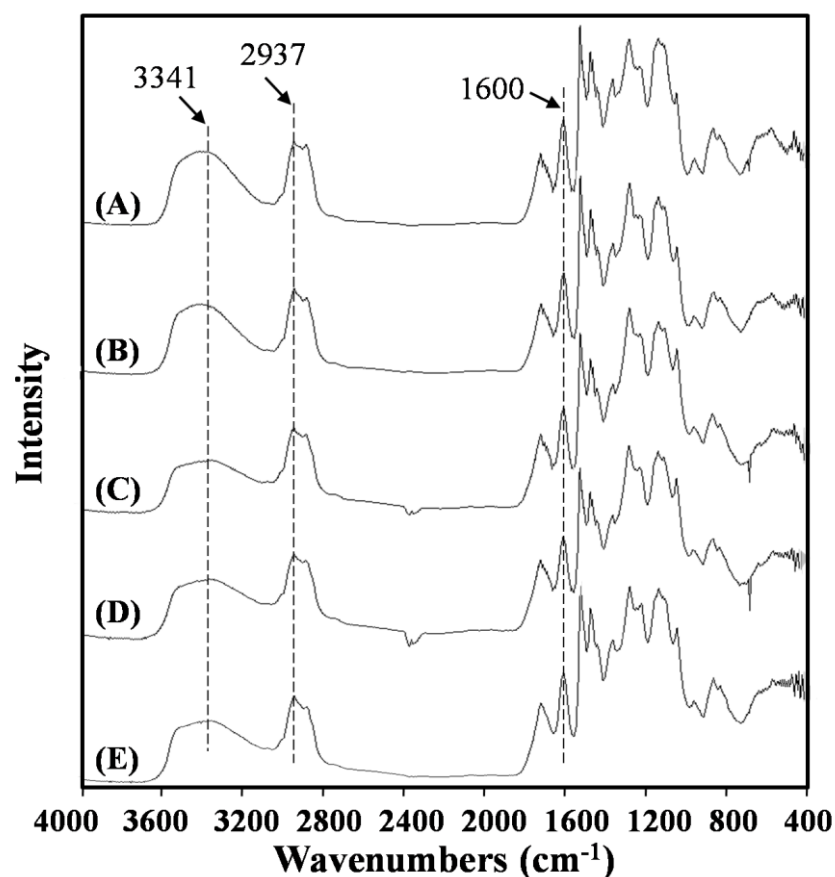


Fig. 3-6. FTIR spectra of PEG-lignin fibers (A) and chemically cured fibers treated under various conditions (B) (0.1 M, 20 g/L), (C) (2 M, 40 g/L), (D) (3 M, 40 g/L) and (E) (3 M, 60 g/L), respectively.

Fig. 3-6 illustrates the FTIR spectra of PEG-lignin fibers and chemically cured fibers. A relative peak intensity of all chemically cured fibers (Fig. 3-6 (B)-(E)) at 2937 cm^{-1} was likely to become stronger than that of the original PEG-lignin fibers (Fig. 3-6 (A)). The ratio of intensity at 2937 cm^{-1} to that at 3341 cm^{-1} (O-H stretching vibration) or that at 1600 cm^{-1} (C=C ring stretching vibration) clearly showed the increase in the relative intensity at 2937 cm^{-1} (Table 3-1), indicating that increasing number of methylene groups was generated by the curing with HMTA under stronger acidic condition and it acted as methylene

bridge for cross-linking (Silverstein *et al.* 2005).

Table 3-1 also shows that PEG content in the cured fibers was slightly but gradually decreased, with an increase in the concentration of acid used for curing. This result may be caused either by the release of PEG by HCl treatment, or by the introduction of methylene group, or both. Accordingly, the cured fibers treated with 3 M of HCl and 60 g/L of HMTA, which has the most amount of methylene group and the lowest PEG content, would probably be converted into the fibers with the densest cross-linking structure and the lowest flexibility.

Table 3-1. Thermal behaviors, FTIR peak intensity ratio and PEG content of PEG-lignin fibers and chemically cured fibers, respectively.

Samples ¹	T_g (°C)	FTIR peak intensity ratio		PEG content (%)	Heating rate ² (°C/min)
		(I_{2937} / I_{3341})	(I_{2937} / I_{1600})		
PEG-lignin fibers	79	1.12	0.789	40.56	< 0.1
CC-F (0.1, 20)	155	1.19	0.796	39.11	0.5
CC-F (2, 40)	158	1.51	0.824	37.50	1.5
CC-F (3, 40)	161	1.38	0.819	37.45	1.5
CC-F (3, 60)	165	1.41	0.850	37.23	2.0

¹ CC-F (0.1, 20), (2, 40), (3, 40), and (3, 60) denote chemically cured fibers treated with various concentration of HCl and HMTA of (0.1 M, 20 g/L), (2 M, 40 g/L), (3 M, 40 g/L), (3 M, 60 g/L), respectively.

