

A New Softening Agent for Melt Spinning of Softwood Kraft Lignin

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ABSTRACT: Kraft lignin obtained from the pulping of wood is an interesting new precursor material for carbon fiber production because of its high carbon content and ready availability. However, continuous spinning of softwood kraft lignin (SKL) has been impossible because of its insufficient softening characteristics and neat hardwood kraft lignin (HKL) has required extensive pretreatments to enable fiber formation. Softwood kraft lignin permeate (SKLP) and hardwood kraft lignin permeate (HKLP), fractionated by membrane filtration, were continuously melt spun into fibers. To improve the spinnability of SKL and HKL, HKLP was added as a softening agent. SKL- and HKL-based fibers were obtained by adding 3–98 wt % HKLP. A suitable temperature range for spinning was 20–85°C above the T_g of the lignin samples, and this range gave a flawless appearance according to the SEM analysis. Smooth, homogeneous fibers of SKLP, HKLP, and SKL with HKLP were successfully processed into solid carbon fibers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1274–1279, 2013

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INTRODUCTION

The demand for carbon fibers (CFs) for structural applications has been steadily increasing since the introduction of light-weight composite materials in the aircraft and aerospace industry.¹ At present, the most common precursors used are predominantly polyacrylonitrile (PAN) and to a lesser extent, coal- or petroleum-derived pitch^{1,2} and regenerated cellulose.³ However, using these precursors limits the expansion of the CF application range, as the raw material and spinning account for approximately 50% of the CF cost.⁴ Additionally, PAN- and tar-derived pitches are petroleum based, and the precursor cost will continue to increase as a result of increases in the crude oil price.⁵ One major area of interest in which CFs are too expensive for large-scale implementation is the automotive industry, which is constantly searching for ways to lower vehicle weight to reduce fuel consumption.^{2,5}

One potential alternative precursor material is lignin,⁶ one of the most abundant natural macromolecules, that is found in all vascular plants.⁷ Wood contains approximately 20–30 wt % lignin, a polyaromatic macromolecule with a carbon content of above 60 wt %.⁸ Lignin is made from two monolignolic units, coniferyl alcohol and sinapyl alcohol (Figure 1). In lignin macromolecules, these units give two different types of phenyl propanes: guaiacyl and syringyl, respectively, which are mainly connected with ether and carbon–carbon bonds.⁷ Softwood lignin contains only guaiacyl units in which one of the ortho-positions next to the

phenol is free. In contrast to softwood, hardwood lignin also contains syringyl units in addition to guaiacyl, which contributes to retaining a more linear structure compared to softwood, during technical delignification and isolation processes thereof, whereas lignins originating from softwoods are more easily branched and/or crosslinked.^{8,9} Not only the origin, but also the isolation methods affect the lignin yield and the final chemical structure,⁷ and thereby influence the thermal behavior of lignins.

The need to find new precursor materials for CF production converges with the current efforts being made by the kraft pulp mills to more efficiently use wood raw materials by utilizing the large amounts of lignin dissolved in the black liquor. Marketing of lignin for high-value applications is one of the most important possibilities for creating a sound economy for pulp mills in the future. Not only the use of lignin as a precursor potentially would reduce the CF cost by up to 35%,⁵ but it would also result in a renewable CF produced from a by-product, that is readily available on a large scale.

Efforts have been made to produce high-quality CF from lignin and thus far, the only commercial lignin-based CF, Kayocarbon, was produced from lignosulfonates by spinning them together with a polyvinyl alcohol.¹⁰ Lignins from various wood pulping methods have been used in previous melt spinning studies, such as steam-explosion lignin,^{11,12} organosolv lignin,¹ and kraft lignin.^{1,5,13} Lignin-based CFs are commonly produced by melt spinning into a precursor fiber.^{1,9,13} The lignin fiber is

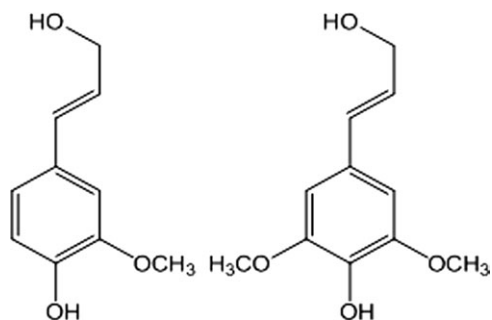


Figure 1. The monomer precursor for softwood lignin is coniferyl alcohol (left), whereas hardwood lignin originates from both coniferyl alcohol and synapyl alcohol (right) monomers.

