

Lignin-based Carbon fiber: effect of softwood kraft lignin separation method on multifilament melt-spinning performance and conversion

Darren Baker¹, Omid Hosseinaei², Maria Sedin²,
Linda Echardt³, Ewellyn Capanema²

¹Baker Consulting, Kingston, TN 37763, USA

²RISE, Box 5604, SE-114 86 Stockholm, SE

³Södra Skogsägarna ekonomisk förening, Södra
Innovation & Nya Affärer, 43286 Väröbacka, SE

ABSTRACT

A reference lignin separated from an industrial softwood Kraft black liquor via an improved LignoBoost process was compared to four other lignins derived from the same liquor. The four lignins were produced by using a) pH-fractionation within the LignoBoost process, b) ultrafiltration of black liquor prior to the LignoBoost process, and c) solvent leaching of the reference lignin using methanol and d) ethanol.

Lignin compositional characteristics and thermal properties were compared, and monofilament extrusion used to assess their potential for successful melt spinning at the 24 filament scale. The lignin prepared by ethanol leaching of the reference lignin was found to be most appropriate for potential pilot scale fibre production. This was owing to a high purity, lower comparative glass transition temperature (T_g), and good spinning performance.

Thermal pretreatments of the ethanol leached lignin gave a selection of enhanced lignins which were characterized for comparison, and melt spun on pilot multifilament equipment. The enhanced lignins could be continuously melt spun giving filaments with diameters as low as 10 μm and with minimal defects. Conversion of selected filaments provided carbon fibres with a tensile strength of 1259 ± 159 MPa, tensile modulus of 67 ± 3 GPa and diameter of 7.3 ± 0.5 μm .

INTRODUCTION

Lignin, due to its high carbon content and aromatic structure, has been studied as a precursor for low-cost carbon fibers for several decades [1]. The preferred, most economically desirable route to

lignin carbon fibre is via melt spinning and this poses several challenges in preparing suitable lignins. It is necessary for a lignin to have optimal melt flow properties for fine filament spinning, a low volatile content at potential extrusion temperatures, and as high a glass transition temperature as possible so that conversion of the fibres to carbon fibre proceeds at an acceptable rate. The need for optimum rheological characteristics together with structural stability in the lignins contrast with the reactivity needed for desirable conversion kinetics [1,2].

Kraft lignins are typically separated from the black liquor with broad molecular weight distributions, impurities, and with the potential for infusible contents. Efforts to control these in a techno-economically viable way are needed, especially for use in high value products such as carbon fibres. In the past, Kraft lignin deficiencies have been addressed by employing methods such as blending it with synthetic polymers or by chemical modifying it to produce fusible and melt-spinnable lignin [1]; though both of these routes have resulted in improvements in melt spinning performance, the resulting carbon fibres were generally poor owing to problems caused by the additives/modification that arise during conversion of the melt spun fibres to carbon fibre.

If successful and economically attractive processes can be developed for the purpose of refining black liquor, there is the potential for lignins to be produced in the pulp mill with properties tailored towards differing products. It has been shown that lignin fractions can be separated from black liquors or lignins using different refining methods [3,4]. Solvent leaching is a common method reported for refining lignins [3], while pH-fractionation and ultrafiltration are two that have been used for producing refined lignins directly from black liquors [4,5]. Optimization of the refining parameters and/or selecting the proper solvent, are very important in preparing lignins for use in lignin-based materials.

In this work we sought to produce a bio-based, renewable carbon fibre from lignin. The target was to provide a basis for the commercial production of lignin, lignin filaments, carbon fibre, and carbon fibre composites. To develop lignin as a precursor for continuous filament carbon fibre, the main challenge to be overcome was to produce melt extrudable lignins which could be techno-

economically favorably converted to carbon. The LignoBoost process, which provides kraft lignins with low inorganic element, carbohydrate, and extractives contents^[6], and variations of the original LignoBoost process were used to produce lignins with improved thermal properties from one commercially produced softwood kraft black liquor. These variations included the incorporation of pH inversion, ultrafiltration, and solvent leaching. Four refined lignins were produced and compared to one made using the standard process. The lignins were tested in terms of thermal, compositional, and structural properties; then monofilament melt spinning and pilot scale melt spinning at the 24 filament scale.

