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Carbon Fibers Based on Cellulose–Lignin Hybrid Filaments: Role of Dehydration Catalyst, Temperature, and Tension during Continuous Stabilization and Carbonization

Christoph Unterweger [1,*], Inge Schlapp-Hackl [2], Christian Fürst [1], Daria Robertson [2], MiJung Cho [2] and Michael Hummel [2,*]

1   Wood K Plus—Kompetenzzentrum Holz GmbH, Altenberger Strasse 69, 4040 Linz, Austria; c.fuerst@wood-kplus.at
2   Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, 00076 Aalto, Finland; inge.schlapp-hackl@aalto.fi (I.S.-H.); daria.robertson@aalto.fi (D.R.); mijung.cho@aalto.fi (M.C.)
*   Correspondence: c.unterweger@wood-kplus.at (C.U.); michael.hummel@aalto.fi (M.H.); Tel.: +43-732-2468-6758 (C.U.); +358-505-12-4198 (M.H.)

Abstract: Lignocellulose has served as precursor material for carbon fibers (CFs) before fossil-based polymers were discovered as superior feedstock. To date, CFs made from polyacrylonitrile have dominated the market. In search of low-cost carbon fibers for applications with medium strength requirements, cellulose and lignin, either as individual macromolecule or in combination, have re-gained interest as renewable raw material. In this study, cellulose with 30 wt% lignin was dry-jet wet-spun into a precursor filament for bio-based carbon fibers. The stabilization and carbonization conditions were first tested offline, using stationary ovens. Diammonium sulfate (DAS) and diammonium hydrogen phosphate were tested as catalysts to enhance the stabilization process. Stabilization is critical as the filaments' strength properties drop in this phase before they rise again at higher temperatures. DAS was identified as a better option and used for subsequent trials on a continuous carbonization line. Carbon fibers with ca. 700 MPa tensile strength and 60–70 GPa tensile modulus were obtained at 1500 °C. Upon further carbonization at 1950 °C, moduli of >100 GPa were achieved.

Keywords: bio-based carbon fibers; cellulose–lignin filaments; carbonization catalyst

1. Introduction

The ubiquitous use of fossil resources during the past decades had a massive impact on the global ecosystem. The dependence on petrochemical products must be reduced quickly and drastically to halt and partially revert their broad negative effect on the environment. Ambitious goals to reduce the use of oil-based products and lower CO_2 emissions have been set by political decision bodies. Amongst others, this affects the transportation and mobility sectors. Lightweight, fuel-efficient vehicles are needed, not only because of sustainability aspects but also in the light of unpredictably volatile energy prices. The outstanding weight-to-strength ratio of carbon fibers (CFs) allows for the production of high-performance lightweight composite materials to reduce weight and energy consumption. Although predominantly produced from fossil-based polyacrylonitrile (PAN), the development of bio-based CFs is experiencing a renaissance. Motivated by the prevailing high costs of high-quality PAN precursor fibers and the need to shift to renewable resources, activities in the field of cellulose and lignin-derived CFs have surged during the past few years. It should be noted that, as of now, it seems unlikely that bio-based carbon fibers will reach the properties offered by standard PAN-based CFs such as the T300 series, with a tensile strength and modulus of 3–4 GPa and 200–300 GPa, respectively. However, CFs from

renewable resources reaching a tenacity of 1.7 GPa and modulus of 170 GPa would have potential to be implemented into mainstream cars [1].

Natural cellulosic fibers had been recognized as CF precursors already at the end of the 19th century, when Swan and Edison were developing incandescent filaments for their light bulbs [2,3]. CFs derived from natural fibers, however, are by nature discontinuous, have an irregular cross section, and moderate mechanical properties. The viscose process offered the first continuous cellulose filaments. Standard viscose fibers are not ideal CF precursors either. Intrinsic characteristics such as an irregular cross section, a low degree of polymerization (DP), and low polymer orientation in the cellulose matrix limit the uniformity and mechanical properties of the resulting CFs [4]. The structural and macromolecular properties of the precursor fibers govern the structure and properties of the CFs [5–7]. Therefore, viscose-derived CFs showed moderate mechanical properties, although it is possible to reach tensile strengths of 1–4 GPa and moduli of 170–690 GPa when graphitized at 2500 °C (Thornel series) [8,9]. These shortcomings are overcome in Lyocell-type fibers. They are spun from a direct cellulose solvent (*N*-methylmorpholine *N*-oxide monohydrate is commercialized; ionic liquids are currently developed by several companies) using a dry-jet wet-spinning set-up. Filament stretching in the air gap induces high polymer orientation, and instant coagulation in the aqueous spin bath leads to a circular cross section with only minor skin–core inhomogeneities [10]. These features are distinct advantages for subsequent carbonization. Yet, the biggest limitation displayed by all cellulose fibers is the low inherent carbon content of 44.4%. During the carbonization process, various volatile carbonaceous compounds are formed, lowering the actual carbon yield even further, sometimes down to 10% [7,11]. Slow heating rates have been recognized as means to increase the char yield since the early days of cellulose-based carbon research. However, they reduce the economic efficiency of a continuous carbonization process significantly [12]. Recently, stabilization of the cellulosic precursor filament under reduced pressure was suggested as an alternative pretreatment strategy [13]. Dehydration and cross-linking reactions can be accelerated by the introduction of catalysts. Essentially, these catalysts are substances known as flame retardants as they suppress the formation of gaseous flammable species such as levoglucosan [14,15]. Common substances are sulfuric and phosphorous acids and salts thereof. Very recently, Jang et al. showed how sulfuric acid can promote the dehydration of cellulose and formation of 5-hydroxymethyl furfural during the carbonization of Lyocell filaments to increase the char yield [16]. Also, ionic liquid (IL) residuals can improve the carbon yield upon pyrolysis [17]. Although this could be attractive when aiming for precursor filaments spun from IL-solution, a thorough analysis of the costs of sacrificed IL is needed before this can be considered as a true asset in the process.

