Carbon Fibers Derived from Dry-Spinning of Modified Lignin Precursors

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ABSTRACT

Cost and environmental concerns arise from the manufacture of carbon fibers using petroleum-based precursors such as polyacrylonitrile (PAN). Toxic by-products such as hydrogen cyanide (HCN) are generated during stabilization and carbonization of PAN-based carbon fibers. These concerns have promoted increasing interest in biomass-based carbon fibers. As the second most abundant biomass material on the earth, lignin is being investigated as a potential carbon fiber precursor. Therefore, this research was focused on converting lignin materials into carbon fibers with enhanced performance properties.

Since the 1960s, various types of lignin have been investigated as carbon fiber precursors. Hardwood kraft lignin and organosolv lignin could be converted into carbon fibers without chemical modification, whereas softwood kraft lignin was very difficult to convert without suitable modification or plasticization. Strength of most of the carbon fibers produced from the above lignin precursors were below 800 MPa, which is much lower than that of commercial carbon fibers derived from PAN precursors. Thus, the overall goal of this study was to produce lignin-based carbon fibers with enhanced mechanical properties by a scalable process. The specific objectives were to: (i) identify different types of lignin precursors for their potential of being carbon fiber precursors; (ii) study the modified lignin-acetone solutions to establish a range of suitable combinations of solution concentrations and spinning temperatures; (iii) establish thermal stabilization and carbonization conditions for lignin-based precursor fibers to enhance the
performance of resulting carbon fibers; and (iv) to develop a UV/thermal dual stabilization route to increase the speed of stabilization.

The lignin precursors investigated in this study included an organosolv lignin, a soda lignin, and a softwood kraft lignin. The organosolv lignin was successfully melt-spun into fibers without any modification of the precursor material. However, it took more than 200 hours for the thermo-oxidative stabilization step. The infusible soda lignin was chemically modified by acetylation into a fusible material, but it could not be cross-linked. The softwood kraft lignin was modified by a similar acetylation reaction and fractionation method, and the resulting material could be melt-spun into fibers, as the melt possessed significant thermal stability. The large extent of acetylation of hydroxyl groups that led to thermal stability also hindered the thermo-oxidative stabilization. Consequently, the melt-spinning approach was abandoned. Instead, to preserve more hydroxyl groups within the precursor material, the acetic anhydride amount used in acetylation of the softwood kraft lignin was reduced from 15 to 0.66 ml per gram lignin. As indicated by FTIR spectroscopy, the hydroxyl peak was significantly increased. In addition, the weight gain of lignin after reaction was reduced from 18% to 5%, indicating a partial acetylation of the hydroxyl groups in softwood kraft lignin. The resulting acetylated softwood kraft (Ace-SKL) lignin could be dry-spun using acetone as solvent, and the fibers could be thermo-oxidatively stabilized.

The rheology of Ace-SKL/acetone solutions prepared with different solid contents was investigated for the purpose of dry-spinning into precursor fibers. The solution viscosity was investigated at high shear rates encountered during fiber spinning. The
solutions displayed a significant shear-thinning behavior at various temperatures studied with power-law exponents ranging from 0.33 to 0.82, confirming the macromolecular nature of the Ace-SKL lignin/acetone solutions. As expected, elevated temperatures led to lower viscosities and facilitated extrusion at moderate pressures.

Dry-spinning was performed over a range of concentrations (1.85 to 2.15 g/ml acetone) and appropriate temperatures (25-50°C). It was observed that all of the resulting dry-spun lignin fibers displayed a crenulated surface pattern, with increased crenulation achieved for fibers spun at higher temperatures. Presence of some doubly-convex and sharp crevices was found on fibers produced from solutions containing lower concentrations (1.85 and 2.00 g lignin/mL solvent). In contrast, no crevices were found on the fibers obtained from the concentrated solution (2.15 g/mL), likely due to the reduced extent of solvent out-diffusion. Dry-spinning at room temperature was also performed to obtained fibers with relatively smooth surface, but the pressure drop was excessive. The results above have established temperature/concentration combinations for dry-spinning of Ace-SKL. About 30% larger surface area could be achieved in the crenulated lignin fibers (as compared with equivalent circular fibers), indicating the potential advantage of such biomass-derived fibers in providing larger fiber/matrix bonding area when used in composites.

During thermo-oxidative stabilization, tension of about 2000-2500 g/(g/cm) was applied on fiber tows that led up to 800% extension. In the carbonization step, tension was also applied using a customized graphite rack and tungsten weights, and stabilized Ace-SKL fibers were successfully carbonized at 1000°C. It was found that the load
needed to be above 20150 g/(g/cm) to prevent shrinkage of fiber tows. Both tensile strength and modulus were measured as a function of extension during carbonization (EDC). As expected, Ace-SKL carbon fibers with larger EDC had better mechanical properties due to preserved molecular orientation. Carbon fibers derived from lignin precursor fibers obtained from 2.15 g/ml Ace-SKL solution (6 μm diameter) displayed a tensile modulus, strength, and strain-to-failure values of 52 ± 2 GPa, 1050 ± 70 GPa, and 2.0 ± 0.2%, respectively. These values are amongst the best reported for lignin-based carbon fibers. In contrast, the carbon fibers spun from 2.00 g/ml solution with sharp crevices displayed a reduced tensile strength of 790 ± 80 MPa due to occlusion-type defects formed by sharp crevices during spinning. The Ace-SKL carbon fibers displayed low crystallinity as investigated by Wide Angle X-ray Diffraction (WAXD) and Raman spectroscopy. The crenulated surface from dry-spinning was preserved, which can provide a larger specific interfacial area for enhanced fiber/matrix bonding in composite applications. Above results elucidate the importance of precursor composition and processing conditions on microstructure and properties of resulting precursor and carbon fibers.

A limitation of the partially acetylated lignin (i.e., with a fraction of hydroxyl moieties converted to acetyl groups) is the slow heating rate during thermal stabilization, which required up to 40 hours due to the slow heating rate needed to prevent the fibers from becoming tacky and sticking to each other. Therefore, a rapid strategy of dual UV-thermoxidative stabilization was developed. The fibers undergo UV-induced reaction close to the surface in a short duration (15 min) such that they can be subsequently
stabilized at a rapid heating rate without fibers fusing together. The glass transition temperature of UV irradiated fibers was about 15°C higher than that of fibers without UV treatment. This strategy reduces the total stabilization time significantly from 40 to 4 hour. Stabilized fibers were successfully carbonized at 1000°C and resulting carbon fibers displayed a tensile strength of 900 ± 100 MPa, which is amongst the highest reported for carbon fibers derived from rapidly stabilized lignin precursors.

In summary, the results from this study established a route for dry-spinning of partially acetylated softwood kraft lignin into precursor fibers and successful stabilization and carbonization. This precursor could be dissolved in acetone for dry-spinning. The lignin/acetone solutions were investigated to establish suitable concentration/temperature combinations for dry-spinning. The dry-spun precursor fibers were thermally treated under tension to convert into a carbon fiber with tensile strength of more than 1 GPa. Those carbon fibers possessed crenulated surface which could provide larger fiber/matrix interfacial bonding area for composite applications. Furthermore, UV/thermal dual stabilization was developed to reduce the time duration of stabilization.
DEDICATION

This work is dedicated to my family who supported me unconditionally during these years.
ACKNOWLEDGEMENTS

I would like to extend my sincere gratitude to everyone who supported and helped me to successfully complete this work.

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CHAPTER ONE
INTRODUCTION

1.1 Overview of carbon fibers

Carbon fibers possess excellent strength, stiffness, low density, and outstanding electrical and thermal conductivities. Also, they are chemically stable and fire-retardant (1-3). In Table 1.1, mechanical properties and specific gravity of different materials are listed for comparison (4-7). When compared with metals like steel, carbon fibers possess an order of magnitude higher specific modulus and strength. When compared on an absolute basis with strong polymer, i.e. Kevlar fibers, they display much higher modulus and strength. Overall, carbon fibers possess an excellent combination of modulus, strength, and conductivities as compared with other materials.
Unlike polymers, carbon cannot be melted and directly extruded into a fiber form. Therefore, a suitable organic precursor material is first processed into "precursor fibers" that subsequently must be “stabilized” to crosslink the precursor material into a thermoset. Finally, the stabilized fibers need to be heat-treated in an inert environment at temperatures above 1000°C to obtain carbon fibers. A schematic of carbon fiber manufacturing process is illustrated in Figure 1.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific gravity (GPa)</th>
<th>Modulus (GPa)</th>
<th>Specific modulus (GPa)</th>
<th>Strength (GPa)</th>
<th>Specific strength (GPa)</th>
<th>Thermal Conductivity (W/m-K)</th>
<th>Electrical resistivity (µΩm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>7.9</td>
<td>200</td>
<td>25</td>
<td>1-1.5</td>
<td>0.1-0.2</td>
<td>50</td>
<td>0.72</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2.7</td>
<td>76</td>
<td>28</td>
<td>0.5</td>
<td>0.2</td>
<td>205</td>
<td>0.003</td>
</tr>
<tr>
<td>Glass (bulk and fiber)</td>
<td>2.5</td>
<td>72</td>
<td>28</td>
<td>2-3</td>
<td>~ 1-1.5</td>
<td>13</td>
<td>$10^{18}$-$10^{19}$</td>
</tr>
<tr>
<td>Kevlar fibers</td>
<td>1.45</td>
<td>135</td>
<td>93</td>
<td>2.3</td>
<td>~ 1.5 – 2</td>
<td>0.04</td>
<td>N/A</td>
</tr>
<tr>
<td>Carbon fibers (high strength)</td>
<td>1.82</td>
<td>294</td>
<td>164</td>
<td>7.1</td>
<td>3.9</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Carbon fibers (ultra high modulus)</td>
<td>2.18</td>
<td>830</td>
<td>380</td>
<td>2.4</td>
<td>1.1</td>
<td>640</td>
<td>2.2</td>
</tr>
</tbody>
</table>
The first carbon fiber or carbon filament was produced by Thomas Edison in 1879 as the heated filament in a light bulb (3). A bamboo sliver (cellulose) was baked at high temperature and formed an all-carbon filament. However, the first carbon fiber with relatively good mechanical properties was invented by Roger Bacon in the late 1950s by growing graphite whiskers using vapor deposition in a high pressure carbon arc (8). Subsequently, Bacon patented another process for carbonization of rayon to produce carbon fibers (9). Almost at the same time, Shindo used polyacrylonitrile (PAN) as precursor material and successfully produced carbon fibers (10). A few years later, carbon fibers were produced from another type of precursor, pitch (11). All of the three precursor materials (PAN, pitch, and rayon) are used for commercial production of carbon fibers, with PAN accounting for over 90% of carbon fibers produced currently (12).
1.2 Carbon Fiber Precursors

1.2.1 Polyacrylonitrile (PAN)

As noted above, high-strength carbon fibers used in current structural composite applications are almost exclusively derived from PAN precursor fibers (1, 2). These precursors are typically copolymers of acrylonitrile and a small amount of other monomers as shown in Figure 1.2 (2). The carbon yield of converting a PAN precursor to carbon fibers is about 45%.

PAN precursor decomposes at a temperature lower than its melting temperature (2, 13). Therefore, it must be converted into fibers via wet-spinning process, as illustrated in Figure 1.3 (14). A solution containing 15-30 wt% PAN is extruded out of a spinneret into a coagulation bath that extracts the solvent out of the extruded solution to solidify the filaments. The mass transfer rate in this step is controlled by temperature and concentration of the coagulant, which leads to differences in the cross-section of precursor fibers. After coagulation, the fibers are subjected to multiple steps of washing and stretching to remove the residual solvent and achieve smaller diameter, respectively. Due to collapse of fiber skin during coagulation, the cross-section of PAN precursor fibers typically has the shape of kidney-beans or dog-bones (2, 15) (Figure 1.4).
<table>
<thead>
<tr>
<th>Monomers</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic Acid</td>
<td><img src="image" alt="Acrylic Acid Structure" /></td>
</tr>
<tr>
<td>Itaconic Acid</td>
<td><img src="image" alt="Itaconic Acid Structure" /></td>
</tr>
<tr>
<td>Methacrylic Acid</td>
<td><img src="image" alt="Methacrylic Acid Structure" /></td>
</tr>
<tr>
<td>Methyl Acrylate</td>
<td><img src="image" alt="Methyl Acrylate Structure" /></td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td><img src="image" alt="Vinyl Acetate Structure" /></td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td><img src="image" alt="Acrylonitrile Structure" /></td>
</tr>
</tbody>
</table>

Figure 1.2 Monomers copolymerized with acrylonitrile to form PAN-based carbon fiber precursor (2)
Figure 1.3 Schematic of typical process for wet-spinning of PAN precursors (14)

Figure 1.4 As-spun fibers from PAN precursor. Reproduced with permission from (15).
In addition to wet-spinning, another solution spinning method to obtain PAN precursor fibers is dry-spinning. In dry-spinning, a PAN copolymer solution is extruded into a hot gas chamber to evaporate the solvent. The temperature of evaporation chamber and hot gas composition need to be well monitored since it will control the mass transfer rate and fiber structure (2, 16). Another route to form PAN fibers is melt-assisted spinning in which the PAN precursor and a plasticizer is fed into extruder. Finally, with significant comonomer content, the melt-spinning can be performed (2, 17).

Stabilization of PAN-based precursor fibers is carried out at 220-280°C in air atmosphere under tension (18). The primary reaction in this step is cyclization as shown in Figure 1.5. In this reaction, the nitrile groups on the polymer chain cyclized and the material became infusible. It can be seen that some toxic by-products, such as hydrogen cyanide (HCN), are generated in this step (14). Once the precursor fibers have been stabilized, carbonization is performed at temperatures ranging from 1000 to 2800°C still in the presence of tension. In this step, HCN also evolved. Accompanied with the fact that large amount of organic solvent is needed during coagulation, the production of PAN-based carbon fiber is not an environmentally friendly procedure.
After carbonization, the kidney-bean or dog-bone cross-section shape is preserved as displayed in Figure 1.6 (19). The microstructure of PAN-based carbon fibers is fibrillar. Figure 1.6 is a schematic 3-D structural model of a PAN-based carbon fibers (20). In Figure 1.7, the ribbon like undulation is displayed. Also, it was found that the undulation structure was highest in the center and lowest near the skin part. As displayed in Figures 1.7 and 1.8, PAN-based carbon fibers display extensively folded turbostratic layers and low degree of graphitization, and the turbostratic layers are not highly aligned along the fiber axis.
Figure 1.6 Representative SEM micrographs of PAN-based carbon fibers. Reproduced with permission from (19).

Figure 1.7 Schematic 3-D structural model of Fortafil 5-Y PAN-based carbon fibers with 345 GPa of tensile modulus. Reproduced with permission from (20).
Figure 1.8 Structure of lignin, cellulose, PAN, and mesophase pitch. The first three precursors generate carbon fibers with noncrystalline/turbostratic structure, whereas mesophase pitch generates graphitic/crystalline structure (adapted from (2), (21))
1.2.2 Mesophase pitch-based carbon fibers

Mesophase pitch could be obtained by polymerization from a petroleum or coal-tar pitch. When heated up to 400-450°C, the isotropic pitch transforms into a mesophase or liquid crystalline phase (22). Also, it could be synthesized from pure aromatic hydrocarbons such as naphthalene and methylnaphthalene (23). Another way to produce mesophase pitch is by extracting a portion of an isotropic pitch and heating the solvent insoluble portion to 230°C to 400°C (2, 24-26). Figure 1.9 is a schematic model of carbonaceous mesophase that shows the nematic liquid-crystal structure (27). The average molecular weight of a mesophase pitch is around 1000 (2).

![Schematic model of the carbonaceous mesophase](image)

Figure 1.9 Schematic model of the carbonaceous mesophase. Reproduced with permission from (27).

In the melt-spinning process of mesophase pitch, the solid pitch is fed into an extruder and heated to produce a melt. Then the molten pitch is pumped into a die head and extruded through spinnerets. As the molten pitch exits the spinneret, it is drawn and
solidified in air at the same time, developing a highly oriented molecular structure along the fiber axis. The spinning temperature needs to be very carefully controlled due to the extreme temperature sensitivity of mesophase pitch viscosity (2, 28, 29).

The mesophase pitch precursor fibers need to be thermally stabilized at a temperature below its softening point in air environment to prevent fusing of fibers. Thus, a precursor with higher softening point is desired to allow higher stabilization temperature and shorter stabilization time (4). In addition, fiber diameter is another parameter that controls the total reaction time during stabilization due to the diffusion of air from fiber surface into the core. Normally, the as-spun fibers are heated to 250-300°C and held for a period ranging from 3-30 h (2, 4).

