Development of lignin carbon fibers: Evaluation of the carbonization process

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ABSTRACT: The use of lignin as a renewable resource for the production of less-expensive carbon fibers has in recent years attracted great interest. In order to develop the strength properties, the stabilization and carbonization processes have to be optimized. For this reason, the process parameters during carbonization have here been studied on stabilized lignin fibers in the temperature interval from 300 to 1300 °C. The effects of temperature, heating rate, and straining of fibers during carbonization on the strength properties of carbon fibers were investigated. The heating rate, in the range from 1 to 40 °C/min, was shown to have no effect on the property development of the fibers. During carbonization with no load applied to the fibers, a shrinkage of 20% was noted. Counteracting the shrinkage by imposing a load on the fibers during the carbonization resulted in fibers with a greater stiffness. The tensile strength was not, however, affected by this loading. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43965.

INTRODUCTION

In order to reduce fuel emissions, there is an increasing interest in the transportation sector for replacing heavy metal parts with lighter carbon-fiber-reinforced structures. However, the costs of carbon fibers are currently too high, making their use only acceptable in highly specialized items. To replace the fossil-derived resources used for carbon fiber production, such as polyacrylonitrile (PAN), pitch, and mesophase pitch, lignin has been considered as an attractive, cheaper alternative raw material.[1,2] Lignin is second to cellulose the in the world, and it is derived as a byproduct in chemical pulp production from forest resources. The potential amount of lignin available from today's production facilities may easily cover the foreseeable market needs for carbon fibers in the near future. Lignin fibers may also be melt-spun, which is a simpler fiber-producing process than the wet- or dry-spinning processes (used for example for PAN) that require dissolution of the polymer. Thus, substantial efforts have been made in recent years to develop lignin-derived carbon fibers.[2–9] Much of the research has been focused on melt-spinning of lignin fibers and how to obtain the most suitable lignin material. The spinnability and thermal behavior of the lignins have been shown to depend on both the source of the lignin and the method used to isolate it.[10,11] In general, hardwood lignins have been rather easy to melt-spin, whereas only recently have kraft softwood lignin fibers been produced without the aid of plasticizers.[2,5,7,12] Kraft lignins are generally rather heterogeneous with regard to their molecular weight distribution, so fractionation of the lignin is advantageous in order to improve spinnability.[4,7,13] For lignin fibers to be carbonized, it is necessary to thermostabilize them to prevent fusion, a process that crosslinks the lignin and increases its glass-transition temperature (T_g).[3,5,14] The lignin structure, which depends on the source of origin and on the extraction process, also has a significant influence on the processing time necessary for this oxidative stabilization process.[2,15] The carbonization processes for converting the stabilized lignin fibers into carbon fibers, that is, the processes for the development of fiber strength properties, have been based mainly on experience of the conversion of the fossil-based precursor to carbon fibers.[16] During the carbonization process, dehydration, decarboxylation, crosslinking, and aromatization reactions take place, and most of the noncarbon elements are released.[17] Since the lignin precursor fibers have a chemical structure very different from that of the traditionally used fossil-based precursors, such as PAN or pitch, process parameters different from those used for these traditional materials should most likely be required. It has been claimed that heating rates affect the properties.[3] However, the manner in which the processing parameters during carbonization affect the carbon structure of lignin-derived fibers is unclear. So far, the lignin fibers produced and converted to carbon fibers have not been able to match conventional carbon fibers in terms of strength properties.[2]

In this study, the process step of carbonization of already stabilized lignin fibers has been investigated at carbonization temperatures from 300 to 1300 °C. The effects of heating rate, final carbonization temperature, and the load applied during carbonization have been studied and related to the strength properties of the carbon fibers.

EXPERIMENTAL

Materials

The lignin material used was derived using the LignoBoost process.[18] In order to improve the melt-spinning operation, a pH-fractionated softwood kraft lignin was taken out between pH 11 and 9.5. The lignin had a molecular weight M_w (weight-average molecular weight) of 51 kDa, a M_n (number-average molecular weight) of 11 kDa, a polydispersity M_w/M_n of 4.6, and a T_g of 140 °C. Prior to extrusion, the lignin had been dried in vacuum at 80 °C for 24 h followed by 2 h at 160 °C and finally dried in N_2 at 180 °C for 1.5 h in order to remove volatile compounds that would otherwise result in uneven fibers during melt-spinning. Melt-spinning was performed at 220 to 230 °C in a multifilament extruder (Alex James & Associates, Greenville, South Caroline). Lignin fibers with a diameter of about 50 μm were retrieved. These lignin precursor fibers are much greater in diameter than typical commercial precursor fibers based on PAN or pitch of around 10 μm, but they are typical of melt-spun kraft lignin fibers.[5] Although work is ongoing to develop techniques giving smaller fiber diameters, the larger fibers were chosen here for easier handling.