Lignin, as the most abundant aromatic biopolymer on Earth and with a higher inherent carbon content ($\geq$60%), attracted interest as CF-precursor material already in the 1960s. Its thermoplastic character offers the possibility to produce continuous filaments through simple melt extrusion [18]. However, lignin is an ill-defined substance class. The macromolecular structure varies for different wood species and can undergo substantial changes during its isolation depending on the pulping process [19,20]. The diversity of lignin is a major challenge as not every lignin type is equally suited for melt shaping. Low-molar-mass lignin does not depict visco-elastic properties suitable for spinning and, hence, cannot be processed into continuous filaments. By contrast, if the MW is too high, the lignin is no longer fusible but rather starts decomposing under heating. Other polymers might be needed to act as a plasticizer [21–24] or the glass transition temperature (T_g) is changed through chemical derivatization [25]. Further, when exposed to elevated temperatures typically required for spinning, lignin can undergo degradation and/or polymerization, altering the visco-elastic properties over time. Melt-spun filaments tend to re-melt again during the pyrolysis process, which leads to the fusion of single precursor fibers upon carbonization. Thus, a costly thermo-stabilization step in air below T_g of the respective lignin (-derivative) prior to the actual carbonization and graphitization is needed to induce

cross-linking reactions and increase T_g [26]. Carbon fibers derived from lignin with tensile strength > 1 GPa and moduli around 100 GPa have been reported [27,28]. However, to arrive at such high values, the lignin substrates require pretreatment such as fractionation or chemical modification and, upon carbonization, the aforementioned slow heating rates. This makes continuous processing virtually impossible and compromises the economic feasibility of commercially viable upscaling notably.

Another challenge is the low orientation of melt-spun lignin filaments resulting from the limited stretchability during the spinning process. Analogous to the draw of filaments in cellulose spinning, the elongational deformation increases the orientation of the respective polymer in the resulting precursor fiber, which facilitates intermolecular cross-linking reactions during pyrolysis [7]. In routine CF production, the precursor filament tow is stretched in the oxidation and carbonization zones to amplify the pre-orientation of the precursor molecules and create highly ordered graphite crystallites in the final CFs.

It was suggested to overcome the limitations of pure cellulose and lignin precursor by blending them into mixed polymer filaments. This is possible through ILs, which can dissolve lignocellulose without prior chemical modification [29–31]. Imidazolium-, amidine-, and guanidine-based ILs were reported as suitable for fiber spinning [32]. Upon dissolution of the lignocellulosic substrate, they provide solutions with visco-elastic properties suitable for wet or dry-jet wet-spinning [33]. The resulting fibers were then converted into bio-based CFs [34,35]. Bengtsson et al. have used 1-ethyl-3-methyl imidazolium acetate to dissolve pulp cellulose and lignin and spin them into precursor fibers [36–38]. They then studied the effect of different heating rates during thermostabilization on the properties of the final CFs [39]. Trogen et al. and Duc et al. used cellulose–lignin filaments spun from 1,5-diazabicyclo[4.3.0]non-5-ene-1-ium acetate ([DBNH]OAc) and converted them to CFs using a continuous pilot carbonization line [40,41]. Catalysts such as phosphates and borates could increase the char yield also in the case of cellulose–lignin precursor fibers [42]. Notably, lignin with a high molar mass performed better in such studies because it was retained to a higher extent in the precursor fiber upon dry-jet wet-spinning. When using lignin with a high fraction of low-molar-mass constituents, a considerable share of it does not coagulate in the fiber and is lost in the spin bath [40]. This material loss affects the fiber yield and can complicate the recovery and purification of the spinning solvent.

In the study at hand, we compare the effects of diammonium hydrogen phosphate (DAHP) and diammonium sulfate (DAS) on the stabilization of a cellulose–lignin mixed polymer filament at three different temperatures (210, 230, and 250 °C). Subsequently, the found optimum parameters were tested in continuous stabilization, followed by continuous two-step carbonization including a variation of fiber tension.

2. Materials and Methods

2.1. Materials

Pre-hydrolyzed kraft (PHK) birch pulp from Stora Enso Enocell mill (Joensuu, Finland) with an intrinsic viscosity of 494 mL/g and Organosolv (ethanol/H_2SO_4) beech lignin received from the Lignocellulosic Biorefinery Pilot Plant, Fraunhofer CBP (Leuna, Germany) were used. The pulp sheets were ground to a fine powder using a Wiley mill, while lignin was used as received. For the preparation of IL, acetic acid (glacial, 100%, Merck, Darmstadt, Germany) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (Fluorochem, Hadfield, UK) were used as received. In the spin bath, tap water regulated at 9 ± 2 °C was used.

For impregnation of the precursor fibers before stabilization, aqueous solutions of diammonium sulfate (DAS) (99.5%, Merck, Germany) and diammonium hydrogen phosphate (DAHP) (>97%, Carl Roth, Karlsruhe, Germany) were used. The as-received chemicals were dissolved in deionized water under stirring at room temperature for at least 10 min before use.