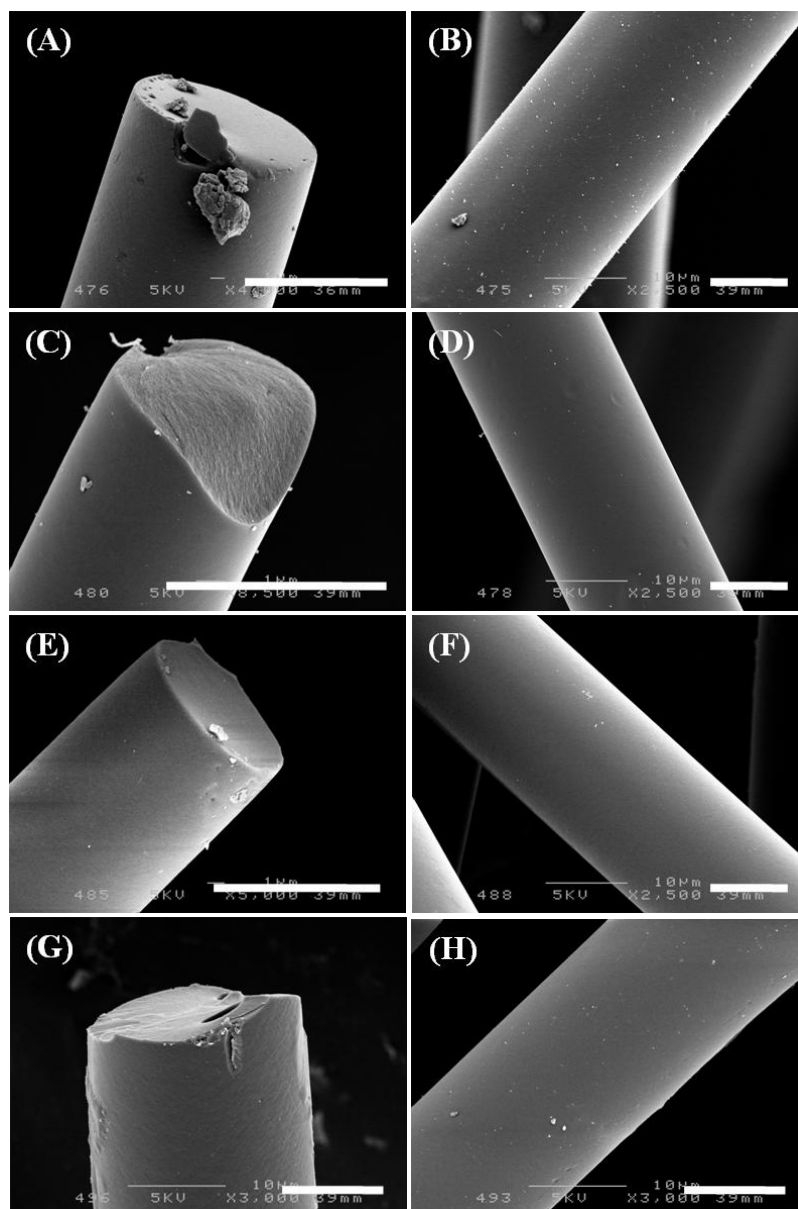


Fig. 3-7. SEM morphology of oxidative thermostabilized fibers derived from chemically cured fibers treated with the mixture system containing HCl and HMTA of (0.1 M, 20 g/L), (2 M, 40 g/L), (3 M, 40 g/L), (3 M, 60 g/L) by heating in air atmosphere from room temperature to 250 °C with the various heating rates of (A) and (B), 0.5 °C/min; (C) and (D), 1.5 °C/min; (E) and (F), 1.5 °C/min; (G) and (H), 2 °C/min, respectively. (White bar = 10 μm).

3.3.4 Oxidative thermostabilization of chemically cured fibers

The existence of T_g and the observed changes in volume in TMA curves of chemically cured fibers (Fig. 3-5) implied that the fibers were not completely infusible. To prevent the fusion of individual fibers upon further carbonization, the oxidative thermostabilization were further attempted. Generally, heating rate is considered to be one of the most significant factors affecting thermal stability of fibers during oxidative thermostabilization (Brodin *et al.* 2012), and production cost for CFs. In chapter 2, PEG-lignin fibers was able to be converted to infusible fibers at low heating rates (< 0.1 °C/min), leading to an infeasible industrial process.

The highest heating rate to cure fibers without losing the fibrous morphology were sought out, by increasing heating rate at an interval of 0.5 °C/min. Results are shown in the last column in Table 3-1. As seen in the table, the highest heating rate was increased with an increase in the concentration of HCl and HMTA in the curing process. Accordingly, the PEG-fibers thermostabilized by the curing with 3 M of HCl and 60 g/L of HMTA (3, 60) followed by oxidative thermostabilization under air atmosphere, showed the highest heating rate of the 2 °C/min. As expected, the resultant fibers had smooth surface without any defect (Fig. 3-7). In addition, TMA profiles also indicated that all the fibers prepared by the curing reaction, followed by oxidative thermostabilization, were converted to completely infusible fibers without showing T_g (OT-Fs in Fig. 3-5).

