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Effect of graphitic additives on the rheology of cellulose solutions for the preparation of templated carbon fiber precursors

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The performance of biobased carbon fiber (CF) can potentially be improved to a new level by enhancing its graphitization by including graphitic additives as structural templates in the precursor. Mixing these additives in the precursor spinning solution can influence the solution rheology and thus its spinning process and ensuing carbonization, though these effects are not well understood. Herein, we analyze the influence of carbon nanotube (CNT) and graphene oxide (GO) additives on the rheology of cellulose solutions in ionic liquid as well as the subsequent precursor and CF preparation. Addition of GO both thickened the solution and clearly increased its elastic (solid-like) nature in comparison to pure cellulose solution in ionic liquid, while CNT only made the solution moderately more elastic. Still, solutions with both additives were spinnable into continuous precursor fibers, though the inclusion of GO somewhat disturbed cellulose alignment in the fiber, as observed through X-ray diffraction. Also, GO induced structural order development, observed as a decrease in the intensity and ratio between the Raman peaks at ~1300 cm\(^{-1}\) (related to disorder) and ~1600 cm\(^{-1}\) (related to sp\(^2\)-hybridised carbon in general).

1. Introduction

Carbon fiber reinforced polymers are essential enablers of a low-carbon economy, as they are optimal materials for applications requiring the combination of high strength with low weight, such as large wind turbine blades, light vehicles, pressure vessels or kinetic energy storage. However, increased use of carbon fiber is currently limited by its high price that fluctuates
following the oil price. Moreover, the conventional process of producing carbon fiber from polyacrylonitrile (PAN) involves harmful solvents, toxic emissions and large energy use.\textsuperscript{[1,2]} The possibility to produce carbon fiber with lower price, environmental impact and health risks could signify a breakthrough in the use of carbon fiber and thus also the green technologies it enables. This makes cellulose-based carbon fiber precursors an attractive prospect.

However, even though cellulose-based carbon fiber has been commercially available for decades,\textsuperscript{[3]} it struggles to compete with the mechanical properties of the PAN-based option. This is because it takes an expensive and low-yield hot stretching process to develop remarkable graphitization in the cellulosic precursor.\textsuperscript{[1]} It has been shown, though, that using an additive with a graphitic surface in the precursor fiber can generate a templating effect, facilitating cellulose\textsuperscript{[4]} and PAN\textsuperscript{[5]} to form graphitic structures even at lower temperatures. However, the validation of this phenomenon on cellulose has been limited to the demonstration of increased conductivity.\textsuperscript{[4]} Moreover, the effects of the additive on the rheological properties of the precursor spinning solution are poorly understood. So far, the studies on the rheology of carbon nanomaterial dispersions have mainly focused on carbon nanotubes (CNT) alone.\textsuperscript{[6-8]} The flow behavior and spinning of graphene oxide (GO) has been studied when dispersed in ionic liquid together with cellulose,\textsuperscript{[9]} but the carbonization of the ensuing cellulose-GO hybrid fibers has not been addressed.

As such, the exploration of the templating approach specifically on regenerated cellulose has been limited despite its well-known performance as a carbon fiber precursor. Recently, cellulosic fibers produced by regeneration from ionic liquids have been demonstrated as promising precursors, both as pure cellulose\textsuperscript{[10]} and as blends with other biopolymers such as lignin\textsuperscript{[11,12]} and chitosan.\textsuperscript{[13,14]} Herein, possibilities are examined to enhance the carbonization of cellulosic precursors from ionic liquids by incorporating carbon nanomaterials.

This approach takes advantage of the ability of ionic liquids to facilitate the dispersion of carbon nanomaterials, as demonstrated previously through graphite exfoliation via ultrasonication\textsuperscript{[15]} as well as electrochemically in ionic liquid containing electrolytes.\textsuperscript{[16,17]} Furthermore, carbon nanotubes (CNT)\textsuperscript{[6]} and graphene oxide (GO)\textsuperscript{[9]} have been used as additives in regenerated cellulose fibers spun from solutions in ionic liquids. Also, both CNT and GO have been applied with and without oxidation as additives in electrospun nylon 6,6 fibers.\textsuperscript{[18]} However, the effect of the morphology and concentration of the nanocarbon additive on the properties of cellulose-
based spinning solutions has not been addressed, specifically considering their rheology, spinning and subsequent carbonization. This makes CNT and GO particularly interesting additives, as their morphological differences (1-dimensional CNT and 2-dimensional GO) may influence the rheological behavior of the solution.