2.2. Preparation of Cellulose–Lignin Precursor Filaments

The Ioncell® process as described by Trogen et al. in detail [40] was used for preparation of the IL and the dope as well as the fiber spinning. In short, pulp cellulose and lignin were dissolved in [DBNH]OAc using a vertical kneader (80 °C, 90 min, 15 wt% total polymer concentration). The dope (dissolved cellulose–lignin mixture) was filtered using a filter press (pore size 5 μm) and subsequently dry-jet wet-spun by means of a piston-spinning unit (Fourné Polymertechnik, Alfter, Germany). An air gap of 1 cm and a spinneret with a capillary diameter of 100 μm, an L/D of 0.02, and 400 holes was used. The temperature and the extrusion rate in the spinning process were 71 ± 5 °C and 5.5 mL/min, respectively. The spun fibers were washed with tap water using a 10 ± 0.25 min retention time at 68 ± 3 °C for washing and a drying temperature of 80 °C. The prepared filament of 70 wt% cellulose and 30 wt% lignin had a titer of 1000 dtex in conditioned state and consisted of 400 single fibers with a diameter of 15 μm.

2.3. Preliminary Stabilization Trials

For impregnation, the tow was continuously dipped into aqueous solutions of DAHP, DAS, or water. Concentrations of 3.25 wt% DAHP and 6.50 wt% DAS were chosen based on previous trials with viscose filaments and should give loadings around 1 wt% P or 2 wt% S. Higher loadings are not expected to result in significant further increase of the carbon yield [43]. The transport speed was 0.061 m/min, resulting in a residence time in the impregnating solution of approximately 1 min. Samples of 15 cm length were cut from the filament after impregnation. The loading was immediately determined gravimetrically using Equation (1), where m is the mass of 15 cm of the tow after impregnation, m_0 is the mass before impregnation. M is the molar mass of P or S and M_{tot} the molar mass of DAHP or DAS. The concentrations (c) of the impregnation agents and rH is the moisture content of the tow before impregnation.

$$\text{Loading} = \frac{(m - m_0) \cdot c \cdot M}{m_0 \cdot (1 - rH) \cdot M_{tot}} \tag{1}$$

The actual loadings obtained in the current trials were 1.10 wt% P and 2.37 wt% S. The gravimetric method was validated by Sørensen formol titration, which was performed immediately after impregnation to avoid distortion of the results due to NH_3 evaporation.

The stabilization conditions were screened in a drying cabinet, pre-heated to the desired stabilization temperatures of 210, 230, or 250 °C. The horizontally placed straight samples were heat-treated in air for 40 min. Mass loss, shrinkage, and tensile properties of the stabilized fibers were determined. All samples were subsequently carbonized in a GERO HTK8 chamber furnace. The filament samples were again placed horizontally in straight sample holders without fixing the ends. The samples were heated in nitrogen atmosphere using the maximum heating rate of 10 °C/min up to 900 °C and held isothermal for 4 min. Again, mass loss, shrinkage, and, if possible, tensile properties of the carbonized fibers were determined.

2.4. Continuous Trials

Based on the results of the discontinuous trials, impregnation with 6.50 wt% DAS and stabilization at 250 °C were chosen for continuous trials. These conditions resulted in the smallest mass loss during the subsequent carbonization and the strongest CFs. The impregnation was performed as described above. Following the impregnation bath, the filament was continuously transported through an FRHT-5-100/2500/300 tube furnace (Linn High Therm, Hirschbach, Germany). All 5 heating zones were set to 250 °C, and an air atmosphere was used. The godet speeds were set to 0.061 m/min before the tube furnace and 0.063 m/min after the furnace, resulting in stretching of 3.2% and a total residence time at 250 °C of 40 min. A stable continuous process could be achieved without any difficulties and kept running for 24 h.

Subsequent low-temperature (LT) carbonization was performed in an FRHT-5-100/ 2500/1050 tube furnace (Linn High Therm, Hirschbach, Germany). The following temperature profile in the 5 heating zones was used: 300–340–380–570–900 °C. The speed of the godet duo after the furnace was set to 0.063 m/min, thus resulting in a residence time of approximately 8 min per zone and 40 min in total. The godet speed before the furnace was varied between 0.063 and 0.065 m/min to achieve a process with no change in length or shrinkage of 3.2%. The applied forces corresponded to 70 and 53 g, respectively. High-temperature carbonization (HT) was performed in an FRH-2-50/1000/1700 tube furnace (Linn High Therm, Hirschbach, Germany). Both zones were set to 1500 °C, and the residence time was 2 min. The tension during this process was varied, applying forces corresponding to 18 or 32 g.

Finally, the already-HT-carbonized filaments were further heat-treated in a GERO HTK8 chamber furnace (Carbolite Gero, Neuhausen, Germany) at 1950 °C in argon atmosphere. The CF filament samples were placed horizontally in straight sample holders without fixing the ends.

2.5. Thermal, Structural, and Mechanical Characterization

For thermogravimetric analysis (TGA), a Netzsch STA 449 F3 Jupiter & QMS 403 Aëolos Quadro thermal analyzer (Netzsch Gerätebau, Selb, Germany) with He atmosphere was used. A heating rate of 10 °C/min from 40 °C to 800 °C was selected.

A Q20 AS (TA Instruments, New Castle, DE, USA) was used for differential scanning calorimetry (DSC). Next, 5–10 mg of sample material was placed in a Tzero pan with a pierced hermetic lid. The temperature program consisted of a drying step at 105 °C for 20 min followed by equilibrating at 40 °C and heating at 10 °C/min up to 250 °C.