3.3.5 Carbonization

The completely thermostabilized fibers were, in turn, carbonized by heating the fibers from room temperature to 1000 °C at a heating rate of 3 °C/min under a stream of nitrogen, and then the temperature was maintained at 1000 °C

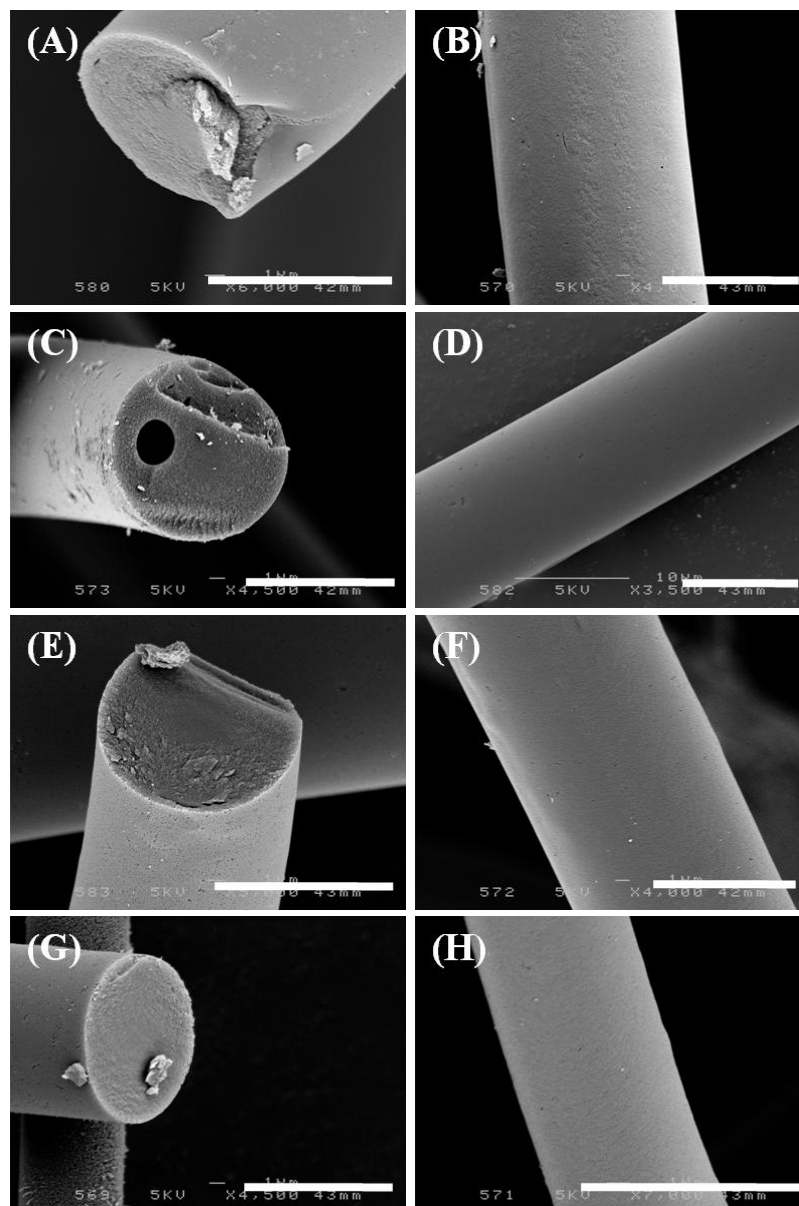


Fig. 3-8. SEM morphology of CFs derived from oxidative thermostabilized fibers which were obtained from PEG-lignin fibers by chemical curing and oxidative thermostabilization under different conditions: (A) and (B), (0.1, 20), 0.5 °C/min; (C) and (D), (2, 40), 1.5 °C/min; (E) and (F), (3, 40), 1.5 °C/min; (G) and (H), (3, 60), 2 °C/min, respectively. (White bar = 10 μm).

for 1 h. As shown in Fig. 3-8, no obvious defect such as split and flabby structures appeared on the surface of CF, which is significantly different from CFs prepared

from chemically thermostabilized fibers (Fig. 2-11). Positive changes in fiber morphology (free of defect) were mainly attributed to less PEG moieties released, and also condensation reaction between lignin molecules through methylene groups during chemical curing process.

Table 3-2. Mechanical properties of CFs based on different precursors.

Samples ¹	Diameter (μm)	Tensile strength (MPa)	Tensile modules (GPa)	Elongation (%)
CFs (0.1, 20)	8.9 ± 1.3	590 ± 63	41.7 ± 9.1	1.47 ± 0.32
CFs (2, 40)	8.4 ± 0.8	620 ± 47	41.9 ± 7.9	1.52 ± 0.25
CFs (3, 40)	8.6 ± 0.9	653 ± 90	47.2 ± 9.4	1.42 ± 0.23
CFs (3, 60)	8.2 ± 1.0	695 ± 124	47.3 ± 11.5	1.51 ± 0.25
PEG-lignin CFs	10.4 ± 1.3	457 ± 188	26.2 ± 13.3	2.11 ± 1.07
HWKL/PET (95/5)	31.0 ± 5.0	669	84.0	1.10

¹ CFs (0.1, 20), (2, 40), (3, 40) and (3, 60) denote carbon fibers from chemically cured fibers (0.1 M HCl, 20 g/L HMTA), (2 M HCl, 40 g/L HMTA), (3 M HCl, 40 g/L HMTA), (3 M HCl, 60 g/L HMTA), respectively. The mechanical properties of PEG-lignin CFs and HWKL/PET (75/25) are derived from literatures (Lin *et al.* 2012; Kadla and Kubo 2005).

Table 3-2 shows the mechanical properties of the CFs from both the chemically cured fibers prepared in this study and the chemically thermostabilized fibers reported in chapter 2. All the CFs prepared in this study showed much stronger tensile strength and modulus than the previously prepared CFs.

Especially CFs derived from chemically cured fibers treated with 3 M of HCl and 60 g/L of HMTA (3, 60) showed 1.5 times greater tensile strength than that of the previous CFs, and its value is almost comparable to that of CFs prepared from hardwood kraft lignin blended with 25 % PET, which was considered as the strongest lignin-based CFs among the CFs reported so far (Kadla and Kubo 2005).