Carbonization of stabilized mesophase pitch precursor fibers usually comprises two steps. First, a pre-carbonization step consists of a few minutes at 900-1000°C in order to reduce the rate of gases evolution. Second, carbonization or graphitization is conducted between 1200-3000°C. For mesophase pitch-based carbon fibers, the tensile strength increases with carbonization temperature until a maximum is reached at about 1500°C. Carbon fibers obtained at high heat treatment temperatures of 2400-3000°C have a higher modulus compared to fibers treated at the lower temperatures (4).

Pitch-based carbon fibers display more variation in microstructures compared with their PAN-based counterparts. Due to the highly oriented graphitic structure as displayed in Figure 1.8 (presented earlier), the tensile modulus of mesophase pitch-based carbon can be as high as 830 GPa (30).
1.2.3 Rayon-based carbon fibers

The chemical structure of cellulose is displayed in Figure 1.10. The carbon content is 44% and the carbon yield is only about 25%. As noted earlier, it was the precursor material for the first carbon fiber produced by Edison for his light bulb. Natural cellulose fibers, such as cotton or flax, in that native state are not good precursors for structural carbon fibers due to their discontinuous character. Instead, regenerated cellulose fibers, such as rayon, can serve as precursors. However, only a small fraction (~1%) of world production of carbon fibers is rayon based.

![Chemical structure of cellulose](image)

Figure 1.10 Chemical structure of cellulose

Rayon precursor fibers are produced from a wet-spinning process. Cellulose was mixed with a basic solution and treated with CS$_2$ to form cellulose xanthate. Cellulose xanthate is then dissolved in NaOH and the solution is extruded through spinneret followed by coagulation in a sulfuric acid solution. Cellulose xanthate hydrolyzed in the acid solution to precipitate the cellulose filaments.
The rayon precursor fibers were stabilized in air at temperatures as high as 400°C. Pyrolysis progressed as heating continues. After oxidation, they were carbonized under similar condition to those of PAN or pitch. In this step, tension is applied to form a molecular orientation which is lost during pyrolysis. Rayon based carbon fibers nominally display a turbostratic structure as displayed in Figure 1.8 (presented earlier). Stretched carbon fibers can achieve a modulus as high as 720 GPa, but this stretching is a very expensive process (32-34). Therefore, only a small fraction (~1%) of world production of carbon fibers is rayon based (2).

As noted in section 1.2.1, the vast majority of commercial carbon fibers are currently produced from polyacrylonitrile (PAN), a synthetic precursor that does not melt, so its solution-spun fibers can be easily crosslinked (also referred to as “stabilized”) and subsequently carbonized, as illustrated in Figure 1.1. However, the wet-spinning process itself involves the use of hazardous solvents, and the nitrile group generates toxic by-products (viz. hydrogen cyanide) during heat-treatment.(2, 4) The environmental concerns and related high costs associated with this process can be partially overcome by using bio-based precursors. Among naturally occurring biomass, lignin are regarded as potential CF precursors due to their low cost and carbon forming chemical structure.

1.3 Overview of lignin

Lignin is the second most abundant natural polymer on the earth (35). Raw wood material nominally consists of 40–50% of cellulose, 23–32% of hemicellulose, and 15–30% lignin (36). It is present in cell walls of vascular plants to impart compressive and flexural
strength to the stems. Over $3 \times 10^{11}$ tons of lignin exits in the biosphere with approximately $2 \times 10^{10}$ tons generated annually (37). In 1838, a French chemist, Anselme Payne, isolated both cellulose and lignin from wood and identified them as two separate components (38). Since then, numerous studies have been performed on the characterization, separation, and application of lignin.

1.3.1 Chemical structure of lignin

Lignin is an amorphous, complex, and random polymer abundant in aromatic rings. It is a natural polymer generated from the enzymatic polymerization of three primary precursor units: coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol. In the polymerized form, they were guaiacyl, syringyl, and p-hydroxyphenyl (21). A lignin model structure is shown in Figure 1.8 (presented earlier) (39). One of the typical building/repeat unit is circled and the commonly used notation of carbon atoms in those units is displayed (40, 41). Guaiacyl alcohol is found predominately in softwood lignins, whereas syringyl alcohol is the dominant structure found in hardwood lignins (21). The content of p-hydroxyphenyl is relatively low in both softwood and hardwood lignins, but occurs more often in annual crops. Above three main structural elements in lignin are linked together by various carbon-carbon and ether bonds. The $\beta$-O-4 linkage is the most dominant one in all types of lignins (42). In softwood type, about 50% of the linkages are $\beta$-O-4 type, whereas in hardwood type these comprise 60% (21, 43). As indicated by the arrows in Figure 1.8, lignin, cellulose, and PAN form a nongraphitic or turbostratic structure within the resulting CFs, whereas a polynuclear aromatic hydrocarbon precursor,
mesophase pitch, forms a highly graphitic/crystalline structure after heat treatment above 2400°C (2).

1.3.2 Lignin derived from different pulping methods

The structure and properties of lignins vary based on different plant source they are separated from, such as hardwood, softwood, wheat straw, or bamboo (44-46). However, the discussion here will be focused on major types of lignins separated by different pulping methods, because chemical pulping brings out the most remarkable differences in the resulting lignin products. Pulping is a process of separating lignin from cellulose in plant materials to produce pulp for the manufacture of paper or other products (47).

Soda pulping and kraft pulping (alkaline processes)

In the soda pulping process, sodium hydroxide (caustic soda) is used as the reactant for making wood pulp at temperature between 130-170°C. Grass species can be treated at milder conditions including ambient temperatures (48). Thus, the soda process is mainly used for pulping of non-wood materials.

Kraft pulping is developed based on soda pulping and has become the dominant commercial process (49). A schematic of the kraft pulping process is displayed in Figure 1.11. It uses sodium hydroxide and sodium sulfide as the chemical for breaking down the matrix (lignin). Aqueous sodium hydroxide and sodium sulfide (white liquor) is added to the wood chips. Pulping is performed at pH above 12 at 160-180°C for 0.5-3 h to reduce the lignin into smaller fragments that are soluble in water/alkaline solution. Cleavages
occur on the linkages that hold the phenylpropane units together, which lead to generation of free phenolic hydroxyl groups in the resulting kraft lignin (50). After pulping, a waste liquor containing mainly lignin, hemicellulose and inorganic pulping chemicals is separated from cellulose. The cellulosic pulp is further treated by bleaching, washing and drying to form paper. This process is suitable for any type of plant material (51).

Figure 1.11 Simplified kraft pulping process

The waste liquor generated from both soda and kraft pulping is called black liquor. Lignins can be precipitated by acidification of black liquor. However, the black liquor is usually concentrated and burned in a recovery boiler to recover the cooking chemicals and generate energy from burning of lignin (organic matter) (48, 51).

*Sulfite pulping (acid processes)*

In a traditional sulfite process, a pulping liquor consisting of sulfur dioxide aqueous solution and suitable bases is prepared. The bases could be hydroxides of
magnesium, sodium, potassium or ammonium. Wood chips are in contact with the pulping liquor with a pH between 1.5 to 5 at temperatures ranging from 130 to 160°C. During pulping, carbocations are formed and react with bisulfite ions (HSO$_3^-$) to generate sulfonates as shown below. Lignin is solubilized by the addition of sulfonate groups (51).

\[
R-\text{O}-R' + H^+ \rightarrow R^+ + R'OH
\]

\[
R^+ + HSO_3^- \rightarrow R-\text{SO}_3H
\]

After washing, the waste liquor that contains lignosulfonates and cooking chemicals is called brown liquor. Like black liquor, the brown liquor is concentrated and burned to provide steam and recover the inorganic chemicals. To recover lignosulfonates from the brown liquor, a widely used method is the Howard process of adding excess calcium hydroxide to precipitate calcium lignosulfonates (52).

*Solvent pulping*

Kraft pulping is a very efficient and versatile process that can be used to treat different type of raw plant materials, but it suffers from several environmental issues such as emission of waste water and malodorous products (sulfur containing). Organic solvent pulping is a good alternative to overcome such problems (53). Multiple studies have been conducted using various organic solvents such as methanol (54), ethanol (55), acetic acid (56), etc. One of the well-developed process is the Alcell process using aqueous ethanol solutions to treat the wood at temperatures from 180-210°C and pressures of 2-3.5 MPa. Solvent is recovered later by evaporation and condensation (57). Lignin is recovered from the spent liquor by precipitation. Since there is no addition of inorganic moieties
and sulfur during the process, oranosolv lignins usually have higher purity compared with kraft lignin and lignosulfonates.

1.3.3 Carbon fibers derived from lignin precursors

Carbon fibers first produced from lignin were patented in 1969 by Otani (58). The patent described both melt-spinning and dry-spinning using different type of lignin precursors. The strength of carbon fiber produced from melt-spun precursor ranged up to 800 MPa. In the examples for dry-spinning, water or sodium hydroxide aqueous solutions were used as solvent for both alkali lignin and thiolignin. Carbon fiber produced from this dry-spinning process possessed strength that ranged only up to 300 MPa.

Since 1990’s, studies have focused on producing carbon fiber from different types of lignin precursors by melt-spinning. Sudo and Shimizu (59) used methanol to extract lignin from a steam exploded birch wood and washed out the hemicellulose. Then, the extracted lignin was modified into a fusible material by hydrogenolysis. Hydrogenolysis of the lignin led to extensive cleavage of alkyl-aryl ether bonds, and the lignin was extracted with chloroform and carbon disulfide. The chloroform soluble and carbon disulfide insoluble fraction was capable of melt-spinning after a heat treatment. The resulting carbon fibers from this process possessed a tensile strength of 660 MPa and modulus of 40.7 ± 6.3 GPa. Sudo and coworkers also modified the steam exploded lignin through phenolysis (60). The tensile strength of carbon fibers derived from phenolized lignin was below 400 MPa.
A series of studies have been performed on lignin precursor produced from acetic acid pulping. A hardwood lignin was extracted using acetic acid (61). This organosolv hardwood lignin is fusible and could be melt spun without any modification by Uraki et al. (62), who also separated softwood lignin from acetic acid pulping. However, the organosolv softwood lignin could not be spun directly due to a large molecular fraction which was infusible. It was further fractionated with aqueous acetic acid and one of the fractions with lower molecular weight could be melt spun into fibers (63, 64). However, the tensile strength of resulting carbon fibers was only 26.4 and 5.8 MPa, from the organosolv softwood and hardwood lignin fractions, respectively. Kubo et al. also studied the processibility of a softwood kraft lignin but failed to convert it into a fusible precursor (64). Based on their fractionation study, the softwood kraft lignin only had 13% of fusible fractions, which could not be spun due to a remarkably low molecular mass. They concluded that softwood kraft lignin is not a suitable raw material for thermoforming of precursor fibers.

Hardwood kraft lignin and Alcell organosolv lignin can be converted into carbon fibers without any chemical modification (65). To increase spinnability, both types of lignin were mixed with 3-5% of poly(ethylene oxide) (PEO). Spinning temperatures for the mixtures could be lowered as the content of PEO increased. The carbon fibers derived from hardwood kraft lignin and PEO blend had a tensile strength of about 460 MPa. Here the possibility of converting softwood kraft lignin into carbon fibers was investigated again. Even with the addition of PEO, the softwood kraft lignin did not soften, instead
charring occurred due to the more highly-crosslinked structure compared with hardwood lignin (65).

Norberg et al. investigated selected grades of softwood and hardwood kraft lignin. Both grades were further fractionated with ultrafiltration of the black liquors to generated permeate lignins (66). This particular grade of fractionated softwood kraft lignin was successfully melt-spun into precursor fibers. Also, 10% of permeate hardwood kraft lignin was added into the unfractionated softwood kraft lignin as a softening agent to achieve melt-spinning. The advantage of this process is the fast stabilization achieved in 85 min, which is faster than most of the lignin fiber stabilization reported in literature. However, the carbonized fibers had large diameters (above 50 μm) and the carbon fiber strength was not reported. The large cross-section area of those carbon fibers would lead to poor tensile strength as observed in prior studies (11). In another study reported by Nordström et al., using the same separation method, the permeate hardwood kraft lignin was blended with different unpermeated softwood kraft lignin with various ratios. They found that the suitable spinning temperature of the mixtures decreased as permeate hardwood fraction increased (67). The tensile strength reported for those lignin based carbon fibers were all below 400 MPa (68).

Several studies have made attempts to introduce acrylonitrile (AN) or polyacrylonitrile (PAN) into lignin to develop carbon fibers. Maradur et al. prepared a copolymer using a hardwood lignin and AN with AN: lignin ratio from 5:5 to 8:2 (69). The lignin-PAN copolymer was dissolved in DMSO and converted into fibers through wet-spinning using a coagulation bath containing water. Xia et al. prepared a
lignosulfonate-AN copolymer which is also soluble in DMSO and insoluble in water (70). They conducted wet-spinning using lignosulfonate/PAN mixture and lignosulfonate-AN copolymer, respectively. Macrovoids were found in the as-spun fibers derived from lignosulfonate/PAN mixture, acting as defect in the resulting carbon fibers. But the as-spun fibers obtained from lignosulfonate-AN copolymer were solid without voids. The resulting carbon fibers from this copolymer displayed a strength of 540 MPa. Similarly, lignosulfonate/PAN blend solution was prepared for wet spinning (71). The lignin content used in this study ranged from 15% to 47%. Voids were still observed in the as-spun fibers.

Qin et al. introduced organoclay (organically modified montmorillonite) into a pyrolysis lignin as a reinforcement (72). When the organoclay loading was below 1.0 wt%, tensile strength of resulting carbon fibers was improved by 12%. The resulting carbon fibers in this study had a large diameter (more than 45 µm), and the tensile strength was below 500 MPa.

Above lignin-based carbon fibers have exhibited relatively low tensile properties, with published tensile strengths of 800 MPa or lower. Carbon fibers derived from softwood kraft lignin by melt-spinning of its acetylated form were patented by Eckert (73). However, in their example, only a small batch of about 200 mg acetylated lignin was melt-spun without any characterization of resulting carbon fibers. In 2010, Baker and coworkers reported their carbon fibers produced from an organic-purified hardwood lignin with tensile strength of 0.51 Gpa and a modulus of 28.6 GPa (74). Also, a value of 1.07 GPa was attributed in a review article to a DOE presentation (75).
Finally, a summary of tensile properties of carbon fibers obtained from different precursors is listed in Table 1.2. All of the lignin-derived carbon fibers have significantly lower mechanical properties as compared with those of pitch or PAN based carbon fiber. The low strength may be attributed to the fact that melt-spun precursor fibers are inherently difficult to stabilize by thermo-oxidative means, and often partially fuse together during the stabilization-carbonization processes that lead to surface defects on the resulting carbon fibers. On the other hand, due to its three-dimensional aromatic structure, native lignin is intractable in its unmodified state, and must be suitably modified into components or products that can be converted into fibers. Therefore, research on modification of lignin is of topical interest.
Table 1.2 A summary of tensile properties of carbon fibers obtained from different precursors in prior studies

<table>
<thead>
<tr>
<th>Precursor Type</th>
<th>Diameter (µm)</th>
<th>Elongation (%)</th>
<th>Modulus (Gpa)</th>
<th>Tensile strength (Mpa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various types of lignin</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>150-800</td>
<td>Otani, 1969 (58)</td>
</tr>
<tr>
<td>Steam exploded hardwood</td>
<td>8 ± 3</td>
<td>1.6 ± 0.2</td>
<td>40.7 ± 6.3</td>
<td>660± 230</td>
<td>Sudo, 1992 (59)</td>
</tr>
<tr>
<td>Steam exploded hardwood</td>
<td>1.2</td>
<td></td>
<td>450</td>
<td></td>
<td>Sudo, 1993 (60)</td>
</tr>
<tr>
<td>Organosolv hardwood</td>
<td>14 ± 1</td>
<td>1.0 ± 0.3</td>
<td>39.1 ± 13.3</td>
<td>355 ± 53</td>
<td>Uraki, 1995 (62)</td>
</tr>
<tr>
<td>Organosolv softwood</td>
<td>84 ± 15</td>
<td>0.7 ± 0.1</td>
<td>3.6 ± 0.4</td>
<td>26.4 ± 3.1</td>
<td></td>
</tr>
<tr>
<td>Kraft hardwood</td>
<td>46 ± 8</td>
<td>1.1 ± 0.2</td>
<td>40 ± 11</td>
<td>422 ± 80</td>
<td>Kadla, 2002 (65)</td>
</tr>
<tr>
<td>Organic purified hardwood</td>
<td>10 ± 1</td>
<td></td>
<td>28.6 ± 3.2</td>
<td>520 ± 182</td>
<td>Baker, 2011 (76)</td>
</tr>
<tr>
<td>Organic purified hardwood</td>
<td>2.0</td>
<td>82.7</td>
<td>1070</td>
<td></td>
<td>Baker, 2013 (75)</td>
</tr>
<tr>
<td>Softwood and hardwood kraft</td>
<td>36-78</td>
<td>0.78-1.20</td>
<td>25-33</td>
<td>233-377</td>
<td>Nordström, 2013 (68)</td>
</tr>
<tr>
<td>Lignosulfonate-AN copolymer</td>
<td>12-20</td>
<td></td>
<td>540</td>
<td></td>
<td>Xia, 2015 (70)</td>
</tr>
<tr>
<td>PAN</td>
<td>5-10</td>
<td>2</td>
<td>100-500</td>
<td>3000-7000</td>
<td>Various</td>
</tr>
<tr>
<td>Mesophase pitch</td>
<td>5-15</td>
<td>0.6</td>
<td>200-800</td>
<td>1000-3000</td>
<td>Various</td>
</tr>
</tbody>
</table>
1.4 Objectives

The current study investigated different lignin precursors for conversion to carbon fibers with a focus on an acetylated version of a softwood kraft lignin. The overall goal of this study was to produce lignin-based carbon fibers with enhanced mechanical properties. The specific objectives of this study were to: (i) identify different types of lignin precursors for their potential of being carbon fiber precursors; (ii) study the modified lignin-acetone solutions to establish a range of suitable combinations of solution concentrations and spinning temperatures; (iii) establish thermal stabilization and carbonization conditions for lignin-based precursor fibers, to enhance the performance of resulting carbon fibers; and (iv) to develop a UV/thermal dual stabilization route to increase the speed of stabilization.