EXPERIMENTAL

Lignin source

Södra Mönsterås industrial softwood kraft black liquor made from 40 % sawmill chips and 60 % pulpwood (30 % pine and 70 % spruce) was used as the primary liquor source for producing five differing lignins according to variations of the LignoBoost process (Figure 1)

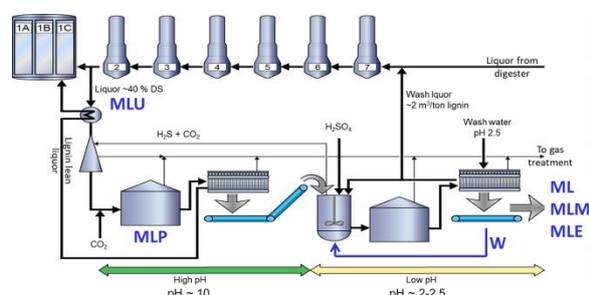


Figure 1: Representation of the LignoBoost process for producing lignins with high purity. An additional purification step was also used (W).

Lignin preparation

The LignoBoost process was used to produce five lignins, in each case an additional purification step was applied to reduce impurities (Figure 1. W). The first was produced using the process without further alteration (ML, Figure 1). The second (MLP, Figure 1), a pH-fractionated lignin, was prepared by reducing the pH of the black liquor to 11.5, instead of 10 which was normally used, and filtered so that higher molecular weight lignin was removed. The filtrate was then adjusted to pH 10 and proceeded through the LignoBoost process to provide MLP.

The third was a permeate via ultrafiltration (50 kDa) of the black liquor prior to LignoBoost processing (MLU, Figure 1). The remaining lignins were prepared via solvent leaching of ML using either methanol (MLM) or ethanol (MLE) so that the filtrate was recovered and evaporated under reduced pressure.

Composition

Lignin purity was calculated on the basis of total lignin content divided by total assay as %. The total assay was the sum of lignin, carbohydrate, extractives, and inorganics minus sulphur; sulphur was assumed to be part of the lignin.

Lignin assays were determined by measuring for moisture (dry mass basis calculations), extractives content (SCAN/CM 67:3), carbohydrate content (SCAN-CM 71:09), and Klason and acid-soluble lignin (TAPPI T222 om-11). The data were normalised.

Inorganic element contents were determined after hydrogen peroxide oxidation, nitric acid microwave digestion, and subsequent separation and dissolution in 6 M HCl. Inductively Coupled Plasma – Optical Emission Spectroscopy was then used to characterise the inorganic content of the lignin. Elements quantified were: Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Si and Zn.

C, H, N, and S contents were measured using combustion elemental analysis. This was measured in triplicate and an average value calculated. The % C portion is reported here.

Thermal properties

Their softening temperatures (T_s) were measured optically using a Fisher-Johns melting point apparatus. A small amount of dried lignin was placed between two microscope cover slips and placed on the heating platform of the instrument. Tests were done using a heating rate $\sim 1-3$ °C/min and temperature values were recorded when full softening of the lignin was observed.

Lignin glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) using a TA Instruments Q1000 apparatus equipped with an RC90 cooling unit. Dried lignin samples (~ 2.5 mg) were placed in a standard Tzero aluminum pan with lid and heated under nitrogen to 85 °C and held for 20 minutes to expel any moisture. The sample was then cooled to 0 °C. A second DTA trace was then obtained on heating the sample to

260 °C at 5 °C/min under nitrogen. The T_g was taken at half width of onset and offset.

Thermogravimetric analyses (TGA) were performed using a TA Instruments Q5000IR TGA. This was used to evaluate and compare any potential volatiles in the lignin and nominal carbon yield. Dried lignin samples (10 mg) were placed in a platinum pan and heated under nitrogen to 105 °C and held for 20 minutes to expel any moisture. The sample was then heated to 1000 °C at a rate of 10 °C/min. Data were normalized against the residual mass measured at 105 °C.

Monofilament trials

Monofilament trials were conducted on a DSM Xplore MC15 twin-screw melt compounder with a 15 ml screw capacity and equipped with a die with one 250 µm diameter orifice. Each lignin was dried at 80 °C under vacuum for 24 hours to remove moisture, and melt extrusion performed using a temperature range appropriate for each lignin, based on T_g and T_s . Extrusion conditions were optimised so that the most continuous extrusion of monofilament was obtained and with the lowest fibre diameter. The equipment was disassembled and cleaned between samples. The success of monofilament spinning was evaluated in terms of extrusion continuity, filament diameter and quality, lignin purity, and thermal properties.