Before carbonization, the melt-extruded lignin fibers were oxidatively thermostabilized. For this purpose, bundles of fibers were mounted between two clamps in a conventional gas chromatograph (GC) oven (Hewlett-Packard 5890 Series II, Palo Alto, CA) in air. The temperature was raised from 25 °C to 140 °C at 3 °C/min and then at 0.2 °C/min up to 250 °C, followed by an isothermal treatment for 60 min. This temperature profile has been well established as suitable for the stabilization of softwood kraft lignin fibers.[3,12,15]

Methods

In order to monitor the weight loss during carbonization, a thermogravimetric analyzer (TGA Q5000, TA Instruments, New Castle, Delaware) was used. Stabilized lignin fibers, 2 mg, were heated in nitrogen at 10 °C/min from 20 to 1100 °C while the weight was monitored. Prior to the measurements, the sample was purged with excess nitrogen for 20 min to remove all air.

Carbonization studies were carried out using a thermomechanical analyzer (TMA 402F1, Netzsch, Selb, Germany). Bundles of fibers, between 30 and 50, were glued together at both ends by applying a carbon paint suspension (SPI Supplies, West Chester, Pennsylvania) and then mounted in aluminum oxide clamps in the TMA. In this case, a small negligible load of 5 mN was applied in order to keep the bundle straight.

When larger loads were applied to the fibers during carbonization, the fibers had to be more securely mounted to avoid slip-out. A set of 5 to 10 fibers was in these cases bonded to graphite plates using a graphite bonding agent (Graphi-Bond 551-RN, Aremco Products , Cradley Heath, UK), which was cured at an elevated temperature. In these studies, an initial load of 10 mN
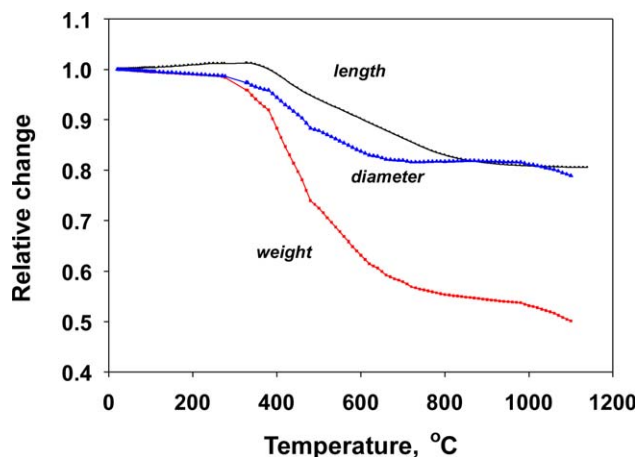
Figure 1. Relative change in weight (recorded by TGA) and length (recorded by TMA) and the calculated diameter of stabilized lignin fibers as a function of temperature. The temperature was increased at a rate of 10 °C/min. The diameter values are calculated from the weight and length changes assuming a constant fiber density and circular cross section of the fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was applied, and the load was further increased at specific temperature intervals.

Prior to carbonization, the TMA was evacuated to a pressure of approximately 4 mbar. The TMA was then filled with pure nitrogen to a slight overpressure before measurements were started under a nitrogen flow of 75 mL/min. During the measurements, both the applied load and the length of the specimen were monitored.

Tensile testing of fibers was carried out using an automated fiber tester (Dia-Stron Ltd., Andover, UK). Fibers were premounted with a gauge length of 12 mm, and the fiber diameter was automatically measured in the equipment using laser diffraction.[19] Thereafter the fiber was automatically moved to a tensile stage, and an initial load of 2 g was applied. The fiber was then stretched at a rate of 0.1 mm/s, equivalent to a strain rate of 0.833%/s.