Diffraction patterns of all samples have been measured by means of a Xenocs Xeuss 3.0 X-ray diffractometer operated in transmission mode at 50 kV and 0.6 mA (CuKα radiation, λ = 1.5406 Å) equipped with an Eiger2 R 1M (Dectris, Baden-Daettwil, Switzerland) detector (sample-to-detector distance: 56 mm). Bundles of fibers were positioned unidirectionally to a sample holder, vertically to the X-ray beam. For each sample, scattering profiles of three different positions were collected. The scattering profiles were corrected by a blank run. The sample profiles were analyzed by OriginPro 2021b (OriginLab, Northampton, MA, USA) and Fityk 1.3.1 software ((Marcin Wojdyr, Warsaw, Poland)) [44,45]. The crystallinity index, the d-spacing (Bragg equation), and the crystallite widths (Scherrer equation) using the shape factors of K = 0.90 and K = 1.84 for (002) and (10) bands were calculated according to that described earlier [46,47].

The carbon, hydrogen, and nitrogen amount was determined by means of a FlashSmart elemental analyzer CHNS/O with MV (Thermo Scientific, Waltham, MA, USA). BBOT (2,5-Bis(5-tert-butyl-2-benzo-oxazol-2-yl)thiophene; CAS: 7128-64-5; M = 430.57 g/mol; $C_{26}H_{26}N_2O_2S$) purchased from Merck (N = 6.49%, C = 72.56%, H = 6.11) was used as calibration standard.

Single fibers were mounted into a paper frame with a slot of 25 mm. For CFs, 24 single-fiber specimens were prepared for each sample, while 12 were prepared for stabilized fibers. All single-fiber specimens were conditioned at 23 °C and 50% relative humidity before measurement. The fiber diameter was determined using an Olympus (Shinjuku, Japan) optical microscope for each single fiber prior to mechanical testing. Single-fiber tensile tests were performed according to ISO 11566 [48] using a Zwick BETA 20. A pre-load force of 5 mN and a test speed of 1 mm/min were used.

The cross sections of the carbon fibers were imaged with a Zeiss Sigma VP scanning electron microscope (Carl Zeiss, Jena, Germany) at an accelerating voltage of 1.00 kV after sputter coating with 80 Au/20 Pd.

3. Results

3.1. Preliminary Trials—Evaluation of Stabilization Conditions

The fibers used in this study contained 70% pulp cellulose and 30% organosolv lignin. Their preparation and properties were discussed in detail earlier [40]. Carbonization of cellulose with direct heating to the final pyrolysis temperature is known to suffer from extremely low yields. This is explained by the so-called two-pathway model, also known as the Broido–Shafizadeh model, postulated based on investigations made in the 1960s and 1970s [12,49–53]. The heating rate plays a decisive role, either favoring the formation of volatile low-molar-mass fractions, or increasing the char yield. In particular, the temperature range from 150 to 250 °C was identified as critical for the final product distribution. Thus, carbonization protocols usually include a stabilization step in which the cellulosic precursor is first heated to moderate temperatures before inducing carbonization at higher temperatures. The intermediate structure is often also referred to as thermostable condensed phase (TSCP) [54]. Table 1 shows the results of the preliminary stabilization trials. For the untreated and washed fibers, almost identical results were obtained. Only slight mass losses (related to the dry precursor) up to 10.6% at 250 °C were observed during stabilization. In the subsequent carbonization step, high mass losses around 80% occurred, thus resulting in total yields below 20%. Oxidative stabilization at 230 or 250 °C yielded only slight improvements compared to carbonization without pre-treatment. Stabilization at 210 °C seems to have no effect on the total yield. Catalysts like sulfates and phosphates are commonly used to increase the char yield [55–57]. With DAHP impregnation, significantly higher mass losses compared to the untreated samples could be observed, especially at 230 and 250 °C. With DAS impregnation, degradation starts at even lower temperatures, with almost 25 wt% mass loss at 210 °C and reaching a maximum value of 38 wt% for stabilization at 250 °C. A previous study by Spörl et al. comparing ammonium dihydrogenphosphate and ammonium tosylate as a stabilization agent for cellulose fibers also found lower degradation temperatures for the sulfonic stabilization agent [58]. In our study, the observed earlier degradation of the DAS-impregnated fibers was demonstrated by TGA-MS and DSC measurements (see Figure 1).
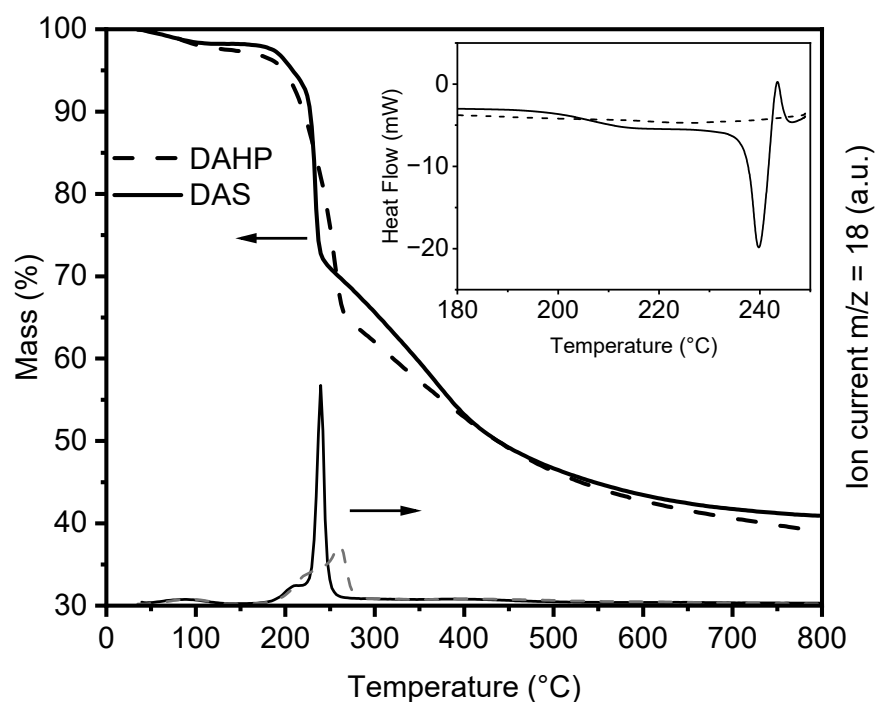

Figure 1. TGA-MS and DSC measurements of DAHP- and DAS-impregnated cellulose/lignin fibers. Arrows indicate the corresponding y-axis.