The organization of the remainder of the dissertation is as follows:

Chapter Two describes the study on three types of bio-derived precursors for the purpose of producing lignin-based carbon fibers. These precursors included soda lignin, organosolv lignin, and softwood kraft lignin. It was concluded that soda lignin and SKL cannot be melt spun without suitable modification. The organosolv ECN lignin was successfully melt spun into lignin fibers, but the thermo-oxidative stabilization took an impractically long time to complete. Therefore, controlled acetylation was performed on softwood kraft lignin, and the resulting precursor could be successfully dry-spun using acetone as a solvent and thermally stabilized in air atmosphere.
In Chapter Three, the shear viscosity of acetylated softwood kraft lignin/acetone solutions was studied and the results were fitted with power-law model. Dry-spinning was performed on solutions with various concentrations under different temperatures. The crenulated surface patterns of resulting as-spun fibers were investigated to establish a suitable concentration/temperature combination for spinning. The results presented in this chapter are reported in reference 77 (77).

In Chapter Four, a systematic study on carbonization of the dry-spun lignin precursor fibers is discussed. The effect of tension during carbonization and stabilization is discussed, because adequate tension significantly improved the mechanical properties of resulting carbon fibers. The crenulated patterns of fiber cross-section shape were preserved in carbon fibers. Also, the microstructure of resulting carbon fibers was studied. The results presented in this chapter have been published in references 78 and 79 (78, 79).

The process described in Chapter Four has drawback of a fairly long thermal stabilization step, which took around 40 hours to complete. Therefore, in Chapter Five, a UV/thermal dual stabilization route was established, which reduced the thermal stabilization time by almost 90% to 4 hours. The effect of UV was investigated using DSC, FTIR and GPC analysis. The results have been published in reference 80 (80). Finally, Chapter Six summarizes conclusions from this study and provides potential future work directions.
CHAPTER TWO

INVESTIGATION OF VARIOUS LIGNINS AS CARBON FIBER PRECURSORS

2.1 Introduction

As noted in Chapter One, high-strength carbon fibers used in structural composite applications are almost exclusively derived from wet-spinning of PAN precursor fibers (3),(2). This wet-spinning process suffers from an inherent limitation: chemical conversion of PAN into carbon proceeds via generation of hydrogen cyanide (HCN) and other toxic gases during the thermal stabilization and carbonization steps. Therefore, additional studies need to investigate the replacement of PAN by an environmentally sustainable precursor such as lignin, which is an abundant biorenewable source. Because of its aromatic nature, lignin may be used to generate a valuable source of aromatic precursors for processing into carbon fibers. However, because of its 3-D aromatic structure, lignin is intractable in its unmodified state and most lignin materials must be suitably modified into components or products that can be processed into fibers.

A detailed description of different types of lignin precursors reported in prior literature studies was provided in section 1.3.3. The goal of studies presented in this chapter was to investigate three types of lignin as potential carbon fiber precursors: a soda lignin, an organosolv lignin, and a softwood kraft lignin. Specifically, the soda lignin was chemically modified to achieve melt-processibility, the organosolv lignin was melt-spun into precursor fibers without modification, and the softwood kraft lignin was also chemically modified to conduct both melt and dry-spinning. Furthermore, the carbon fiber formation potential of above precursor fibers was investigated.
2.2 Experimental

2.2.1 Analysis of lignin samples

Three grades of lignin were investigated in the first phase of this research as potential precursors. The first lignin precursor was a commercial soda lignin, Protobind 1000 (GreenValue Enterprises LLC, Media, PA), which was derived from wheat straw and grass. The second lignin was an organosolv hardwood lignin provided courtesy of Energy Research Centre, Netherlands (ECN lignin). The ECN lignin was derived from poplar with an ethanol-organosolv process resulting in lower than 0.1% ash content. The third lignin was a commercial softwood kraft lignin, Indulin AT (SKL, Mead-Westvaco, Charleston, SC).

The softening point of lignin samples was measured with a METTLER TOLEDO FP900 Thermosystem using the Mettler Cup and Ball method according to ASTM D 3461. ASTM D 3461 was originally designed for testing of pitch materials that do not have a true melting point. It is appropriate to use this method to study the fusing behavior of lignin materials, which are amorphous and do not have a true melting point either. Before the softening point test, lignin samples were put into a vacuum oven at 60°C under vacuum of 20 inHg for 12 h to remove the low molecular volatiles. If volatiles were not removed sufficiently, lignin foamed during heating and plugged the furnace chamber illustrated in Figure 2.1 (METTLER TOLEDO FP900 Thermosystem).

In a typical test, the sample cup is filled with lignin powder and the powder is compressed several times with a spatula. After lignin is loaded, the surface of compressed
powder should be solid and flat. The sample cup is inserted into the furnace with a metal ball placed on the top. As shown in Figure 2.1, there is a light source in the lower part of the furnace chamber. The furnace was heated at a heating rate of 10°C/min. When the temperature is high enough to soften the sample, an extended droplet is formed that blocks the light path, which triggers the recording of temperature, and referred to as the “softening point” (SP). It is noted that this SP is a good indicator of the temperature above which the material will flow.

Figure 2.1 The structure of the heating furnace in METTLER TOLEDO FP900 Thermosystem

Ash content and elemental analysis determination were performed following ASTM D 5630 at the Agricultural Service Laboratory, Clemson University.
Thermogravimetric analysis (TGA) was conducted using a Pyris 1 instrument. The lignin powder samples were heated at a heating rate of 20°C/min under nitrogen purge. Differential scanning calorimetry (DSC) was conducted using a Pyris 1 DSC (Perkin Elmer Instruments) using volatile sample pans from Perkin Elmer. The sample pans loaded with lignin powder were heated from room temperature to 250°C under nitrogen at a heating rate of 30°C/min and cooled to room temperature at the same rate. For each sample, the second heating run was used to calculate $T_g$ using the half $\Delta C_p$ method. FT-IR spectroscopy was performed in the transmission mode with a Nexus spectrophotometer using KBr pellets containing 1% samples.

Rheological testing of lignin samples was carried out on an ARES rheometer (TA Instruments) using a cone-and-plate fixture under a steady shear rate range of 1 to 10 s$^{-1}$. Lignin melts were tested at temperatures approximately 5°C above their SP in a nitrogen environment.

2.2.2 Acetylation Reaction

Acetylation was carried out by reacting dry Soda or SKL lignin powder with acetic anhydride (AA) in a round-bottomed flask. The flask was connected with a reflux condenser and immersed into a water bath set at 85°C with continuous stirring. After conducting the reaction for a desired duration, the solvent remaining in the reaction mixture was evaporated under reduced pressure (6 torr) using a vacuum pump to obtain the acetylated lignin (Ace-Soda or Ace-SKL). Further, Ace-SKL was also fractionated.
with 75% aqueous acetic acid, and the dissolved fraction was obtained by evaporation of the aqueous acetic acid under reduced pressure (6 torr).

2.2.3 Carbon fiber preparation

Melt spinning of lignin precursors was initially performed using an Instron rheometer modified as a fiber spinning device with a capillary die of 0.25 mm diameter. The maximum take-up speed was about 3 m/s. When the barrel temperature reached the target value, the sample was loaded into the barrel. The plunger was fitted into the barrel, and the melt was extruded out of the capillary die. A take-up roll was positioned below to draw down the melt into fibers. The total heating time was controlled in this manner to prevent the formation of high-viscosity material before spinning.

The lignin precursor fibers were placed in a programmable air oven and heated from room temperature up to 220°C at various heating rates ranging from 0.01 to 0.5°C/min for different batches of samples. Different intermediate holding temperatures were necessary to prevent fibers from sticking to each other. After stabilization, the fibers were wrapped in graphite foil and placed in a RED DEVIL furnace. Carbonization was performed by heating at a rate of 4.5°C/min up to 1000°C in a stream of argon and held at 1000°C for 1 h. A limited number of samples were also carbonized at 2500°C.

2.2.4 Characterization of carbon fibers

To measure tensile properties, individual fibers were tested in a Phoenix tensile testing device following the ASTM test method D-3379-5. The load cell of the MTS
apparatus has a maximum capacity of 500 g, and the crosshead speed was set to 0.5 mm/min. Individual filaments were mounted in paper tabs with gage length of 25 mm. The fiber diameter was measured by a laser diffraction method. Each paper tab was secured in the upper and lower jaws of the MTS. To prevent the accidental breakage of fiber prior to test failure, an electrically heated wire was used to burn the paper tab.

To measure electrical resistivity, individual fibers were mounted using the same paper tabs for tensile test. A mounted single filament sample was put across two parallel copper wires 10 mm apart, using silver paint (SPI) at the cross points to ensure contact. The resistance was measured using a two-point probe technique with a micro-ohmmeter. Fiber diameters were measured using the same laser diffraction method for tensile tests.

Optical microscopy (Olympus BX60) was used in transmission mode to investigate the surface of fibers and check the fiber size. Scanning electron microscopy (SEM, Hitachi S4800) was used to study the morphology of fibers. A clear cross-sectional cut was generated by soaking the carbon fibers in liquid nitrogen for 1 minute. 10 kV was used for SEM analysis.

2.3 Results and Discussion

2.3.1 Soda lignin precursor

The soda lignin Protobind 1000 had a softening temperature of 245°C. Because of degradation, the residue after heating of this lignin was a foam, as displayed in Figure 2.2. Based on a thermogravimetric analysis (TGA), it began to degrade at 200°C, as displayed
in Figure 2.3. The carbon yield as indicated from TGA was only about 20%. The ash content was measured at 1.66%. Thus, melt spinning of as-received soda lignin is not a desirable process because degradation occurs before the sample softens. As a result, it is necessary to reduce the softening point to below 200°C.

Figure 2.2 Residue of Soda lignin after heating at 250°C for 5 minutes
Acetylation was carried out to enhance the flow characteristics of soda lignin. Excess acetic anhydride was reacted with soda lignin, i.e., 15 ml acetic anhydride per gram of soda lignin, to allow a high degree of acetylation. After the reaction mixture was cooled down from 95°C to room temperature, an insoluble fraction precipitated from the reaction mixture. This fraction was the large molecular weight component and was removed by filtration. The recovered soluble fraction, referred to as Ace-Soda, had a SP between 130 and 142°C. It displayed a relatively stable melt viscosity when tested at 148°C, i.e., about 5°C higher than the SP, as displayed in Figure 2.4. We desire 30 min of stable viscosity to process the fibers. However, the material must also increase in
viscosity significantly after 30 min, which would indicate that the precursor has some reactivity that is desired during fiber stabilization.

![Figure 2.4 Transient shear viscosity of Ace-Soda at 148 °C]

The Ace-Soda was then melt spun into fibers. The resulting fibers, shown in Figure 2.5, had a fiber diameter of 22 ± 3 µm. These melt-spun Ace-Soda fibers were tacky during thermostabilization even at a heating rate as low as 0.01°C/min. In retrospect, the stable melt viscosity, displayed in Figure 2.4, indicates that little cross-linking of the lignin can occur upon heating, likely as a result of too much acetylation (and too little residual hydroxyl groups) to have enough dehydration induced cross-linking.

To help the thermostabilization, the material was heated in a vacuum oven for different durations to increase its T_g. SP of Ace-Soda increased from 145°C to around 190°C after 2.5 h of devolatilization in a vacuum oven (20 inHg vacuum) at 160°C, as shown in Figure 2.6.
Figure 2.5 As-spun fibers of Ace-Soda

Figure 2.6 SP change with devolatilization time for Ace-Soda
The transient viscosity curve of Ace-Soda after different time periods of devolatilization is shown in Figure 2.7. The results indicate long periods over which a constant viscosity was observed, allowing for a significant duration available processing. This was followed by a significant rise in viscosity, indicating decreased thermostabilization with increased devolatilization time. However, fibers spun using the highest SP (191°C) material still could not be cross-linked even with an extremely low heating rate. The fibers could not be maintained in their glassy state and became tacky at around 150°C. Once the precursor becomes tacky, it is not possible to retain individual precursor fibers. This is likely due to the lower concentration of hydroxyl groups on soda lignin after acetylation. Substitution of hydroxyl groups by the stable acetyl groups prevented any significant cross-linking and thermal stabilization of the macromolecules within the precursor fibers. We emphasize that molecular cross-linking within precursor fibers is an essential step in transforming the fiber into a thermoset before it can be carbonized. This confirms that the composition is not suitable for producing high-performance carbon fibers.
Figure 2.7 Transient shear viscosity of Ace_Soda with 0, 2, and 2.5 h of heat treatment.

2.3.2 ECN organosolv lignin

ECN lignin was an organosolv lignin separated from hardwood using ethanol as solvent. It had a SP of 155°C. The transient shear viscosity of ECN lignin tested at 160°C is shown in Figure 2.8. The viscosity increased gradually with time, but shear viscosity had not exceeded 200 Pa·s after 1 hour, which indicates that the material is more thermally stable compared with soda lignin that was discussed earlier. The results of thermogravimetric analysis, displayed in Figure 2.9, indicate a decomposition temperature of ECN lignin at about 280°C.
Figure 2.8 Transient shear viscosity of ECN lignin at 1 and 3 s\(^{-1}\), 160\(^\circ\)C.

Figure 2.9 Thermogravimetric analysis of ECN lignin
Melt spinning of ECN lignin was performed at 160°C. The resulting fibers were uniform and circular with an average diameter of 29.3 ± 1.1 µm, as displayed in Figure 2.10.

![Figure 2.10 ECN lignin fibers as seen on the take-up wheel (left) and as observed by light microscopy in the transmission mode (right)](image)

The initial stabilization trial was performed at a heating rate of 0.1°C/min. Fiber became tacky at around 125°C. The second stabilization trial was performed carefully with a relatively long procedure; the temperature profile is shown in Figure 2.11. The fiber survived during stabilization, and the final oxidation temperature was 240°C. It took more than 200 h (over 1 week) to stabilize the fibers to prevent fibers from being tacky. This duration is much longer than that needed for most commercial PAN precursor fibers that require about 2 h. The slow oxidation rate was attributed to relatively low hydroxyl content in hardwood organosolv lignin.
The average fiber size after oxidation reduced to 23.5 ± 0.5 µm due to the weight loss during thermal oxidation. After stabilization, the ECN lignin fiber became infusible. The stabilized fibers did not dissolve in acetone, indicating their cross-linked structure after thermo-oxidation.

The stabilized fibers were carbonized at 1000°C. The resulting carbon fibers were nominally 14 ± 1 µm in diameter, as shown in Figure 2.12. The SEM images show that the carbon fibers had smooth surfaces and circular cross sections. The carbonized ECN fibers displayed a tensile modulus, strength, and strain-to-failure values of 32 ± 4 GPa, 450 ± 130 MPa, and 1.4 ± 0.4%, respectively. The electrical resistivity of these fibers was
about 60 $\mu\Omega$-m. Although the tensile properties are not high enough for structural applications, the electrical resistivity is similar to that of rayon-based fibers. Rayon is no longer produced in the United States because of the hazards and environmental regulations in its manufacturing. Rayon-based carbon fibers are used in missile casings where lightweight and low-thermal conductivity is desired. Such ECN-based carbon fibers may serve as a substitute, but the drawback of this ECN process is the extremely slow stabilization step.

![SEM micrographs of carbon fibers derived from ECN lignin](image)

Figure 2.12 SEM micrographs of carbon fibers derived from ECN lignin

2.3.3 SKL lignin

As-received SKL showed no melting behavior during the entire heating procedure even when the temperature reached 300°C at the end of the SP test. Instead, degradation was observed, and the residue was a foamed state indicating the generation of volatiles during heating. Above results are in agreement with those reported in previous literature.
studies in which softwood lignin has been shown to possess poor thermal mobility because it has higher cross-linked structure than does hardwood lignin (65). The hydroxyl groups result in dehydration reaction between molecules. Thus, SKL cannot be melt-spun without appropriate modification.