The structure and composition of the fibers were monitored using scanning electron microscopy (SEM) (Quanta FEG 650, Hillsboro, Oregon) coupled with energy dispersive X-ray analysis (EDXA) and spectroscopy (EDS Oxford Instruments, Abingdon, UK). Carbonized fibers were attached to the sample holder using double-coated PELCO carbon tape (Ted Pella Inc., Redding, CA). Measurements were performed at a pressure of 1 mbar using an acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

Carbonization of thermally stabilized fibers is a process where mostly oxygen and hydrogen are removed in an inert atmosphere at temperatures of 1000 °C or above. The mass loss during carbonization of the stabilized lignin fibers is illustrated in Figure 1. Nearly 50% of the material was pyrolyzed, as was also previously noted in the case of lignin-derived fibers.[20] The mass loss started to be significant above 300 °C, and the highest rate of mass loss was at about 420 °C. At temperatures above 800 °C, the material loss was rather small, but it increased somewhat above 1000 °C.

Table I. Relative Atomic Composition of Stabilized Lignin Fibers Carbonized to Different Temperatures

Temperature (°C)	Carbon (atom %)	Oxygen (atom %)	Sulfur (atom %)	Temperature (°C)
20	74.8	24.8	0.4	20
300	76.0	23.6	0.4	300
500	84.3	15.3	0.4	500
1000	90.7	9.0	0.3	1000
1200	90.8	8.9	0.3	1200

Only atom numbers equal to or higher than that of sodium are detected by EDXA. Hydrogen atoms present in the original sample are thus not included in the relative atom % composition given.

This behavior is typical for lignin carbonization, where the fastest stage below 500 °C is due to pyrolysis, the second stage up to 900 °C to amorphous carbon formation, and the third stage above 900 °C to re-forming of the carbon structure.[21]

The chemical composition of the fibers (measured on the axial surface of the samples by EDXA) taken at different positions during the carbonization showed that the oxygen was mainly released in the temperature interval between 300 and 1000 °C (see Table I), where pyrolysis gave rise to CO_2 and CO, and the further formation of an amorphous structure at the higher temperatures released CO.[21,22] The sulfur present in small amounts in the stabilized fibers seemed to be difficult to remove at the temperatures used here. It should also be noted that the fibers carbonized up to 1200 °C still contained about 10 wt % oxygen (about 9 atom % oxygen), although CO is usually released at this temperature.[21] Temperatures of 1400 °C or above may be needed for complete removal of the oxygen-containing structures.[21]

The pyrolysis of the fibers, manifested in the material loss, also resulted in shrinkage of the fiber in its length direction (recorded during carbonization with the TMA equipment), with the highest rate of shrinkage occurring at around 400 °C (see Figure 1). At lower temperatures, a slight increase in fiber length, probably related to a general thermal expansion, was seen. In general, the length changes may be said to follow a behavior typical of carbonization processes.[23] The diameter changes during carbonization may as a first approximation be calculated from the measured weight (taken from TGA recordings) and length changes (taken from TMA recordings), assuming that the density of the stabilized lignin fibers did not change significantly during the carbonization. As indicated in Figure 1, the calculated diameter changes (assuming constant density) seem to be related more to the weight changes than to the observed changes in fiber length. If the estimated diameter changes (from the weight and length changes as in Figure 1) are compared with the actual diameter measurements (recorded using laser diffraction on a Dia-Stron fiber tester) on fibers taken out at different temperatures during carbonization, it seems that at temperatures of 600 °C and above, the fiber diameters obtained were smaller than those calculated from the weight loss (Figure 2). It should be noted that the data for each temperature are for a new set of fibers and that there was some variation in the initial diameter of the stabilized lignin fibers. It

nevertheless seems obvious that for all the fibers with a carbonization temperature exceeding 600 °C the measured fiber diameters were smaller than those calculated based on a constant density of the material. This appears to indicate that the carbon fiber structure increased in density during the latter phase of the carbonization. In the SEM images of stabilized and carbonized lignin fibers in Figure 3, no larger pores or cavities are visible that could account for the changes in diameter measured. However, it is not possible to exclude the presence of micropores that are not detected by SEM. Based on the differences in diameter between the actual carbonized fibers and the calculated diameter, based on the weight loss, an increase of 35% in the material density during the carbonization of stabilized lignin fibers can be estimated. This may support the hypothesis of an increase in crosslinking or aromatization of the structure.