2. Experimental Section

2.1. Materials

Birch prehydrolysis kraft pulp (Enocell, Stora Enso, Finland) was supplied in sheet form and ground into a powder (dry matter content 90-94%, moisture content 6-10%). Graphene oxide (GO) flakes and single-walled carbon nanotubes (CNT) were purchased from Merck, Germany. Ethanol (grade Etax A 94%) was obtained from Anora, and HNO₃ and H₂SO₄ from Merck, Germany. 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH][OAc]), used as a solvent for cellulose and dispersant for the nanocarbon, was synthesized from 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 99%, Fluorochem, UK) and acetic acid (glacial, 100%, Merck, Germany), as described previously.[19,20]

2.2. Preparation of spin solution

153 mg of GO flakes were manually ground in a mortar and mixed with 20.30 g of [DBNH][OAc] melted at 80 °C. The suspension was sonicated for 30 min at 80 °C in a bath sonicator. 2.91 g (dry weight) of ground cellulose fibers were slowly added to the suspension and the mixture was kneaded at 80 °C at a reduced pressure of 8-40 mbar for 2h. The obtained solution of 12.5 wt.% cellulose in [DBNH][OAc], with total solids 13.1 wt.%, GO content 4.9 wt.% out of solids, was sonicated again for 30 min at 80 °C. Finally, the dispersion was filtered at 80 °C through a metal filter mesh with 5 μm absolute fineness (Gebr. Kufferath AG, Germany). The obtained spinning solution or dope was formed into the shapes needed for further experiments, wrapped air-tight in plastic and parafilm, and refrigerated. Similarly, a solution was prepared with total solids of 13.0 wt.%, containing less GO (1.9 wt.% out of solids).

To compare carbon nanomaterials in different forms, dope was also prepared with CNT. Prior to dispersion in the ionic liquid, the CNT were first refluxed in acid in order to purify them and potentially introduce oxidized groups on the surface as follows. Approx. 1 g of CNT were immersed in 160 ml of 1:1 mixture of 2 M HNO₃ and 1 M H₂SO₄. The suspension was sonicated for 5 min. Subsequently, it was heated to 120 °C in an oil bath and refluxed for 4h. Thus purified
CNT were filtered through a filter membrane and washed with deionized water until neutral pH. Finally, the CNT were immersed in ethanol, sonicated for 30 min and filtered. The obtained CNT were covered with a foil with holes and dried at 105 °C overnight.

190 mg of the purified CNT was mixed with 25.73 g of [DBNH][OAc]. After sonication of 30 min at 80 °C in a bath sonicator, 3.65 g (dry weight) of cellulose powder was slowly added to attain a solution of 12.4 wt.% cellulose in [DBNH][OAc], with total solids 13.0 wt.%, CNT content 4.9 wt.% out of solids. This dope was kneaded at 80 °C in a reduced pressure of 8-40 mbar for 2h and sonicated again for 30 min at 80 °C. However, as this solution solidified during the sonication, it was remelted in a larger water bath at 80 °C and sonicated once more for 30 min. Subsequently, the dope was filtered, shaped and stored as above. Similarly, a solution was prepared with total solids of 12.8 wt.%, containing less CNT (1.9 wt.% out of solids), though without the additional melting and sonication steps, as this dope did not solidify during preparation.

A control sample without additive was prepared similarly, only omitting the sonication steps. 2.83 g (dry weight) of cellulose powder was dissolved in 18.94 g of [DBNH][OAc] to attain a 13.0 wt.% solution. The sample compositions are summarized in Table 1.