subsequently stabilized to hinder the fiber from melting during the carbonization treatment, yielding a fiber containing above 90 atomic-% C.¹⁴

For a long time, kraft lignin was considered unsuitable as a precursor for CF production because of impurities, such as particles, high amounts of carbohydrates, and inorganics. However, methods have been developed to remove impurities that improve the processability of kraft lignin.⁵ Kadla and coworkers have shown that HKL can be successfully transformed into CFs by pretreating the lignin under vacuum to remove the volatile compounds before blending it with various additives, such as poly(ethylene terephthalate) and poly(ethylene oxide).^{1,6}

In contrast, softwood kraft lignin (SKL) has been more difficult to process into fibers even with the addition of softening agents,⁶ supposedly because of the branched and/or crosslinked structures, compared with HKL.⁹ Overcoming the spinning difficulties is an important challenge, as softwood is the main raw material for the wood pulping industry in the Northern hemisphere.

It has been shown that isolated kraft lignin permeate obtained from fractionated black liquor has a lower glass transition temperature than that of its unfractionated counterpart, indicating improved melt properties.⁸ This article shows how the thermal behavior of fractionated kraft lignin can have a beneficial impact on the melt spinning of SKL and HKL.

EXPERIMENTAL

Materials

SKL and HKL were isolated from industrial black liquor according to the LignoBoost-concept, in which lignin is precipitated using carbon dioxide and re-slurried prior to further washing with acid.¹⁵ Softwood kraft lignin permeate (SKLP) and hardwood kraft lignin permeate (HKLP) were produced by ultrafiltration of the respective black liquor through a 15-kD ceramic membrane (Groupe Novasep, Saint-Maurice-de-Beynost, France) prior to isolation.⁸ The yields for unfractionated lignins was 80% and the yield for fractionated lignin was approximately 40%.⁸ The lignins were dried in air at room temperature to a dry content above 90 wt % (hereafter denoted %). All chemicals used were of analytical grade.

Thermal Characterization

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) using a Q1000 V9.4 Build

287 (TA Instruments, New Castle, DE). Samples of 1–2 mg of lignin powders and pre-extruded SKL, SKLP, HKLP, and SKL/HKLP blends were placed in hermetic aluminium pans, and the covers were pierced after sealing. The samples were dried in the DSC equipment by heating at 1°C/min to 105°C and then isothermally treated for 20 min before cooling to room temperature. For analysis, the samples were heated to 250°C by modulated reversed calorimetry at a heating rate of 3°C/min. T_g was defined as the inflection point in the DSC curve and evaluated with the software Universal Analysis 2000, version 4.5A Build 4.5.0.5 (TA Instruments, New Castle, DE). The reported T_g values are the mean values based on the five measurements.

The decomposition temperature (T_d) was determined by thermogravimetric analysis (TGA). Samples of approximately 4 mg of lignin were placed in an aluminum pan and analyzed with a TGA instrument (TGA7, Perkin Elmer, MA). After drying at 105°C for 20 min, the samples were heated at 15°C/min to 400°C. T_d was defined as the temperature when 95% of the dried sample remained. Duplicates of each sample were measured.

Molecular Mass Distribution

The lignins were derivatized by acetylation with acetic acid anhydride prior to size exclusion chromatography (SEC).¹⁶ The analysis was performed using tetrahydrofuran as a solvent at a flow rate of 0.8 mL/min (515 HPLC pump, Waters, Milford, PA). Three Styragel columns (Waters) were connected in series: HR1, HR2, and HR4. The refractive index (Waters 410) was used as a detector. Five polystyrene standards (Macherey-Nagel, Düren, Germany) covering the molecular mass range of 1.38–115 kD were used to calibrate the chromatographic system. The weight average molecular mass (M_w), number average molecular mass (M_n), and the polydispersity ($PD = M_w/M_n$) were determined using PL Cirrus GPC software, version 3.1, Varian, Palo Alto, CA.