Table 1. Results of the pre-studies regarding impregnation agents and stabilization temperature: mass change during stabilization or carbonization, total yield and mechanical properties (tensile strength TS, tensile modulus TM and elongation at break EB including the 95% confidence interval) of stabilized and carbonized fibers.

Sample (Impr_$T_{stab.}$)	$\Delta m_{stab.}$ [g/g]	$\Delta m_{carb.}$ [g/g]	yield $_{tot.}$ [g/g]	TS $_{stab.}$ [MPa]	TM $_{stab.}$ [GPa]	EB $_{stab.}$ [m/m]	TS $_{carb.}$ [MPa]	TM $_{carb.}$ [GPa]	EB $_{carb.}$ [m/m]
H_2O_X *	X	−83.3%	16.7%	X	X	X	– **	–	–
H_2O_210	−8.2%	−81.6%	16.7%	312 ± 31	17.1 ± 0.7	7.4 ± 1.1%	–	–	–
H_2O_230	−7.6%	−79.3%	19.2%	294 ± 32	22.9 ± 0.9	4.4 ± 1.1%	323 ± 86	29.2 ± 4.9	1.0 ± 0.4%
H_2O_250	−10.6%	−79.3%	18.3%	272 ± 20	24.1 ± 1.4	3.2 ± 0.5%	–	–	–
DAHP_X	X	−61.2%	38.8%	X	X	X	–	–	–
DAHP_210	−10.8%	−57.9%	37.3%	153 ± 6	16.0 ± 0.8	1.9 ± 0.4%	459 ± 32	30.7 ± 1.6	1.4 ± 0.2%
DAHP_230	−16.6%	−52.1%	39.8%	199 ± 12	16.4 ± 0.9	2.8 ± 0.6%	540 ± 89	33.5 ± 2.1	1.6 ± 0.3%
DAHP_250	−28.1%	−47.0%	38.5%	135 ± 13	6.4 ± 1.1	6.8 ± 1.7%	533 ± 88	33.4 ± 2.0	2.2 ± 0.7%
DAS_X	X	−64.8%	35.2%	X	X	X	457 ± 114	32.6 ± 1.8	3.5 ± 1.3%
DAS_210	−24.7%	−54.8%	33.9%	77 ± 12	8.4 ± 0.3	0.7 ± 0.2%	501 ± 53	30.8 ± 1.5	1.5 ± 0.2%
DAS_230	−34.9%	−48.1%	34.0%	112 ± 4	4.3 ± 0.2	3.1 ± 0.4%	559 ± 80	31.6 ± 1.9	1.8 ± 0.3%
DAS_250	−38.2%	−39.4%	37.0%	122 ± 10	4.2 ± 0.3	5.7 ± 1.3%	593 ± 83	32.0 ± 2.1	1.8 ± 0.2%

* "X" indicates that no stabilization was performed. Thus, no mass change for stabilization and mechanical data for stabilized fibers are available. ** "–" mechanical testing not possible due to low stability.

In TGA measurements, faster degradation of the DAS-impregnated sample could be observed with a stronger MS signal correlated to more pronounced dehydration reactions. Additional DSC measurements up to 250 °C corroborate these findings. The DAS-impregnated sample showed a strong endothermic peak could, while no detectable reactions in the analyzed temperature range seem to occur in the DAHP-impregnated sample.

For the impregnated fibers, significantly reduced mass losses were observed in the subsequent carbonization process, with all samples achieving yields in the range of 33.9–39.8%. Similar yield improvements have been observed for various types of cellulose and cellulose/lignin fibers before [39,58–60].

Regarding the mechanical properties, some correlation with the mass loss can be found for the stabilized fibers, with non-impregnated samples being superior to DAHP- and finally DAS-impregnated ones corresponding to increasing mass loss. For the non-impregnated samples, even an improved modulus compared to the precursor fibers (17.0 ± 1.3 GPa) could be observed, while all stabilized fibers showed decreased tensile strength and elongation at break values compared to the precursor (412 ± 26 MPa, 11.5 ± 0.8%). Interestingly, increasing elongation at higher stabilization temperature was observed for the impregnated samples. This is in line with the recent observation showing pronounced cellulose chain cleavage through the formation of levoglucosan moieties at the reducing end [54]. As a result, the tensile strength decreases and elongation at break increases. Concomitantly, cross-linking reactions take place in the temperature range of 200–250 °C, resulting in a thermostabilized condensed phase, which gradually leads to an increase in tensile strength and modulus [61]. Similar to previous studies, the carbonized fibers were very brittle in the case of the non-impregnated fibers, with only one sample allowing preparation of specimens for single-fiber testing [58]. The impregnated samples yielded better CFs with no significant differences regarding mechanical properties, except for the non-stabilized DAHP-impregnated sample, which showed extremely brittle behavior similar to the non-impregnated samples. It should be noted that the mechanical performance of all prepared CFs is generally poor due to the lack of tension related to the discontinuous processes used in this preliminary evaluation of stabilization conditions. Based on the obtained results, impregnation with DAS and stabilization at 250 °C was chosen for continuous trials. This was motivated by the observed lowest mass loss during carbonization, which contributes significantly to the stability of a continuous process. In addition, the highest average tensile strength (even though not statistically significant) and very good total yield of 32% after carbonization at 900 °C could be obtained. The choice of DAS instead of DAHP is further supported by previous studies reporting defects

in the carbon structures due to the incorporation of phosphor [62], an effect that is not expected from S-based stabilization aids as a high carbon content is already obtained at lower temperatures [58].