Figure 4 shows the effect of the heating rate during carbonization on the actual fiber length during the carbonization process. Fiber bundles of stabilized lignin fibers were here carbonized with a negligible, constant force of 5 mN. The general pattern of fiber length changes was very similar for the different heating rates, although there seems to be an offset between the curves for 10 and 20 °C/min with respect to the other curves. This may be an effect of differences in the alignment of the fibers when mounted. At low temperatures, the fibers expanded, as do most materials when heated. At temperatures above 300 °C, when carbonization started to lead to a weight loss, the length decreased considerably, the shrinkage reaching a value of around −20% at 800 °C. Above this temperature, shrinkage was negligible. This shrinkage is comparable with that seen, for instance, in the carbonization of PAN fibers.[24]

When the temperature of carbonization was increased, the strength and stiffness of the fibers started to increase while the strain to failure decreased, as shown in Figure 5. The most abrupt change seemed to be the reduction in the strain to failure above 400 °C, indicating a substantial embrittlement of
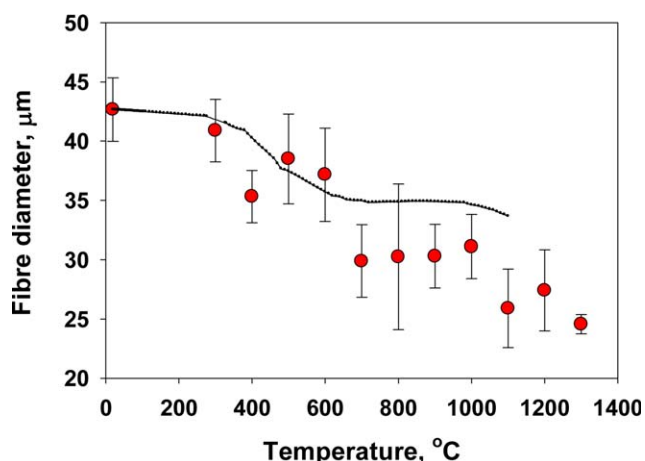
Figure 2. Fiber diameter, measured by laser diffraction on a Dia-Stron fiber tester, of stabilized lignin fibers as a function of carbonization temperature (standard deviation indicated). The line indicates the diameter calculated from the weight loss and fiber length shrinkage assuming a constant fiber density. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
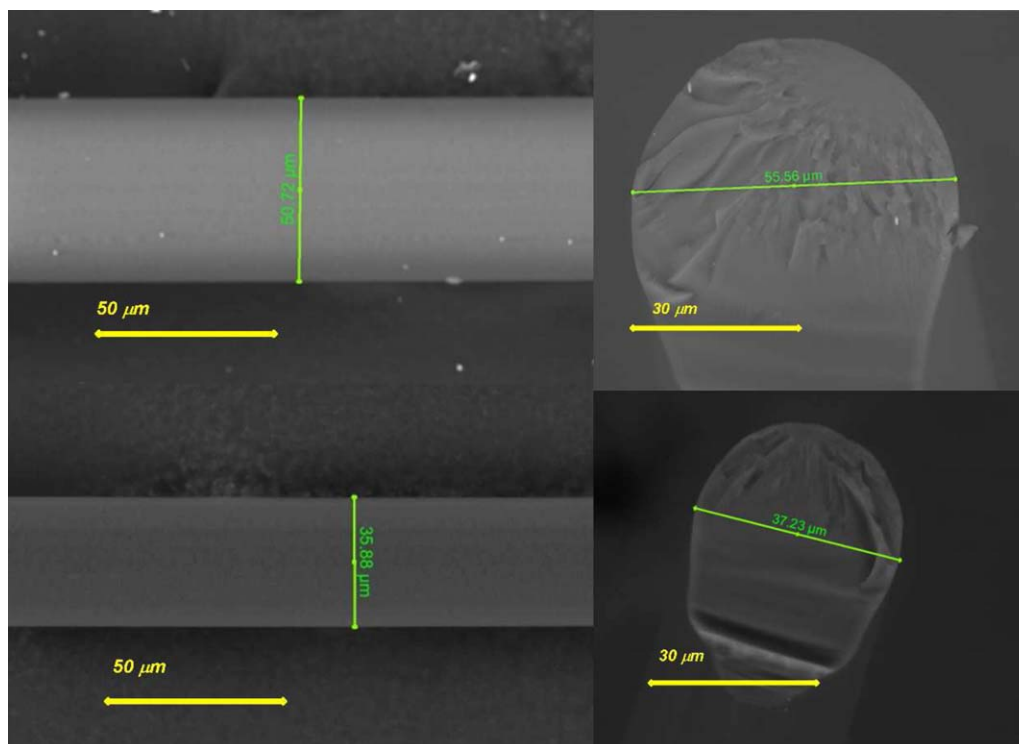
Figure 3. SEM images of (top) a stabilized lignin fiber, surface and cross section; and (bottom) a carbon lignin fiber carbonized at 1 °C/min to 1000 °C, surface and cross section. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the fiber. This may be a typical effect of a crosslinking reaction.[25] The elastic modulus also increased with higher carbonization temperatures but was mostly affected in the temperature interval between 600 and 900 °C. Carbonization temperatures above 900 °C seemed to have little effect on the elastic modulus. The tensile strength increased above 600 °C and reached its highest value at temperatures of 1000 °C and above, where the strength leveled out. This behavior was different from that reported, for instance, for the carbonization of PAN, for which the maximum tensile strength was reached at temperatures of about 1500 °C.[16,26] The strength increase in the carbon fibers