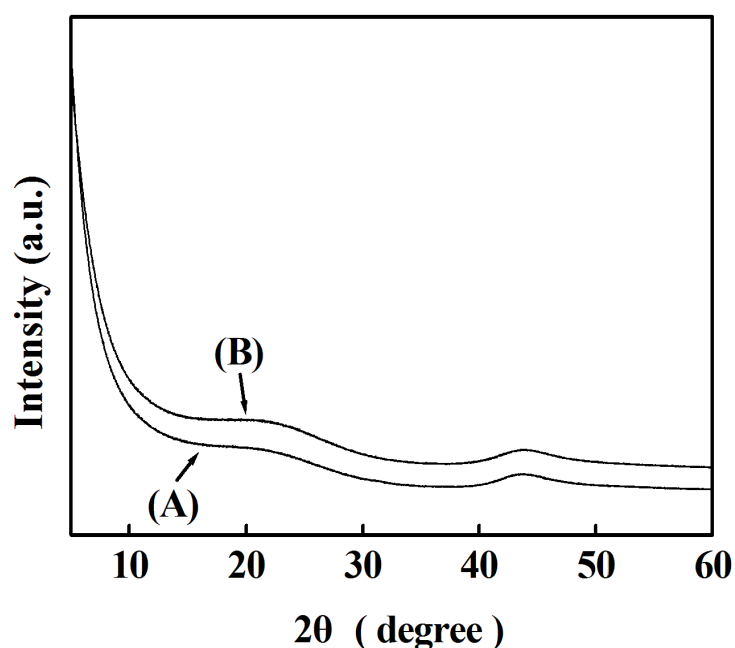


Fig. 3-9. XRD of PEG-lignin based carbon fibers (CFs) prepared from the cured and oxidatively thermostabilized fibers (A), and CFs from chemically thermostabilized fibers (B).

The XRD profiles of CFs derived from chemically cured fibers (3, 60) and chemically thermostabilized fibers with Cu-K α irradiation are shown in Fig. 3-9. Although a weak broad peak was observed at around $2\theta = 44^\circ$ that nearly corresponds to the diffraction of turbostratic carbon (Kubo *et al.* 2003), there was no clear peak at about 22° in both diffractograms. This result suggests there is no

development of graphite structure developed during carbonization process. Consequently, the enhancement of the tensile strength for CFs prepared from the chemically cured fibers is not attributed to the development of graphite structure, but to the defect-free, smooth surface of the CFs.

3.4 Summary

Hexamethylenetetramine (HMTA) was found to act as an effective cross-linker for the chemical curing of PEG-lignin fibers. HMTA in aqueous HCl solution accelerated the curing for PEG-lignin. PEG-lignin fibers were successfully converted to completely thermostabilized fibers without defect by the chemical curing with HMTA in aqueous HCl solution, followed by the oxidative thermostabilization under air atmosphere. The oxidative thermostabilization of the fibers chemically cured with a mixed solution of 3 M of HCl aq. and 60 g/L of HMTA, was carried out at a heating rate of 2 °C/min. These results suggested that all thermostabilization process was completed for 3 h. The resultant defect-free CFs showed the highest tensile strength of about 700 MPa, which was comparable to the strongest lignin-based CFs previously reported.

CHAPTER 4

General discussion

This study has brought a new insight that high-performance CFs are able to be produced from softwood-derived lignin, which, compared to hardwood-derived lignin, was considered to be an unsuitable raw material for CF production before. The softwood-derived lignin was first necessary to be modified, prior to melt-spinning process. An acid-catalyzed cooking process with PEG employed in this study demonstrated that softwood PEG-lignin isolated from Japanese cedar wood was easily converted into lignin-based fibers without any other modification. The fibers were further modified to fabricate CFs successfully, by stabilization and carbonization processes. Here is a detailed discussion about some important findings obtained in this study.

In chapter 2, a novel solvolysis pulping of cedar wood chips with a mixture of PEG 400 and sulfuric acid was applied to obtain softwood PEG-lignin, which was found to be thermally fusible and show good spinnability. The powderous PEG-lignin was easily transformed into the corresponding fibers with a diameter of 23 to 38 μm by conventional melt-spinning. The lignin fibers were subjected to oxidative thermostabilization under an air atmosphere or a stream of oxygen to obtain infusible fibers, but all the oxidatively thermostabilized fibers melted and adhered to each other even at the slowest heating rate of 0.1 $^{\circ}\text{C}/\text{min}$ (> 2 days). Thereby, an alternative thermostabilization process, termed as “chemical thermostabilization” was developed to replace the general oxidative thermostabilization. When PEG-lignin fibers were immersed in a concentrated HCl aqueous solution (6 M) at 100 $^{\circ}\text{C}$ for 2 h, PEG moieties were partially

liberated from the lignin fibers by the cleavage of ether bond in between, resulting in the conversion of fusible fibers to infusible fibers. However, several defects were generated on the surface of fibers by the treatment, and also remained in the resulting CFs, which brought low tensile strength of 450 MPa. When the resultant CFs were further subjected to steam activation at 900 °C for a short period (30 min), ACFs with a specific BET surface area of larger than 2000 m²/g were easily obtained. By prolonged activation time to 90 min, the BET surface area reached up to 3060 m²/g. Thus, high-performance ACF were successfully obtained.

