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Potential of producing carbon fiber from biorefinery corn stover lignin with high ash content

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ABSTRACT: The possibility of producing carbon fiber from an industrial corn stover lignin was investigated in the present study. As-received, high-ash containing lignin was subjected to methanol fractionation, acetylation, and thermal treatment prior to melt spinning and the changes in physiochemical and thermal properties were evaluated. Methanol fractionation removed most of the impurities in the raw lignin and also selectively removed the molecules with high melting points. However, neither methanol fractionation nor thermal treatment rendered melt-spinnable precursors. The precursors were highly viscous and decomposed easily at low temperatures, attributed to the presence of H, G phenolic units, and abundant hydroxycinnamate groups in herbaceous lignin. A two-step acetylation of methanol fractionated lignin greatly improved the mobility of lignin, while enhancing the thermal stability of the precursor during melt-spinning. Fourier Transform Infrared and 2D-NMR analysis showed that the contents of phenolic and aliphatic hydroxyls, as well as the hydroxycinnamates, decreased in the acetylated precursors. The optimum precursor was a partially acetylated lignin with a glass transition temperature of 85 °C. Upon oxidative stabilization and carbonization, the carbon fibers with an average tensile strength of 454 MPa and modulus of 62 GPa were obtained. The Raman spectroscopy showed the I_D/I_G ratio of the carbon fiber was 2.53. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *134*, 45736.

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INTRODUCTION

Carbon fiber is a corrosion-resistant material with many potential applications because of its high ratio of tensile strength to density, along with its unique thermal and electrical properties.[1,2] Despite the advantages, carbon fiber is currently used in limited areas due to the high price of polyacrylonitrile (PAN), which accounts for more than 50% of the total production cost of carbon fiber.[3–5] Also, PAN is derived from petroleum and emits hazardous gas during carbon fiber manufacturing. Thus, finding alternative precursors of carbon fiber has been of great interest for decades.[6] Among potential alternatives, lignin has received significant attention because it is a renewable biopolymer available in large quantities at low costs.[4,7–12] Similar to PAN, lignin can be spun into fibers followed by oxidative stabilization and carbonization to produce carbon fibers with a turbostratic carbon structure.[6] Compared to PAN, lignin could provide a higher carbon fiber yield because of its relatively high carbon content. The partly oxidized lignin molecules also potentially reduce the time required for stabilizing the as-spun fiber. The ability to melt-spin lignin also provides cost effectiveness, compared to wet-spinning of PAN.

To date, woody biomass-derived lignins produced from the pulping process have been extensively studied for carbon fiber processing. Previous studies showed that the lignin structure has a significant implication in carbon fiber processing.[6,13] Lignin is an amorphous aromatic polymer and its physiochemical and thermal properties highly depend on the biomass origin and lignin isolation method.[14] Although lignin in general is biosynthesized from three main units, which are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, the ratios of H, G, and S units vary by biomass species.[15] S unit is dominant in hardwood lignin; thus hardwood lignin is chemically stable and less likely to crosslink when it is thermally processed. Accordingly, hardwood lignin has a moderate glass transition temperature (T_g) and can be melt-spun at ease.[16] However, as-spun fiber from hardwood lignin tends to fuse during stabilization due to its low ability to develop oxidative crosslinking. Unlike hardwood lignin, G unit is the major unit in softwood lignin. Due to its imbalanced aromatic ring structure in G unit, softwood lignin has a strong tendency to develop crosslinking. Thus, softwood lignin is difficult to spin due to its high T_g and thermal instability. On the other hand, the crosslinking of softwood lignin fiber promotes solidification of the fiber during stabilization.[13,17] In the previous studies, lignin has been pretreated or chemically modified to improve the processibility as precursor and the quality of the resulting carbon fibers. For example, Baker *et al.*[9] fractionated a hardwood kraft lignin in an organic solvent followed by thermal treatment to obtain the precursor with more defined properties. Zhang *et al.*[11] spun fiber from a mixture of an acetylated softwood kraft lignin and acetone. Softwood and hardwood lignin were also mixed with other co-polymers, such as poly(ethylene oxide), poly(ethylene terephthalate), polypropylene, poly(vinyl alcohol), and PAN to improve the spinnability of the precursors, as well as mechanical properties of the resulting carbon fibers.[18–21] Despite these efforts, the quality of lignin-based carbon fiber was found to be much lower than PAN-based carbon fiber, whose tensile strength is typically above 3 GPa. Baker and Rials[6] produced a carbon fiber with a tensile strength of 1070 MPa from an experimental hardwood lignin and it is so far the lignin-based carbon fiber with highest quality. Other lignin-based carbon fibers mostly have lower tensile strengths in the range 150–700 MPa.[6,22] The lack of well-defined molecular orientation in lignin is mainly responsible for the low mechanical properties of lignin-based carbon fiber compared to PAN-based carbon fiber. Although replacing PAN-based carbon fiber for structural applications is currently challenging, as a low cost and greener product, lignin-based carbon fiber could still be considered in many general applications where materials with moderately high mechanical properties, low density, high temperature tolerance, low thermal expansion, and thermal conductivity are of interest. For instance, it has been reported that lignin-based carbon fiber is used to produce a high-temperature-tolerant insulation material.[17]

Compared to woody biomass-derived lignin, herbaceous lignin was seldom used in carbon fiber production. Herbaceous lignin is available from cellulosic biorefineries as a byproduct when agricultural residues and energy crops are used to produce biofuels and chemicals. Herbaceous biomass are popular feedstocks in biorefineries because they can be harvested annually and are the largest biomass sources available in many regions.[23] As biorefineries are rapidly expanding, producing value-added products from herbaceous lignin becomes an urgent need in order to maintain the economic sustainability in many biorefineries. Accordingly, exploring herbaceous lignin-based carbon fiber could provide a potential opportunity for value-added product from lignin. Herbaceous lignin consists of both H and G units in relatively higher contents, thus its thermal and physiochemical properties differ from wood-based lignin.[4] Recently, Hosseinaei *et al.* produced a carbon fiber with tensile strength up to 370 MPa from switchgrass lignin[4], and it is currently the only published study regarding carbon fiber from herbaceous lignin. In their study, an experimental organosolv lignin with high purity was used as the starting material.