3.2. Continuous Preparation of Carbon Fibers

The cellulose–lignin precursor filaments were successfully impregnated with DAS and converted to carbon fibers using continuous thermal processing. Stabilization could be performed under high tension, thus resulting in 3.2% elongation of the filaments upon this first thermal processing step. The first LT carbonization was performed under mild conditions allowing a shrinkage of the filament of 3.2%, but an additional trial under higher load preventing shrinkage of the filament was possible, too. Both processes were stable and produced filaments in sufficient amount and mechanical performance enabling subsequent continuous HT carbonizations under varying tensions. Fibers were sampled after each stage and analyzed in terms of their mechanical and morphological properties (see Table 2).

Table 2. Development of the mechanical and structural properties of carbon fibers throughout the different stages in the continuous carbonization process. Single-fiber mechanical properties (tensile strength, tensile modulus, and elongation at break), single-fiber diameter D, morphological properties (crystallinity index CI, crystallite size Lc (002), and interlayer distance d (002) by XRD). The given deviations represent 95% confidence intervals.

Sample	Last Process	Description	TS [MPa]	TM [GPa]	EB [m/m]	D [μm]	CI [−]	Lc (002) [Å]	d (002) [Å]
Precursor	-	No processing	412 ± 26	17.0 ± 1.3	11.5 ± 0.8%	14.8 ± 0.4			
DAS_250	Stab.	3.2% strain	150 ± 9	4.6 ± 0.4	7.8 ± 1.9%	12.4 ± 0.5	58.06 ± 0.29	5.84 ± 0.30	4.64 ± 0.06
DAS_250_lt	LT	3.2% shrinkage	801 ± 59	44.8 ± 1.3	1.8 ± 0.2%	9.4 ± 0.2	25.64 ± 0.39	9.52 ± 0.70	3.92 ± 0.04
DAS_250_lt_ht	HT	18 g @HT	660 ± 52	59.2 ± 1.7	1.1 ± 0.1%	8.5 ± 0.2	43.43 ± 0.24	10.06 ± 0.11	3.83 ± 0.00
DAS_250_lt_HT	HT	32 g @HT	695 ± 84	60.5 ± 3.2	1.1 ± 0.1%	8.8 ± 0.2	42.79 ± 0.55	9.61 ± 0.12	3.85 ± 0.00
DAS_250_lt_ht_1950	1950 °C	no tension	430 ± 72	83.9 ± 5.4	0.6 ± 0.1%	8.5 ± 0.3	87.64 ± 0.12	26.08 ± 0.60	3.45 ± 0.00
DAS_250_lt_HT_1950	1950 °C	no tension	558 ± 87	86.9 ± 6.7	0.7 ± 0.1%	8.4 ± 0.3	88.76 ± 0.30	28.60 ± 0.34	3.45 ± 0.00
DAS_250 *	Stab.	3.2% strain	152 ± 6	4.5 ± 0.3	12.5 ± 4.1%	12.5 ± 0.5	57.76 ± 0.46	5.74 ± 0.11	4.68 ± 0.01
DAS_250_LT	LT	0% shrinkage	834 ± 122	55.6 ± 1.7	1.5 ± 0.2%	8.8 ± 0.2	25.58 ± 0.41	9.31 ± 0.53	3.93 ± 0.00
DAS_250_LT_ht	HT	18 g @HT	703 ± 81	67.7 ± 2.8	1.0 ± 0.1%	8.2 ± 0.3	44.91 ± 0.21	9.79 ± 0.11	3.79 ± 0.01
DAS_250_LT_HT	HT	32 g @HT	722 ± 75	66.5 ± 2.9	1.0 ± 0.1%	8.3 ± 0.3	46.17 ± 0.53	9.74 ± 0.31	3.78 ± 0.01
DAS_250_LT_ht_1950	1950 °C	no tension	493 ± 68	99.5 ± 6.8	0.6 ± 0.1%	8.1 ± 0.2	89.50 ± 0.60	31.57 ± 0.32	3.47 ± 0.00
DAS_250_LT_HT_1950	1950 °C	no tension	611 ± 84	113.6 ± 9.2	0.6 ± 0.1%	7.7 ± 0.2	89.24 ± 0.22	28.99 ± 0.17	3.45 ± 0.00

* The stabilization was repeated under identical conditions. All samples mentioned below were prepared from this repeated sample.

In comparison to the preliminary trials in batch mode, higher yields were obtained in the continuous trials. The mass loss during stabilization was just 29.4%, while after LT carbonization, yields of 39.6–40.8% were obtained. The total yield after HT carbonization at 1500 °C was in the range of 35.7–36.4%.