2.3. Optical microscopy
The quality of the dispersion was assessed with Axio Zeiss A1 optical microscope equipped with a heating stage. During imaging, the samples were heated to 80 °C.

2.4. Rheometry
The shear rheological properties of the spin solutions were analyzed using Anton Paar MCR 302 rheometer in oscillatory mode, with a plate diameter of 25 mm and a gap of 1 mm. The edge of the sample was sealed with silicon oil in order to prevent the solution from regenerating under the humidity of the surrounding air. The temperature was altered from 65 to 95 °C, at intervals of 10 °C. At each temperature, an angular frequency sweep was conducted from 100 to 0.1 Hz at a constant shear strain amplitude of 1% (within the linear viscoelastic region of the dope samples). The zero shear viscosity $\eta_0$ at each temperature was determined based on the complex viscosity data, assuming that the dopes follow the Cox-Merz rule. The data of complex viscosity $\eta^*$ as a function of angular frequency $\omega$ was fitted with the Cross model:
\[ \eta^* = \frac{\eta_0 - \eta_\infty}{1 + (K_c \omega)^m} + \eta_\infty, \]  

(1)

where \( \eta^* \) is limiting complex viscosity when \( \omega \) approaches infinity, \( K_c \) is the cross constant (i.e., time constant describing the onset of shear-thinning) and \( m \) is the shear thinning index. Further, the activation energy \( E_a \) of each solution was calculated by plotting \( \eta_0^* \) as a function of the inverse temperature \( T^{-1} \). The plots were fitted with the Arrhenius equation:

\[ \eta_0^* = A \exp \left( \frac{E_a}{RT} \right), \]  

(2)

where \( A \) is a constant and \( R \) the molar gas constant.

**Table 1. Sample compositions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Additive</th>
<th>Total solid content (wt.%)</th>
<th>Additive content out of solids (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO2%</td>
<td>Graphene oxide</td>
<td>13</td>
<td>1.9</td>
</tr>
<tr>
<td>GO5%</td>
<td>Graphene oxide</td>
<td>13</td>
<td>4.9</td>
</tr>
<tr>
<td>CNT2%</td>
<td>Carbon nanotubes</td>
<td>13</td>
<td>1.9</td>
</tr>
<tr>
<td>CNT5%</td>
<td>Carbon nanotubes</td>
<td>13</td>
<td>4.9</td>
</tr>
<tr>
<td>Ref</td>
<td>None</td>
<td>13</td>
<td>0</td>
</tr>
</tbody>
</table>

**2.5. Preparation of carbon fiber**

Precursor fibers were spun out of the dopes using a custom-made dry-jet wet-spinning line described previously.\(^{[21]}\) The dope was placed in the spinning cylinder and heated to 85 °C (GO5%), 75 °C (CNT2%), 72 °C (CNT5%) or 70 °C (GO2% and reference without additive). The melted dope was extruded at a volumetric speed of 0.015 cm\(^3\) min\(^{-1}\) through a spinneret.
with one orifice, diameter 0.1 mm and length 0.2 mm, corresponding to an extrusion speed of 1.9 m min\(^{-1}\) (i.e., volumetric speed divided by orifice area). The extruded filament was stretched in an air gap of \(~50\) mm before coagulation in water at 10 °C and collection on a double godet. The draw ratio (i.e., ratio of collection speed to extrusion speed) was altered between 1-12 by adjusting the godet speed between 1.9-22.9 m min\(^{-1}\). The obtained filaments were cut off the godet and soaked in deionized water to remove remaining [DBNH][OAc] for \(~20\) min and dried in ambient air.

Cellulosic and GO-containing precursor fibers were carbonized in a tube furnace under nitrogen atmosphere. Firstly, the temperature was increased to 350 °C in 350 min (0.94 °C min\(^{-1}\)). From 350 °C, the temperature was further increased to 700 °C in 70 min (5 °C min\(^{-1}\)). The temperature was held steady at 700 °C for 30 min, after which it was increased to 800 or 900 °C in 30 min (3.3-6.7 °C min\(^{-1}\)). At 800 or 900 °C, the temperature was held steady for 30 min before letting the fibers cool down to room temperature. Also, plain GO flakes were ground and exposed to the same carbonization programs to prepare control samples with GO only.