In this study, an industrial corn stover lignin was used as the raw material to investigate the possibility of producing carbon fiber from a popular herbaceous lignin. Corn stover is the most abundant cellulosic-agricultural residue in the United States[24] and currently being used as the biomass feedstock by several biorefineries in the country. To produce a melt-spinnable precursor, as-received lignin was subjected to solvent fractionation, acetylation, and thermal treatment. The pretreated precursors were characterized and the resulting carbon fiber was evaluated.

EXPERIMENTAL

Materials

Corn stover organosolv lignin was provided by Archer Daniels Midland (ADM) Company. The lignin was isolated from corn stover using an acetosolv extraction process in the plant. The lignin is free from carbohydrate residue. Methanol, hydrochloride acid (HCl), acetic anhydride (AA), and tetrahydrofuran (THF) used in this study were purchased from Fisher Scientific.

Lignin Pretreatment

For methanol fractionation, 50 g of raw lignin was dissolved in 250 mL methanol and stirred with a magnetic rod for 15 min at room temperature. After stirring, the solution was filtered twice using a 0.7 μm filter paper followed by a 0.45 μm filter paper to remove insoluble lignin particles and impurities. The methanol soluble lignin was then placed in a vacuum oven at 40 °C overnight to evaporate methanol. The resulting methanol fractionated lignin is denoted as "ML" in this study.

For the acid-washing of lignin, raw lignin was washed with a 0.1 N HCl acid solution at a ratio of 10 mL of the acid solution to 1 g of the lignin and stirred for 30 min. The procedure was repeated three times and the filtered solid lignin was rinsed with deionized water until the rinsed water became neutral.

Acetylation of the methanol fractionated lignin was performed in two steps. In the first step, different amounts of AA were added to ML and kept at 85 °C for 2 h. In the second step, the acetylated samples were subsequently heated at 140 °C for an additional 0.5 h under vacuum ventilation. During the entire process, the mixtures were stirred at 150 rpm. After the two-stage treatments, the acetylated precursors were pelletized and stored at room temperature. Different levels of acetylation were performed at 0.5, 0.75, 1, 2, and 3 mL g^{-1} of ML, respectively. The resulting precursors are denoted as "0.5AT-ML", "0.75AT-ML", "1AT-ML", "2AT-ML", and "3AT-ML", respectively. ML was also treated under identical temperatures and reaction times in the absence of AA, and the thermally treated precursor is denoted as "0AT-ML".

Fiber Spinning and Processing

Raw lignin and pretreated lignins were extruded using a twin-screw extruder (DACA Instruments, Santa Barbara, CA). The precursors were fed into the extruder preheated to 130 °C and circulated within the extruder for 5 min prior to drawing the fibers. The drawn fiber was wound on a roller (DSM, Geleen, the Netherlands). During the spinning process, the temperature and rotation speed of the twin-screw, as well as the winding speed at the roller, were adjusted for different types of precursors. Several hundred meters of the fiber were collected during each test.

The as-spun fibers were mounted on a metal rack inside a muffle furnace and subjected to oxidative stabilization at a heating rate of 0.1 °C min^{-1} from room temperature up to 250 °C, and then held at the same temperature for 1 h. The as-spun fiber from 0.75AT-ML was also subjected to a step-wise stabilization by dwelling the fiber at 100, 120, 14, 160, 180, and 200 °C for 6 h, respectively. The stabilized fibers were placed on a porcelain crucible and carbonized in a tubular furnace. During carbonization, the stabilized fiber was heated from room temperature to 1000 °C at 3 °C $\min^{-1}$ and then held isothermally for 1 h. Argon was used to maintain an inert environment inside the tube furnace.

Characterizations

Proximate analyses of lignin precursors were performed in thermal gravimetric analyzer (TGA/DSC 1 STARe system, Mettler Toledo) using nitrogen with a flow rate of 100 mL $\min^{-1}$. Approximately 30 mg of lignin samples were heated from room temperature to 105 °C at 10 °C $\min^{-1}$ and then held at constant temperature for 40 min to remove moisture. The samples were further heated to 900 °C at a heating rate of 10 °C $\min^{-1}$ and then held for 20 min. Finally, air was introduced to combust the solid residue. Thermal stability of the samples was also evaluated using the TGA. Approximately 30 mg of each sample was heated under a nitrogen environment from room temperature to 900 °C with a heating rate of 10 °C $\min^{-1}$.

Ultimate analysis of the sample was conducted using an elemental analyzer (Vario Micro Cube, Elementar, Germany). Carbon, hydrogen, nitrogen and sulfur contents were measured and oxygen content was determined by the difference. The ash content of the raw lignin was subtracted prior to calculating the elemental compositions. Each test was triplicated and the average results were reported.

Gel permeation chromatography (GPC) analysis was conducted using Dionex Ultimate 3000 series high performance liquid chromatography equipped with a Shodex Refractive Index (RI), and Diode Array Detectors. Two GPC columns (3 μm, 100 Å, 300 × 7.5 mm; PLgel, Agilent, p/n PL1110–6320) were calibrated with six monodispersed polystyrene standards ranging from 162 to 38640 g mol^{-1}. THF was used as the solvent for samples and the eluent in the columns.

Fourier Transform Infrared (FTIR) analysis was conducted using a Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) equipped with a Smart iTR accessory. The wave numbers of the FTIR analysis ranged from 750 to 4000 cm^{-1} and each sample was scanned 32 times at a resolution of 4 cm^{-1} and interval of 1 cm^{-1}. All FTIR spectra were normalized at 1510 cm^{-1} (aromatic-skeleton vibration) for comparison.

Glass transition temperature (T_g) was determined using a differential scanning calorimeter (DSC, Q2000, TA instruments). Each sample was first rapidly heated to 200 °C and cooled to 25 °C to eliminate thermal history, and then reheated to 200 °C at a heating rate of 10 °C $\min^{-1}$. Nitrogen with a flow rate of 50 mL $\min^{-1}$ was used as the purge gas. The midpoint T_g of the precursor was determined using a TA software.

Mechanical properties of carbon fiber were determined according to ASTM standard (ASTM C1557-03) using a Discovery hybrid rheometer (DHR-2, TA Instruments) with dynamic mechanical analysis clamps. The reported results are the average of 20 single fibers.