Lignin thermal treatments

It is known ^[1,2] that there is an inverse relationship between filament conversion time and lignin T_g . For lignin to be techno-economically successful as a precursor for carbon fibre, the oxidative thermostabilization step using conventional conversion techniques should take less than 2-4 hours, depending on the economic balance between each step (lignin cost, spinning and so on). Therefore, it is economically favourable for a lignin to have as high a T_g as possible while permitting the continuous multifilament melt extrusion of fine, high quality filaments.

A way to achieve this is to employ controlled vacuum degassing during twin-screw pelletisation, which removes a portion of the lower T_g lignin resulting in an increased T_g lignin with much reduced volatile content at desirable melt spinning temperatures, and an increased rate of oxidative thermostabilization.

In this preliminary work, a vacuum oven was used to remove volatiles. Evaluation of the effect of

vacuum degassing on lignin thermal properties was performed over temperatures around 200 °C to 260 °C. Selected thermally treated lignin samples were then prepared and their thermal and purity properties were measured prior to melt spinning.

Multifilament spinning

Multi-filament spinning trials were conducted using a custom pilot scale mesophase pitch melt-spinning unit equipped with a 12-48 holes spinnerets with 150 µm diameter holes (Alex James and Associates).

Prior to any extrusion, lignins were dried at 80 °C under vacuum, and placed into the nitrogen purged hopper for a minimum of two hours. Manipulation of barrel, spin head and pack temperatures were used to optimize extrusion performance, while increases in winding speed were used to reduce fiber diameter.

Conversion to carbon fiber

Thermogravimetric analysis (TGA; TA Instruments Q5000IR) was used to investigate permissible oxidative thermostabilization rates of selected lignin filament samples and their carbon yields at 950 °C. Lignin filaments (2.0 mg) were placed in a platinum pan and heated under nitrogen to 105 °C and held for 20 min to expel any remaining moisture in the sample. They were then heated to 250 °C under an air atmosphere at rate of between 0.1 °C/min to 10 °C/min. The sample was carbonized to 1000 °C at rate of 10 °C/min under nitrogen. After treatment a visual observation was made to determine the condition of the fibers. The data were normalized against the residual mass measured at 105 °C.

Preliminary carbon fibre samples were prepared in this work owing to an ongoing scale up of another MLE type lignin, which would be the basis for a more complete investigation. However, selected filaments were mounted on a fixed graphite frame (to create tension during conversion), oxidatively thermostabilized, and carbonized. Thermo stabilization was performed by heating the fibers from 100 °C to 250 °C at rates of ~0.1 °C/min in an MTI KSL-1200X-M Box Furnace under air and held isothermally for 15 min. The thermostabilized fibers were carbonized under nitrogen in an Entek 70/18-III three zone tube furnace by heating to 1000 °C at 3 °C/min. A Dia-stron LEX820 tensile testing system was used to measure the tensile properties of the carbon fibers according to ASTM

standard C1557-03. Morphologies were studied by light microscopy and a SU3500 Hitachi scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Lignin composition

The double wash LignoBoost process provided ML lignin with a relatively high purity of 97.7 % (Table 1) in comparison to other Kraft lignins and regular LignoBoost lignins^[7]. The 2nd wash (a second hot water resuspension and filtration) reduced carbohydrates (3.6 mg/g), extractives (17.8 mg/g), and inorganics (1.2 mg/g) effectively. In melt spinning, extractives, carbohydrates, together with smaller lignin oligomers contribute to volatiles being formed that are detrimental to fine filament formation and integrity. Carbohydrates cause flaws and voids to be formed during oxidative thermostabilization at temperatures around their decomposition temperatures. Inorganics cause activation and porosity formation during carbonization which reduces tensile properties.

The pH-fractionated MLP had an improved purity (99.5 %) owing to a 17 mg/g reduction in extractives, but still contained relatively high carbohydrate (3.2 mg/g) and inorganic (1.0 mg/g) contents. This reduction in extractives (fatty acids, rosin acids, phenolics, waxes and inorganics) was thought to be due their prior precipitation with the material precipitated at pH 11.5.