2.6. Transmission electron microscopy

In preparation for transmission electron microscopy (TEM), pieces of the fibers were embedded in an epoxy embedding medium. The fiber-containing epoxy blocks were cut in thin slices placed on TEM grids to enable imaging of the cross-sections. Transmission electron micrographs were recorded with FEI Tecnai T12 microscope (Eindhoven, Netherlands) operating at 120 kV.

2.7. Raman spectroscopy

To evaluate the quality of the obtained carbon structures, Raman spectra were obtained with Renishaw inVia Confocal Raman Microscope. Laser wavelength was 785 nm, power 0.5 mW and grating 1800 l min\(^{-1}\). Spectra were recorded for an exposure time of 10 s, and 3 acquisitions were averaged. The spectra were baseline corrected and peaks fitted with Lorentzian function. The intensity ratio (i.e., D:G ratio) between the bands at wavenumbers \(~1300\) cm\(^{-1}\) and \(~1600\) cm\(^{-1}\) (i.e., D and G bands, respectively) was calculated by comparing the peak heights at these wavenumbers.

2.8. X-ray diffraction (XRD)
The development of carbon crystallites with the carbonization temperature was monitored with Xenocs Xeuss 3.0 X-ray diffractometer in transmission mode with Cu Kα radiation, wavelength 1.54189 Å, operated at 50 kV and 0.6 mA. Bundles of fibers were cut into a length of 1-2 cm and positioned unidirectionally in the sample holder, vertically against the X-ray beam. Powders (GO without treatment and after the carbonization procedure at 800 and 900 °C) were loaded inside metal rings between layers of kapton tape.

The scattering patterns were collected using three horizontally arranged detector positions, and the collected patterns were merged to cover a wide horizontal range. Subsequently, the globular averaged scattering intensities were obtained from the merged scattering pattern. In this experimental geometry, the scattering vector of the horizontal side extended up to 4.5 Å⁻¹ (scattering angle or 2θ of 67°), with sample-to-detector distance of 56 mm and exposure time of 120 s. A blank measurement was conducted without sample and the acquired background scattering profile subtracted from the sample profiles. In the case of GO powders, two layers of kapton tape were used as the background.

The amorphous contribution was subtracted from the scattering profile using a smoothing procedure[22] applying Savitzky-Golay filter, over a 2θ range from 2° to 55°, for each diffraction profile. Window size and polynomial order for the Savitzky-Golay filter were set to 51 and 1, respectively. Iteration for the background estimation was repeated 150 times. Then the crystallinity index CI was estimated using the ratio of the area of total intensity $S_{total}$ and of the above estimated background intensity $S_{bkg}$ over a 2θ range from 9° to 50°:

$$CI = \frac{S_{total}}{S_{bkg}}$$

(3)

The diffraction profile was fitted with two pseudo-Voigt functions for (002) and (10) diffraction peaks. The software lmfit[23] was used for the fitting. Scherrer equation was used to estimate the crystal widths $Lc$ for (002) peak and $La$ for (10) band, as follows:

$$Lc \text{ or } La = \frac{K\lambda}{\beta_{hkl}\cos \theta},$$

(4)

where $\lambda$ is the X-ray wavelength, $\beta_{hkl}$ is the full width at half maximum (FWHM) of the diffraction peak in radians and $\theta$ is the diffraction angle of the peak. Shape factors of $K = 0.90$
and $K = 1.84$ were used for the (002) lattice plane and (10) bands, respectively. The d-spacing $d_{002}$ of the (002) peak was calculated by the Bragg equation:

$$d_{002} = \frac{\lambda}{2\sin \theta}$$  \hspace{1cm} (5)

3. Results and discussion

3.1. Additive type governs its effect on spinning dope rheology

The behavior of the prepared dopes under oscillatory shear was analyzed in order to predict their spinnability. Figure 1 shows the storage and loss moduli as a function of angular frequency for cellulose solutions with two different concentrations of CNT and GO as well as reference data with no additive. Figure 1a and c show that replacing 2% of the cellulose in the reference solution (Figure 1e) with an additive did not significantly change the viscoelastic behavior of the solution, apart from 2% of GO moving the crossover of storage and loss modulus ($G'$ and $G''$) to higher angular frequencies, especially at high temperatures (Table 2).