[^{1}H^{13}C] 2D-NMR heteronuclear single-quantum coherence (HSQC) spectroscopies of selected lignins were obtained at 25 °C on a Bruker Biospin Advance 600 MHz spectrometer incorporated with a 5 mm cryogenically cooled z-gradient probe using the Bruker pulse sequence "hsqcetg-psisp.2". A sample concentration of 100 mg lignin per 1 mL of solvent mixture was used. The solvent mixture was composed of dimethyl sulfoxide (DMSO)-d_6 and pyridine-d_5 (v/v: 4/1). The sample was prepared by dissolving 100 mg of sample in the solvent mixture and then holding it in the shaker for 20 min to enhance sample dissolution. Different structural compounds were identified by comparing the acquired 2 D-NMR signals with the available literature.[25–29]

Raman spectrum of carbon fiber was characterized using a confocal Raman system (Voyage, B&W Tek, Inc. and Olympus BX51). A 532 nm Raman laser of 16mW was focused on the fiber with a 50× lens. A 20 s integration time was used to obtain the spectrum and origin software was used to analyze the acquired Raman spectra with Gaussian–Lorentzian curve fitting.

RESULTS AND DISCUSSION

Proximate and Ultimate Analysis of Raw Lignin and ML

The results of the proximate and ultimate analyses for as-received raw lignin and the ML are given in Table I. The ash content of raw lignin is 6.07%, significantly higher than the ash contents in experimental organosolv lignins, which are usually <0.2%.[30] The compositions of ash are mainly inorganic salts. Herbaceous biomass is known to contain significantly more impurities than woody biomass contains.[31] Lignin isolation method and the scale of lignin production also affect the impurity content in lignin. Lignin must be pretreated to remove the impurities prior to fiber spinning. Otherwise, the impurities remaining in carbon fiber could become the source of mechanical defects. The inorganics could also promote the volatile release and the formation of pores in the fibers due to their catalytic effect for thermal decomposition of lignin. Elemental analysis showed that the raw lignin also contained 2% of

Table I. Proximate and Ultimate Analyses of Raw Lignin and ML

	Raw lignin	ML
Proximate analysis (%)		
Moisture content	3.87	3.66
Volatiles	62.52	65.03
Fixed carbon	27.55	31.04
Ash	6.07	0.27
Ultimate analysis (%)		
Carbon	61.34	58.66
Hydrogen	4.67	5.32
Nitrogen	2.00	0.72
Sulfur	0.20	0.06
Oxygen[a]	31.79	35.24

[a] By difference.

nitrogen and 0.2% of sulfur. Nitrogen and sulfur in the precursor may react with oxygen to form hazardous gases.

The raw lignin was initially subjected to acid washing with 0.1 N HCl. Since the acidic solution dissolves many inorganic salts, acid washing is a common method to purify lignin[1]. However, the ash content after three rounds of washing was still as high as 3.97%. It is likely that the raw lignin contained a high amount of acid-insoluble impurities. For example, silica and silicates are not soluble and calcium salts also have lower solubility in acidic solution.[32] Therefore, the raw lignin must be purified by alternative methods. Methanol fractionation was chosen because inorganic impurities have no or low solubility in alcohols.[33] After the fractionation, the ash content reduced to 0.27% in ML, indicating that most impurities remained in methanol-insoluble fraction.

The volatile and fixed carbon contents were both higher in ML in comparison to raw lignin, mainly due to the reduced ash content. Carbon content in ML was 58.66%, which is lower than 61.37% in the raw lignin. Hydrogen and oxygen contents, on the other hand, increased in ML. Considering that oxygen atoms only appear at the side chains of aromatic rings, ML could have a less aromatically condensed structure than raw lignin. Nitrogen and sulfur contents were also reduced to 0.72% and 0.06% in ML. The ML was further subjected to acetylation and thermal treatment and the characterizations of different precursors are described below.

FTIR Analysis

FTIR spectra of raw lignin, ML, and pretreated lignins are given in Figure 1. The peak appearing at 3250–3400 cm^{-1} is for phenolic and aliphatic hydroxyl groups, and the peak at 2842–3000 cm^{-1} is for C—H in methyl and methylene attached to aromatic rings. The relative peak ratio 2842–3000 to 3250–3400 cm^{-1} of the raw lignin was higher than the corresponding ratios of hardwood and softwood lignins in their respective FTIR spectra reported in literature.[11,16,34,35] This is because herbaceous lignin contains higher amounts of side chain carbon than woody biomass-based lignin. Coumarate and ferulate groups, commonly found in herbaceous lignin contribute to the C—H peak.[4,36,37] In comparison to raw lignin, ML contains a higher amount of hydroxyl group, ascribing to selective extraction of lignin molecules by methanol. Saito *et al.*[38] also reported that methanol-extracted lignin contains a higher content of hydroxyl group than original lignin. The increased peak at 1709–1738 cm^{-1} corresponds to unconjugated ketones, carbonyls, and conjugated aldehydes and carboxylic acids groups. In herbaceous lignin, γ-positions of lignin side chains are naturally acetylated,[23] which also contribute to this peak. In addition, the peak at 2842–3000 cm^{-1} for C—H, 1221–1230 cm^{-1} for C—C, C—O, and C═O stretch, 1166 cm^{-1} for conjugated C═O in ester group, and 1030–1035 cm^{-1} for C—O deformation in primary alcohols and unconjugated C═O stretch also increased in ML. ML contains more oxygen containing groups, such as hydroxyl, carboxyl, and carbonyl groups, which correspond to the higher oxygen content in ML compared to the raw lignin. Since the signals of the side chains became stronger relative to the peak intensity of the aromatic skeleton (1510 cm^{-1}), the result also confirms that ML has a less aromatically condensed structure than raw lignin. The higher amount of side chain could increase the mobility of lignin during fiber spinning.

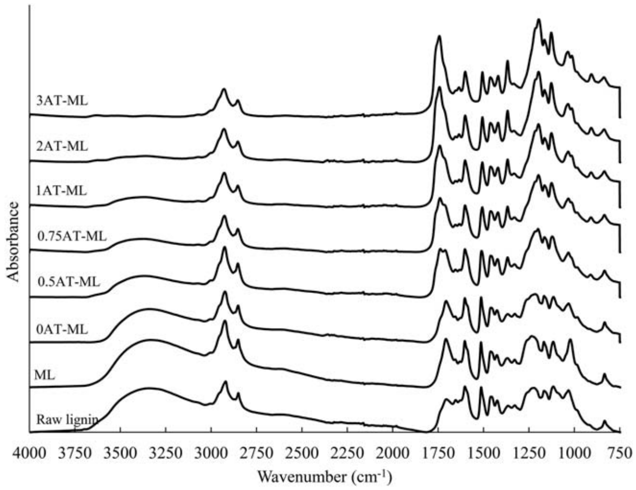

Figure 1. FTIR spectra of different lignin precursors.