3.2.1. Effect of Temperature

During continuous carbonization, the filaments underwent several stages of heat treatment after being impregnated with DAS. First, the filaments were stabilized at 250 °C under tension, which resulted in an elongation of 3.2%. In this heat regime, dehydration is initiated, and the carbon content of the stabilized fibers rises to 58–60%. The mass loss is most pronounced during this step, visible through the significant reduction of the filament diameter (Figure 2) from 14.8 to 12.5 μm. As mentioned earlier in the discussion of the stationary carbonization trials, the cellulose chains also undergo fragmentation, which reduces the mechanical properties drastically. This is in line with earlier observations for pure cellulose precursor filaments [7] and lignin–cellulose mixed matrix filaments [35,41]. Upon further heating in the LT furnace, cross-linking reactions are promoted, leading first to the TSCP from which a predominantly carbonaceous matrix evolves. The carbon content of the filaments after LT treatment is around 86–88% and rises further to 95%

and higher after passing the HT furnace. XRD analyses showed that the carbon matrix gradually assumes a higher-order configuration as the filaments pass through the various zones. The overall crystallinity increases, and the d-spacing of the (002) peak decreases slowly (Figure 3 and Table 2). This is directly reflected in the mechanical properties of the fibers. Both tensile strength and modulus increase instantly after LT treatment, and the elongation at break reduces. The tensile properties are slightly higher than those reported earlier by Bengtsson et al. [62]. Starting from a wet-spun precursor fiber with a lignin content of 50%, they reported properties of <800 MPa and <50 GPa for tensile strength and modulus, respectively, and significantly lower yields of 29–30% after carbonization at 1000 °C. However, they used a slightly smaller furnace and did not impregnate their fibers. A longer furnace and the use of DAS as catalyst in the stabilization phase both would have likely also increased the yield and the mechanical properties of their fibers. Further heating in the HT furnace does not improve the tensile strength but does lead to higher moduli, which again is in line with the evolution of macromolecular structure, as observed through XRD.
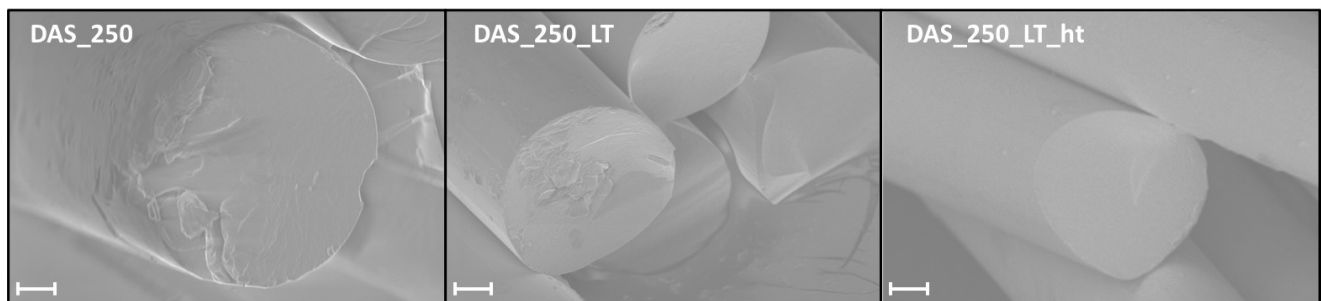

Figure 2. SEM images of the cellulose–lignin fiber impregnated with diammonium sulfate and: stabilized at 250 °C (**left**); stabilized and heat-treated under tension in the low-temperature furnace at 900 °C (**middle**); stabilized, heat-treated under tension in the low-temperature furnace at 900 °C and subsequent heat treatment under low tension in the high-temperature furnace at 1500 °C (**right**). Scale bars represent 2 μm.
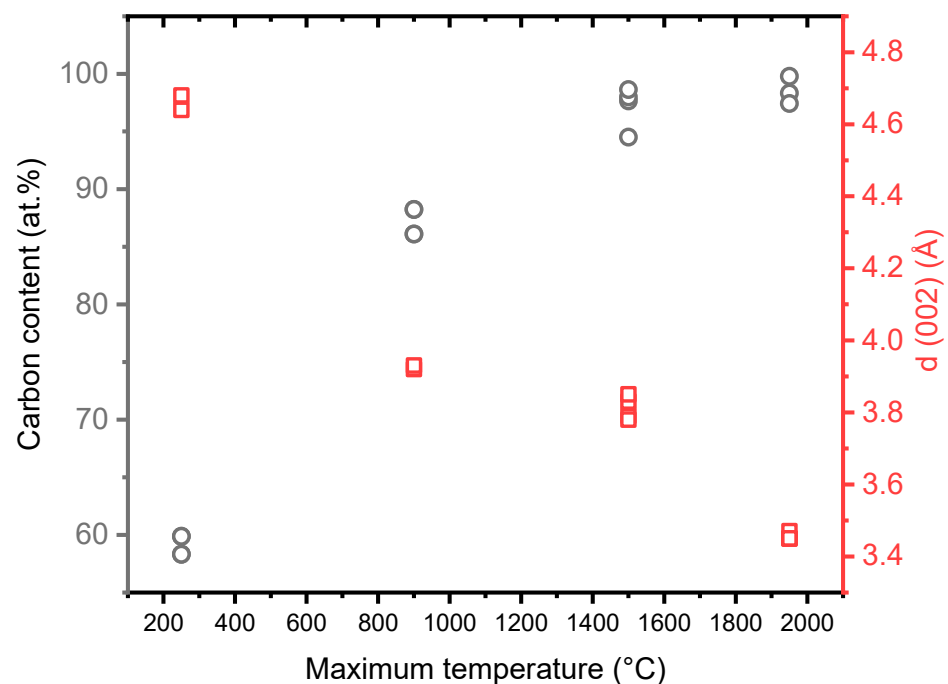

Figure 3. Carbon content and d-spacing distances of fibers treated at different maximum processing temperature. Black circles represent carbon content and red squares represent d-spacing data.

Ultimately, we investigated the effect of an even higher heat treatment at 1950 °C. Due to equipment limitations, this step was performed offline and without applying any tension in a chamber furnace. The carbon matrix develops a significantly higher order as seen by the crystallinity index, crystallite dimensions, and d-spacing distances. The carbon content increases to 98% and higher. Due to the lack of tension, the tensile strength drops slightly, but the modulus increases dramatically. In the case of DAS_250_LT_HT_1950 (DAS-impregnated filament, stabilized at 250 °C, no shrinkage allowed in the LT furnace, 32 g load in the HT furnace, and tension-free treatment at 1950 °C), the filaments' modulus surpassed 100 GPa, reaching up to 113.6 (±9.2) GPa.