Extrusion

A 7 g sample of neat lignin or lignin blends was premixed prior to manually feeding the powder into a counter-rotating twin-screw laboratory compounder with conical 110 mm long screws with decreasing diameter from 10 to 4 mm. (HAAKE MiniLab II CTW5, Thermo Fischer Scientific, Waltham, Germany).

For lignin fiber spinning, a 0.5 mm single filament die was used, and either blends of SKL or HKL containing 1–95% HKLP, neat SKLP, or HKLP were recirculated in the extruder for 10 min prior to extrusion at 25 rpm and temperatures ranging from 140 to 220°C, depending on the composition. The lignin fiber was collected on a bobbin (TUS, Dynisco, Franklin, MA) at a winding speed of 76 m/min.

Thermal Treatment

Lignin fibers of neat SKLP, HKLP, and SKL with 3 or 10% HKLP were oxidatively stabilized in a conventional gas chromatography oven (HP 5890, Hewlett Packard, Palo Alto, CA). The fibers were heated at 0.2°C/min up to 250°C and held for 1 h before cooling to room temperature.¹⁷

The stabilized fibers were subsequently carbonized in a tube furnace (VTF 50/15-L, Entech, Ångelholm, Sweden) in a nitrogen atmosphere at a flow rate of 10–20 mL/min. The temperature

Table I. Thermal Properties and Molecular Mass Characteristics for SKL, HKL and Corresponding Permeates: SKLP and HKLP

Lignin	T_g (°C)	T_d (°C)	M_w	M_n	PD
SKL	150	273	6400	1300	5.0
SKLP	146	273	3300	1300	2.6
HKL	139	273	3500	1100	3.2
HKLP	114	274	1700	780	2.2

was increased by 1°C/min to 600°C and 3°C/min to 1000°C before cooling to room temperature.

Fiber Characterization

The lignin and carbonized fibers were characterized using field-emission scanning electron microscopy (SEM) (JSM-6460, Jeol, Tokyo, Japan) at an acceleration voltage of 15 kV. The fibers were gold-plated prior to analysis to avoid charging of the sample.

The elemental composition of the carbonized fibers was determined for three fibers using X-ray/energy dispersive spectroscopy (EDS) (INCA Energy, Oxford Instruments, Oxfordshire, United Kingdom) connected to the SEM instrument.

RESULTS AND DISCUSSION

Thermal Properties

In this article, T_g , T_d , M_w , M_n , and PD were initially determined for all lignins (Table I). As previously reported by Brodin et al.,⁸ fractionation has a great impact on the lignin properties. As expected, higher T_g were found for the unfractionated SKL and fractionated SKL (SKLP) than for the unfractionated HKL and fractionated HKL (HKLP). The thermal properties were affected only slightly by the ultrafiltration, as shown by the T_g of SKL and SKLP, respectively, whereas the T_g of the corresponding HKLP was clearly lower compared to HKL. T_d was determined, as processing the lignin at temperatures too close to T_d can result in thermal degradation and/or a significant material loss, resulting in a low yield in the final product,⁶ and thus should be avoided.

Fractionation by ultrafiltration removes particles and the largest lignin molecules and decreases the amount of carbohydrate in

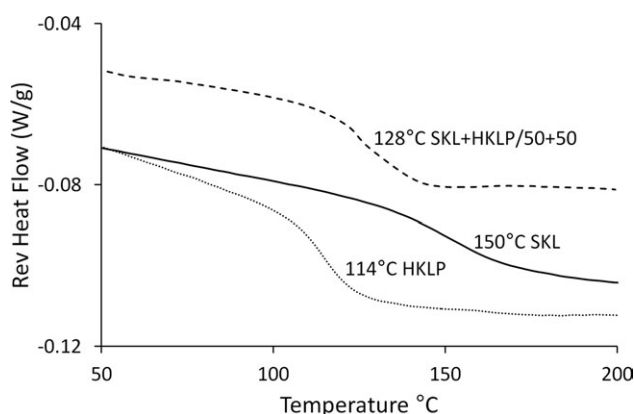


Figure 2. DSC curves of neat SKL, HKLP, and a blend thereof (50% SKL with 50% HKLP). The glass transition temperature (T_g and $T_{g(\text{blend})}$) is specified at the transitions (EXPERIMENTAL section).