The lignin recovered from a 50 kDa permeate of the black liquor, MLU also had an increased purity (98.7 %) in comparison to ML (97.7 %). A substantial decrease in both carbohydrate (0.8 mg/g cf. 3.6 mg/g) and inorganic (0.6 mg/g cf. 1.2 mg/g) contents were observed. In contrast, the reduction in extractives content was much less so that MLU contained 11.6 mg/g in comparison to 0.6 mg/g for MLP. It is thought that since MLU was recovered by size exclusion, the nature of the extractives is such that they are able to pass through the membrane. However, the extractives could later easily be removed during heat treatments under vacuum.

In the case of MLM and MLE, whose purities were 99.8 % it is likely that the extractives are only sparingly soluble in polar solvents and therefore are much reduced (0.2 mg/g) in the solvent leached lignins. A reduction in both carbohydrate and inorganic contents were also found.

Comparison of the lignins sulphur contents showed a slight increase in comparison to ML, and this is consistent with the assumed reduced molecular weights of the other lignins. It is hypothesized that the increase in sulphur is associated with the portions of the biomass more accessible and/or lignin entities more readily depolymerised during pulping.

Table 1 Composition of the five lignins.

| Sample | Lignin ¹ | Car. ² | Ext. ³ | Inorg - S ⁴ | Purity | S ⁵ | C ⁶ |
|--------|---------------------|-------------------|-------------------|---------------------------|--------|----------------|----------------|
| | mg/g | | | | % | | |
| ML | 977.4 | 3.6 | 17.8 | 1.2 | 97.7 | 2.0 | 64.9 |
| MLP | 995.2 | 3.2 | 0.6 | 1.0 | 99.5 | 2.2 | 65.1 |
| MLU | 987.1 | 0.8 | 11.6 | 0.6 | 98.7 | 2.0 | 65.9 |
| MLM | 997.9 | 1.1 | 0.2 | 0.8 | 99.8 | 2.3 | 66.0 |
| MLE | 998.0 | 1.6 | 0.2 | 0.2 | 99.8 | 2.4 | 66.1 |

¹Total lignin, ²carbohydrates, ³extractives, ⁴inorganics excl. sulphur, ⁵sulphur, and ⁶carbon (combustion elemental analysis)

The carbon contents of the lignins increased in the order shown in Table 1. Since the level of impurities which have reduced carbon content, i.e. carbohydrates and extractives, found in the lignins was very low and in the order of 0.48 % for ML and 0.14 % for MLU, these could not possibly contribute to the differences found in carbon content. This increase must therefore be because of structural features which provide increasing C content.

Thermal properties

Lignin T_g 's and T_s 's are well known to be related to their molecular weights, and comparisons can be made provided the lignins are of similar structure (i.e. softwood, hardwood, and so on). It is surprising that both MLP and MLU have T_g 's and T_s 's close to that of ML (Table 2). However, it is likely that ML contained substantial infusible lignin components

The ML contained much more extractives than the other lignins which could plasticize the lignin and reduce its T_g and T_s ; it would be interesting to see if removal of these compounds via non-polar solvent leaching would result in a substantially increased T_g . Both of the solvent leached lignins had a much reduced T_g and a low extractives content.

Volatiles are thought to arise due to a balance of evaporation of low molecular mass lignin oligomers,

the decomposition of carbohydrate impurities, and the loss of extractives on increasing temperatures.

Table 2 Thermal properties of the five lignins

| Sample | T_g | T_s | C Yld ¹ | Volatiles at °C | | | | | |
|--------|-------|-------|--------------------|-----------------|-----|-----|-----|-----|-----|
| | | | | 200 | 210 | 220 | 230 | 240 | 250 |
| | °C | % | % | | | | | | |
| ML | 142 | 177 | 36.6 | 2.3 | 2.7 | 3.1 | 3.6 | 4.3 | 5.1 |
| MLP | 140 | 180 | 37.4 | 1.4 | 1.6 | 1.9 | 2.4 | 2.9 | 3.6 |
| MLU | 135 | 171 | 35.5 | 1.8 | 2.1 | 2.6 | 3.1 | 3.7 | 4.6 |
| MLM | 116 | 145 | 35.1 | 1.9 | 2.4 | 2.9 | 3.6 | 4.6 | 5.7 |
| MLE | 97 | 134 | 30.6 | 3.9 | 4.9 | 6.0 | 7.2 | 8.5 | 9.9 |

¹nominal carbon yield measured by TGA at 950°C

Comparison of the modified lignins (MLP, MLU, MLM, and MLE) reveal an increasing evolution of volatiles with decreasing T_g , and it is therefore likely that the main contributor to this are low molecular mass monomers and oligomers. The initially high evolution of volatiles for ML (and also for MLU) in comparison to its T_g is most likely because of the relatively high extractives content (Table 1). Their nominal carbon yields were found to decrease with decreasing T_g , and again this is thought to be due to lignin and extractives volatility.