To achieve melt processability, acetylation of SKL was attempted. SKL was reacted with acetic anhydride for 2 h to convert the hydroxyl groups into acetyl groups using a reaction solution of 15 ml of acetic anhydride per gram of SKL. The resulting acetylated softwood Kraft lignin, referred to as “Ace-SKL”, showed a softening temperature between 156 and 167°C. However, the viscosity of molten Ace-SKL at 170°C increased from about 80 Pa·s to 8,000 Pa·s within 30 min as shown in Figure 2.13 (a). The test finally ended due to overloading of the torque transducer. During heating, several types of reactions can occur including dehydration, condensation, and addition that induce an increase of molecular weight. Consequently, the viscosity increases significantly and causes the failure of rheology test.

Ace-SKL was extracted with 75% acetic acid, and a fraction with relatively large molecular weight was removed. A similar study has been reported by Saito et al. (16) using methanol to obtain a hardwood lignin fraction with a much lower molecular weight, which displayed a SP. After extraction, the fraction soluble in 75% acetic acid in the current study had a SP between 136-145°C. The viscosity remained below 500 Pa·s for the first 30 min at 145°C, as shown in Figure 2.13 (b), as a result of the lower molecular weight. This indicates that subsequent melt spinning may proceed as a stable process.
The extracted Ace-SKL was melt-spun into fibers, as illustrated in Figure 2.14 (a). Although the extracted Ace-SKL was easy to spin into fibers, it was virtually impossible to stabilize them by thermo-oxidative stabilization. Similar to Ace-Soda lignin, substitution of hydroxyl groups by the stable acetyl groups prevented any significant crosslinking and thermal stabilization of the macromolecules within the precursor fibers. Although an extremely slow ramp heating rate of 0.01°C/min was applied, the fibers could not be maintained in their glassy state and became tacky at around 150°C, as shown in Figure 2.14 (b). Therefore, this composition is not well-suited for producing carbon fibers due to the difficulty in its stabilization.
Based on the above discussion on highly acetylated lignin samples, it is evident that the melt stability achieved by significant conversion of hydroxyl end-group to stable acetyl-groups is also a major limitation in the subsequent stabilization step. A potential alternative is to retain some hydroxyl groups by partial acetylation of SKL (whose melt will not be thermally stable), but attempt to convert this lignin into fibers by a process other than melt-spinning. Dry-spinning is such a process where the precursor can be dissolved in a solvent, the solution spun into fibers, and the solvent evaporated simultaneously. Such a process is used commercially to produce cellulose acetate fibers (81), so it is a scalable process. A similar strategy was adopted here, as described next.

SKL was reacted with gradually decreased concentrations of AA (from 15 down to 0.66 mL/g lignin) and reduced reaction times (from 2 h to 15 min), while retaining solubility in acetone. The presence of residual hydroxyl groups was confirmed by FTIR spectra of precursors at different acetylation levels as displayed in Figure 2.15. All the
spectra were normalized with respect to the peaks at 856 cm$^{-1}$, which is attributed to C-H bending on aromatic rings. As the amount of acetic anhydride decreased from 15 ml to 0.66 ml per gram of lignin, intensity of the hydroxyl peak at 3400 cm$^{-1}$ increased significantly. Also, the weight gain of lignin after reaction moderated from 18% to 5%.

![FTIR spectra of SKL at different acetylation levels](image)

**Figure 2.15 FTIR spectra of SKL at different acetylation levels**

Softening point was also measured for Ace-SKL with different reaction composition. As displayed in Figure 2.16, as the extent of acetylation decreased, resulting material had elevated SPs exceeding 200°C, which is favorable for subsequent thermo-oxidative stabilization. 0.66 ml AA/gram lignin was found to be a practical low limit. This grade was miscible in an acetone and could be formed into a viscous solution that
could be manually drawn into filaments and acetone evaporated rapidly. Glass transition temperature, as estimated using DSC, is displayed in Figure 2.17. $T_g$ of Ace-SKL reacted from 1.5-15 ml acetic anhydride per gram SKL were all between 90-105°C, but was noticeably higher at 112°C for Ace-SKL obtained using 0.66 ml acetic anhydride per gram of SKL. The increase of $T_g$ was attributed to stronger intermolecular hydroxyl group interactions, i.e., when less hydroxyl groups were reacted away with acetic anhydride. The presence of such interactions is favorable for the following thermo-oxidative stabilization reactions.

![Figure 2.16 Softening points of Ace-SKL with different reaction composition](image)

Figure 2.16 Softening points of Ace-SKL with different reaction composition
The Ace-SKL with low extent of acetylation was mixed with acetone to form a viscous solution that could be manually drawn into filaments and acetone evaporated rapidly. The solidified filaments had diameter range from 20 to 70 μm, as shown in Figure 2.18, indicating its dry-spinning potential.
Figure 2.18 Ace_SKL filaments manually drawn from acetone solution

Thermo-oxidation was attempted to stabilize the filaments. The following general heating procedure was used to thermo-oxidatively stabilize the fiber: heating from 70 to 140°C, at a heating rate of 0.4°C/min; holding at 140°C for 10 h; heating from 140 to 220°C, at a heating rate of 0.1°C/min with holding time of 3 hours at intermediate temperatures of 150, 160, 170, 180, and 220°C. Larger content of hydroxyl group increased the reactivity and enabled crosslinking during thermo-oxidation, and filament shape was preserved without fibers becoming tacky. The stabilized filaments heated to 1000°C. The interesting observation is that the filament survived the carbonization step and led to the initial production of carbon fibers from dry-spun precursor fibers.
2.4 Conclusions

In the initial phase of this research study, three types of lignins (soda lignin, organosolv lignin and softwood kraft lignin) were investigated as precursors for converting into carbon fibers, as summarized in Table 2.1. Without suitable modification, soda lignin and SKL could not be melt spun due to the existence of large molecules or a large content of hydroxyl groups, which could lead to dehydration reaction. ECN lignin could be converted into carbon fiber, but required impractically slow heating rate during stabilization. Acetylation and fractionation was performed on soda lignin and SKL, and the resulting materials possessed relatively stable melt viscosity and were capable of being melt-spun. However, high extent of substitution of hydroxyl groups into thermally stable acetyl group prevented the subsequent thermal stabilization. SKL with limited acetylation was found to have the potential of being solution spun and successfully thermo-oxidatively stabilized and carbonized. This Ace-SKL with limited extent of acetylation was systematically investigated. The flowing chapters present the rheology and dry-spinning (Chapter Three), carbonization and properties of carbon fibers (Chapter Four), and dual UV-thermal stabilization route (Chapter Five) for rapid stabilization.
Table 2.1 Carbon fiber potential of lignin and modified lignin precursors

<table>
<thead>
<tr>
<th>Lignin Type</th>
<th>SP</th>
<th>Spinning Potential</th>
<th>Stabilization Potential</th>
<th>Carbon Fiber Potential?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda lignin</td>
<td>As-received</td>
<td>245°C</td>
<td>Not melt spinnable</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Acetylated</td>
<td>145°C</td>
<td>Melt spinnable</td>
<td>X</td>
</tr>
<tr>
<td>Acetylated (Ace-Soda)</td>
<td></td>
<td></td>
<td>Not able to cross-link</td>
<td></td>
</tr>
<tr>
<td>ECN organosolv lignin</td>
<td>As-received</td>
<td>155°C</td>
<td>Melt spinnable</td>
<td>√ converted to carbon fibers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Very slow stabilization procedure</td>
<td></td>
</tr>
<tr>
<td>Softwood Kraft Lignin (SKL)</td>
<td>As-received</td>
<td>No SP</td>
<td>Not melt spinnable</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Ace-SKL</td>
<td>136-167°C</td>
<td>Melt spinnable</td>
<td>X</td>
</tr>
<tr>
<td>Ace-SKL (high extent of substitution followed by fractionation)</td>
<td></td>
<td></td>
<td>Not able to cross-link</td>
<td></td>
</tr>
<tr>
<td>Ace_SKL (low extent of substitution)</td>
<td>205°C</td>
<td>Not melt spinnable, can be solution spun</td>
<td>Can be thermo-oxidative stabilized</td>
<td>√ converted to carbon fibers</td>
</tr>
</tbody>
</table>
CHAPTER THREE

EFFECT OF TEMPERATURE AND CONCENTRATION ON FLOW CHARACTERISTICS OF ACETYLATED-LIGNIN SOLUTIONS

3.1 Introduction

This chapter discusses the rheology of lignin solutions and processing of these solutions into precursor fibers by dry-spinning. In the previous chapter (Section 2.3.3), partial acetylation of softwood kraft lignin (SKL) was discussed as a strategy to preserve a fraction of hydroxyl groups. The partially acetylated lignin could be dissolved into acetone and formed into thin filaments, and the resulting material could be successfully stabilized and carbonized. These results indicated the potential of dry-spinning using this partially acetylated Ace-SKL. Whereby, lignin fibers solidify in air while acetone evaporates rapidly. Acetone is a benign solvent that can be recovered, condensed and recycled, and is used in scalable industrial processes such as those used to produce cellulose acetate fibers (81).

To determine the dry-spinning potential of Ace-SKL, the flow characteristics and mass-transfer issues associated with Ace-SKL/acetone solutions need to be studied, since they play an important role during fiber spinning, including evaporation of solvent, to form solid filaments. Therefore, the goal of the study reported in this chapter was to investigate Ace-SKL/acetone solutions to establish a range of suitable combinations of solution concentrations and spinning temperatures. Thus, dry-spinning was conducted under various conditions to determine their effect on the morphology of the resulting lignin precursor fibers.
3.2 Experimental

3.2.1 Materials

As described earlier in Section 2.3.3, softwood Kraft lignin, Indulin\textsuperscript{AT} (SKL), was used throughout this study. The commercial availability of this raw material from Mead-Westvaco, Charleston, SC, indicates its potential in conversion to carbon fibers by an industrially scalable process.

However, for use as a carbon precursor, SKL lignin had to be purified because its ash content was 2.85%, which is too high to produce carbon fibers without defects. The non-carbon content of such precursors can play a significant role in creating defects in the resulting carbon fibers. Thus, before acetylation, washing was performed on SKL lignin to reduce the ash content. Different combinations of mixing time, liquid to solid ratio, and washing solution pH value were studied to determine a suitable protocol for washing.

SKL was washed with acidified DI water under different conditions, and ash contents thus obtained are listed in Table 3.1. The results indicate that larger liquid-to-solid ratio, pH value of 2, and mixing time of 15 min is favorable to efficiently reduce the ash content. When this cycle was repeated, it was also found that using 10 ml acidified DI water (pH=2) per gram of SKL and 15 min of mixing time for each wash resulted in ash content of around 0.15% after 25 cycles. After 5 more washes, there was no substantial reduction of ash content. Thus, 10 ml acidified DI water (pH=2) per gram of SKL, 15 min of mixing time, and 25 washing cycles were established as the standard protocol for each batch of SKL purification. After washing under above conditions, the ash content
was reduced to 0.15%, and a comparison of main metal impurities before and after washing is listed in Table 3.2.

Table 3.1 Ash content resulting after different washing conditions

<table>
<thead>
<tr>
<th>ml liquid/gram of SKL</th>
<th>pH</th>
<th>Mixing time (min)</th>
<th>Ash%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2</td>
<td>30</td>
<td>1.73</td>
</tr>
<tr>
<td>12.5</td>
<td>2</td>
<td>30</td>
<td>1.56</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>30</td>
<td>1.29</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>30</td>
<td>1.09</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>30</td>
<td>1.29</td>
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<td>30</td>
<td>1.29</td>
</tr>
<tr>
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<td>15</td>
<td>1.30</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>30</td>
<td>1.29</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>30</td>
<td>1.33</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>30</td>
<td>1.29</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>30</td>
<td>1.98</td>
</tr>
</tbody>
</table>

Table 3.2 Elemental analysis result of SKL before and after wash

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>S</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
</tr>
<tr>
<td>SKL</td>
<td>0.105</td>
<td>0.014</td>
<td>0.017</td>
<td>0.005</td>
<td>1.219</td>
<td>0.753</td>
<td>0.015</td>
<td>0.023</td>
</tr>
<tr>
<td>Washed SKL</td>
<td>0.003</td>
<td>0.008</td>
<td>0.012</td>
<td>0.004</td>
<td>0.684</td>
<td>0.007</td>
<td>0.014</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Starting with the purified SKL, limited acetylation was conducted. Details of the modification process were discussed earlier in Sections 2.2.2 and 2.3.3. Thirty grams of
purified SKL was mixed with 20 mL acetic anhydride in a round-bottomed flask. The flask was connected with a reflux condenser and dipped into a water bath set at 85-90°C with continuous stirring. In the initial stage of mixing, manual stirring was necessary to wet the dry lignin powders. The mixture was reacted for 15 min. The partially acetylated SKL (Ace-SKL) was capable of crosslinking during thermal oxidation.

Ace-SKL/acetone solution was prepared by mixing 50 g of Ace-SKL dry powder with 100 ml acetone. The mixture was manually stirred and solvent evaporated until solution was concentrated to above 1.7 g solids/mL acetone. Also, the concentrated solutions were put into ultrasonic tank to achieve homogeneity. To measure the concentration of various solutions, the solutions were weighed precisely, vacuum dried at 95°C for 2 hours, and re-weighed.

3.2.2 Rheology and spinning

The viscosity of Ace-SKL solutions at various concentrations and temperatures was measured using an ACER 2000 capillary rheometer (Rheometric Scientific). High shear measurements were conducted at shear rates ranging from 3,000 to 10,000 s⁻¹. In an attempt to measure more fundamental rheological properties of the Ace-SKL solutions, tests were also conducted at low shear rates using a cone-plate fixture. Unfortunately, the rapid evaporation of acetone from edges led to inaccurate and unrepeatable results. Therefore, only the high shear results obtained reliably from capillary rheometer are discussed, as these are also of greater relevance for the extrusion step during fiber spinning. Capillaries of 1 mm diameter and three L/D ratios (5, 15, and 25) were used to
perform the Bagley correction \(^{(82)}\) for entrance pressure drop. In a Bagley plot, the measured pressure drop under selected shear rates is plot against L/D as shown in Figure 3.1, which was obtained from a 2.15 g/ml acetone Ace-SKL solution. The corrected shear stress was calculated using equation (3.1), in which \(\Delta P_{app}\) is the measured pressure drop, \(\tau_R\) is the shear stress, and \(\Delta P_{ent}\) is the pressure drop caused by entrance effect. The slope of trendlines in Figure 3.1 equals to \(4 \tau_R\) and the intercept equals to \(\Delta P_{end}\). After corrected shear stress \(\tau_R\) is calculated, the shear viscosity \(\eta\) at a certain shear rate \(\dot{\gamma}_R\) can be calculated using equation (3.2).

\[
\Delta P_{app} = \tau_R \frac{4L}{D} + \Delta P_{ent} \tag{3.1}
\]

\[
\eta = \frac{\tau_R}{\dot{\gamma}_R} \tag{3.2}
\]
Dry-spinning was performed using a batch unit custom-designed by AJA Inc. (Greenville, SC). The viscous solution was transferred into a spinning barrel fitted with a 4-hole die, with each hole having a diameter of 75 μm and a length of 225 μm. The spinning barrel had a diameter of 18 mm. In this lab-scale process, the solvent was vented, but in a commercial process, the solvent can be condensed and recycled.

The Ace-SKL / acetone solutions could be drawn into filaments when the concentration exceeds 1.7 g solids/mL acetone. Thus, Ace-SKL / acetone solutions were prepared at three concentrations: 1.85, 2.00, and 2.15 g solids/mL acetone. These solutions were dry-spun at temperatures ranging from ambient (25°C) to 52°C. During

Figure 3.1 Bagley plot of 2.15 g/ml Ace-SKL solution
spinning, the draw-down ratio (DDR) was controlled between 5.7-6.9 at a nominal roll speed of 130 m/min.

Scanning electron microscopy (SEM, Hitachi S4800) was used to analyze the cross-section shape and dimension. The perimeter and area of single fibers were measured using Quartz PCI software and “Freenhand shape measuring tool”. For each group of as-spun fibers, 10 fiber samples were measured to obtain the average cross-sectional area and perimeter, as well as other features of fiber shape.

3.3 Results and Discussion

3.3.1 Viscosity and flow characteristics

After purification, the SKL with an ash content of about 0.15% was modified by acetylation, as described earlier in Chapter Two. Ace-SKL/acetone solutions were prepared for dry-spinning. In typical commercial fiber spinning equipment, pressure drop across spinnerets must be limited to about 14 MPa (2,000 psi). In preliminary experiments, it was found that the pressure drop across the spinneret was excessive even at the lowest concentration (1.85 g/mL) when the experiment was conducted at ambient temperature (25°C). Therefore, flow characteristics were needed at elevated temperatures to determine the extent of viscosity reduction and resulting pressure drop.