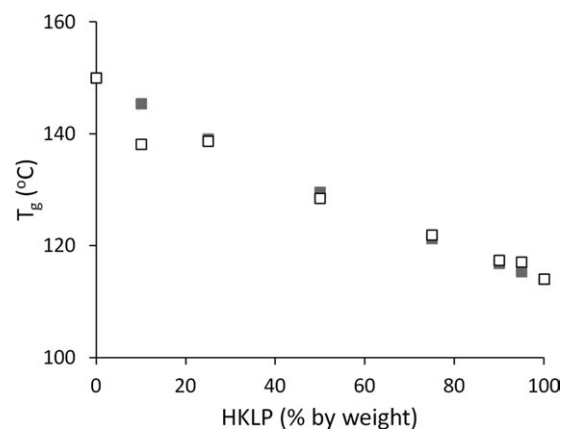


Figure 3. Experimentally determined glass transition temperature (T_g) of the extrudates of SKL and HKLP and blends thereof (open squares). Theoretical T_g values were determined using a semi-empirical model, the Fox equation (gray squares), are shown for comparison.

the permeate.⁸ Accordingly, the SEC analysis revealed lower average molecular masses and PD for the lignin permeates compared with the unfractionated counterparts. Based on its structure and characteristics,^{7–9} HKL is, in general, assumed to have a more linear structure and lower T_g than SKL. As membrane filtration accentuate the structural and thermal differences,⁸ HKLP was tested as a softening agent by blending with either SKL or HKL.

DSC graphs can also be used to determine whether polymer components are miscible on a molecular level.^{6,18} In case of a two-component homogeneous polymer blend, the analysis will reveal a single T_g for the blend ($T_{g(\text{blend})}$) at a temperature intermediate of the T_g values of the neat compounds. This theory appeared to be applicable also for lignin blends, as smooth curves with intermediate T_g values could be determined for all SKL/HKLP blends. Neat SKL, HKLP, and a blend thereof (50% SKL and 50% HKLP) are shown for comparison in Figure 2. For mixtures containing >10% of one component, the intermediate $T_{g(\text{blend})}$ can be determined using a semi-empirical expression [eq. (1)], where $T_{g(\text{blend})}$ is based on the weight fractions (w_i) and T_g values (T_{gi}) of the neat components.¹⁸

$$\frac{1}{T_{g(\text{blend})}} = \sum_i \frac{w_i}{T_{gi}} \quad (1)$$

A clear trend can be observed in which $T_{g(\text{blend})}$ decreases as larger amounts of HKLP are added to SKL (Figure 3) and although the temperature steps were rather small between the $T_{g(\text{blend})}$ values for different compositions, these were clearly distinguished as the standard deviation was <2°C ($n = 5$). Values determined with eq. (1) corresponded well with the experimental $T_{g(\text{blend})}$ values.

Previous reports have shown that lignin can be processed into fibers by melt extrusion,^{4,6,9} one of the most common processing techniques for thermoplastic materials.¹⁸ Lignin is an amorphous material, and similar to many amorphous polymers, it does not have a distinct melting temperature. However, amorphous materials often have a detectable T_g , the temperature at which the material goes from a glassy solid to a rubbery state owing to micro-Brownian motion, and a softening temperature

(T_s), at which the molecular mobility (macro-Brownian motion) becomes high enough for viscous flow.^{19,20} It has been difficult to determine the softening temperature for lignin using DSC analysis, especially for softwood lignin.^{9,13}

Consequently, the spinning temperature should be adjusted relative to $T_{g(\text{blend})}$ to obtain a lignin blend with adequate thermal properties for fiber spinning.

Fiber Spinning of Neat Lignins and Permeates

As the fracture of brittle fibers such as CFs is initiated at flaws, it is important to minimize the number of defects.²¹ Thus, a prerequisite to obtaining acceptable mechanical properties of CFs is solid and homogeneous precursor fibers.

For extrusions of neat lignins, the initial processing temperature studied was 50°C above T_g , a minimum processing temperature for many amorphous resins.²² Neat SKL, HKL, SKLP, and HKLP, respectively, were tested for melt spinning into fibers at temperatures 50°C above their respective T_g s: at 200 and 165°C. Both SKLP and HKLP could easily be melt spun, but when extruding SKL, extensive foaming occurred. For neat HKL, the brittleness of the fibers hindered continuous spinning.