In chapter 3, two types of chemical curing reactions for the fibers with HMTA as a curing reagent were carried out to prepare defect-free lignin-fibers. The first trial was that PEG-lignin powder was mixed with HMTA, and then the mixture was subjected to melt-spinning. However, PEG-lignin seemed to be converted to an infusible material on the spot by crosslinking reaction by the heating process, and no fiber was obtained even at the smallest addition (1 % on PEG-lignin) of HMTA. As a second trial, the PEG-lignin fibers were immersed and heated in aqueous HMTA solution, and then the resultant fibers were subjected to the general oxidative thermostabilization. As a result, all the oxidatively thermostabilized fibers melted and adhered to each other, and could not be converted to infusible ones even at a heating rate of 0.5 °C/min.

Finally, the chemical curing of PEG-lignin fibers were carried out by immersing the fibers in an aqueous mixed solution of HMTA (60 g/L) and hydrochloric acid (3 M) at 85 °C for 1 h, followed by oxidative thermostabilization at a heating rate of 2 °C/min. As expected, no defect was observed on the surface of the stabilized fibers and the corresponding CFs. The tensile strength of the CFs was increased to around 700 MPa, which was almost

equal to that of the strongest lignin-based CFs ever reported before.

According to these results obtained from this study, I will conclude this study with a brief background.

It had been a general thought that softwood lignin was quite difficult to be transformed into fibers due to its more condensed structures than hardwood lignin, until the pre-treatment for softwood lignin was performed. But in the current study, softwood PEG-lignin prepared from solvolysis pulping with PEG 400, was able to be directly melt-spun into fibers. The good thermal spinnability of PEG-lignin would probably be caused by the introduced PEG moiety which may not only inhibits the formation of intra- and/or intermolecular hydrogen bonding of lignin, but also acts as an internal plasticizer of the lignin.

To obtain infusible fibers for further carbonization at high temperature, it is necessary to conduct the conversion of fusible PEG-lignin based fibers into infusible fibers. Unexceptedly, the general oxidative thermostabilization under an air atmosphere or an oxygen stream was found to be unsuitable for the conversion of PEG-lignin fibers because it was found a time-consuming process. Thereby, new methods of chemical thermostabilization or a combination of chemical curing and oxidative thermostablization were developed, in which only a very short period (within 3 h) was required for the conversion of PEG-lignin fibers to infusible fibers.

During chemical thermostabilization, ether bonding between lignin and PEG was promoted by protonizing action of concentrated HCl, followed by the cleavage of the ether bonding, resulting in the formation of a significant amount of defects, including splits and flabby structure, on the surface and in the interior part of lignin fibers. The defects remained in CFs, leading to relatively low

mechanical properties which were not as high as those of other types of lignin-based CFs. However, these defects on the surface of CF were assumed to be used as advantageous reaction site for production of ACF. Large specific surface area of the resultant ACF was easily obtained, indicating its usefulness as a potential precursor of ACF.

On the other hand, I assumed that when defect-free thermostabilized fibers are obtained, CFs with high mechanical strength would be prepared. Thus, PEG-lignin fibers were successfully converted to defect-free, completely thermostabilized fibers by chemical curing, followed by the oxidative thermostabilization under an air atmosphere. Improvement of surface morphology was achieved by avoiding the formation of the defects on fibers, by the reduction of PEG moiety as well as the formation of cross-linkages among lignin molecular structures. The infusible defect-free fibers were, in turn, successfully transformed into CFs with high mechanical properties, which were comparable to those of the strongest lignin-based CFs previously produced.

Thus, I developed a novel process for the manufacture of CFs with relatively high tensile strength from Japanese softwood. This current research, therefore, contributes to the effective conversion of a by-product from the pulping of softwood to valuable materials, leading to viable biorefinery of woody biomass.

REFERENCES

- Ago, M., Okajima, K., Jakes, J.E., Park, S., Rojas, O.J. (2012a). Lignin-based electrospun nanofibers reinforced with cellulose nanocrystals. *Biomacromolecules*. 13: 918-926.
- Ago, M., Jakes, J.E., Johansson, L.S., Park, S., Rojas, O.J. (2012b). Interfacial properties of lignin-based electrospun nanofibers and films reinforced with cellulose nanocrystals. *Appl. Mater. Interfaces*. 4: 6849-6856.
- Alma, M. K., Kelley, S. S. (2000). Thermal stability of novolak-type thermosettings made by the condensation of bark and phenol. *Polym. Degrad. Stabil.* 68: 413-418.
- Azargohar, R., Dalai, A.K. (2008). Steam and KOH activation of biochar: Experimental and modeling studies. *Micropor. Mesopor. Mat.* 110: 413-421.
- Bahl, O.P., Shen, Z., Lavin, J.G., Ross, R.A. (1998). Manufacture of Carbon Fibers, In: *Carbon Fibers*, Donnet, J.-B., Wang, T.K., Peng, J.C.M., and Reboulliat, S. (ed.), Marcel Dekker: New York, 1-83.
- Baker, D.A., Gallego, N.C., Baker, F.S. (2012). On the characterization and spinning of an organic-purified lignin toward the manufacture of low-cost carbon fiber. *J. Appl. Polym. Sci.* 124: 227-234.
- Bengisu, M., Yilmaz, E. (2002). Oxidation and pyrolysis of chitosan as a route for carbon fiber derivation. *Carbohydr. Polym.* 50: 165-175.
- Blazzevic, N., Kolbah, D., Belin, B., Sunjic, V., Kajfez, F. (1979). Hexamethylenetetramine, A versatile reagent in organic synthesis. *Synthesis-stuttgart*. 03: 161-176.
- Bozell, J.J, Moens, L., Elliott, D.C., Wang, Y., Neuenschwander, G.G., Fitzpatrick,