Figure 3.2 (a) displays the viscosity of the three solutions at ambient and elevated temperatures. For these results, entrance pressure drop was subtracted using Bagley correction method (82). Results show clearly that Ace-SKL / acetone solutions are shear-
thinning at all temperatures and concentrations investigated. As expected, viscosity increased as Ace-SKL concentration increased (ambient temperature = solid symbols). Also, viscosity of all three solutions could be reduced significantly by increasing the temperature (open symbols). The extent of temperature increase was higher for the most concentrated solution.

The viscosity curves were fitted to a power-law model. It should be noted that for a Newtonian fluid the power law exponent (n) equals 1, whereas for polymeric solutions n < 1. For Ace-SKL solutions at various concentrations and temperatures, the power-law exponent was found to range from 0.33 to 0.82, which confirms the macromolecular nature of the Ace-SKL lignin precursor.

The power-law parameters were also used to predict pressure drops (ΔP) expected in the spinnerets using the following equation for a power-law fluid (83):

\[ Q = \frac{\pi R^3}{1/n + 3} \left( \frac{R \Delta P}{2mL} \right)^{1/n} \]

(3.3)

where Q is the flow rate, R is the capillary diameter, L is the capillary length, m and n are the power law parameters. Calculations were performed using power-law parameters obtained for the three combinations: 1.85 g/mL at 35°C, 2.00 g/mL at 40°C, and 2.15 g/mL at 50°C. For the three concentrations, (1.85, 2.0 and 2.15 g/mL), the predicted ΔP were 4.1 MPa (590 psi), 3.4 MPa (490 psi), and 3.4 MPa (500 psi). Because these predicted ΔP values do not include end-effects, viscosity results from the short L/D
5 capillary [Figure 3.2 (b)] were also used. The predicted values were 12.0 MPa (1740 psi), 11.8 MPa (1710 psi) and 11.5 MPa (1670 psi), which are fairly consistent with the measured values of 10.1 MPa (1460 psi), 10.0 MPa (1450 psi) and 8.4 MPa (1220 psi) during the fiber spinning experiments, discussed next.

Figure 3.2 Shear viscosity of Ace-SKL solutions over a range of shear rates. (a) Viscosity obtained after Bagley correction using capillaries with L/D = 5, 15 and 20; (b) Viscosity obtained from capillaries with L/D = 5, without Bagley correction.

3.3.2 Fiber spinning

Figure 3.3 displays SEM images of lignin fibers obtained from a 1.85 g/mL solution. Continuous filaments could be drawn consistently at a roll-speed of 130 m/min
and spinning temperatures of approximately 30°C from this lowest concentration solution. It is noted that the as-spun fiber diameters were quite fine, about 30 to 40 μm. In Chapter Four, the post-stretching and stabilization of these lignin fibers will be discussed. Subsequently, such lignin-based precursor fibers can be successfully carbonized. Another interesting feature of the dry-spun lignin-based precursor fibers, as well as the resulting carbon fibers, is their crenulated shape. When used in polymeric composites, the crenulated shape can enhance the interfacial bonding between carbon fibers and resin by providing increased contact area, and is a desirable feature. Therefore, these characteristics were studied further.

As displayed in Figure 3.3 (also at a concentration of 1.85 g/mL), as the spinning temperature increases, fibers developed more crenulations. Also, some crenulations became doubly convex crevices, such as that identified by the encircled region in the SEM images displayed in Figure 3.3. A SEM image of a crevice at higher magnification is shown in Figure 3.4. Such sharp crevices are not desired as these would be difficult to infuse with polymeric resins and result in inadequate fiber-surface wetting if such carbon fibers were converted into composites. Therefore, other dry-spinning conditions were investigated next.
Figure 3.3 SEM images of Ace-SKL lignin fibers from a 1.85 g/mL solution, at various spinning temperatures.
Figure 3.4 Magnified SEM image of a sharp crevice on the surface of as-spun lignin fiber obtained from 1.85 g/mL solution.

Figure 3.5 displays the SEM images from a more concentrated solution, 2.00 g/mL. Higher spinning temperature was required to achieve lower viscosity and better processability. Stable filament winding could be achieved for spinning temperatures of about 35°C and higher. Again, the crevices started to show up when spinning temperature was above 40°C. The sharp notches on the surface of some fibers fused together at the outer edge, leaving a hollow space/void.
Figure 3.5 SEM images of Ace-SKL lignin fibers from a 2.00 g/mL solution, at various spinning temperatures
The highest concentration of solution used in this study was 2.15 g/mL, and Figure 3.6 displays SEM micrographs of fibers obtained from this solution. Fibers could be continuously spun when solution temperature approached 40°C. Due to a lower fraction of solvent in this concentrated solution, a smaller volume reduction resulted in fibers during the drying step. Consequently, the collapse of fiber surface during diffusion was not as significant as for the more dilute concentrations. Thus, fibers produced from this concentrated solution did not possess sharp crevices at any of the spinning temperatures. Clearly, 2.15 g lignin/mL solvent is a suitable concentration for the given Ace-SKL to produce fibers with the desired morphology. These results establish the importance of precursor solution concentration in determining the shape and features of the resulting lignin fibers.
Figure 3.6 Ace-SKL lignin fibers from dry-spinning of 2.15 g/mL solution at various spinning temperatures.

A quantitative analysis of fiber microstructure is listed in Table 3.3. The average number of crenulations on each fiber ($C_N$) are reported because the exact number varies from fiber to fiber. Another measure of the surface undulation is the ratio of the enhanced lateral surface area of the crenulated fibers compared with circular fibers possessing equal cross-sectional area, which is reported in Table 3.3 as SR. This represents the enhancement of fiber-matrix surface area due to crenulations for a given volume fraction of the reinforcing fibers in a composite material. For all concentrations, current results
confirm that fibers spun at a higher temperature had a larger number of crenulations, which facilitates rapid out-diffusion of solvent. As discussed previously, higher spinning temperatures also helped reduce the solution viscosity and resulting pressure drop within spinnerets.

Table 3.3 Fiber surface characteristics of Ace-SKL as-spun fibers at various concentrations and appropriate processing temperatures. $C_N$ is the average number of crenulations on each fiber, and SR is the ratio of the enhanced surface area of the crenulated fibers compared with circular fibers possessing equal cross-sectional area.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>35°C ± 2°C</th>
<th>40°C ± 1°C</th>
<th>50°C ± 2°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.85 g/mL C$_N$ (Average number of crenulations per fiber)</td>
<td>15.1 ± 0.4</td>
<td>19.1 ± 1.2</td>
<td>24.6 ± 0.8</td>
</tr>
<tr>
<td>1.85 g/mL SR (%) (Enhancement of lateral surface area)</td>
<td>135.1% ± 1.2%</td>
<td>134.2% ± 1.9%</td>
<td>132.4% ± 0.9%</td>
</tr>
<tr>
<td>2.00 g/mL C$_N$ (Average number of crenulations per fiber)</td>
<td>11.8 ± 0.6</td>
<td>16.1 ± 0.4</td>
<td>19.4 ± 0.5</td>
</tr>
<tr>
<td>2.00 g/mL SR (%) (Enhancement of lateral surface area)</td>
<td>131.2% ± 1.2%</td>
<td>133.5% ± 1.4%</td>
<td>136.4% ± 1.1%</td>
</tr>
<tr>
<td>2.15 g/mL C$_N$ (Average number of crenulations per fiber)</td>
<td>Too viscous</td>
<td>13.6 ± 0.4</td>
<td>17.3 ± 0.1</td>
</tr>
<tr>
<td>2.15 g/mL SR (%) (Enhancement of lateral surface area)</td>
<td>Too viscous</td>
<td>127.1% ± 1.5%</td>
<td>136.5% ± 1.7%</td>
</tr>
</tbody>
</table>

Dry-spinning is a complex process that includes three simultaneous phenomena: non-Newtonian fluid flow (fiber extrusion and draw-down), heat-transfer (fiber cooling), and mass transfer (solvent evaporation). So, exact mathematical modeling is beyond the
scope of this work, but the development of crenulations can be explained semi-quantitatively as follows.

During evaporation of acetone through the circular (nominal) fiber, the radial mass flux

\[ n_{Ar} \text{ scales with the concentration gradient:} \]

\[ n_{Ar} \sim D_{AB} \frac{\partial \omega_A}{\partial r} \]

(3.4)

where \( D_{AB} \) is the mass diffusivity of acetone in the solution, and \( \omega_A \) is the weight fraction of acetone. As the solvent diffuses out, the volume of the fiber decreases and so does its surface area, which for a circular cross-section would lead to a decrease in overall evaporation rate (mass/time). However, to facilitate the overall mass-transfer rate, the fiber cross-section changes from smooth (circular) to crenulated, which increases the specific area. As demonstrated in Table 3.3, crenulated fibers possess about 35% more external specific surface area compared with circular fibers with the same cross-sectional area (SR).

For carbon fibers, it is known that smooth circular cross-section leads to better strength than the ones containing sharp crevices such as that observed in the MP-based CFs that possess a “pac-man” split (84). For dry-spun Ace-SKL precursor fibers, it is not possible to obtain circular fibers because the finite rate of out-diffusion of solvent (at any temperature or solvent concentration) still produces a wavy surface. In an attempt to
produce fibers with smooth surface and shapes close to circular from dry-spinning, a 2.15 g/ml solution was dry-spun at room temperature for slower diffusion of acetone. The spinning was extremely difficult and the process had to stop due to plugging of spinneret hole as the pressure drop approached the high alarm value of 24 MPa (3,500 psi). The limited fibers that were collected are illustrated in Figure 3.7 (a). Although the as-spun fibers displayed a ribbon-like shape and smooth surface, the extrudate could not be drawn-down to fine fiber diameters below about 30 µm that are highly desired for producing high strength carbon fibers.

To enable dry-spinning at room temperature (25°C), a solution at a lower lignin concentration of 2.00 g/ml was prepared. The spinning was still difficult due to a high pressure drop of 2700 psi within the spinneret. The as-spun fibers, shown in Figure 3.7 (b), displayed a relatively smooth lateral surface but noncircular cross-section.

The crenulated pattern from dry-spinning at elevated temperatures was preserved in the carbonized fibers, and the carbonization of these precursor fibers and properties of the resulting carbon fibers are discussed next in Chapter Four.
Figure 3.7 As-spun fibers from dry-spinning of Ace-SKL/acetone solutions at room temperature at two different concentrations: (a) 2.15 g/ml and (b) 2.00 g/ml

3.4 Conclusions

Shear viscosity of Ace-SKL solutions displayed a significant shear-thinning behavior at all temperatures studied. The viscosity results could be modeled with power-law exponents ranging from 0.33 to 0.82, confirming the macromolecular nature of the Ace-SKL lignin/acetone solutions. As expected, elevated temperatures lead to lower viscosities and facilitate extrusion at pressures under 10 MPa (about 1500 psi). As-spun fibers produced from dilute solutions (1.85 and 2.00 g/mL) developed some sharp crevices on the fiber surface. These are undesirable for subsequent processing of resulting carbon fibers into composites by resin-infusion. For the most concentrated solution investigated in this study, 2.15 g/mL, the resulting fibers contained no sharp crevice. All fibers produced by the dry-spinning process led to crenulated fiber surface, with the
highest spinning temperature leading to most crenulations. Room temperature spinning was also attempted for the purpose of obtaining fibers with circular cross-section, but resulted in excessive pressure drop during dry-spinning that is not suited for scaled-up processes. About 35% larger surface area could be achieved in Ace-SKL as-spun fibers (as compared with equivalent circular fibers), indicating the potential of such biomass-derived fibers in providing larger fiber/matrix bonding area when used in composites.
CHAPTER FOUR
CARBON FIBER DERIVED FROM ACE-SKL: HEAT TREATMENT AND CARBON FIBER CHARACTERIZATION

4.1 Introduction

As discussed in Chapter One, production of carbon fibers is a complex process that requires a series of steps. During the heat treatment step, tension must be applied to the fibers to improve mechanical properties. Stretching is necessary during the stabilization and carbonization of PAN precursors, and results in improvement of modulus and strength of resulting carbon fiber due to the preserved molecular orientation (85-87). Also, for the production of rayon based carbon fibers, stretching is a significant protocol during carbonization to achieve orientation within the carbon fibers (32-34). Only for mesophase pitch based carbon fibers, there is no need to apply tension during stabilization and carbonization as the discotic pitch molecules align in the fiber axis during melt spinning and cannot relax subsequently (2, 4).

Most of prior studies on lignin-based carbon fibers have focused on the fiber-forming step by the modification of lignin precursors. Although different types of lignin precursors have been explored to produce carbon fibers, the highest tensile strength reported for those lignin-based carbon fibers was only 660 MPa (59, 62, 65, 66, 74, 88, 89). It is necessary to improve the conditions during the entire process of carbon fiber production process to achieve better mechanical properties. An investigation of dry-spinning conditions to obtain the derived microstructure was discussed in Chapter Three.
Stabilization and carbonization step will be discussed in this chapter, particularly with attention to applied tension/stretching during heat treatment. The microstructure and properties of resulting carbon fibers are finally discussed.

4.2 Experimental

4.2.1 Thermal stabilization

Ace-SKL as-spun fibers were obtained by the method discussed in Chapter Three. To “stabilize” these fibers into a thermoset state, they were placed in a programmable air oven. The heating cycle was: heating from 70 to 140°C at a heating rate of 0.4°C/min; holding at 140°C for 10 h; heating from 140 to 150°C at a heating rate of 0.1°C/min; holding at 150°C for 4 h; heating from 150 to 160°C at a heating rate of 0.1°C/min; holding at 160°C for 4 h; heating from 160 to 170°C at a heating rate of 0.1°C/min; holding at 170°C for 3 h; heating from 170 to 180°C at a heating rate of 0.1°C/min; holding at 180°C for 3 h; heating from 180 to 220°C at a heating rate of 0.2°C/min; holding at 220°C for 3 h.

Tension was applied during heat treatment. Ace-SKL precursor fibers were mounted within graphite end-tabs at both ends using fast-cure epoxy. The mounting procedure is illustrated in Figures 4.1 (a) and (b). In Figure 4.1 (a), a fiber tow with about 0.01-0.03 gram weight and 3-5 cm length was cut and weighed in balance. One end of the aligned fiber tow was placed in the graphite end tab, with fast cure epoxy applied on the tab. Another layer of graphite end tab was bonded beyond those fibers to form a “sandwich” structure. The fiber tow, with one end glued, was weighed again and the
weight of the end tabs factored into load applied during stabilization. After the other side was glued, the fiber tows were loaded in tension, as illustrated in Figure 4.1 (c).

![Figure 4.1 Stabilization of Ace-SKL fiber tow under tension](image)

4.2.2 Carbonization

After stabilization, the fiber tows were mounted again with graphite end tabs but using a ceramic based glue Ceramabond 671 (Aremco Products Inc.) that could survive the high carbonization temperature. As shown in Figure 4.2, ends of the stabilized fiber
tows were fixed on a layer of graphite sheet with scotch tape. The tows were maintained under slight tension to keep a good alignment of fibers. One piece of a new end tab for carbonization was carefully inserted under the fiber tow, and Ceramabond 671 was applied on top of the end tab. Another piece of end tab was glued on top of the fibers. After two ends were glued with Ceramabond 671, the newly mounted tows were put into oxidation oven at 94°C for two hours for curing of the adhesive.

Figure 4.2 Mounting of stabilized fiber tows with Ceramabond 671
Then carbonization was performed under tension using a customized graphite rack, as illustrated in Figure 4.3. Fiber tows were suspended on the rack, and appropriate tungsten weights were loaded at the bottom using tungsten wires. The rack with fiber tows was put into a cup made with graphite sheet. If the tows broke during carbonization, the graphite cup could catch the dropped tungsten weight. Most of the Ace-SKL based carbon fibers in this study were obtained from carbonization performed at 1000°C for 1 h, with a ramp from room temperature to 1000°C of 3.5 h. Also, one batch of carbonized fibers were further carbonized to 2400°C.

Figure 4.3 Carbonization of Ace-SKL fiber tow under tension using customized graphite rack
4.2.3 Characterization

To measure the density of Ace-SKL based carbon fibers, a series of density floats was used to prepare cesium formate solutions with densities ranging from 1.50 to 2.25 g/cm³ in increments of 0.05 g/cm³ (Figure 4.4). Ace-SKL derived carbon fibers were immersed into these solutions and allowed to settle for 24 h. Based on the solution in which the fibers sunk as opposed to the next denser solution where the fiber floated enabled density measurements to within ± 0.025 g/cm³. For carbon fibers produced in this study (1000°C), fibers floated on surface of solutions with density larger than 1.75 g/ml and sank to the bottom of solutions with density lower than 1.70 g/ml. Thus, the density of Ace-SKL carbon fibers could be bracketed between 1.70 and 1.75 g/cm³.