The crossover frequency signifies the inverse of the timescale at which the viscoelastic behavior of the system changes from predominantly elastic to viscous. When the timescale of observation is sufficiently short (high frequency), all polymer systems appear elastic, as there is no time for individual polymers to significantly move in relation to each other and thus cause a viscous response. Instead, deformations occur via stretching of the existing polymer arrangement, which is seen as elastic; i.e., the system behaves principally like a solid material. In contrast, at a long timescale of observation (low frequency), deformations proceed so slowly that the polymers have time to move in response to the deformation, as in a predominantly liquid system.

The increase of the crossover frequency with 2% of GO implies that a small amount of GO addition can make the cellulose chains slightly freer to move, as viscous effects start dominating the elastic ones already at a smaller timescale (i.e., higher angular frequency). However, this effect is only subtle, as it is not coupled with a clear increase in loss tangent (Figure S2), as expected when viscous effects are significantly enhanced.
Figure 1. Storage and loss moduli ($G'$ and $G''$, respectively) as a function of angular frequency at different temperatures for solutions with 2% of CNT (a), 5% of CNT (b), 2% of GO (c), 5% of GO (d) and no additive (e). The insets show corresponding optical microscope images.

However, replacing 5% with CNT brought the values of storage and loss modulus closer to each other at low angular frequencies (Figure 1b). This signifies that CNT enhanced the elastic (solid-like) nature of the solution, which is further highlighted by a lower loss tangent compared to the samples with no or only 2% of additive (Figure S2). This effect was even more pronounced with 5% of GO (Figure 1d). Moreover, besides further decreasing the loss tangent (Figure S2), the 5% substitution with GO moved the crossover of $G'$ and $G''$ to lower angular frequencies (Figure 1, Table 2) associated with enhanced elastic behavior. These findings imply that, at a sufficiently high concentration, CNT and GO contributed to the elasticity of the solution more than a corresponding amount of cellulose - especially GO, as a larger timescale
(i.e., lower angular frequency) was necessary to initiate the dominance of viscous (liquid-like) behavior.

Table 2. Crossover angular frequencies (in Hz) of $G'$ and $G''$ for the studied solutions at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>65 °C</th>
<th>70 °C</th>
<th>75 °C</th>
<th>80 °C</th>
<th>85 °C</th>
<th>90 °C</th>
<th>95 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT2%</td>
<td>0.4</td>
<td>0.5</td>
<td>0.8</td>
<td>1.1</td>
<td>1.4</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td>CNT5%</td>
<td>0.3</td>
<td>0.5</td>
<td>0.8</td>
<td>1.1</td>
<td>1.4</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>GO2%</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>1.3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.5</td>
</tr>
<tr>
<td>GO5%</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Ref</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>1.3</td>
<td>1.7</td>
<td>2.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Since 2% of additive was too little to increase elasticity, this amount was, assumedly, below the critical concentration where the additive would start forming an elastic, gel-like network. In the CNT2% and GO2% samples, the concentration of additive in $[DBNH][OAc]$ was 0.3 wt.%, whereas in the CNT5% and GO5% samples, it was 0.7 wt.%. This suggests that, at a concentration between 0.3-0.7 wt.%, the CNT or GO would reach sufficient percolation for the structural network formation. This is consistent with the previous report of CNT gelation in ionic liquids occurring at concentrations between 0.5-1 wt.%, depending on the applied ionic liquid.[24]