As foaming causes pores in the formed fiber, it must be avoided to achieve a high-quality CF. Foaming of lignin during extrusion has been observed previously and has been suggested to be owing to the emission of volatile compounds.^{4,9} These compounds can be removed by heat treatments prior to extrusion.^{6,13} In this study, however, heat treatments were avoided as heating to temperatures above T_g can induce branching and/or crosslinking of the SKL which leads to an unstable material unsuitable for fiber spinning.¹³

To evaluate the impact of spinning temperature on foaming for SKL, extrusion of neat SKL was also performed at 180 and 220°C. None of these temperatures made fiber spinning possible owing to foaming. Additionally, the viscosity of SKL at 180°C was too high for continuous melt spinning.

Pelletizing by pre-extruding SKL through the twin-screw extruder at 200°C was used in an attempt to minimize the foaming by removing the volatile compounds. This pretreatment decreased the foaming when the SKL pellets were re-extruded at 200°C but not sufficiently to make neat SKL suitable for transformation into continuous and solid lignin fibers. In contrast, continuous fiber spinning of SKLP is an important breakthrough as this is the first 100% SKL-based fiber ever reported. However, although both HKLP and SKLP could be continuously spun, it is more economically sound to use permeate lignin as a softening agent for unfractionated lignins, such as SKL and HKL, as the fractionation process is both energy intensive and costly.²³

Fiber Spinning of Kraft Lignin With HKLP as a Softening Agent

HKL could be continuously spun into thin filaments with the addition of 5% HKLP at 180°C, giving nonheat pretreated kraft lignin-based fibers. In earlier studies, synthetic softeners have been used.^{1,6}

To improve the spinnability of SKL, HKLP was added as a softening agent. Initially, a blend containing 50% SKL and 50% HKLP was prepared for fiber spinning at 200°C. The resulting fiber could be continuously spun, and SEM analysis revealed a homogeneous

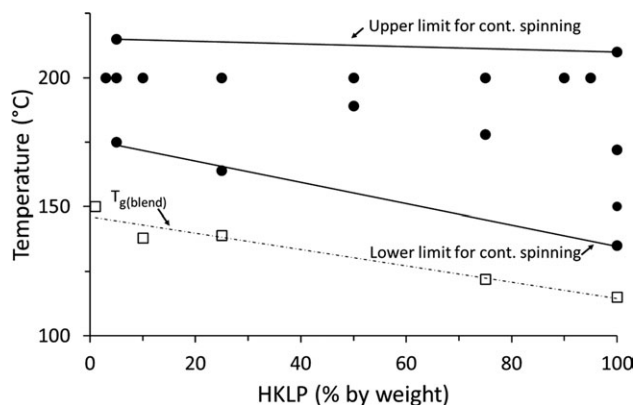


Figure 4. Suggested upper and lower limits (solid lines) for continuous fiber spinning of SKL, with addition of HKLP, and for neat HKLP. The filled circles show the composition and spinning temperature for successfully continuous spun fibers. The open squares show the measured $T_{g(\text{blend})}$ values for different compositions and are included for comparison.

and solid fiber. One assumption of the beneficial impact of HKLP on foaming is that a decreased viscosity of the melt facilitates the emission of volatiles from the material before it exits the die. However, as there are no reports about the origin of thermally induced foaming of lignin, this needs to be further investigated.

To establish the minimum amount of HKLP required to obtain a lignin blend suitable for fiber spinning of SKL, several experiments were performed by adding different amounts of HKLP corresponding to fractions ranging between 1 and 95% HKLP. All compositions were initially spun at 200°C. Blends composed of SKL with 3–95% HKLP added were successfully spun into continuous fibers, and no foaming was observed. For SKL with 3% HKLP, the high viscosity required a low winding speed for continuous spinning, approximately 30 m/min compared with the maximum speed of the equipment (76 m/min). The melt viscosity during extrusion decreased as larger amounts of HKLP were added to SKL because the spinning temperature relative to the $T_{g(\text{blend})}$ increased. For high amounts (75–95%) of HKLP, fiber spinning was difficult because of the low melt viscosity, which is a typical behavior also for amorphous polymers.^{24,25} This relationship between melt viscosity and spinning temperature was not observed for SKL. The difference in softening characteristics can be related to the fundamental differences in the molecular structures and the composition of softwood and hardwood lignin, respectively,^{7,9} which persists in the isolated kraft lignins. The blend with 1% HKLP as a softening agent was not suitable for spinning as this lignin blend exhibited foaming, which hindered the drawing of fibers, similarly to neat SKL.