Monofilament preparation

The reference lignin ML was evaluated for monofilament extrusion. Monofilaments could only be obtained over several seconds at temperatures of up to 230 °C, the viscosity of the extrudate was such that fibre diameters of ~70 µm were obtained. Efforts to improve filament properties by increasing the temperature to more than 230 °C resulted in the evolution of volatiles and filaments could not be produced.

MLP only improved a little in comparison to ML. The viscosity of the extrudate was such that feeding, and screw rotation only became continuously possible as the temperature was increased to 225 °C. Continuous monofilaments could be obtained from around 230 °C for several minutes, but had large diameters >30 µm and voids were to be found along the fibres. Efforts to decrease diameter by increasing temperatures above 235 °C gave rise to an excessive release of volatiles and ultimately poor continuity.

MLU, on the other hand, provided an improved

melt spinning performance. Monofilaments could be obtained from 220 to 224 °C of about 24 µm diameter and were defect free. Efforts to decrease diameter by increasing the temperature did not visually cause volatiles to be formed but filaments could not be continuously recovered.

MLM, which possessed a lower T_g , could be spun readily from 200 °C to 230 °C and provided continuous filaments of ~25 µm to 15 µm diameter with increasing temperature and collection speed. Temperatures above 230 °C gave rise to substantial volatiles which prevented filament collection.

Both ML and MLP were excluded from further study because they would not be able to be melt spun at the 24 filament scale to provide fine filaments (< 12 µm), without increasing temperatures which would result in excessive volatile formation and therefore discontinuous fibre spinning. Removal of potential volatiles prior to extrusion would raise their already high T_g 's substantially. In addition to this, excluding the extractives data, both contained a relatively high level of impurities.

Evaluation of the thermal properties of MLU and MLM indicated that although they provided fine monofilaments, there were volatiles evolved at potential melt spinning temperatures. Therefore, some level of heat treatment (under vacuum) would have to be employed prior to spinning to remove them. Heat treatment studies and multifilament trials were performed on MLU but were ultimately unsuccessful. Upon 24 filament spinning, the filaments were either discontinuous and fibre spinning could not be maintained for more than 5 minutes without at least one filament rupturing, or the filament diameters were unacceptably large, or too many volatiles were generated. Similarly, and informed by the MLU studies, MLM could not provide a robust melt spinning platform.

Ultimately, it was decided that a differing lignin preparation would be required to ensure a robust melt spinning process. MLE was prepared with a reduced T_g , thermal treatments were investigated, and multifilament trials performed.

Heat treatment of MLE

Several heat-treated lignins were prepared for multifilament melt spinning and a comparison of the compositional characteristics of some of the lignins is shown in Table 3. It is clear that the heat treatments brought about the decomposition of

carbohydrates because of the reduction of content from 1.6 mg/g in MLE to 0.1 in its derivatives, and this is desirable. In addition to this, carbon contents were found to increase with severity so that they increased from 66.1 % in MLE to 69.7 % in MLE treated at 260 °C for 2 hours (MLE-260t02). Sulphur contents were found to be reduced with increasing temperature.

Table 3 Comparison of some compositional characteristics of selected heat treated derivatives of MLE. (Key: 240t02 indicates a vacuum treatment at 240 °C for 2 hours).

| Sample | Lignin ¹ | Car. ² | Ext. ³ | Inorg -S ⁴ | Purity | S ⁵ | C ⁶ |
|------------|---------------------|-------------------|-------------------|-----------------------|--------|----------------|----------------|
| | mg/g | | | | % | | |
| MLE | 998,0 | 1,6 | 0,2 | 0,2 | 99,8 | 2,4 | 66,1 |
| MLE-240t02 | 998,8 | 0,1 | 0,8 | 0,2 | 99,9 | 1,8 | 69,0 |
| MLE-250t01 | 998,7 | 0,1 | 0,9 | 0,3 | 99,9 | 1,8 | 68,9 |
| MLE-260t02 | 999,6 | 0,1 | 0,1 | 0,3 | 100,0 | 1,6 | 69,7 |