Similar effects have been observed on the same concentration scale for GO in ethylene glycol. Hadadian and coworkers reported that 0.3 wt.% of GO in ethylene glycol was sufficient to establish a clear non-Newtonian regime at low shear rates, which became more pronounced at higher concentrations.[25] The enhancement of non-Newtonian behavior indicates strengthening of sheet–sheet and multi-sheet interactions,[25] which can also explain the increase in elastic behavior when the GO concentration in $[DBNH][OAc]$ was increased from 0.3 wt.% (sample GO2%) to 0.7 wt.% (sample GO5%) in the present study.
Also in nanocomposites, the percolation threshold of multiwalled CNT has been reported as 0.1-0.4 wt.%.\textsuperscript{[26]} Even though a nanocomposite is a different system compared to an ionic liquid dispersion, this implies that the observed scale of the percolation concentration is realistic for a critical amount of entanglement to occur.

On the other hand, also higher gelation concentrations have been reported, reaching as high as >2 wt%.\textsuperscript{[6]} The differences may arise from the specifics of the systems, including the type and aspect ratio of the CNT as well as the ionic liquid used. Moreover, in the present study, the cellulose chains are likely to also contribute synergistically to the network formation.

As GO enhanced the elasticity more than CNT (i.e., lowered the loss tangent more, Figure S2, and changed the crossover of storage and loss modulus to lower angular frequencies, Figure 1), the structure of the network formed upon the percolation of GO appears to be more solid than that formed by CNT. This is expectable, as the GO was obtained by manual grinding of rigid flakes. As such, the GO sheets are probably still largely included in stiff aggregates, as supported by optical microscopy (inset of Figure 1d). Furthermore, as a one-dimensional additive (visible as ribbon-like in the inset of Figure 1b), the morphology of CNT resembles more closely that of cellulose chains despite being more rigid. As such, replacing 5% of the cellulose with CNT can be expected to alter the viscoelastic behavior less than using two-dimensional GO.

Besides the additive morphology, its surface chemistry can also influence its effects on the solution. In particular, as GO has more chemical resemblance to cellulose than CNT (see Figure S1 and associated supplementary discussion), it can be expected to interact more readily with the cellulose and thus produce synergistic effects on the rheology of the dispersion. This can explain the stronger structural network formation with GO present. A schematic representation of the supposed microstructures of the solutions with different forms of nanocarbon is presented in Figure 2a.
Figure 2. Schematic illustration of the supposed microstructure of the cellulose solutions with different nanocarbon additives, following Yao et al.[28] (a). Complex shear modulus $G^*$ as a function of angular frequency at 65 °C (b), 80 °C (c) and 95 °C (d).

Too elastic behavior has been previously shown to be disadvantageous for another spinning setup.[27] Moreover, the optical microscope images of the samples show aggregates remaining in the spin solutions (Figure 1, insets). These observations suggest that the inclusion of the additive may make it more challenging to form uniform fibers with effective cellulose alignment during the spinning, as discussed below.

The effects of the carbon additive morphology and amount are further highlighted by plotting the complex shear modulus ($G^*$, i.e., square root of the sum of the squares of storage and loss moduli) as a function of angular frequency (Figure 2b-d). This Figure shows how $G^*$ largely overlaps for all the other samples except for GO5%, which contains enough of a rigid and sufficiently cellulose-compatible additive to increase the modulus by forming a solid-like structure in the solution (Figure 2a).
Complex viscosities of the dopes were analyzed in order to determine their viscous flow activation energies and appropriate spinning temperatures. Figure S3 shows the complex viscosity of each sample as a function of angular frequency at varying temperature and Figure 3a the zero shear viscosity as a function of temperature, calculated based on the complex viscosity data, according to Equation (1). As seen in Figure S3a and 3a, replacing 2% of the cellulose in the solution with GO maintained the complex viscosity similar to the reference with cellulose and [DBNH][OAc] only (Figure S3e). As such, the same spinning temperature (70 °C) was selected for both GO2% and reference dopes.

![Figure 3](image)

**Figure 3.** Zero shear viscosity as a function of temperature for samples with different carbon additives and no additive, including the zero shear viscosity targeted for spinning (a). Transmission electron micrographs of GO5% fiber cross-sections without draw (b) and with a draw ratio of 12 (c).