The spinnability for SKL/HKLP blends was improved by adapting the temperature for fiber spinning relative to the $T_{g(\text{blend})}$ values. Blends containing SKL with 5–75% HKLP and neat HKLP were successfully spun into continuous fibers at 50°C above the $T_{g(\text{blend})}$ or T_g , respectively. Thus, the simple approach presented by Dumoulin et al.,²² consisting of choosing a processing temperature 50°C above the T_g , was also applicable for lignin for these SKL blends.

In Figure 4, all successful continuously spun samples of SKL/HKLP blends and neat HKLP are shown as filled circles. To find

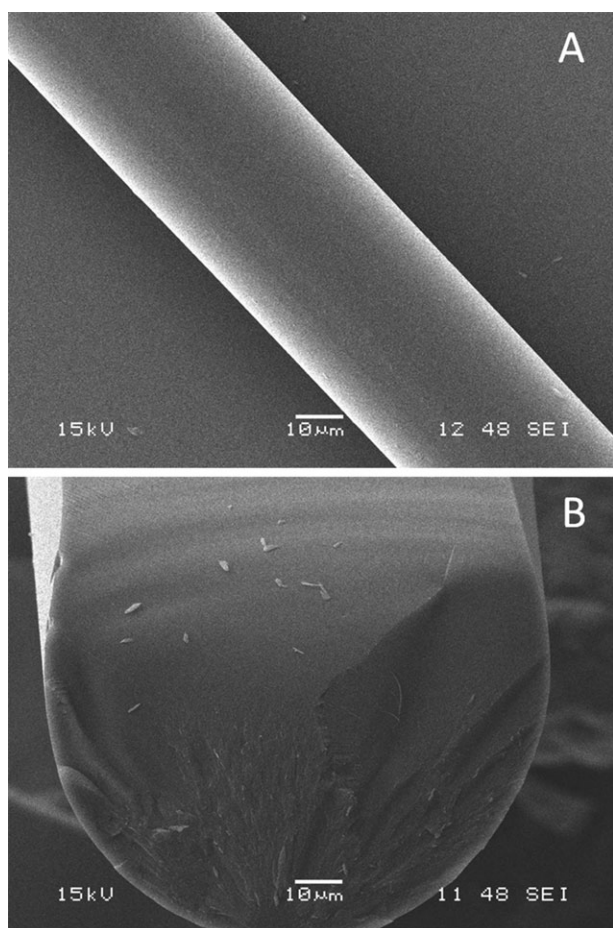


Figure 5. SEM image at 15 kV of a HKLP fiber (A), and a SKL fiber with 5% HKLP (B).

the upper and lower temperature limits, fiber spinning of SKL with 5 or 25% HKLP and neat HKLP, thus covering the whole blend range, was performed at 130–225°C and the temperature range of 135–215°C resulted in successfully continuous spun fibers. From these results, temperature limits, implying a suitable temperature range for continuous spinning are shown as solid lines in Figure 4. The open squares representing the measured $T_{g(\text{blend})}$ values are included for comparison. The processing temperatures span from 25 to 85°C above the T_g values of the lignin blends containing 3–98% HKLP, respectively. An increasing temperature range for successful spinning was observed as the HKLP fraction increased and neat HKLP could be continuously spun up to 210°C, that is, 95°C above its T_g . Fiber surfaces and cross-sections of all fibers were investigated with SEM to evaluate the fiber quality with respect to homogeneity and solidity. All neat permeate fibers and all blend fibers (HKL/HKLP and SKL/HKLP), appeared to be solid and without pores, and had a smooth surface without inclusions or irregularities (Figure 5). The fiber diameters ranged from 20 to 90 μm. It is expected that the diameters can be decreased by, for example, using smaller spin dies and by increasing the winding speed.