- S.W. et al. (2000). Production of levulinic acid and use as a platform chemical for derived products. *Resour. Conserv. Recy.* 28: 227-239.
- Braun, J. L., Holtman, K. M., Kadla, J. F. (2005). Lignin-based CF: Oxidative thermostabilization of kraft lignin. *Carbon.* 43(2): 385-394.
- Brodin, I., Ernstsson, M., Gellerstedt, G., Sjöholm, E. (2012). Oxidative stabilization of kraft lignin for carbon fibre production. *Holzforschung.* 66: 141-147.
- Choi, M. H., Chung, I. J., Lee, J. D. (2000). Morphology and curing behaviors of phenolic resin-layered silicate nanocomposites prepared by melt intercalation. *Chem. Mater.* 12(10): 2977-2983.
- Christina, C., Small, Z. H., Ulrich, A.C. (2012). Preparation and characterization of activated carbon from oil sands coke. *Fuel.* 92: 69-76.
- Dallmeyer, I., Ko, F., Kadla, J.F. (2010). Electrospinning of technical lignins for the production of fibrous networks. *J. Wood Chem. Technol.* 30: 315-329.
- Dence, C. W. (1992). *Methods in Lignin Chemistry.* Lin, S.Y., Dence, C.W. (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.
- Drbohlav, J., Stevenson, W.T.K. (1995). The oxidative stabilization and carbonization of a synthetic mesophase Pitch, Part I: The Oxidative stabilization process. *Carbon.* 33(5): 693-711.
- Ek, M., Gellerstedt, G., 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.
- Frank, E., Hermanutz, F., Buchmeiser, M.R. (2012). Carbon Fibers: Precursors,

- manufacturing, and properties. *Macromol. Mater. Eng.* 297: 493-501.
- Foston, M., Nunnery, G. A., Meng, X. Z., Sun, Q. N., Baker, F. S., Ragauskas, A. (2013). NMR a critical tool to study the production of carbon fiber from lignin. *Carbon*. 52: 65-73.
- Gao, G.Z., Dallmeyer, J.I., Kadla, J.F. (2012). Synthesis of Lignin Nanofibers with Ionic-Responsive Shells: Water-Expandable Lignin-based Nanofibrous Mats. *Biomacromolecules*. 13: 3602-3610.
- Gosselink, R.J.A., DeJong, E., Guran, B., Abacherli, A. (2004). Coordination network for lignin—standardization, production and applications adapted to market requirements. *Ind. Crops Prod.* 20: 121-129.
- Homma, H., Kubo, S., Yamada, T., Matsushita, Y., Uraki, Y. (2008). Preparation and characterization of amphiphilic lignin derivatives as surfactants. *J. Wood Chem. Technol.* 28(4): 270-282.
- Horikiri, S., Iseki, J., Minobe, M. (1978). Process for production of carbon fiber. *US Pat.* 4070446.
- Huang, X.S. (2009). Fabrication and properties of carbon fibers. *Materials*. 2: 2369-2403.
- Inagaki, M. (2000). Old but New Materials: “Carbons”, In: *New Carbon: Control of Structure and Functions*. Inagaki, M. (ed.), Elsevier Oxford, 1-29.
- Kadla, J.F., Kubo, S. (2004). Lignin-based polymer blends: analysis of intermolecular interaction in lignin-synthetic polymer blends. *Composites: Part A*. 35: 395-400.
- Kadla, J.F., Kubo, S. (2005). Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties. *J. Polym. Environ.* 13(2): 97-104.
- Kadla, J.F., Kubo, S., Venditti, R.A., Gilbert, R.D. (2002). Novel hollow core