¹Total lignin, ²carbohydrates, ³extractives, ⁴inorganics excl. sulphur, ⁵sulphur, and ⁶carbon (combustion elemental analysis)

Selected thermal properties of the heat treated derivatives of MLE are provided in Table 4. Heat treatments brought about a progressive increase in both T_g and T_s with increasing treatment severity. The difference between T_g and T_s can indicate an increase in polydispersity or a broader molecular weight distribution. In the case of MLE this difference was 37 °C and for MLE-260t02 it was 51 °C. This indicated that the heat treatment was too severe and resulted in an undesirable amount of lignin condensation reactions to occur.

Measurement of the volatiles evolved by the heat treated lignins at temperatures between 200 °C and 250 °C using TGA, showed that they were much reduced in comparison to both ML and MLE, as desired. Their nominal carbon yields increased with increasing severity from 30.6 % for MLE up to 37.4 % for MLE-260t02. This was due to both the prior removal of volatile components and also the formation of a more condensed lignin which resulted in an increased thermal stability.

Therefore, by using heat treatments under vacuum, derivatives of MLE were produced which had very low impurities, a desirable range of T_g 's for comparison, and a reduced potential for volatile component generation during melt extrusion.

Table 4 Comparison of some thermal properties of selected heat-treated derivatives of MLE.

| Sample | T_g | T_s | C Yld ¹ | Volatiles at T ^C | | | | | |
|------------|-------|-------|--------------------|-----------------------------|-----|-----|-----|-----|-----|
| | | | | 200 | 210 | 220 | 230 | 240 | 250 |
| | °C | | % | | % | | | | |
| ML | 142 | 177 | 36,6 | 2,3 | 2,7 | 3,1 | 3,6 | 4,3 | 5,1 |
| MLE | 97 | 134 | 30,6 | 3,9 | 4,9 | 6,0 | 7,2 | 8,5 | 9,9 |
| MLE-220t01 | 117 | ~ | 33,5 | 0,3 | 0,4 | 0,6 | 1,0 | 1,6 | 2,5 |
| MLE-240t02 | 135 | ~ | 35,5 | 0,2 | 0,3 | 0,3 | 0,3 | 0,4 | 0,5 |
| MLE-250t01 | 129 | 171 | 37,0 | 0,2 | 0,3 | 0,3 | 0,5 | 0,6 | 0,8 |
| MLE-260t02 | 141 | 192 | 37,4 | 0,2 | 0,3 | 0,4 | 0,5 | 0,6 | 0,8 |

¹nominal carbon yield measured by TGA at 950°C

Multifilament spinning

Owing to the sample masses to be spun (~500 g), the first trial of MLE-220t01 was performed using a 12 hole die to provide more time for adjustment of spinning parameters (Table 5). Material throughput was halved in comparison to the other trials which consequently doubled residence time from ~12 min to ~24 min. This likely resulted in an increase in chemical changes in the lignin so that a reduced normalized winding speed resulted in comparison to the second trial of the same lignin. MLE-220t01 was spun using a 48 hole die and provided for a much increased normalized winding speed. Even though the spinning performance of this sample was good, it was anticipated that relatively low T_g of MLE-220t01 could result in longer oxidative thermostabilization times compared to the samples heat-treated at higher severity treatments.

Lignins that were produced using more severe heat treatments were used to explore the upper limits of lignin T_g for successful extrusion. MLE-240t02 provided filaments with a relatively slow winding speed and exhibited problems with volatile generation upon increasing T_{spin} , while MLE-260t02 could not reasonably be melt spun at all owing to high viscosities at temperatures below 254 °C and the generation of large amounts of volatiles above it; continuous filament spinning could not be achieved. MLE-250t01, on the other hand, could be melt spun at an acceptable speed so that 24 fine filaments could be continuously produced over > 10 min. This lignin also had a reasonably high T_g which implied that conversion to CF would proceed more rapidly. Comparison of the melt spinning performance data revealed that the most desirable T_g would be around 130 °C for MLE which had been thermally treated using the particular equipment used.