Conversion of Lignin Fiber into CF

Fibers of neat SKLP, HKLP, and SKL with 3 or 10% HKLP were further processed into CFs. The lignin fibers were oxidatively sta-

bilized prior to carbonization to prevent fiber fusion,^{4,14} using conditions adopted from the literature.¹⁷ The carbonization conditions were adopted from the literature where it is stated that a two-step process, where the first slow step up to 600°C, is crucial to allow efficient mass transfer of volatiles formed.¹⁴

After carbonization, all fibers retained their fibrous shape, indicating that they had been successfully stabilized.

To fully characterize the softwood-based CFs, a thorough evaluation of the mechanical properties is currently being performed. However, processing conditions such as stabilization and carbonization may have a great influence on the mechanical properties of CFs and thus should be optimized to improve the fiber quality.^{14,26}

The composition and quality of the carbonized fibers were evaluated using X-ray/EDS and SEM (Figure 6). The elemental composition confirmed that CFs had been obtained, as the carbonized fibers contained 93–97 atomic-% carbon. The other components were mainly oxygen and sulfur, the latter originating from the kraft pulping process. X-ray/EDS and SEM analyses showed that the first continuous SKL-based CFs had

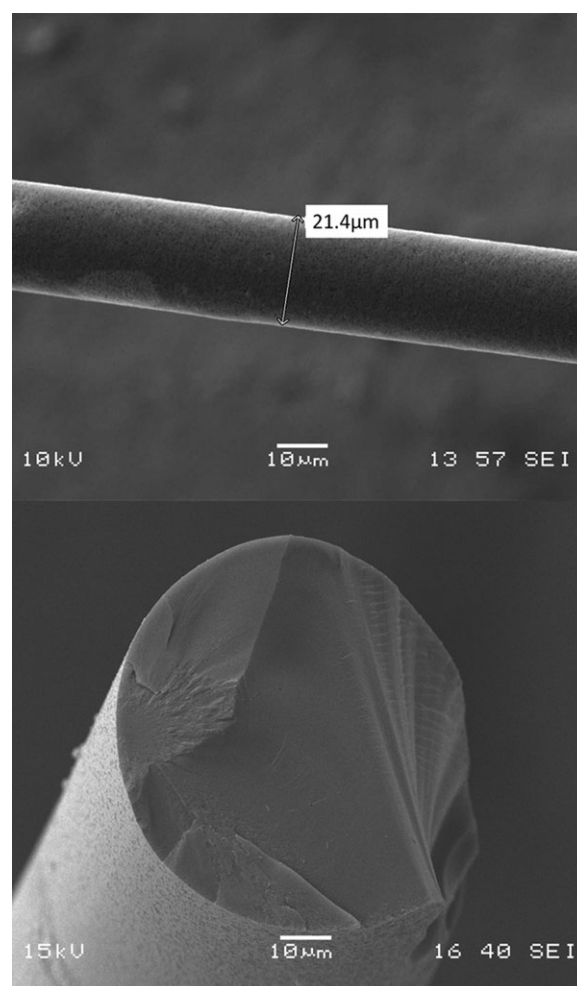


Figure 6. Cross-section and fiber surface of a carbonized SKL fiber with 10% HKLP.

successfully been produced, without visible defects at the surface or in the cross section of the fibers.

CONCLUSIONS

For the first time, solid and smooth CFs made from SKL have successfully been produced. This was accomplished either by direct spinning of SKLP or by the addition of HKLP, as a softening agent, to unfractionated SKL. The studied fraction of HKLP ranged from 1 to 100%, that is, the latter being only HKLP. The T_g characteristics of the lignin blends were suitable to use for optimization of the spinning temperature of the lignin materials. The suitable spinning temperature of the SKL/HKLP blends, decreased with the increasing fraction of HKLP. In addition, it was found that HKLP can be suitable as a softening agent for unfractionated HKL.

All of the above lignin samples and lignin blends were continuously spun into smooth and solid filaments and the SKL-derived fibers were further transformed into CFs. Thus, kraft lignin-based CFs with a carbon content ranging from 93 to 97 atomic-% was produced, and the fibers were all of good quality, as revealed by SEM analysis.

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