Compared to ML, the intensities of the hydroxyl peak (3250–3400 cm^{-1}) and carbonyl peak (1709–1738 cm^{-1}) decreased in the thermally treated precursor (0AT-ML). The peak around 1030–1035 cm^{-1} also decreased. The changes in the peak intensities indicate that lignin structure became condensed upon thermal treatment. Phenolic/aliphatic hydroxyls, and C—O groups participated in the condensation reactions.

The precursors, including 0.5AT-ML, 0.75AT-ML, 1AT-ML, 2AT-ML, and 3AT-ML, were produced by the two-step acetylation. Acetylation is frequently used to treat lignin as it could improve solubility of lignin in organic solvents. Acetylation was also used to inhibit yellowing of paper caused by the formation of free radicals from lignin.[39] In terms of carbon fiber production, a softwood kraft lignin was acetylated to reduce the reactivity and enhance the mobility of the lignin molecules.[40] Corn stover lignin has an increased amount of side chains in comparison to softwood lignin, and thus may have better precursor mobility. However, G and H units in corn stover lignin also promote crosslinking. The reactivity of H unit is higher than G unit because both of the ortho positions in P-hydroxylphenol become the potential sites for crosslinking. Crosslinking of lignin molecules during melt-spinning increases the precursor viscosity, causing a difficulty of fiber spinning. Thus, capping the hydroxyl group by acetylation could improve the melt-spinnablity of lignin.[11] The intensities of the peak at 3250–3400 cm^{-1} remarkably decreased in the acetylated precursors even with the lowest amount of AA. On the other hand, the intensities of the peaks shown at 1702 cm^{-1} for C═O, 1360–1365 cm^{-1} for aliphatic C—H stretch in CH_3, and 1221–1230 cm^{-1} for C—C, C—O, and C═O increased with the increasing degree of acetylation. This confirms that phenolic and aliphatic hydroxyl groups are acetylated, and that carbonyl and methyl groups are newly added. The hydroxyl peak nearly disappeared at 3AT-ML, indicating that hydroxyl groups were almost completely acetylated under the reaction condition.

The degree of acetylation in the acetylated precursor was estimated based on the FTIR spectra using following equation[41]:

$$\text{Acetylation degree } (\theta) = 1 - \frac{(H_{OH}/H_{aromatic}) \text{ after acetylation}}{(H_{OH}/H_{aromatic}) \text{ before acetylation}}$$

where H_{OH} is the peak intensity of hydroxyl stretching at approximately 3400 cm^{-1} and $H_{aromatic}$ is the peak intensity of aromatic skeleton vibration at 1510 cm^{-1}. The results are plotted in Figure 2. The value of θ is 0 in ML and 0.96 in 3AT-ML. Although θ monotonically increased with increasing concentrations of AA, the increases were faster with lower concentrations of AA. As the concentration of AA further increased above 1 mL g^{-1} lignin, θ values increased slowly. This result is likely related to the variations in the reactivity of different types of hydroxyl groups in lignin toward to acetylation. According to Pu and Ragauskas,[39] phenolic OH is preferentially acetylated within a shorter reaction time. The preference of acetylation is in the order of phenolic OH > β-side chain OH > α-side chain OH.

Nevertheless, it should also be noted that fully acetylating lignin may not be desirable since the absence of hydroxyl groups could hinder the ability of the as-spun fiber to crosslink during oxidative stabilization. As a result, the fiber will fuse together with elevating temperature. Previously, Zhang *et al.*[42] also reported that a fully acetylated softwood lignin fiber could not be stabilized even with a heating rate as low as 0.01 °C min^{-1}. Therefore, the softwood lignin was partially acetylated in their study so the acetylated fibers could be stabilized. In this study, processability of all the acetylated precursors was tested. Among the acetylated lignins, 0.75AT-ML with the θ value of 0.59 was characterized in greater detail in below to evaluate the effect of acetylation on the precursor properties and performance.

2D-NMR Analysis

The 2D-NMR of ML, 0AT-ML, and 0.75AT-ML are compared in Figure 3. Raw lignin was also tested, but the results are not shown. The signals of some lignin structures were not clearly observed with raw lignin, possibly affected by strong solvent peaks and the presence of high impurity content.

Aryl ether linkages, methoxyl group, S, G, and H groups were detected in ML as they are characteristics in lignin. Ferulate, courmaric groups, and tricin structures were also detected in ML lignin. Due to the abundancy of ferulate and courmaric groups, herbaceous lignin has overall longer aliphatic side chains than woody biomass-based lignin. Particularly, corn stover contains higher amounts of the hydroxycinnamate acids than many other herbaceous biomass plants.[43] These longer and linear side chain groups may provide some molecular linearity in the lignin, which is potentially beneficial for improving the quality of carbon fiber. However, the aliphatic side chain linkages are also susceptible for thermal decomposition, causing lignin instability. The signal of polysaccharide residue was also found in ML. The presence of polysaccharide residue in lignin is undesired because polysaccharides can decompose during thermal processing to form pores in the fibers.

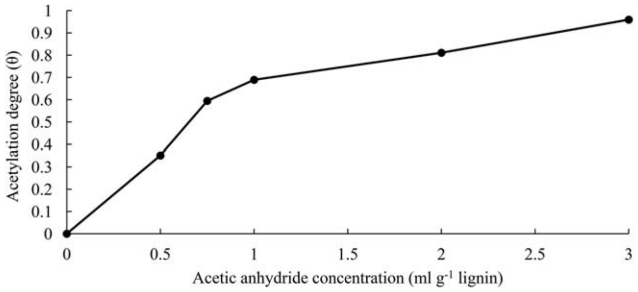

Figure 2. Correlation between acetic anhydride concentrations and acetylation degrees.