follows the general pattern of strength improvement during carbonization of materials, but the specific temperatures and temperature profiles seem to be highly dependent on the precursor material used.[25–27]

The effect on the strength properties of the heating rate during carbonization is illustrated in Figure 6 for the elastic modulus of carbonized fibers withdrawn at different carbonization temperatures. Although there were some small differences in the behavior toward complete carbonization, no significant difference in elastic modulus could be seen between samples reaching carbonization temperatures of 900 °C and higher. The same was true for the tensile strength and strain to failure, which are not shown here. For the higher heating rates, samples were withdrawn only at temperatures of 900 °C and above. Faster heating rates could thus preferably be used in the carbonization of stabilized lignin fibers, as shorter times would be required for the carbonization.

Since the stabilized fibers shrank considerably in length during carbonization, it was of interest to investigate the implication of restraining this shrinkage to different extents during carbonization. This strategy is illustrated in Figure 7 with the application of a load ramp during carbonization in order to reduce the length shrinkage of the fibers. With the equipment used, a TMA, it is only possible to control the applied load, whereas in a production facility it would be more suitable to control the strain in different temperature steps. In this way, it is hoped that an increased orientation of the lignin molecules could be obtained, which could lead to improved strength properties.[24,28] The critical factor when applying a load to the fibers, or restraining its shrinkage, is the choice of temperature at which
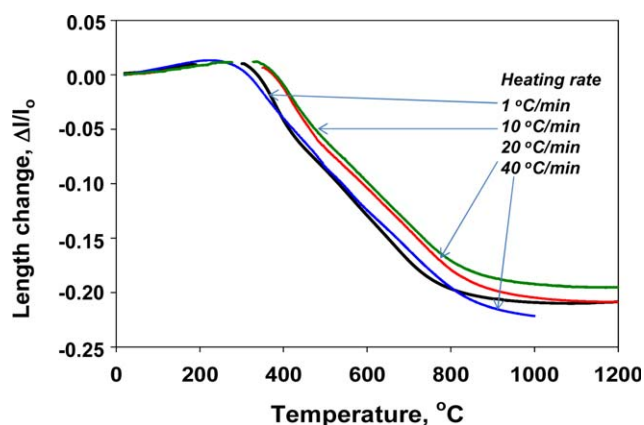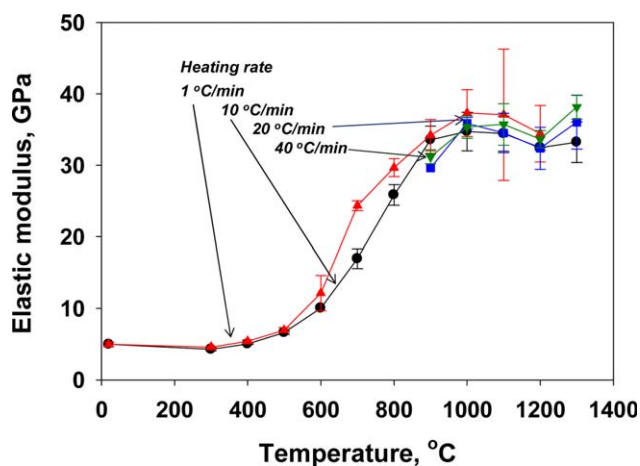