Table 5 Comparison of some melt spinning parameters for heat treated derivatives of MLE.

| Sample | T _g | T _s | T _{spin} ¹ | Pump speed ² | Winding speed ³ | Normalized winding speed ⁴ |
|-------------------------|----------------|----------------|--------------------------------|-------------------------|----------------------------|---------------------------------------|
| | °C | | | rpm | m/min | m/min |
| MLE | 97,3 | 134,0 | ~ | ~ | ~ | ~ |
| MLE-220t01 ⁵ | 116,7 | ~ | 206 | 3,0 | 600 (800) | 600 (800) |
| MLE-220t01 ⁶ | 116,7 | ~ | 205 | 6,0 | 500 (600) | 1000 (1200) |
| MLE-240t02 | 135,2 | 178 | 225 | 5,0 | 500 (600) | 600 (720) |
| MLE-250t01 | 129,3 | 171 | 233 | 6,0 | 800 (1000) | 800 (1000) |
| MLE-260t02 | 141,1 | 192 | 254 | 6,0 | (variable) | (variable) |

¹Die pack temperature during extrusion, ²material extrusion speed (1 rpm = 0.576 ml), ³continuous for >10 min (continuous for <1 min) ⁴normalised for equivalent volume throughput at each orifice, ⁵12 hole die used instead of otherwise identical 24 hole die, ⁶48 hole die used instead of otherwise identical 24 hole die

Conversion and properties of the carbon fibers

Simulated conversion (TGA) of the fibres obtained from MLE-250t01 suggested that they might be successfully oxidatively thermostabilized using rates up to 0.5 °C/min (time ~300 min) (Figure 2), while those prepared from MLE-240t02 might be stabilized at an even higher rate of up to 2 °C/min (75 min). In comparison, MLE-220-t01 filaments could only be (practically) oxidatively thermostabilized at rates of up to 0.1 °C/min (not presented in this figure).

The data collected for both MLE-250t01 and MLE-260t02 filaments (Table 2) followed similar trends to those previously reported [1,2].

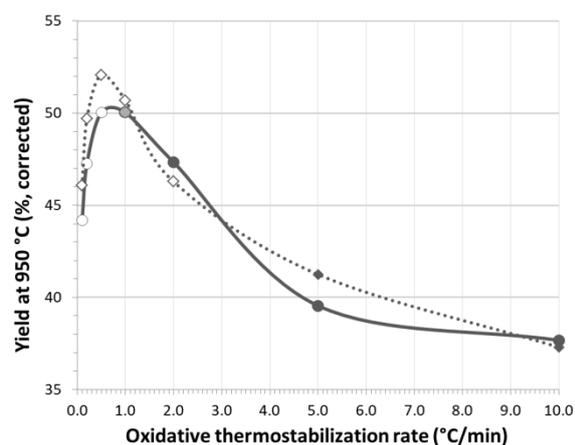


Figure 2 Relationship between conversion yield (lignin fibre to carbon fibre) and oxidative thermostabilization rate for MLE-240t02 (dotted line) and MLE-250t01 filaments (solid line). Open data point indicates fibre form maintained, checkered indicates fusion between filaments, filled indicates filament melt.

To provide information on the potential tensile properties expected, selected filaments were converted to carbon fibre. However, comparison of the tensile properties of carbon fibres obtained from the conversion of MLE-220t01, MLE-250t01, and MLE-260t02 lignin filaments revealed the dependence of tensile properties on filament diameters (Table 5). Tensile strengths and moduli of up to 1259±160 MPa and 67±3 GPa were recorded and are among the highest values reported for lignin-based carbon fibers [1,8]. Highest tensile properties of the carbon fibers MLE-220t01 could be due to lowest diameter of these fibers. It is possible that improved conversion conditions, especially optimized tension, could result in producing fibers with further increased properties.

The diameters of carbon fibers produced from both MLE-220t01 and MLE-250t01 were found to be commercially acceptable (Table 6 and Figure 3).