3.2.2. Effect of Tension during Carbonization

The development of the properties depends greatly on the tension that is applied during carbonization. Cellulose fibers carbonized tension-free or under minimum tension show a longitudinal contraction. In our study, the fibers shrunk by 3.2% in the LT furnace when only the minimum tension needed for continuous processing was applied. Preventing shrinkage and preserving the original length of the stabilized fibers was also possible when applying higher load in continuous LT carbonization. This had no statistically significant effect on the tensile strength but did increase the modulus of the fibers (Figure 4 and Table 2). In addition, the fiber diameter was significantly reduced at higher tension. When passing the HT furnace, the filament tow was kept at two different loads, 18 and 32 g, respectively. These different loads did not result in statistically different properties. However, in both cases the resulting filaments that were kept at 0% shrinkage in the LT furnace retained their significantly higher tensile moduli even at the improved values after the HT treatment. Despite significant differences in the mechanical properties, no changes in the morphological properties related to the applied tension could be observed by XRD analysis. Just some single values (e.g., when comparing the d-spacing distances after the HT process) indicate a higher order, but overall, the morphological properties are predominately determined by the maximum temperature rather than the applied tension.
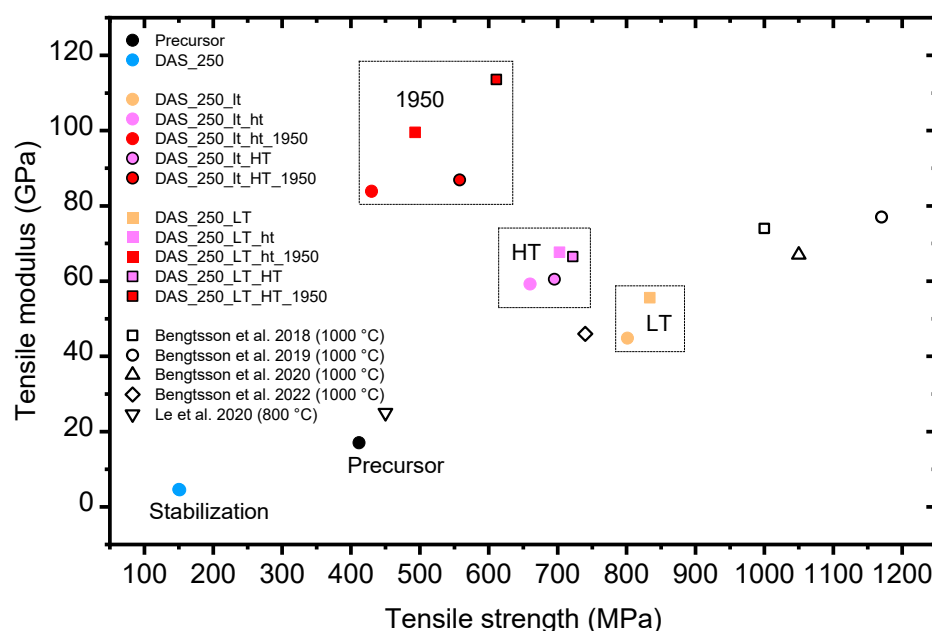

Figure 4. Tensile strength and modulus in relation to processing conditions (light orange symbols: treated at 900 °C; pink symbols: treated at 1500 °C; red symbols: treated at 1950 °C; filled symbols with black edge represent fibers that have undergone tension); open symbols are values of CFs from cellulose–lignin precursors published earlier [39,41,62–64]; only in the work from Bengtsson et al., 2022 [62], continuous processing has been used.

4. Conclusions

Carbon fibers could be continuously prepared from cellulose/lignin precursor filaments. The main findings are summarized below.

- Pretreatment with dehydration catalysts DAS or DAHP allows doubling of the yield compared to carbonization of neat cellulose/lignin precursor filaments.
- Impregnation with a DAS solution and thermal treatment at 250 °C were found as optimum stabilization conditions. DAS leads to higher mass loss during stabilization and a more stable LT carbonization process compared to DAHP as dehydration catalyst.
- With increasing processing temperature, improved modulus values were obtained, accompanied by decreasing fiber diameters and d-spacing of the (002) peak.
- Subsequent heating to 1950 °C without tension leads to huge improvements of the tensile modulus with slight reductions in the tensile strength.
- Tension during LT carbonization had a clear impact. Higher tension led to a significantly higher tensile modulus and smaller fiber diameters.

The applied tension during the HT process had no visible impact on the fiber properties. Overall, the prepared carbon fibers from cellulose/lignin precursor filaments offer a very interesting property profile. The obtained tensile properties after LT carbonization are already superior compared to a previous study [62] and can be improved by further treatment at higher temperatures, which has not been reported before for a cellulose/lignin precursor. The achieved modulus values >100 GPa are especially promising. Continuous processing at temperatures above 2000 °C should allow for further improvements, while also avoiding the observed reduction in the tensile strength. The obtained yields of approximately 35% at 1950 °C are among the highest reported for bio-based carbon fibers. A further increase should be achievable by higher lignin contents in the precursor, even though limitations regarding spinnability and fiber properties must be considered. Ideally, a lignocellulosic substrate that contains the original lignin (e.g., unbleached kraft pulp) should be used to reduce the costs and environmental impact of the starting material. Based on the good mechanical properties and the high yields achieved in this study, cellulose/lignin precursor filaments can be considered a very promising candidate for preparation of low-cost carbon fibers.

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