There were no significant changes in the signals of methoxyl and aryl ether linkage in 0AT-ML after ML was thermally treated. The temperature for thermal treatment was 140 °C, not high enough to cause β-O-4 cleavage or demethoxylation. Ferurate and courmate groups were also not affected by thermal treatment. Polysaccharides still remained in this precursor. In 0.75AT-ML, the signals for acetyl group (AcMe) newly appeared. Due to acetylation of phenolic and aliphatic hydroxyl groups, the signals of H and G groups, as well as aryl ether and tricin groups, decreased. Compared to the corresponding signals in 0AT-ML, the signals of C_α and C_β in ferulate and p-coumarate groups decreased significantly after acetylation. This change was unexpected, since the acetylation of phenolic OH in the hydroxycinnamates should not shift the signals of C_α and C_β. The disappearance of the signals suggests that the unsaturated $C_\alpha{=}C_\beta$ is either cleaved or saturated during the acetylation. Considering that acetic acid is the byproduct of acetylation and is known to catalyze repolymerization of lignin-derived bio-oil,[44] it is likely that acetic acid catalyzed repolymerization reactions to saturate the $C_\alpha{=}C_\beta$ bonds. Attachment of other groups at $C_\alpha{=}C_\beta$ may result in a lignin with a slightly more branched structure. However, it also results in more stable lignin structure. It is also found that the signals of polysaccharide disappeared at 0.75AT-ML, probably because OH groups in polysaccharides were also acetylated.

GPC Analysis

The molecular weight distributions of selected lignins are given in Table II. Weight average molecular weights (M_w) and polydispersity index (PDI) of raw lignin are 3263 Da and 2.91, which are typical for organosolv lignins.[32] The average M_w of ML was 1299 Da, significantly lower than that of the raw lignin. The PDI also decreased to 1.89, indicating that large M_w components were selectively removed along with the impurities by methanol fractionation. Although precursors with lower M_w usually have better mobility, low M_w lignin could also easily devolatilize at relatively low temperatures during spinning or cause fiber fusion during oxidative stabilization. For that reason, solvent fractionated lignins and other low M_w precursors were often thermally treated prior to fiber spinning in previous studies to increase its M_w and thermal stability.[12]

The M_w of 0AT-ML was 3180 Da, indicating thermal treatment of ML caused repolymerization. The PDI of the precursor also increased to 3.19. The reactivity toward repolymerization varies by the functional groups in individual lignin molecules, which resulted in the thermally treated precursor with a broader

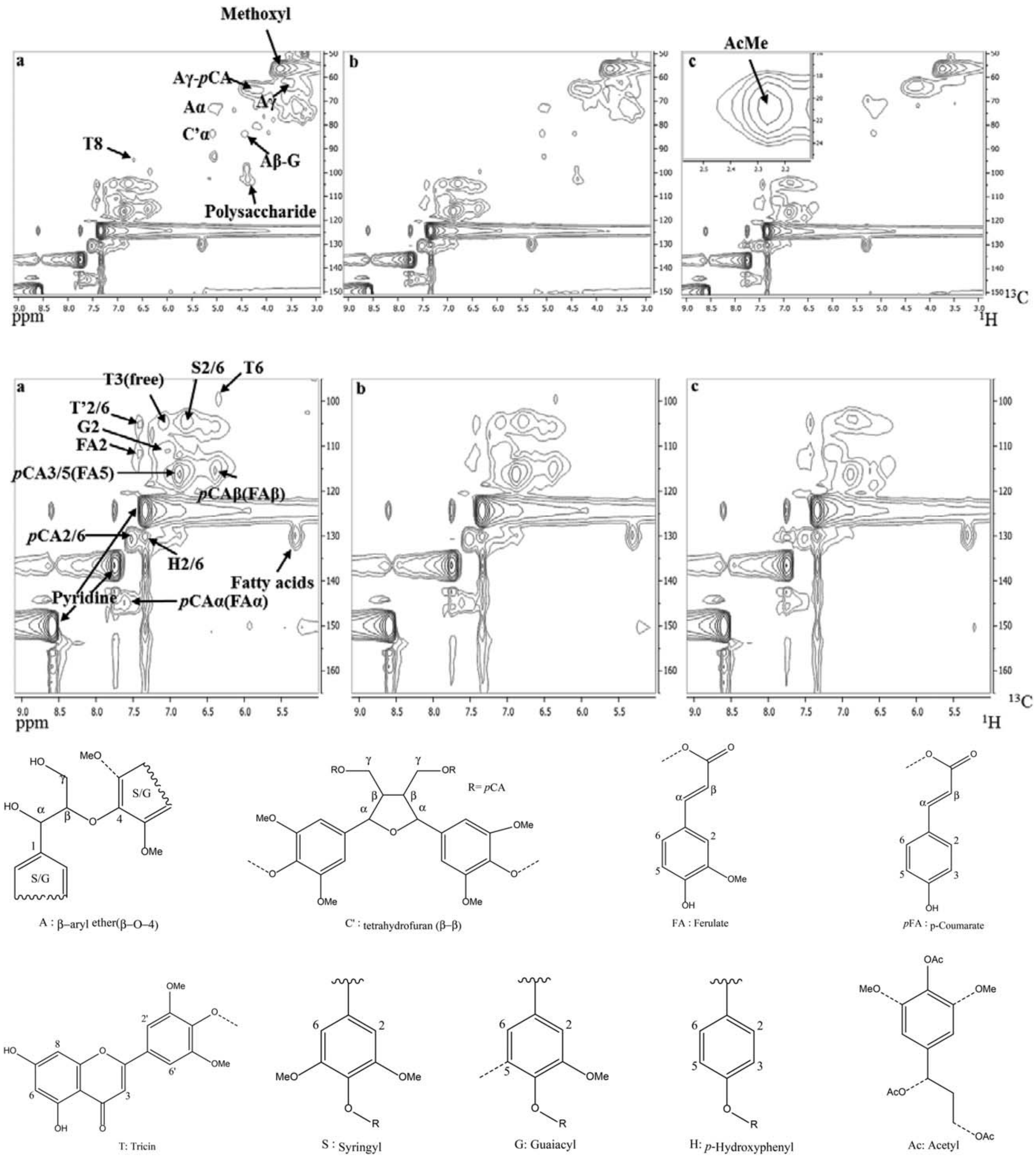

Figure 3. 2D-NMR spectra of selected lignin precursors [(a) ML. (b) 0AT-ML. (c) 0.75AT-ML Top: Full region. Bottom: Selected region].