Figure 4. Length changes during carbonization (recorded by TMA) of stabilized lignin fibers as a function of temperature for different heating rates during carbonization (a constant negligible load was applied). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
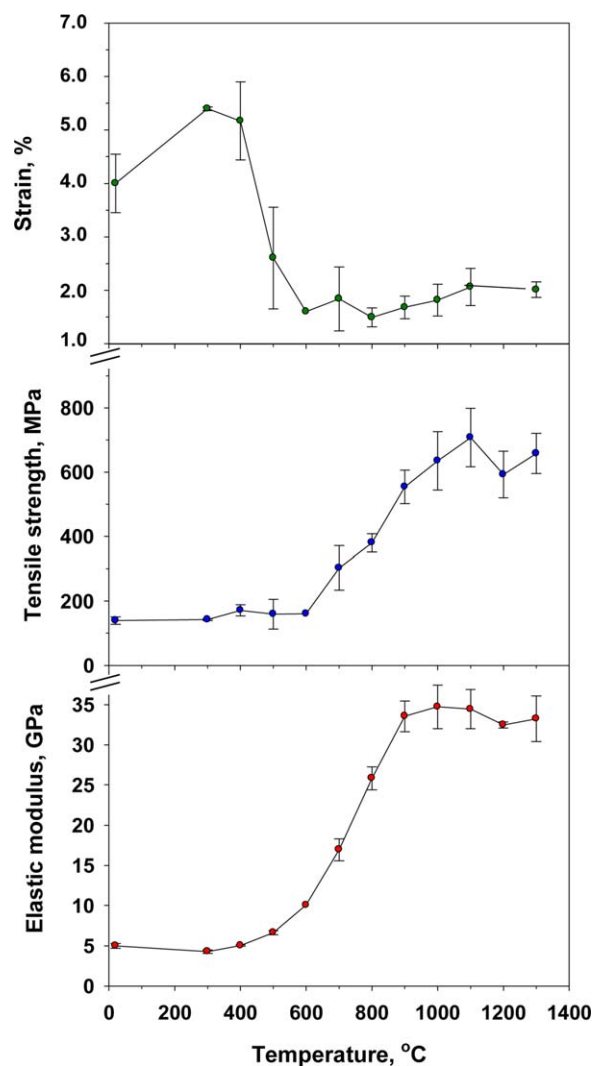
Figure 5. E-modulus, tensile strength, and strain to failure (recorded in a Dia-Stron fiber tester) of lignin fibers as a function of temperature during carbonization of stabilized lignin fibers under a constant negligible load (standard deviation indicated). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to apply the load and the magnitude of the load in order not to break the fiber during processing. Loads were here applied at temperatures of about 300 to 400 °C, where fiber shrinkage has been found to occur in fibers carbonized with the negligible load (see Figure 4). A loading ramp was used to ensure that too-high forces were not applied prior to the strength improvement of the fibers. The load at the end of the loading ramp, when final carbonization was reached, was estimated to be in the range of 100 MPa, based on the calculated fiber diameter. With higher loads, the fiber shrinkage could be substantially reduced (see Figure 7). Obviously the load applied at the lower temperatures of 300 to 400 °C, where the fibers are rather weak, may be critical, as the strain to failure at this temperature was less than 2% (see Figure 5).

Figure 8 shows the tensile strength versus elastic modulus for carbonized fibers. For the fibers carbonized to a given temperature, no difference with regard to heating rate was noted, and
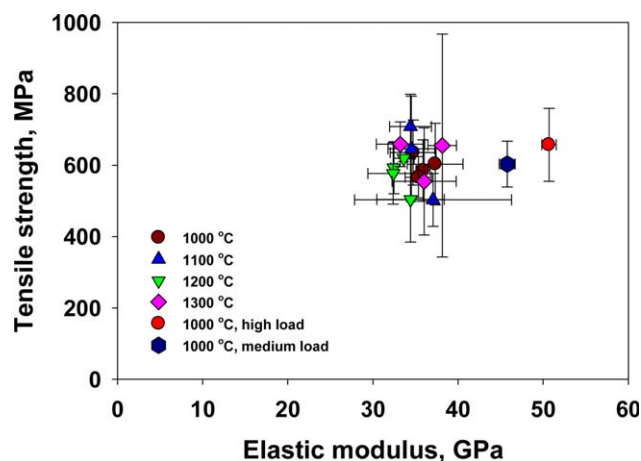