- fibers prepared from lignin polypropylene blends. *J. Appl. Polym. Sci.* 85: 1353-1355.
- Kadla, J. F., Kubo, S., Venditti, R. A., Gilbert, R. D., Compere, A. L., Griffith, W. (2002). Lignin-based carbon fiber for composite fiber applications. *Carbon*. 40(15): 2913-2920.
- Kishimoto, T., Uraki, Y., Ubukata, M. (2006). Chemical synthesis of β -O-4 type artificial lignin. *Org. Biomol. Chem.* 4: 1343-1347.
- Kubo, S., Kadla, J.F. (2004). Poly(ethylene Oxide)/organosolv lignin blends: relationship between thermal properties, chemical structure, and blend behavior. *Macromolecules*. 37(18): 6904-6911.
- Kubo, S., Kadla, J.F. (2005). Kraft lignin/poly(ethylene oxide) blends: Effect of lignin structure on miscibility and hydrogen bonding. *J. Appl. Polym. Sci.* 98: 1437-1444.
- Kubo, S., Kadla, J.F. (2005). Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties. *J. Polym. Environ.* 13(2): 97-105.
- Kubo, S., Kadla, J.F. (2006). Effect of poly(ethylene oxide) molecular mass on miscibility and hydrogen bonding with lignin. *Holzforschung*. 60: 245-252.
- Kubo, S., Uraki, Y., Sano, Y. (1996). Thermomechanical analysis of isolated lignins. *Holzforschung*. 50(2): 144-150.
- Kubo, S., Uraki, Y., Sano, Y. (1998). Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping. *Carbon*. 36(7-8): 1119-1124.
- Kubo, S., Uraki, Y., Sano, Y. (2003). Catalytic graphitization of hardwood acetic acid lignin with nickel acetate. *J. Wood Sci.* 49: 188-192.
- Kubo, S., Yamada, T., Hashida, K., 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., Tamura, Y. (1999). Species effects on wood-liquefaction in polyhydric alcohols. *Holzforschung*. 53(6): 617-622.
- Kurimoto, Y., Shirakawa, K., Yoshioka, M., 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.
- Luo, J., Genco, J., Cole, B., Fort, R. (2012). Lignin recovered from the near-neutral hemicellulose extraction process as a precursor for carbon fiber. *BioResources*. 6(4): 4566-4593.
- Lv, Y.G., Wu, D., Zha, Q.F., Liu, L., Yang, C.L. (1998). Skin-core structure in mesophase pitch-based carbon fibers: Causes and prevention. *Carbon*. 36(12): 1719-1724.
- Lysenko, A.A., Lysenko, V.A., Astashkina, O.V., Gladunova, O.I. (2011). Resource-conserving carbon fiber technologies. *Fibre Chemistry*. 42: 278-286.
- Mai, C., Milstein, O., Huttermann, A. (2000). Chemoenzymatical grafting of acrylamide onto lignin. *J. Biotechnol.* 79(2): 173-183.
- Majibur, M., Khan, R., Gotoh, Y., Morikawa, H., Miura, M., Fujimori, Y., Nagura, M. (2007). Carbon fiber from natural biopolymer *Bombyx mori* silk fibroin with iodine treatment. *Carbon*. 45:1035-1042.
- Martin, C.H. and Jones Prather, K.L. (2009). High-titer production of monomeric hydroxyvalerates from levulinic acid in *Pseudomonas putida*. *J. Biotechnol.* 139: 61-67.

- Matsumoto, T. and Mochida, I. (1992). A Structural study on oxidative stabilization of mesophase pitch fibers derived from coaltar. *Carbon*. 30(7): 1041-1046.
- Mavinkurve, A., Visser, S., Pennings, A.J. (1995). An initial evaluation of poly(vinylacetylene) as a carbon-fiber precursor. *Carbon*. 33: 757-761.
- Ma, X. J. and Zhao, G. J. (2008). Structure and performance of fibers prepared from liquefied wood in phenol. *Fiber. Polym.* 9(4): 405-409.
- Ma, X. J. and Zhao, G. J. (2010). Preparation of carbon fibers from liquefied wood. *Wood Sci. Technol.* 44: 3-11.
- Mohan, D., Pittman, C.U., Steele, P.H. (2006). Single, binary and multicomponent adsorption of copper and cadmium from aqueous solutions on kraft lignin—a biosorbent. *J. Colloid Interf. Sci.* 297(2): 489-504.
- Morgan, P.W. (1946). 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., Hiramatsu, T. (1981). Stabilization of acrylic fibers by sulfur atoms mechanism of stabilization. *Carbon*. 19(1): 11-18.
- Nagasaka, A., Ashitaka, H., Kusuki, Y., Oda, D., Yoshinaga, T. (1978). Process for producing carbon fiber. *US Pat.* 4131644.
- Norberg, I., Nordstrom, Y., Drougge, R., Gellerstedt, G., Sjöholm, E. (2013). A new method for stabilizing softwood kraft lignin fibers for carbon fiber production. *J. Appl. Polym. Sci.* 128(6): 3824-3830.
- Olivares, M., Guzmán, J. A., Natho, A., Saavedra, A. (1988). Kraft lignin utilization in adhesives. *Wood Sci. Technol.* 22: 157-165.
- Okada, K., Yamamoto, N., Kameshima, Y., Yasumori, A. (2003). Porous

- properties of activated carbons from waste newspaper prepared by chemical and physical activation. *J. Colloid Interf. Sci.* 262: 179-193.
- Otani, S., Fukuoka, Y., Igarashi, B., Sasaki, K. (1969). Method for producing carbonized lignin fiber. *US Patent*. 3461082.
- Ouyang, X. P., Ke, L. X., Qiu, X. Q., Guo, Y. X., Pang, Y. X. (2009). Sulfonation of alkali lignin and its potential use in dispersant for cement. *J. Disper. Sci. Technol.* 30(1): 1-6.
- Pearl, I. A. (1967). *The Chemistry of Lignin*. New York: Marcel Dekker, 298-307.
- Pierson, H.O. (1995). Graphite Structure and Properties. In: *Handbook of Carbon, Graphite, Diamonds and Fullerenes: Processing, Properties and Applications*. Inagaki, M. (ed.), William Andrew, 43-69.
- Prauchner, M. J., Pasa, V. M. D., Otani, S., Otani, C. (2005). Biopitch-based general purpose carbon fibers: Processing and properties. *Carbon*. 43(3): 591-597.
- Qin, W. and Kadla, J.F. (2011). Carbon fibers based on pyrolytic lignin. *J. Appl. Polym. Sci.* 126: E203-E212.
- Rodriguez-Reinoso, F., Lopez-Gonzalez, J.D., Berenguer, C. (1982). Activated carbon from almost shells. *Carbon*. 20: 513-518.
- Rozman, H. D., Koay, E. L., Tay, G. S. (2011). Preliminary study on the utilization of lignin as filler in ultra-violet (UV) curable system. *J. Appl. Polym. Sci.* 120(5): 2527-2533.
- Ruiz-Rosas, R., Bedia, J., Lallave, M., Loscertales, I. G., Barrero, A., Rodríguez-Mirasol, J. *et al.* (2010). The production of submicron diameter carbon fibers by the electrospinning of lignin. *Carbon*. 48(3): 696-705.
- Shen, Q. and Zhong, L. (2007). Lignin-based carbon films and controllable pore