Table 6 Examples of the tensile properties of carbon fibers prepared from derivatives of MLE.

| Lignin filament | Diam. (µm) | Tensile str. (MPa) | Tensile mod. (GPa) | Elongation at break (%) |
|-----------------|----------------|--------------------|--------------------|-------------------------|
| MLE-220t01 | 7.27 (0.54) | 1259 (159) | 67.4 (3.0) | 1.90 (0.27) |
| MLE-250t01 | 9.38 (0.38) | 1133 (172) | 75.1 (2.8) | 1.50 (0.21) |
| MLE-260t02 | 11.5 (0.62) | 950 (192) | 67.1 (1.9) | 1.41 (0.26) |

Standard deviations are shown in parenthesis.

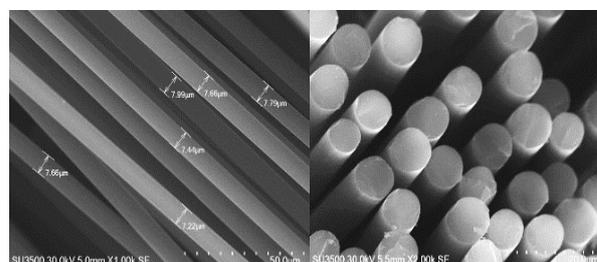


Figure 3 SEM images of carbon fibers produced from MLE-220t01 filament

CONCLUSIONS

Lignin-based carbon fibers were produced from softwood kraft lignins separated from an industrial black liquor by various means. All lignins had a

higher purity compared to standard LignoBoost lignin. The ethanol extracted lignin had the best spinnability among all samples as the spinning was continuous and small diameter fibers (up to about 11 μm) were produced. The resulting carbon fibers from this lignin had some of the highest tensile properties ever reported for lignin-based carbon fibers, with tensile strength of 1259 MPa and tensile modulus of 67 GPa. Results shows ethanol leaching is a suitable refining method to produce a melt-spinnable lignin from a not-spinnable softwood kraft lignin. Further investigation on spinning in pilot-scale units and continuous conversion can even results in producing stronger fibers.

ACKNOWLEDGEMENTS

This project has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No 667501.

REFERENCES

- [1] Baker, D. A.; Rials, T. G. Recent Advances in Low-Cost Carbon Fiber Manufacture from Lignin. *J. Appl. Polym. Sci.* **2013**, *130* (2), 713–728. <https://doi.org/10.1002/app.39273>.
- [2] Baker, D. A.; Baker, F. S.; Gallego, N. C. *Thermal Engineering of Lignin for Low-Cost Production of Carbon Fiber*; 2009.
- [3] Yoshida, H.; Morck, R.; Kringstad, K. P.; Hatakeyama, H. Fractionation of Kraft Lignin by Successive Extraction with Organic Solvents. II. Thermal Properties of Kraft Lignin Fractions. *Holzforschung* **1987**, *41* (3), 171–176. <https://doi.org/10.1515/hfsg.1987.41.3.171>.
- [4] Brodin, I.; Sjöholm, E.; Gellerstedt, G. Kraft Lignin as Feedstock for Chemical Products: The Effects of Membrane Filtration. *Holzforschung* **2009**, *63* (3), 290–297. <https://doi.org/10.1515/hf.2009.049>.
- [5] Lourençon, T. V.; Hansel, F. A.; da Silva, T. A.; Ramos, L. P.; de Muniz, G. I. B.; Magalhães, W. L. E. Hardwood and Softwood Kraft Lignins Fractionation by Simple Sequential Acid Precipitation. *Sep. Purif. Technol.* **2015**, *154*, 82–88. <https://doi.org/http://dx.doi.org/10.1016/j.seppur.2015.09.015>.
- [6] Tomani, P. The LignoBoost Process. *Cellul. Chem. Technol.* **2010**, *44* (1–3), 53–58.
- [7] Mansouri, N.-E. El; Salvadó, J. Structural Characterization of Technical Lignins for the Production of Adhesives: Application to Lignosulfonate, Kraft, Soda-Anthraquinone, Organosolv and Ethanol Process Lignins. *Ind. Crops Prod.* **2006**, *24* (1), 8–16. <https://doi.org/http://dx.doi.org/10.1016/j.indcrop.2005.10.002>.
- [8] Aiti, M. Al; Jehnichen, D.; Fischer, D.; Brüning, H.; Heinrich, G. On the Morphology and Structure Formation of Carbon Fibers from Polymer Precursor Systems. *Prog. Mater. Sci.* **2018**, *98*, 477–551. <https://doi.org/https://doi.org/10.1016/j.pmatsci.2018.07.004>.