Figure 6. Elastic modulus (recorded in a Dia-Stron fiber tester) of carbonized lignin fibers as a function of temperature for different heating rates during carbonization of stabilized lignin fibers under a constant negligible load (standard deviation indicated). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

they are therefore shown with the same symbol. It is clear that the fibers subjected to increasing loads during carbonization showed a greater increase in elastic modulus than the fibers carbonized under only a constant negligible load. This improvement in strength properties due to loading is in line with the general ideas of orienting structures and is comparable, for example, to the results reported by Zhang and Ogale[27] for the extension of acetylated lignin-based fibers during carbonization. No information was, however, given as to what restraint was applied. No increase in tensile strength was seen for the samples investigated here. This could perhaps be due to impurities still left in the fibers or smaller pores created by the evolution of volatiles during fiber spinning or the subsequent stabilization operation.[3,12] Although the fibers seemed in the SEM analysis
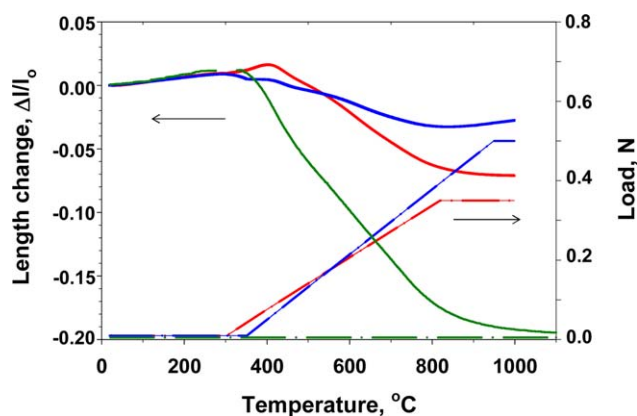
Figure 7. Length change (recorded by TMA) of stabilized lignin fibers as a function of temperature for different loading patterns applied during carbonization. Three loading schemes are compared: green: no load applied; blue and red: load ramp applied at 300 and 350 °C, respectively. For the samples loaded during carbonization, the force at the end of the process, when the load was at its maximum, was estimated to be about 100 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Tensile strength versus elastic modulus (recorded in a Dia-Stron fiber tester) for carbonized lignin fibers (standard deviation indicated). The centered clustered data show fibers that were carbonized at different temperatures under a negligible constant load. At each temperature, the sets of data include all different heating rates used for which no systematic difference in properties was seen. The set of samples subjected to increasing loads (to the right of the clustered data) are those for which the shrinkage during carbonization is shown in Figure 7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to be rather uniform, the existence of small pores or impurities cannot be excluded. No significant difference in strength properties was noted being due to either carbonization temperature (between 1000 and 1300 °C) or heating rate (1 to 40 °C/min). The strength properties of fibers carbonized without any load were similar to the values previously reported for carbonized lignin fibers.[3,5,12,28,29] The increase in the elastic modulus, here shown, when the shrinkage of the fibers during carbonization was restrained indicates that it may be possible to improve the properties of lignin-based carbon fibers during processing. It should, however, be remembered that these carbon fibers have properties far from those of commercial PAN-based carbon fibers.[2,16,26] Thus carbonized lignin fibers are not yet suitable to meet the requirements of the automotive industries in the range of 2 GPa in strength and 200 GPa in modulus.[2] However, the strength properties of carbon fibers are in general highly dependent on the fiber diameter: the smaller the diameter, the higher are the strength properties.[5,30] With improved processing being developed, diameters of carbon lignin fibers down to 10 μm are well foreseen, and this should lead to considerably improved strength properties of the carbon fibers produced. With the application and control of strain during carbonization, the prospects of improving the strength properties of lignin fibers should be promising.

CONCLUSIONS

It has been shown here that the strength properties of stabilized lignin precursor fibers start to increase at carbonization temperatures above 600 °C. The highest strength values were obtained at a carbonization temperature of 1000 °C, and a further increase in temperature up to 1300 °C showed no improvement in properties. The heating rate during carbonization, in the interval from 1 to 40 °C/min, had no effect on the strength

development. Hindering the shrinkage of the fibers during carbonization by a controlled loading increased the elastic modulus of the fibers by 50%, but no effect on tensile strength was noticed as a result of different loading conditions during carbonization. This could probably be related to impurities present in the lignin-produced fibers.

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