Table II. Molecular Weights and Polydispersity Index (PDI) of Different Lignin Precursors

	Raw lignin	ML	0AT-ML	0.75AT-ML
M_w (Da)	3263	1278	3180	3594
M_n (Da)	1121	674	997	1060
PDI	2.91	1.89	3.19	3.39

Table III. Glass Transition Temperatures (T_g) and Decomposition Temperatures (T_d) of Different Lignin Precursors

	Raw lignin	ML	0AT-ML	0.75AT-ML
T_g (°C)	147	93	111	85
T_d (°C)^a	194	160	197	233

[a] Determined by the TGA profiles, the temperatures correspond to 5% of weight losses.

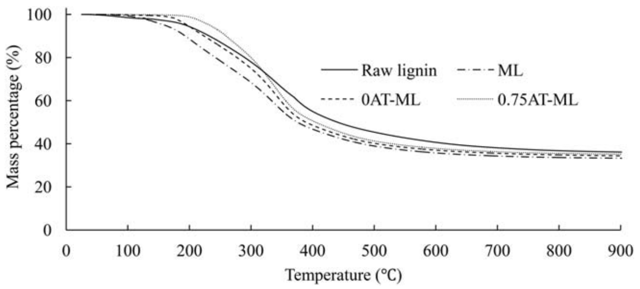

Figure 4. TGA curves of selected lignin precursors.

molecular distribution. Ideally, a carbon fiber precursor should have a high M_w and low PDI for structural uniformity.[6]

The average M_w and PDI of 0.75AT-ML were 3594 Da and 3.39, both slightly higher than the corresponding values of 0AT-ML. Although acetylation could suppress the crosslinking polymerization of the molecules, replacing phenolic and aliphatic hydroxyls in individual molecules by acetyl groups increases the M_w. Also, since 0.75AT-ML is a partially acetylated precursor ($\theta = 0.59$), the unacetylated free OH groups allow crosslinking during the thermal treatment catlyzed by acetic acid. The possibility of acetic acid catalyzed repolymerization of $C{=}C$ bonds was described above.

Glass Transition Temperature

Glass transition temperatures (T_g) of different precursors are compared in Table III. For fiber spinning, T_g of the precursor has to be low enough so the precursor can melt before it decomposes. However, the T_g of the as-spun fiber also has to be high enough so the fiber can be stabilized during oxidation process without fusion or liquid droplet formation. The T_g of the raw lignin was 147 °C, which is similar to the T_g of a previously reported softwood kraft lignin,[10] although its M_w is only about a half of the softwood lignin. Baker and Rials[6] previously indicated that the T_g of the lignin precursor relates to the ratio of G and S unit. The precursor with higher G to S ratio has higher T_g, because G unit is reactive for crosslinking whereas S unit is relatively stable. The corn stover lignin contains H unit in addition to G unit, thus leading to a high T_g even though the M_w of the corn stover lignin was much lower. The impurities in the raw lignin also contribute to the increased T_g of lignin.[45] The T_g decreased to 93 °C in ML, because low M_w molecules have better mobility in the same type of lignin. For example, Saito *et al.* reported that T_g of a softwood kraft lignin decreased from 153 to 117 °C after methanol extraction due to a decreased M_w.[38] After thermal treatment, T_g increased to 111 °C for 0AT-ML. Repolymerization increased M_w and crosslinking among the molecules, which reduced the mobility of the precursor molecules. In comparison, the T_g of 0.75AT-ML was only 85 °C, despite the fact that the average M_w of the acetylated precursor was even higher than the M_w of 0AT-ML. This result confirms that the presence of hydroxyl groups in lignin greatly contributes to the intermolecular force and limits the mobility of molecules.[4] Replacing hydroxyls with acetyl groups has weakened the intermolecular forces and lowered the T_g of the lignin.

Thermal Stability

TGA curves of raw lignin, ML, 0AT-ML, and 0.75AT-ML are given in Figure 4 to compare the thermal stability of different precursors. Decomposition temperatures (T_d) are determined as the temperature corresponding to 5% mass losses in the samples and are also listed in Table III. Thermal stability plays an important role in determining the spinning performance of precursor.[46] In general, a precursor should have high thermal stability at the spinning temperatures, so that the melt-spinning is not interrupted by the formation of bubbles. Bubbling and devolatilization during precursor spinning could create pores in the fiber and eventually lower the mechanical properties of the carbon fiber. The thermal treatment could increase the M_w of the precursor, thus improving thermal stability of the precursor during fiber processing.[47] However, the lignin with high M_w and T_g may become difficult to melt spin and could also decompose before it melts. In the case of raw lignin, the mass loss started at a temperature below 100 °C and T_d was 194 °C. In addition to the evaporated moisture, the high content of inorganic impurities in raw lignin could have catalyzed thermal decomposition of lignin occurring at lower temperatures.

ML also started to devolatilize at low temperatures and T_d decreased to 160 °C mainly due to its lower M_w. Since melt-spinning of lignin is usually conducted at a temperature range below 200 °C (because aryl ether linkages in lignin cleave at temperatures above 200 °C), the mass loss of the precursors at this temperature range could be indicative of undesired bubbling and volatile release during the melt-spinning process. For 0AT-ML, no mass loss was observed at temperatures below 150 °C, showing an improved thermal stability after thermal treatment. However, further increasing the temperature reduced the stability of the precursor and T_d was recorded at 197 °C. Previously, Sun *et al.*[48] investigated rheology of softwood lignin at different melting temperatures and indicated that repolymerization is the main reaction at temperatures below 190 °C, and thermal decomposition becomes dominant at higher temperatures. Herbaceous lignin contains a higher amount of side chain than softwood lignin, and decomposition reaction preferentially occurs at lower temperatures. Ferulate and coumarate groups are still abundant in the thermally pretreated precursor and could contribute to the release volatiles. Decomposition of

Table IV. Spinning and Stabilization Conditions of Different Lignin Precursors

Samples	3AT-ML	2AT-ML	1AT-ML	0.75AT-ML	0.5AT-ML	0AT-ML	Raw lignin
Melt spinning temperature (°C)	135–140	140–145	165–170	165–170	NS[a]	NS	NS
Fiber fusion[b]	S	S	M	L	—	—	—

[a] Not spinnable.
[b] Based on observation ("S" = Severe, "M" = Medium, "L" = Light).