![Figure 4.4 Cesium formate solution prepared with density floats](image-url)
Raman spectra were recorded on a Renishaw System (Gloucestershire, UK) using a near infrared 780 nm-diode laser. The Raman shift was calibrated with a silicon standard centered at 520 cm\(^{-1}\). Raman spectra were analyzed using WiRE software v3.2 to integrate the peaks.

Wide angle X-ray diffraction (WAXD) patterns were obtained from a Rigaku CuK\(_{\alpha}\) X-ray source at wavelength of 0.15406 nm, with the X-ray source operated at 45 kV and 0.65 mA. Fiber bundles were mounted on a paper tab and sprinkled with NIST-grade silicon standard powder for accurate identification of 2\(\theta\) position on integrated azimuthal scan. The exposure time per sample was 1 h. The spacing of (0 0 2) plane \((d_{002})\) were calculated according to Bragg’s law with the following equation (4.1):

\[
d_{002} = \frac{\lambda}{2 \sin \theta}
\]  

(4.1)

where \(\lambda\) corresponds to the wavelength of the X-ray beam (0.15406 nm), and \(\theta\) is the angle of incidence of the X-ray beam. According to the model given by Maire and Mering (102), degree of graphitization was calculated using the equation (4.2):

\[
g(\%) = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100
\]  

(4.2)

where \(g\) is the degree of graphitization (\%).
The Herman’s orientation factor $f_a$ was calculated from equation (4.3), where $\phi$ is the azimuthal angle and $\langle \cos^2 \phi \rangle$ is obtained from equation (4.4). In equation 4.4, $I(\phi)$ is the peak intensity at angle $\phi$.

$$f_a = \frac{3\langle \cos^2 \phi \rangle - 1}{2}$$

(4.3)

$$\langle \cos^2 \phi \rangle = \frac{\sum_{\phi=0^\circ}^{90^\circ} I(\phi) \sin \phi \cos^2 \phi}{\sum_{\phi=0^\circ}^{90^\circ} I(\phi) \sin \phi}$$

(4.4)

SEM images were captured using a Hitachi S-4800. To measure tensile properties, individual fibers were tested in a Phoenix tensile testing device following the ASTM test method D-3379-5. The load cell of the MTS apparatus has a maximum capacity of 500 g, and the crosshead speed was set to 0.5 mm/min. Filaments 25 mm in length were mounted in the paper frame. The fiber diameter was measured by laser diffraction method. Each paper tab was secured in the upper and lower jaws of the MTS. To prevent the accidental breakage of fiber prior to test failure, an electric hot wire (instead of scissors) was used to burn the paper tab.

Also, to eliminate the effect of end-tab slippage during tensile test, for some batches of carbon fiber samples, compliance tests were conducted using samples with 5 mm, 10 mm, and 25 mm of gauge lengths. Because carbon fibers display a linear stress-strain response to failure, equation (4.5) is used to calculate tensile modulus from tensile
strength (\(\sigma\)) and strain to failure (\(\varepsilon\)), where \(f\) is the breaking force, \(A\) is the cross-sectional area, \(\Delta l\) is the length change of fiber sample and \(l\) is the gauge length.

\[
E = \frac{\sigma}{\varepsilon} = \frac{f/A}{\Delta l/l}
\]  

(4.5)

4.3 Results and Discussion

In Chapter Three, the suitable solution concentration of Ace-SKL solution was established at 2.15 g/ml to prevent the occurrence of crevices on fiber surfaces. Therefore, most of the as-spun fibers that were converted into carbon fibers were obtained from dry-spinning of 2.15 g/ml solutions at 35-50°C. A limited amount of carbon fibers were also obtained from a lower concentration of 2.00 g/ml precursor solution.

4.3.1 Tension effect

Ace-SKL fibers were thermo-oxidatively stabilized using a temperature ramp with several hours of dwell time from ambient to a maximum temperature of 220°C. The slow ramp heating program allowed the fibers to maintain their shape without becoming tacky. Tension was applied and the normalized load level is defined in equation (4.6). A range of load levels between 2000-2500 g/(g/cm) led to different extents of stretching.
Normalized Load level_{stabilization}(cm)

\[
\text{Normalized Load level}_{stabilization}(cm) = \frac{Weight \ of \ load \ during \ stabilization \ (gram)}{Linear \ density \ of \ fiber \ taws \ (\frac{gram}{cm})}
\]

(4.6)

After thermal stabilization under tension, Ace-SKL precursor fibers can have an extension up to 800% as shown in Figure 4.5. Stretching and crosslinking occurred at the same time during stabilization process. Figure 4.6 is a plot of fiber length change at different temperatures during one batch of stabilization. To prevent fibers from becoming tacky, several dwells were required and the total stabilization time was about 40 h.

Figure 4.5 Stretched fiber tows after thermal stabilization under tension
Figure 4.6 Fiber length change at different temperatures during one batch of stabilization

Tension was also applied during carbonization. The load level during carbonization ($Load\ level_{carb.}$) was calculated using equation (4.7), wherein $d$ is the fiber diameter after stabilization, $d_0$ is the as-spun fiber diameter before stabilization, and “linear density of fiber tows” is the same as in equation (4.6).
Load level\textsubscript{\text{carb}} (cm)

\[
\text{Load level}_{\text{carb}} (cm) = \frac{\text{Weight of load during carbonization (gram)}}{\text{Linear density of fiber tows (gram/cm)}} \times \frac{d^2}{d_0^2} \tag{4.7}
\]

In Figure 4.7, the extent of fiber extension-during-carbonization (EDC) is plotted against load level applied. When the load level exceeded 21000 g/(g/cm), all of the fiber tows broke during carbonization. The status of the fiber tows in furnace could be monitored through an observation window. However, as a safety precaution, it is emphasized that this should not be done when furnace temperature exceeds 1300°C. Tow breakages typically occurred between 640-820°C, and most of the tows broke at 700-730°C. When fibers broke, they lost the applied tension. But it should be noted that, at 700-730°C, carbonization was partially completed, so certain level of orientation could be preserved within the broke fibers. Although in Figure 4.8, fiber tows with load level less than 20150 g/(g/cm) survived after carbonization without breakage, most of these fibers displayed a negative extension (shrinkage). As expected, larger load levels resulted in larger EDC values. An extension of up to 26% could be achieved although some fiber tows broke during carbonization.
Figure 4.8 displays modulus and strength of various carbon fibers as a function of EDC. As expected, the overall trend is that carbon fibers with larger EDC displayed better tensile properties, due to a higher textural orientation within the fibers. In Figure 4.9, the two batches of carbon fibers with highest strength were not from the largest EDC batch, but with an EDC around 5%. One of those two batches of fibers broke at 820°C,
while another survived after carbonization without breakage. Thus, they underwent tension during the whole or most of carbonization process, and the orientation was greatly preserved. The fiber tows with 14% and 26% EDC both broke between 700-730°C, thus an extent of molecular orientation lost after breakage occurred.

For the results discussed in this chapter, tension was applied to fiber tows in the batch process using dead weight loading. The limitation of this batch process is that there is no way to change the load level during carbonization. If the load level could be adjusted during carbonization, a relatively smaller amount of tension could be applied when temperature reaches 600°C, where intense reactions and weight loss occur in the fibers. When scaled up to a continuous process, varying levels of tension can be applied by using a series of take up rolls rotating at various speeds.
Figure 4.8 Tensile strength and modulus of Ace-SKL carbon fibers under various levels of tension during carbonization.
Table 4.1 lists the tensile properties of Ace-SKL derived carbon fiber from different batches stabilized and carbonized with or without tension; the values are before compliance correction. With applied tension, fibers with thinner diameter and better tensile properties were obtained. Fibers processed without any tension during both stabilization and carbonization displayed only half of the tensile strength as compared with fibers processed with tension during both steps. After compliance correction for modulus, carbon fibers that underwent significant EDC displayed a tensile modulus, strength, and strain-to-failure values of 52±2 GPa, 1.05±0.07 GPa, and 2.0±0.2%, respectively. The largest individual filament tensile strength was 1.3 GPa.

Table 4.1: Ace-SKL carbon fiber properties of fiber processed with and without tension

<table>
<thead>
<tr>
<th></th>
<th>Diameter (µm)</th>
<th>Strength (MPa)</th>
<th>Apparent Modulus (GPa)</th>
<th>Apparent strain to failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilized and carbonized without tension</td>
<td>22.5 ± 0.4</td>
<td>510 ± 50</td>
<td>30 ± 2</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Stabilized with tension, carbonized without tension</td>
<td>8.6 ± 0.2</td>
<td>700 ± 30</td>
<td>28 ± 1</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>Stabilized and carbonized with tension</td>
<td>5.9 ± 0.2</td>
<td>1050 ± 70</td>
<td>35 ± 3</td>
<td>3.0 ± 0.2</td>
</tr>
</tbody>
</table>

4.3.2 Microstructure

To study the effect of carbonization temperature on microstructure, one group of Ace-SKL carbon fibers was further heat treated to 2400°C (without tension from 1000-
2400°C). After this high temperature carbonization, the tensile strength dropped to 210 ± 30 MPa. This is consistent with other precursors (such as PAN), where out-diffusion of non-carbonaceous elements leave behind voids and defects.

Representative Raman spectra for Ace-SKL carbon fibers carbonized at 1000 and 2400°C are displayed in Figure 4.9. The ratio of integrated intensity value of disordered (D) to graphitic (G) peaks (I_D/I_G) was measured to be about 2.88 and 1.02 for 1000 and 2400°C treated fibers respectively. Both values indicate a low degree of graphitic crystallinity development within the carbon fibers. This is consistent with the nonhomogeneous chemical structure of the lignin precursor, which is not as conducive to formation of the graphitic layer planes (0 0 2) as is mesophase pitch. It should be noted that a higher graphitic crystallinity enhances lattice-dominated properties such as the modulus and thermal conductivity, but adversely affects the tensile strength.
Figure 4.9 Raman spectra of Ace-SKL carbon fibers carbonized at 2400 and 1000°C. Intensity values on the ordinate scale are in arbitrary units.

A representative wide angle X-ray diffraction pattern for Ace-SKL carbon fibers (after Fraser-correction) is shown in Figure 4.10, with (0 0 2) peak and silicon (1 1 1) peak marked on the diffractogram. The 2θ scans (integrated azimuthal profiles) for Ace-SKL carbon fibers treated to 1000°C and 2400°C are presented in Figure 4.11. The three small, sharp peaks (first appearing at 28.4°) marked in circles are from NIST-grade silicon powder sprinkled on the carbon fiber samples for accurate location of 2θ peak positions. For 1000°C carbonized Ace-SKL fibers, the 2-theta (integrated azimuthal) profiles from WAXD for fibers carbonized with and without tension displayed (0 0 2) peaks at 2θ value of approximately 24.3° and 23.3°, respectively, as shown in Figure 4.11.
These 2-theta values are even smaller than that observed for turbostratic carbon generated in PAN-based carbon fibers. Therefore, the 1000°C carbonized fibers possessed no measurable degree of graphitic crystallinity. For 2400°C carbonized fibers, the (0 0 2) peak was located at 26.0°, with d_{002} spacing calculated as 0.3424 nm, and the corresponding degree of graphitization at 18%. These WAXD results are consistent with those obtained from Raman spectroscopy. Further, the azimuthal profile of the (0 0 2) peak, Figure 4.11 (b), shows virtually no molecular orientation in fibers carbonized without tension. The Herman’s orientation factor $f_a$ was measured at about 0.1. In contrast, for fibers carbonized under tension, the peak at $\phi \sim 0^\circ$ indicates an observable extent of molecular orientation with a significantly higher Herman’s orientation factor of about 0.3. The 2400°C carbonized fiber also preserved the orientation with Herman’s orientation factor still as 0.3. In Figure 4.12, the WAXD profiles of Ace-SKL based, PAN-based, and mesophase pitch-based carbon fibers are plotted together for comparison. It is evident that the Ace-SKL based carbon fibers have the smallest 2-theta value and virtually no graphitic three-dimensional order.
Figure 4.10 A 2-D wide-angle X-ray diffraction pattern after Fraser-correction
Figure 4.11 Wide-angle x-ray diffraction of Ace-SKL carbon fibers. Intensity values on the ordinate scale are in arbitrary units. Azimuthal scans have been shifted vertically for visual clarity. The encircled peaks (a) are silicon peaks.
The Ace-SKL based carbon fibers heat treated at 1000°C had a resistivity of 106 ± 12 µΩ·m, whereas the 2400°C heat treated fibers had a resistivity of 63 ± 3 µΩ·m. The electrical conductivity of PAN-based T-300 carbon fibers is 18 µΩ·m, whereas that of pitch-based carbon fibers P-120 is 2.2 µΩ·m (4). Ace-SKL carbon fibers heat treated at both temperatures (1000 and 2400°C) had lower conductivity indicating than even that of PAN-based carbon fibers, indicating a very low 3-D order in these fibers. These results are consistent with the Raman and WAXD result.

As discussed in section 3.3.2, Ace-SKL precursor fibers developed crenulations on the surface. From the SEM micrographs of Ace-SKL based carbon fibers, shown in Figure 4.13, it is evident that the crenulated pattern was preserved. An analysis of carbon
fibers obtained from 2.15 g/ml Ace-SKL solution spun at 45°C shows that it has 35% larger surface area as compared with equivalent circular fiber (same cross-sectional area) that would be typically obtained by melt-spinning. Larger interfacial area could ultimately lead to higher fiber-matrix interfacial bond strength in composites.

The SEM images of Ace-SKL carbon fibers carbonized at 2400°C are shown in Figure 4.14. These fibers displayed a tensile strength, modulus, and strain to failure of 158 ± 17 MPa, 29 ± 3 GPa, and 0.6 ± 0.1%. It was observed that these carbon fibers had a significantly rougher surface as compared with fibers carbonized at 1000°C. These defects were likely caused by the out-diffusion of non-carbonaceous elements during graphitization and led to their very low strength of 210 MPa and low strain-to-failure of only 0.6%. It is possible that the very low levels of force and displacement measured for such fibers could have led to the low level of apparent modulus, observed for porous microstructure. In summary, although these fibers had a relatively larger graphitic content (as inferred from a larger 2-theta angle), the defect-ridden microstructure obtained at 2400°C led to lower tensile properties (including the apparent modulus) that those obtained from fibers carbonized at 1000°C.
Figure 4.13 SEM of Ace-SKL carbon fibers from 2.15 g/ml Ace-SKL solution spun at 45°C
Figure 4.14 SEM of Ace-SKL carbon fibers carbonized at 2400°C
As reported in Section 3.3.2, the as-spun fibers obtained from 1.85 and 2.00 g/ml solutions displayed sharp crevices on the fiber surfaces. One batch of such fibers (dry spun at 50°C from 2.00 g/ml solution) was also heat treated to 1,000°C to study the effect of microstructure on the mechanical properties. Their SEM micrographs are displayed in Figures 4.15. It is evident that the carbon fibers retained the cross-sectional pattern from their as-spun state, as the occlusions were formed within the carbon fibers from sharp notches present on the precursor fiber surface.

Figure 4.15 Carbon fibers obtained from precursor fibers dry spun at 50°C of 2.00 g/ml solution
Stress-strain curves of two representative single carbon fibers derived from the 2.00 and 2.15 g/ml precursor solutions are displayed in Figure 4.16. Both types of carbon fibers display an almost linear/elastic response to failure, with similar slopes (moduli) but different stress values at failure (strengths). As reported previously in Section 4.3.1, carbon fibers derived from the concentrated solution (2.15 g/mL) and possessing smooth crenulations displayed a tensile modulus of about 35 GPa (without system compliance correction or 50 GPa after correction) and a tensile strength of 1,050 MPa. The strength value is amongst highest reported for carbon fibers derived solely from lignin biomass. In contrast, carbon fibers derived lower concentration of 2.00 g/ml solution displayed a similar modulus of about 35 ± 1 GPa (without compliance correction), but their strength was only about 790 ± 80 MPa. The similar moduli are consistent with numerous prior observations that carbon fiber modulus is not affected by defects but usually controlled by the extent of carbonization, which in turn is governed by the carbonization temperature for a given type of precursor (1),(2),(3). However, carbon fiber strength is a strong function of defects, and the lowered tensile strength observed for current carbon fibers with occlusion-type defects can be attributed to precursor fibers containing sharp crevices.
Figure 4.16 Representative stress-strain curves of single carbon fibers, obtained from two different precursor solution concentrations (2.00 and 2.15 g/ml), displaying an almost linear/elastic response to failure.