- size and properties. *Mat. Sci. Eng. A.* 445-446: 731-735.
- Shimada, M., Hamabe, H., Iida, T., Kawarada, K., Okayama, T. (1999). The properties of activated carbon made from waste newsprint paper. *J. Porous Mat.* 6: 191-196.
- Shimada, M., Iida, T., Kawarada, K., Chiba, Y., Mamoto, T., Okayama, T. (2000). Porous structure of activated carbon prepared from waste newspaper. *J Mater. Cycles. Waste Manag.* 2: 100-108.
- Silverstein, R. M., Webster, F. X., Kiemle, D. J. (2005). Infrared Spectrometry, In: *Spectrometric identification of organic compounds*, Silverstein, R. M., Webster, F. X., Kiemle, D. J. (7th ed.), Hoboken: Wiley, 72-126.
- Sliva, D.E. and Selley, W. (1975). Continuous method for making spinnable polyacetylene solutions convertible to high strength carbon fiber. *US Pat.* 3928516.
- Sudo, K., and Shimizu, K. (1992). A new carbon fiber from lignin. *J. Appl. Polym. Sci.* 44(1): 127-134.
- Sudo, K., Shimizu, K., Nakashima, N., Yokoyama, A. (1993). A new modification method of exploded lignin for the preparation of a carbon fiber precursor. *J. Appl. Polym. Sci.* 48(8): 1485-1491.
- Swift, L. P., Cutts, S. M., Rephaeli, A., Nudelman, A., Phillips, D. R. (2003). Activation of adriamycin by the pH-dependent formaldehyde-releasing prodrug hexamethylenetetramine. *Mol. Cancer Ther.* 2: 189-198.
- Tagawa, T., and Miyata, T. (1997). Size effect on tensile strength of carbon fibers. *Mat. Sci. Eng. A.* 238(2): 336-342.
- Uraki, Y., Kubo, S., Nigo, N., Sano, Y., 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. Chem. Technol.* 30(4): 348-359.

Uraki, Y., Sugiyama, Y., Koda, K., Kubo, S., Kishimoto, T., Kadla, J.F. (2012).

Thermal mobility of β -O-4 type artificial lignin. *Biomacromolecules* 13: 867-872.

Uslu, H., Gok, A., Kirbaslar, S.I. (2009). Phase equilibria of (water + levulinic acid + dibasic esters) ternary systems. *Fluid Phase Equilib.* 282: 20-24.

Vishtal, A., and Kraslawski, A. (2011). Challenges in industrial applications of technical lignin. *BioResources*. 6(3): 3547-3568.

Wang, J. Q., Wang, Y. Z., Qiao, M. H., Xie, S. H., Fan, K. (2007). A novel sol-gel synthetic route to alumina nanofibers via aluminum nitrate and hexamethylenetetramine. *Mater. Lett.* 61: 5074-5077.

Wang, M. C., Yuan, Z. S., Cheng, S. N., Leitch, M., Xu, C. B. C. (2010).

Synthesis of novolac-type phenolic resins using glucose as the substitute for formaldehyde. *J. Appl. Polym. Sci.* 118: 1191-1197.

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

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

Yan, C.Q. and Simms, J.R. (1993). Infrared spectroscopy studies of the petroleum pitch carbon fiber. I: The raw materials, the stabilization, and carbonization processes. *Carbon*. 31(3): 451-459.

Zimovets, I. P. and Imarov, A. K. (1996). Production and utilization of generator gas from lignin. *Chem. Tech. Fuels Oil.* 32(6): 288-289.

ACKNOWLEDGEMENTS

The research summarized in this work has been carried out at the Laboratory of Forest Chemistry, Graduate School of Agriculture, Hokkaido University during the years of 2010–2013 under the Ph.D course of “Special Postgraduate Programme in Bio-Systems Sustainability (SPPBSS)”.

First and foremost I would like to express my deepest appreciation to my supervisor Prof. Yasumitsu Uraki for allowing me the opportunity to work in this lab and for guiding me during three years. It is my honor to be his Ph.D. student. I also want to thank Dr. Keiichi Koda, Dr. Satoshi Kubo, Dr. Tatsuhiko Yamada, Prof. Seiichi Tokura and Dr. Masato Ogawa for all their support, help and valuable discussions during this course.

All the members in the Lab of Forest Chemistry have contributed immensely to my personal and professional time in Hokudai. They are a good source of friendships in my daily life and good advice as well as collaboration in the experiment and seminars.

I would also like to thank all the faculty staff for their help to make my work easier, and my kind friends here for giving me so wonderful days.

Great acknowledgement is given to my family for all their love and encouragement.

At last, I am very grateful to both Hokkaido University and China Scholarship Council for providing tuition fee and living expenses for me during my study period, respectively. I would also thank Consulate-General of the People’s Republic of China in Sapporo for caring of my life in Japan.