Table V. Mass Yields during Carbon Fiber Processing (with 0.75AT-ML)

Step	Methanol fractionation	Pretreatment	Stabilization	Carbonization
Yield	42%	92%	103%	47%

ferulate and courmarate produces CO_2 and vinyl phenols as the major products.

Compared to non-acetylated precursors, 0.75AT-ML had a remarkably better thermal stability. Negligible mass loss was observed at temperatures below 200 °C and the T_d increased to 233 °C. Thermal decomposition of acetylated lignin occurs at higher temperatures compared to non-acetylated sample because acetylation hinders the cleavage of aryl ether linkages and other weaker bonds.[39] In a previous study, it was suggested that hydroxycinnamate groups and aliphatic OH are the main causes of volatile release in switchgrass lignin.[4] Acetylation of phenolic OH on coumarate and ferulates and saturation of $C_\alpha{=}C_\beta$ also likely increased thermal stability of the acetylated precursor.

The lignin with low T_g usually results in lower carbon fiber yield. However, it may not be the case with the acetylated precursor of corn stover lignin. It was found that the amount of residue carbon at 900 °C for 0.75AT-ML was higher than the carbon residues of ML and 0AT-ML. Raw lignin produced similar amount of solid residue, but 6.07% of it was inorganic ash. Higher residue carbon in acetylated lignin could be an indicator of a higher carbon fiber yield. The two-step acetylation increased thermal stability and carbonization of the precursor, which are both beneficial to carbon fiber processing.

Performance of Fiber Processing and Properties of Carbon Fiber

All precursors produced in this study, including raw lignin and the pretreated precursors (ML, 0AT-ML, 0.5AT-ML, 0.75AT-ML, 1AT-ML, 2AT-ML, and 3AT-ML), were subjected to melt-spinning. The raw lignin did not melt below 200 °C. Further raising the extruder temperature slightly improved the melting of the lignin, but the lignin also started to decompose. It is likely that the melting temperature of raw lignin is higher than its decomposition temperature. The similar melting behavior was also reported with a softwood kraft lignin.[11] ML melted better than raw lignin at lower temperatures, indicating the lignin molecules with higher melting temperatures were selectively removed as a methanol-insoluble part during the solvent fractionation. However, severe devolatilization took place with the extruder temperature of 150 °C, while the viscosity of the melted ML at this temperature was still too high to extrude.

The 0AT-ML could be extruded at a temperature range 140–200 °C due to its improved thermal stability and precursor mobility at higher extrusion temperatures. However, spinning fiber for an extended time was still difficult due to the high viscosity of the precursor. The as-spun fiber was also too brittle to handle. The high viscosity of 0AT-ML is due to the crosslinking polymerization of the lignin at elevated temperatures. Previously, Hosseinaei *et al.*[4] reported that switchgrass organosolv lignin with T_g of 118 °C could be melt-spun at 190–195 °C. Although 0AT-ML has a lower T_g than the switchgrass lignin reported in the literature, it could not be spun at a similar temperature range. When the extruder temperature exceeded 200 °C, bubbling and forming of the precursor at the extruder outlet was significant and fiber spinning became impractical. The excessive bubbling and forming at higher temperatures could be attributed to decomposition of aryl ether, hydroxylcinamates, and other aliphatic side chain groups. Poor spinning performances of the above precursors were predictable based on their TGA profiles in Figure 4. Because the melt-spinning process is conducted in air, oxygen further enhances the thermal decomposition of lignin. For instance, in addition to CO_2 and vinylphenols, vanillin, acetovanillone, and vanillic acid can also form during the oxidative thermal decomposition of ferulate acid.[49]

All acetylated precursors, except 0.5AT-ML, demonstrated better melt-spinnability than the non-acetylated lignins. The precursor of 0.5AT-ML was still thermally instable and too viscous for spinning, attributed to its low acetylation degree ($\theta = 0.35$). It was also found that the extruder temperature had to be adjusted with different acetylated precursors in order to obtain the best spinning performance. As shown in Table IV, the optimum spinning temperatures were lower for the precursors with higher degrees of acetylation. Apparently, the decreased intermolecular forces in acetylated precursors reduced the viscosity of the precursors, so the fiber could be spun at lower temperatures.

The as-spun fibers of the acetylated precursors were subjected to oxidative stabilization. The extent of fiber fusion upon stabilization is also summarized in Table IV. The as-spun fibers from 3AT-ML and 2AT-ML fused severely after stabilization at a heating rate of 0.1 °C min^{-1}. The fibers from 1AT-ML and 0.75AT-ML also stuck together, but fused less significantly. Ideally, the as-spun fiber should turn into non-fusible, solid fiber by oxidative stabilization within a reasonable time. At this stage, crosslinking among the fiber molecules is highly desired in order to form a rigid fiber structure. Oxygen is mainly introduced into the as-spun fiber molecules as carbonyl and carboxyl groups, although some minor degrees of dehydration, decarboxylation, and decarbonyzation could be expected. Since acetylated precursor has a reduced ability to crosslink, the as-spun fiber molecules still have mobility and fuse together during stabilization at

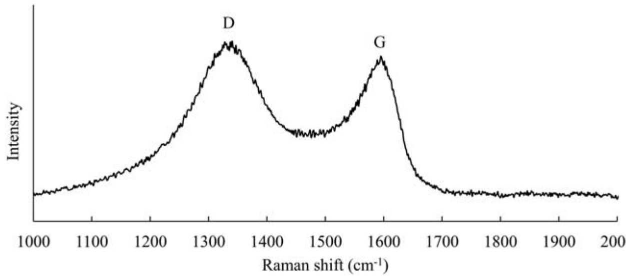

Figure 5. Raman spectrum of carbon fiber produced from 0.75AT-ML.

Table VI. Mechanical Properties of Carbon Fibers Produced from 0.75AT-ML

Properties	Diameter (μm)	Tensile stength (MPa)	Modulus (GPa)	Strain (%)
μ ± σa	39.1 ± 5.4	454 ± 98	62 ± 14	0.73 ± 0.08

μ, mean value; σ, standard deviation.

elevated temperatures. Apparently, the lignin has to be acetylated at the optimum degree to ensure the acetylated precursor is spinnable yet the as-spun fiber can be stabilized within an acceptable time. Among the actylated presursor fibers, 0.75AT-ML was least fusible due to its lower degree of acetylation. Thus, this as-spun fiber was selected and subjected to the stepwise stablization. Upon stablization for prolonged time, fiber fusion was greatly diminished and the integrity of the stabilized fiber was much enhanced. The stablized fiber was further carbonized to produce carbon fiber. The carbon content in the resulting carbon fiber was 90.27%. The yields during the carbon fiber processing steps are given in Table V.