Another aspect that needs to be noted here is the effect of ash content. In Section 3.2.1, purification of SKL was conducted to reduce the ash content to 0.15%. Carbon fibers produced from this purified precursor material could achieve the high strength noted above (1050 MPa). However, in a previous batch where the ash content was 0.3%, even with adequate tension during carbonization, the highest average strength obtained from various batches was only 620 MPa. Thus, strength of lignin-based carbon fibers is very sensitive to the composition of the precursor material, as metals can create defects during carbonization, and reduce the mechanical properties dramatically. Overall, the mechanical properties of Ace-SKL carbon fibers are much lower compared with
commercial PAN-based carbon fibers such as T300 that have a tensile strength of 3.5 GPa, or mesophase pitch based carbon fibers such as P55 with a tensile modulus of 380 GPa (4). However, the mechanical properties for Ace-SKL based carbon fibers reported here are still amongst the highest values reported for solely lignin-based carbon fibers. To further increase the mechanical properties, a lignin precursor with high purity (ash content below 0.1%) is required. Thus, cost-effective methods need to be developed for purification of lignin together with other improvements, as listed in the next chapter (in Future Work).

4.4 Conclusions

Tension was applied during thermal treatment, and resulted in a tensile strength, modulus and strain-to-failure of 52±2 GPa, 1.05±0.07 GPa, and 2.0±0.2%, respectively. These mechanical properties are amongst the highest values reported in the literature for lignin-derived carbon fibers. It is also noted that the cross-section shape can be controlled during dry-spinning, and crenulated carbon fibers obtained in this study have up to 35% larger surface area as compared with equivalent circular fibers that are typically obtained by melt-spinning. Due to the lack of graphitic crystallinity in these lignin-derived carbon fibers, their surface is expected to be more reactive than that of carbon fibers processing from graphitic precursors. Surface reactivity and larger surface area could both lead to better fiber-matrix interfacial bonding in composites. After heat treatment at 2400°C, the tensile strength was reduced to only 210 ± 30 MPa due to out-diffusion of noncarboneous elements during graphitization. The Ace-SKL based carbon fibers heat treated at 1000°C
had a resistivity of 106 ± 12 μΩ·m, while the 2400°C heat treated fibers had a resistivity of 63 ± 3 μΩ·m. This result is consistent with the low crystallinity in Ace-SKL carbon fibers. Also, the low concentration precursor solution (2.00 g/ml solution) led to the formation of carbon fibers with occlusions and resulted in reduced tensile strength as compared with that with smooth crenulations (from 2.15 g/ml solution). In summary, the results reported here establish the important effects of precursor composition and processing conditions on microstructure and properties of resulting carbon fibers.
CHAPTER FIVE

UV-ASSISTED STABILIZATION OF ACE-SKL PRECURSOR FIBERS

5.1 Introduction

As described in Chapter 4, the stabilization of Ace-SKL based carbon fibers consisted of a slow heating ramp that took more than 40 h to complete. The low glass transition temperatures ($T_g$) of lignin precursors required a slow heating rate to achieve crosslinking without fibers becoming tacky. Therefore, in this Chapter, ultraviolet irradiation was used as a pre-stabilization step to help accelerate the stabilization process.

According to Braun’s analysis for continuous heating transformation (90), heating rate during thermal stabilization needs to be below 0.06°C/min to maintain the operating temperature below $T_g$ of the reacting hardwood kraft lignin. Thus, it was reported that a slower heating rate led to higher $T_g$ (90). Kadla et al. (65) showed that hardwood kraft lignin fibers could be thermally stabilized at a heating rate of 2°C/min. Sudo and Shimizu (59) converted a steam exploded lignin into carbon fiber using a heating rate between 1-2°C/min. Uraki et al. (62) prepared carbon fiber using lignin from aqueous acetic acid pulping of hardwood with a stabilization heating rate of 0.5°C/min.

Eckert and Abdullah described carbon fibers produced from melt-spinning of a thermally-stable acetylated softwood kraft lignin, but no tensile properties were reported for the carbon fibers thus produced. Organosolv lignin has also been found to be sensitive to the heating rate during thermal stabilization. A heating rate below 0.2°C/min for Alcell lignin fibers was needed to prevent the fibers from fusing together (65). Also, in a study
reported by Baker et al. (74), an organic purified lignin even required a heating rate as
care required a heating rate as
0.01°C/min to crosslink. Organosolv lignin is readily processed compared with
other lignin precursors due to its low T_g and stable melt viscosity imparted by
substituents, but it lacks the ability to crosslink rapidly.

A DOE presentation reported on melt-spun precursor fibers obtained from a
“modified technical lignin”, with carbon fiber strength of 1.07 GPa (91). However,
further development efforts appear to be restricted by the unavailability of precursors
(lignin grades not specified) that meet stringent melt spinning requirements (75). Norberg
et al. reported a fast oxidative-stabilization using 15°C/min with fibers melt-spun from a
selected type of softwood kraft lignin, but the diameter of resulting precursor and
carbonized fibers were too thick, and no tensile properties were reported (66).

In other prior studies, UV-assisted stabilization of PAN precursor fibers was
investigated to accelerate the stabilization process using photo-sensitive precursors (19,
92-94). However, the role of UV irradiation for stabilization of lignin precursor fibers
has not been systematically addressed. Many studies have focused on reducing photo-
yellowing effect caused by light-induced deterioration of wood surfaces (95-98), but none
have taken advantage of UV irradiation to increase kinetics of stabilization for the
production of lignin-based carbon fiber. Therefore, the effect of UV radiation on
accelerating the stabilization was investigated and the results are presented in this
chapter.
5.2 Experimental

5.2.1 UV/Thermal dual stabilization

As-spun Ace-SKL fibers were mounted using the protocol described in section 4.2.1. The mounted fibers were hung in an oxidation oven with temperature set to 147.5°C. Weight was loaded at the bottom of fiber tows using load level of 2000 g/(g/cm) (Load level was calculated using the equation 4.6 defined earlier). Normally, fibers stretched up to eight times of the original length within 10 minutes of hanging, as shown in (Figure 5.1). In this way, fiber diameter was reduced from 35 μm to about 15 μm. Also, better alignment was achieved in the stretched fiber tows, which is desired for the following UV treatment.

Figure 5.1 Ace-SKL fiber tows before stretching (left) and after stretching (right)

Then the stretched fiber tows were mounted in a fixture for UV irradiation, as illustrated in Figure 5.2. One side of the tow was fixed, whereas the free end was loaded to apply tension during UV treatment. The fiber tows were put into a UV chamber and irradiated with a Nordson 4.5 kW UV curing lamp having a mercury bulb radiation source. Cooling air was blown into the chamber during the irradiation procedure to maintain the chamber temperature below 50°C, as illustrated in Figure 5.3.
Figure 5.2 Fiber tows mounted on UV irradiation fixture

Figure 5.3 Fiber tows in the UV chamber for irradiation
The UV-treated fiber tows were removed from the UV irradiation fixture and thermo-oxidatively stabilization up to 250°C under tension and subsequently carbonized using the method described earlier in section 4.2.1.

5.2.2 Characterization

For the FT-IR study, freshly prepared Ace-SKL powder was dissolved in acetone to prepare a 0.03g/ml solution. 500 mg pure KBr was pressed into a 13-mm diameter pellet using a hydraulic press. Two drops of the Ace-SKL solution were applied on the surface of KBr pellet using a pipette and the Ace-SKL coated pellets were put into vacuum oven at 50°C for 2 hours to fully evaporate the acetone. FT-IR spectroscopy was performed in the transmission mode with a Thermo Nicolet Nexus 870 spectrophotometer.

Differential scanning calorimetry (DSC) was performed using a Pyris 1 DSC (Perkin Elmer Instruments). The samples consisted of UV irradiated Ace-SKL fibers and “control” fibers that were purposely blocked from UV radiation. The fibers were ground into powder and the sample pans containing grounded fiber were heated from room temperature to 250°C under N₂ at a heating rate of 30°C/min and cooled to room temperature at the same rate. For each sample, the second heating run was used to calculate $T_g$ using the half $\Delta C_p$ method.

Gel permeation chromatography (GPC) was conducted for Ace-SKL fibers using a Waters Alliance GPCV 2000 model equipped with a Stylegel HT4 column (Waters) and Polargel (Agilent) column. Fibers were ground into powder and dissolved in
dimethylformamide solution containing 0.05 M lithium bromide at a concentration of 1 mg/mL.

5.3 Results and Discussion

5.3.1 FTIR

The Ace-SKL coated KBr pellets were irradiated in the UV chamber for 3, 10, 15, 20, and 25 min total exposure time. Also, an Ace-SKL coated “control” pellet was wrapped in aluminum foil to block the UV but kept in the UV chamber for the same exposure time. The FTIR spectra for various samples are displayed in Figure 5.4. For the UV irradiated pellets, the spectra were normalized with the intensity of 1369 cm\(^{-1}\) band attributed to C-H stretch in -CH\(_3\) group (44, 99), which is expected to remain fairly unchanged due to the relatively stable –CH\(_3\) group.
There was no measurable change in the FTIR spectrum of the control pellet. For UV irradiated samples, absorbance of 1740 cm$^{-1}$ and 1599 cm$^{-1}$ band increased significantly indicating the formation of new carbonyl groups (44, 99). The 1512 cm$^{-1}$ peak, attributed to the aromatic skeletal vibration (44, 99), decreased during UV treatment, which indicates the degradation of aromatic rings. Relative intensities of $I_{1740}/I_{1369}$ and $I_{1512}/I_{1369}$ are plotted in Figure 5.5 against the irritation time. Within the first 3 min, $I_{1740}/I_{1369}$ increased from 1.04 to 1.25, whereas the $I_{1512}/I_{1369}$ decreased from 1.31
to 1.16. Then the change of relative intensities slowed down for larger reactions times of up to 25 min.

Figure 5.5 Relative intensity change of 1740 cm\(^{-1}\) and 1512 cm\(^{-1}\) peaks as a ratio of 1369 cm\(^{-1}\) peak after UV treatment for different durations

It has been reported in prior literature studies that esterification is an effective way to prevent the photo-yellowing of paper due to the reduced formation of phenoxy radicals (44, 99). In the literature studies, the sensitivity of lignin to UV was dramatically reduced when hydroxyl groups were completely substituted by ester groups. However, our study is aimed towards increasing thermo-oxidative stabilization speed, thus hydroxyl groups were needed in the precursor fibers. Therefore, as noted earlier in section 2.3.3, acetylation was performed using a low acetic anhydride to lignin ratio (0.66 ml acetic anhydride per gram of lignin) (79). Thus, the acetylation in this study was a partial
esterification where acetyl substituents enhanced solubility of the resulting precursor in acetone that allowed for subsequent dry-spinning, and yet preserved a fraction of hydroxyl groups for subsequent stabilization. As shown in the FTIR spectra, the Ace-SKL retained sensitivity to UV and the positive effect of UV to stabilization was proven in the following studies.

5.3.2 Thermal analysis

A 15-min UV treated fiber tow and a control fiber tow with UV blocked were both put into oxidation oven for thermo-oxidative stabilization and subjected to a 1.2°C/min heating rate. A portion of such fibers were taken out of the oven at 100, 130, 160, 190, and 220°C, for DSC testing. Those fibers retained fiber shape without became tacky during the entire heat treatment, as they could be separated from the bundle as shown in Figure 5.6 (a). Control fibers removed at 160°C and higher temperatures were almost completely fused together, as displayed in Figure 5.6 (b). An SEM image of the fused control fibers is shown in Figure 5.7.

Figure 5.6 After thermal-oxidation up to 160°C at a heating rate of 1.2°C/min, (a) with prior UV treatment of fibers; (b) control fibers
The DSC thermograms are displayed in Figure 5.8. The results for fibers heat treated to 250°C are not shown because the highly crosslinked samples did not give a clear $T_g$ transition from DSC. After UV treatment, the UV treated fibers had a higher $T_g$ of 134°C as compared with 118°C for control fibers. $T_g$ for both group of fibers increased gradually as the thermo-oxidative crosslinking increased. After 160°C, $T_g$ increased faster as shown in Figure 5.9 due to the higher reaction rate at elevated temperatures. Although the $T_g$ increase followed the same trend for control fibers, it was far below the oven temperature after reaching 160°C, which caused fusing of the fibers.
Figure 5.8 DSC thermograms of various lignin-based precursor fibers thermally treated up to different temperatures. Solid curves: thermograms of fibers after UV irradiation; dashed curves: thermograms of control fibers without UV exposure.

Figure 5.9 $T_g$ shift of UV treated and control fibers as a function of thermal stabilization temperature
5.3.3 GPC

Ace-SKL fibers UV-treated for 3 and 15 min, and a control group of fibers were studied using GPC. The chromatograms, displayed in Figure 5.10, enabled computation of the number average molecular weights ($M_n$) of 7790, 8756, and 10636 for control (no UV), 3-min, and 15-min UV-treated samples, respectively. The corresponding weight-average molecular weight ($M_w$) values were 63209, 72797, and 87163, confirming that the molecular weight of Ace-SKL fibers after UV treatment was higher than that for the control fibers.

Although the difference was small, the resulting molecular weights were obtained from the whole fibers including UV-affected surface, but partially affected inner fiber cores. Broadened peaks for fibers with 15 min UV treatment clearly indicate the presence of a small portion of larger molecular weight fraction. This result matches with that from previous studies which indicated that long term of UV irradiation can result in decomposition of lignin, but at the beginning of light treatment a higher molecular weight fraction can form due to secondary reactions (100, 101).
Figure 5.10 GPC chromatograms of Ace-SKL fiber samples with different UV treatment time

5.3.4 UV/Thermal dual stabilization

As shown in Figure 5.11, the fiber diameter of stretched as-spun lignin fibers was less than 15 µm. The crenulations on the surface described in Chapter Three were preserved in the stretched fibers.

Figure 5.11 SEM micrographs of stretched as-spun Ace-SKL fibers at (a) low and (b) high magnification levels.
SEM images of UV irradiated fibers are shown in Figure 5.12. Compared with fibers before UV treatment, the UV treated fibers displayed a smoother surface and the crenulations were somewhat flattened. The results also demonstrate that surface of those fibers underwent exothermic reactions, and the heat led to some degree of softening on the fiber surface. Tension was applied during UV irradiation to preserve molecular orientation, as the absence of tension or inadequate tension results in shrinkage of the fiber after UV treatment.

![SEM images of UV-treated Ace-SKL fibers at low and high magnification levels.](image)

Figure 5.12 SEM images of UV-treated Ace-SKL fibers at (a) low and (b) high magnification levels.

Tension was also applied during the following thermal oxidative stabilization. For Ace-SKL fibers using a thermal stabilization alone, a slow heating ramp of 0.1-0.2°C/min with several dwelling times was required to prevent fiber from being tacky. In contrast, UV-treated fibers in the present study could be thermally stabilized with a fast heating rate of 1.2°C/min without any dwell time. It is emphasized that at this fast heating rate of 1.2°C/min, the control fibers that had not been UV irradiated completely lost the fiber
shape when oven temperature reached 160°C and multiple fibers fused together, as was shown earlier in Figure 5.13. The SEM image of stabilized fibers obtained using only thermo-oxidative stabilization (i.e., no UV pretreatment), but a slow heating rate that took 40 hours, are shown next in Fig 5.13 (a). Fibers stabilized by a UV/thermal dual mechanism at a fast heating rate of 1.2°C/min are shown in Fig 5.13 (b). The flattened crenulations due to UV treatment are also displayed by the dual stabilized fibers.

Figure 5.13 SEM images of stabilized Ace-SKL fibers: (a) fibers without any prior UV treatment stabilized at a slow rate of 0.2°C/min; (b) fibers with 15-min prior UV treatment stabilized at a fast rate of 1.2°C/min
The stabilized fibers obtained after UV treatment could be successfully carbonized. Figure 5.14 (a) displays carbon fibers obtained after thermal/UV dual stabilization involving 15 min UV irradiation followed by a fast stabilization rate (1.2°C/min) involving only 4 hours of total stabilization time. These carbon fibers prepared from dual stabilization method retained the crenulated shape of as-spun fibers. For comparison purpose, carbonized fibers obtained after a slow thermal oxidative stabilization (0.2°C/min) over 40 hours total are displayed in the micrograph of Figure 5.14 (b), which has many similarities to that in Fig 5.14 (a). Thus, the microstructural features of carbon fibers produced from UV/rapid oxidative stabilization are similar to those generated after single-step slow oxidative stabilization. When compared to circular fibers with the same cross-section area, rapidly stabilized fibers in Figure 5.14 (a) have about 15% larger surface area, which is slightly smaller than 21% larger area for carbon fibers obtained from slow stabilization, shown in Figure 5.14 (b). When such (lignin-based) carbon fibers will be embedded in an epoxy matrix to prepare a composite, the larger surface area will afford a larger interfacial bonding area and will lead to better fiber-matrix bonding.