Raman spectrum of the carbon fiber is shown in Figure 5. The G band (1595 cm^{-1}) is related to the stretching of the C—C bond in graphitic materials and the D band (1365 cm^{-1}) is associated with structural disorder. The ratio of peak intensities of I_D/I_G is often used to estimate the level of disorder in the fiber. A higher ratio of I_D/I_G corresponds to the fiber with more defects. The I_D/I_G ratio of the carbon fiber produced from 0.75AT-ML was 2.53. This ratio is lower than the corresponding ratio value of acetylated softwood lignin-based carbon fibers carbonized at same temperature, which was reported to be 2.88.[42] Li *et al.*[50] suggested that a lignin precursor with a higher content of linear molecular linkages could result in a carbon fiber with better crystallinity and lower I_D/I_G. The lengths of aliphatic side chains are overall longer in corn stover lignin in comparison to softwood lignin, which may explain the lower I_D/I_G ratio obtained in this study. However, further research is needed to confirm this theory. Frank *et al.*[22] previously pointed out that the molecular linearity is the most critical factor in determining the quality of carbon fiber and must be established before the fiber is oxidized and carbonized.

The average diameter and mechanical properties of the carbon fibers produced from 0.75AT-ML are summarized in Table VI. Distributions of the tensile strength with diameter of the 20 single fibers are also plotted in Figure 6. The carbon fiber has an average tensile strength of 454 MPa and modulus of 62 GPa. The average strain of the carbon fiber is 0.73%, which is similar to that of switchgrass lignin-based carbon fiber,[4] but lower than the corresponding value of carbon fibers produced from woody biomass-based lignins.[6] As it can be seen from Figure 6, some fibers had relatively lower tensile strength than other fibers despite their similar diameters, suggesting these fibers have more structural defects. Recall that the ash content in ML was 0.27%, still higher than the recommended ash content in lignin as a carbon fiber precursor (<0.1%).[1] As described earlier, the carbon fiber with inorganic impurities result in lower mechanical properties. In this study, the average diameter of carbon fiber was 39.1 μm, considerably larger than the diameters of commercial grade carbon fibers. In general, the mechanical properties of carbon fiber is inversely correlated to the diameter of the fiber. During stabilization, oxidization occurs from the outermost layer of the fiber to form a hard shell. The hard shell could then act as a physical barrier to prevent oxygen from penetrating into the inner side of the fiber, preventing the fiber from being sufficienctly stablized. Thus, the fiber with a thinner diameter is highly preferred in order to achieve higher mechanical properties. It has been reported that reducing the fiber diameter from 22.5 to 5.8 μm increased the tensile strength of an acetylated softwood lignin-based carbon fiber from 520 to 1040 MPa.[11] Applying tension during stabilization and carbonization on fiber may reduce the diameter of the fibers and potentially improve the mechanical properties of corn stover lignin-based carbon fiber. However, it should also be noted that the detrimental effects of pores and impurities on mechanical properties of the fiber could also be magnified in the fiber with smaller diameters. Thus, the lignin must have a high purity prior to fiber spinning. The purity of the corn stover lignin could be improved in future studies by repreating the solvent fractionation process or using other filtration methods.

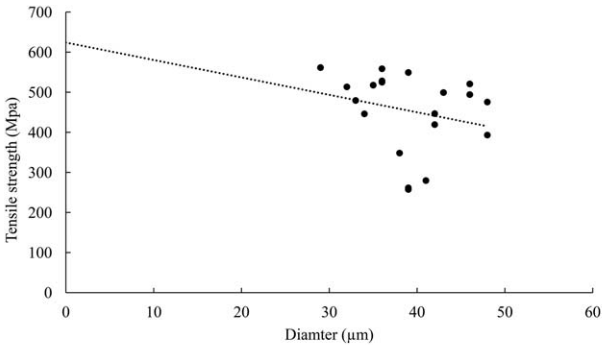

Figure 6. Tensile strengths and corresponding diameters of carbon fibers produced from 0.75AT-ML.

CONCLUSIONS

In the present study, an industrial corn-stover lignin with a high ash content was successfully converted into carbon fiber. Methanol fractionation was used to purify raw lignin and selectively remove the lignin with high M_w. However, neither ML nor thermally pretreated ML (0AT-ML) was spinnable, due to the coupled effect of high viscosity of the precursors upon melting and precursor devolatilzations at low temperatures. These problems were caused by the crosslinking of G, H units and thermal decomposition of aliphatic side chains in the corn stover lignin. On the other hand, the two-step acetylation of ML rendered thermally stable and spinnable precursors. Substitution of phenolic and aliphatic hydroxyl groups by acetylation reduced intermolecular forces to enhance the mobility of the precursor. The hydroxycinnamate groups also decreased upon acetylation, which contributed to the improved thermal stability of the precursor. However, partial acetylation of the lignin was recommended since the lignin with a low acetylation degree was not spinnable, whereas highly acetylated as-spun fibers easily fused during stabilization. The optimum precursor in this study had an acetylation degree of 0.59, T_g of 85 °C, and M_w of 3594 Da. The average tensile strength and modulus of the carbon fiber produced upon oxidative stabilization of the 0.75AT-ML as-spun fiber followed by carbonization at 1000 °C were 454 MPa and 62 GPa. The I_D/I_G ratio of the carbon fiber was 2.53 based on Raman spectroscopy.

Overall, this study demonstrated a potential use of a biorefinery agricultural-residue lignin for carbon fiber and showed challenging issues to tackle. Lignin pretreatment was necessary to increase thermal stability of the lignin caused by decomposition of hydroxycinnamate groups and other aliphatic side chain groups. The ash content was 0.27% in the present study after methanol extraction, which is still higher than the recommended ash content in a lignin precursor for carbon fiber. Improving the precursor purity and optimizing manufacturing processes in future studies could lead to corn stover lignin-based carbon fiber with higher mechanical properties.

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