The carbon fibers obtained from thermal/UV dual stabilization displayed a tensile strength, modulus and strain-to-failure values of 900 ± 100 MPa, 34 ± 2 GPa, and 2.6 ± 0.2%, respectively (modulus value was without compliance correction). The corresponding values for carbon fibers obtained after a single-step slow stabilization process were 1050 ± 100 MPa, 35 ± 2 GPa, and 2.0 ± 0.2%, as reported earlier in Chapter Four. Carbon fibers produced after the rapid stabilization process display about 10-20%
reduction in tensile strength and modulus, but about 20% increase in strain-to-failure. The heat generated from exothermic reactions during UV treatment likely led to some molecular relaxation within the oriented structure of the fibers, and resulted in the slight decrease in stiffness and strength. In future studies using a continuous process, such limitations can be overcome by increased draw-down throughout the entire process. It is noted, however, that the tensile strength reported here is still amongst the highest ones reported for lignin-derived carbon fibers obtained from rapid stabilization (i.e., heating rate exceeding 1°C/min) of precursors derived from commercially available softwood kraft lignin. As discussed earlier, some prior literature studies have reported high heating rates of 1-2°C/min for hardwood kraft and steam exploded lignins, but those have resulted in lower tensile strengths of 422 and 660 MPa, respectively (65),(59).
5.4 Conclusions

An acetylated softwood kraft lignin was dry-spun into fibers and UV irradiated to induce crosslinking. The reactions induced with only 0.25 hour (15 mins) of irradiation effectively shortened the subsequent oxidative-stabilization time from 40 to 4 hours, which is amongst the fastest stabilization processes reported for lignin-based carbon fibers. The increased extent of crosslinking reactions was confirmed using FTIR and GPC analysis, and it manifested into increased glass transition temperature. Stabilized fibers were successfully carbonized at 1000°C, and resulting carbon fibers displayed a
tensile strength 900 ± 100 MPa, which is amongst the highest reported for carbon fibers derived from softwood lignin-based precursors. These results illustrate that UV irradiation is a rapid route for shortening the stabilization time, which is often the rate-limiting step for production of lignin-derived carbon fibers.
CHAPTER SIX
CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

Three types of lignin were investigated in this research for the purpose of producing bio-based carbon fibers. These included soda lignin, organosolv lignin and softwood kraft lignin (SKL). It was concluded that soda lignin and SKL cannot be melt spun without suitable modification. After acetylation and fractionation, soda lignin and acetylated SKL (Ace-SKL) lignin were met spinnable but high extent of acetyl substitution prevented the subsequent thermal stabilization. It was shown that ECN lignin was successfully melt spun into as-spun fibers. However, the thermally oxidative stabilization took a very long time to complete. Controlled acetylation was performed on SKL. The resulting precursor could be dry-spun using acetone as solvent and thermally stabilized in air atmosphere, a method that has not been reported in prior literature. The stabilized fibers were successfully carbonized, and it established a novel route for producing carbon fibers from softwood kraft lignin.

Shear viscosity of Ace-SKL solutions displayed a significant shear-thinning behavior at all temperatures studied. The viscosity results could be modeled with power-law exponents ranging from 0.33 to 0.82, confirming the macromolecular nature of the Ace-SKL lignin/acetone solutions. As expected, elevated temperatures led to lower viscosities and facilitated extrusion at pressures under 10 MPa (about 1500 psi). As-spun fibers produced from dilute solutions (1.85 and 2.00 g/mL) developed some sharp crevices on the fiber surface. These are undesirable for subsequent processing of resulting
carbon fibers into composites by resin-infusion. For the most concentrated solution investigated in this study, 2.15 g/mL, the resulting fibers contained no sharp crevice. All fibers produced by the dry-spinning process led to crenulated fiber surface, with the highest spinning temperature leading to most crenulations. About 35% larger surface area could be achieved in Ace-SKL as-spun fibers (as compared with equivalent circular fibers), indicating the potential of such biomass-derived fibers in providing larger fiber/matrix bonding area when used in composites.

Tension was applied during both stabilization and carbonization steps. With adequate tension, Ace-SKL based carbon fibers displayed tensile strength, modulus and strain-to-failure of 52±2 GPa, 1.05±0.07 GPa, and 2.0±0.2 %, respectively. These tensile properties are amongst the highest values reported in the literature for lignin-derived carbon fibers. The crenulated patterns of precursor fiber cross-section shape were preserved in carbon fibers, and up to 35 % larger surface area was obtained as compared with equivalent circular fibers. The Ace-SKL carbon fibers had low graphitic crystallinity, so their surface is expected to be more active than that of carbon fibers possessing a higher graphitic structure. Larger surface area and surface reactivity could both lead to better fiber-matrix interfacial bonding when such carbon fibers are used in composites.

One limitation of the above process is that the thermal stabilization took around 40 hours to complete. To reduce the time duration required for stabilization, UV irradiation was employed as a way to induce crosslinking. Ace-SKL as-spun fibers were irradiated with UV for 0.25 hours (15 min) followed by thermo-oxidative stabilization, which took only 4 hours. It is amongst the fastest stabilization processes reported for
lignin-based carbon fibers. The effect of UV was investigated using DSC, FTIR and GPC analysis. The resulting carbon fibers from UV/thermal dual stabilization displayed a tensile strength of 900 ± 100 MPa, which is amongst the highest reported for carbon fibers derived from softwood lignin-based precursors. UV irradiation was confirmed as a useful way for shortening the stabilization time of lignin-based carbon fibers.

6.2 Future Work

The SKL used in this study has a wide molecular weight distribution. It is desired that narrower molecular weight distribution be obtained by a suitable fractionation method, either before or after the acetylation reaction. Also, 0.66 g lignin per ml acetic anhydride was used in the acetylation reaction in this study. The content of acetic anhydride could be reduced further in order to preserve more hydroxyl groups within the precursor material. Higher content of hydroxyl group means faster stabilization. Since the reaction mixture was already in a very thick and viscous status, adding certain solvents into the reaction mixture could dilute the acetic anhydride and improve mixing.

Other precursors such as soda lignin and ECN organosolv lignin has been explored in this work, but the study mainly focused on melt-spinning. It is possible that the acetylated soda lignin could be dry spun using acetone as a solvent. Also, proper solvent for the modified or unmodified ECN lignin could possibly be found for dry-spinning. The compatibility of various types of lignin and solvents such as acetic acid could be studied. It would be a good potential for another lignin/solvent system which is
capable of dry-spinning, as carbon fibers derived from dry-spinning has increased surface area which is favorable for fiber/matrix bonding with epoxy.

In Chapter Three, the rheology of Ace-SKL solutions under high shear rate was studied but accurate results for low-shear viscosity was difficult to obtain due to solvent evaporation using cone and plate rheometer. In addition, dynamic rheology results of the Ace-SKL solutions were not available due to the same evaporation problem. Proper design of enclosure system outside the cone and plate or parallel plate fixture would be needed for those types of measurement. Further more, the extensional viscosity is an important rheological property for spinning solutions. A suitable lubricant system needs to be developed to reduce shear effect between the solution and the wall of hyperbolic die, to provide a nearly pure extensional flow.

Some preliminary work has been done to convert Ace-SKL based carbon fibers into composites. Due to limitations of lab-scale experiments, Ace-SKL carbon fibers were produced at a small scale (up to 150 mg per batch), which is not enough for the preparation of a relatively large piece of composite sample. Several 1 cm × 5 cm Ace-SKL carbon fibers/epoxy composites were prepared but resulted in poor alignment of fibers in the composite samples. If the Ace-SKL carbon fibers could be prepared in a continuous form, better alignment can be achieved, which is important for producing high performance composites.

To properly scale up the process, a purification unit with larger capacity is needed. Currently, only 50 gram of SKL could be obtained after each purification batch with 25 cycles of washing and filtration. Larger amount of raw material is necessary to feed into a
continuous spinning unit. Also, a reactor is needed to replace the flask currently used for acetylation reaction. Finally, continuous carbonization and stabilization facility equipped with multiple rolls to provide tension during heat treatment can lead to significant process improvement. Adjustable tension during heat treatment, especially carbonization, is crucial to prevent fiber breakage.

While the positive role that the crenulated surface morphology can play has been noted earlier, the fiber/matrix bonding behavior of Ace-SKL carbon fibers in epoxy resin was not studied yet. In future studies, carbon fibers derived from Ace-SKL should be surface treated and then the fiber interfacial bonding strength could be measured using micro-bead method or fragmentation method. If micro-bead method is used, appropriate technique need to be developed to generate a small enough epoxy bead around a single carbon fiber. Fragmentation method also requires a sophisticated sample preparation with single fiber aligned and embedded in epoxy. In addition, the surface chemistry properties of Ace-SKL carbon fibers could be studied using proper techniques.

UV irradiation assisted stabilization was performed in this study on Ace-SKL as-spun fibers, but it could be applied on other lignin precursors such as organosolv lignin or hardwood kraft lignin. Also, UV initiator could be introduced into the lignin precursors which have been chemically modified with UV-sensitive functional groups. In this way, the stabilization time could be significantly reduced by UV-induced cross-linking.

In summary, lab-scale studies were conducted in a batch-mode during the course of this research and have elucidated several scientific aspects of dry-spinning of
acetylated lignin. Subsequently, the precursor fibers were successfully carbonized to produce carbon fibers with tensile properties that are amongst the best reported in the literature for lignin-derived carbon fibers. Future improvement in precursor composition and processing step suggested above can help with further improvements in resulting carbon fibers and push their application into industrially relevant composite materials.
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APPENDICES
A.1 Bagley correction of Ace-SKL solutions

In Chapter three, the viscosity of Ace-SKL solutions with different concentrations was discussed. High shear viscosities were obtained from capillary rheometer after Bagley correction. The shear rate ($\dot{\gamma}$), measured pressure drop ($\Delta P_{app}$), slope of trend lines obtained from plotting $\Delta P_{app}$ against L/D, corrected shear stress $\tau_R$, and corrected viscosity $\eta$ are listed in Table A.1. Figure A.1 lists Bagley plots of various concentration / temperature combinations. As noted in Section 3.2.2, $\Delta P_{app}$ obtained under selected shear rates was plot against L/D. For each $\dot{\gamma}$, the slopes of trend lines in Figure A.1 equal to $4\tau_R$, thus $\tau_R$ was calculated from the slope values, and corrected shear viscosity was obtained with $\tau_R/\dot{\gamma}$. 
Table A.1 Original data obtained from capillary rheometer for Bagley correction

<table>
<thead>
<tr>
<th>Concentration, temperature</th>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>$\Delta P_{app}$ (MPa)</th>
<th>Slope (MPa)</th>
<th>$\tau_R$ (MPa)</th>
<th>$\eta$ (Pa·s)</th>
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<td></td>
<td></td>
<td>L/D=25</td>
<td>L/D=15</td>
<td>L/D=5</td>
<td></td>
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<td>30.2</td>
<td>20.6</td>
<td>0.97</td>
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<td>5.7</td>
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</table>
2.15 g Ace-SKL / mL acetone, 25°C

ΔP (MPa)

L/D

2.15 g Ace-SKL / mL acetone, 50°C

ΔP (MPa)

L/D

2.00 g Ace-SKL/mL acetone, 25°C

ΔP (MPa)

L/D
Figure A.1 Bagley plots of various concentration / temperature combinations

1.85 g Ace-SKL/mL acetone, 25°C

1.85 g Ace-SKL/mL acetone, 35°C

Figure A.1 Bagley plots of various concentration / temperature combinations
A.2 Elongational viscosity measurement

Elongational viscosity was measured with ACER 2000 capillary rheometer equipped with hyperbolic dies. In this measurement, the extensional rate was calculated using equation (A.1), where $\dot{\varepsilon}$ is the elongational rate, $v_0$ is the initial velocity of fluid at the die entrance, $L$ is the length of the hyperbolic die, and $\varepsilon_H$ is the Hencky strain. The effective elongational viscosity ($\eta_{eff}$) was calculated using equation (A.2), where $\Delta P$ is the measured pressure drop. The Hencky strain of hyperbolic die used was 4.

$$\dot{\varepsilon} = \left(\frac{v_0}{L}\right)(\exp\varepsilon_H - 1)$$  \hspace{1cm} (A.1)

$$\eta_{eff} = \frac{\Delta P}{\varepsilon_H \dot{\varepsilon}}$$  \hspace{1cm} (A.2)

Other than the well-developed shear rheometry, another aspect that is significant to spinning is the elongational rheology. In this study, hyperbolic die was applied to create a controlled flow field with constant elongational rate. However, equation (1) and (2) was applied assuming that there is no shear flow within the hyperbolic die, which is almost impossible without adequate lubrication between die wall and fluid. The measured $\eta_{eff}$ of a 2.15 g/ml acetone Ace-solution at different $\dot{\varepsilon}$ is shown in Figure A.3. It can be seen that, $\eta_{eff}$ at $\dot{\varepsilon}$ of 1 s$^{-1}$ was above 100,000 Pa·s, which is much higher than the predicted value of 2000-3000 Pa·s, because in the Troutons’s rule ($\eta_e = 3 \eta(\dot{\gamma})$). The extremely high $\eta_{eff}$ is attributed to a large shear component within the flow. This leads to
an excess pressure drop than that generated by pure extensional flow and results in possible inaccurate extensional viscosity.

![Graph showing effective extensional viscosity](image)

**Figure A.2 Effective extensional viscosity of 2.15 g/ml acetone Ace-SKL solution measured at 25°C**

Several trials were performed to induce slip between die wall and Ace-SKL solution. For example, the die wall was sprayed with mold release or coated with a thin layer of Vaseline, but the results were similar with that shown in Figure A.2. In another trial, Ace-SKL solution was shaped into long cylinder and Vaseline was applied on the surface of shaped solution. However, Vaseline worked as a plasticizer which obviously softened the solution thus the data was not reliable.
A.3 Ace-SKL as-spun fibers shape analysis using SEM

Scanning electron microscopy (SEM, Hitachi S4800) was used to analyze the cross-section shape and dimension. The as-spun fibers were coated with platinum using a sputter coater. To obtain accurate cross-section areas and perimeters, the fibers need to be aligned perpendicular to the lens of microscope. In this section, the adjustment procedure of fiber orientation will be described.

After regular sample loading of SEM, a single fiber needs to be roughly focused as shown in Figure A.3(a). The fiber in this image was not perpendicular to the lens. The first step is to rotate the sample stage and get the lateral surface of fiber be perpendicular to the horizontal line of screen. The “rotation” and “tilt” feature in the SEM software was shown in Figure A.4, and “Eucentric” need to be checked. In this example, the fiber was rotated 292 degrees (Figure A.3 (b)). Then the sample stage needs to be tilted. Input a proper tilt angle as shown in Figure A.3. Figure A.3 (c) is the resulting image of this fiber tilt 2 degrees, and Figure A.3 (d) is the resulting image of 4.5 degrees tilting. It can be seen that in Figure A.3 (d), no lateral surface could be observed, which means a good alignment of the fiber. Then this single fiber could be furtherly focused under higher magnification.
Figure A.3 Adjustment of single fiber alignment using “rotation” and “tilt” feature of SEM
Once an image is captured for a single fiber, it will be exported to Quartz PCI software for analysis. The “freehand shape measuring tool” is shown in Figure A.5. After click this tool, the mouse cursor will change to pen-shape. A closed line could be drawn along the fiber edge and the cross-sectional area and perimeter will displayed. Ten images was captured and analyzed for each group of fibers. An example group of images for Ace-SKL as-spun fibers is displayed in Figure A.6.
Figure A.5 “Freehand shape measuring tool” in Quartz PCI.
Figure A.6 Example group of images for Ace-SKL as-spun fibers (dry-spun from 2.00 g/ml acetone solution under 40°C)
A.4 Compliance Measurement

In equation (A.3), $\Delta l$ is calculated from total length change $\Delta l_t$ by subtracting the slippage distance $\Delta l_s$. Equation (A.3) is rearranged to equation (A.5), thus in equation (A.6), compliance $C$ was calculated as $\Delta l_t/f$, and system compliance $C_S$ was calculated as $\Delta l_s/f$. $C$ was plotted against $l/A$, and the slope is $1/E$. In this way the corrected $E$ can be calculated. Figure A.7 is one of the compliance plot example.

\[
E = \frac{\sigma}{\varepsilon} = \frac{f/A}{\Delta l/l} \tag{A.3}
\]

\[
\frac{1}{E} = \frac{\sigma}{\varepsilon} = \frac{\Delta l/l}{f/A} = \frac{(\Delta l_t - \Delta l_s)/l}{f/A} = \frac{(\Delta l_t - \Delta l_s)/f}{l/A} \tag{A.4}
\]

\[
\frac{\Delta l_t}{f} = \frac{l}{A} \cdot \frac{1}{E} + \frac{\Delta l_s}{f} \tag{A.5}
\]

\[
C = \frac{l}{A} \cdot \frac{1}{E} + C_S \tag{A.6}
\]
Figure A.0.7 Compliance $C$ plot against $l/A$