This observation is in line with the results of oscillatory rheometry discussed above, showing that 2% was not enough of GO to interact sufficiently to increase the elasticity of the solution (Figure 1c). At low temperatures, the GO2% sample even showed qualitatively lowered viscosity, as it failed to fully solidify during refrigeration. Also previously, GO contents up to 2 wt.% of cellulose have been shown to decrease the viscosity of a cellulose solution because of the slip properties of the GO - ionic liquid system.\(^9\) Yao et al. reported a slight thinning with
2 wt.% of GO in cellulose carbamate but thickening at higher GO contents.\cite{28} This was explained by the long-range interactions between the GO sheets causing their alignment at 2\%, while at higher GO contents, the increased physical interactions between GO sheets and cellulose carbamate chains induce the formation of a 3D network observed as increased viscosity and elasticity.

In line with the findings of Yao et al., thickening was observed here with a sufficiently high GO content of 5\%, as this amount of GO raised the complex viscosity (Figure S3b and 3a) higher than that of the reference sample (Figure S3e). This implies that at a sufficient GO inclusion, the GO and/or the GO-cellulose combination has a stronger thickening effect than the cellulose alone. As such, a higher spinning temperature (85 °C) was necessary for this dope to attain a suitable viscosity (Figure 3a). Thickening with GO addition has also been reported in hydrolyzed polyacrylamide (HPAM) solutions, at GO:HPAM ratios varying from 1:5 to 2:1.\cite{29}

In the case of CNT, only slight thickening occurred at both 2\% and 5\% loadings in comparison to the reference, no observable difference between the different CNT contents. As discussed above, the CNT have one-dimensional morphology, like the dissolved cellulose chains, as well as low chemical affinity with cellulose. As such, replacing part of the cellulose with CNT does not significantly alter the solution structure (Figure 2a) and thus the viscosity of the hybrid dispersion. Because of the slight thickening effect, though, the spinning temperatures were moderately elevated for these dopes (72 °C for CNT5\% and 75 °C for CNT2\%).

The zero shear viscosity as a function of the inverse of temperature (Figure S4a) was also fitted exponentially in order to calculate the viscous flow activation energy (Figure S4b). The activation energy quantifies the temperature sensitivity of the sample viscosity. Differences in the activation energy in comparison to the reference were only visible at an additive concentration of 5\% (Figure S4b) and small even in that case. GO subtly increased the activation energy (i.e., susceptibility to temperature), whereas CNT slightly decreased it. This has implications on spinning, as a more temperature-sensitive dope requires a more extensive adjustment of the spinning temperature to reach suitable conditions.

Optical micrographs of CNT (Figure 1b, inset) and GO (Figure 1d, inset) distributions in the cellulose solution show that both carbon materials form visible aggregates. Nevertheless,
comparison between the two types of additives in [DBNH][OAc] before (Figure S5a, b) and after sonication (Figure S5c, d) shows that, especially in the case of CNT (Figure S5b, d), the sonication enhanced the distribution of the nanocarbon in the ionic liquid. This implies that, when fed with energy, the ionic liquid and CNT can interact in a way that facilitates CNT dispersion.

Also previously, ionic liquids have been reported to interact with CNT to form bucky gels.[24,30,31] This effect has been explained by the ability of an imidazolium-based ionic liquid to form Van der Waals interactions with the CNT surface and thus shield the π-π stacking between adjacent CNT.[30] Possibly, a related effect occurs in [DBNH][OAc]. As such, sonication over lengthened time or with enhanced power could potentially further improve the CNT dispersion in the spinning dopes. However, this may result in an overly elastic dope, unless the CNT concentration is reduced.

Possibly, a more uniform additive distribution could be achieved by using an ionic liquid with a fluorine-containing anion, such as [BF4]− or [FP6]−, as typically used in previous reports concerning carbon nanomaterial dispersion.[15-17] These authors have hypothesized that the interactions between graphitic surfaces and ionic liquids arise from π-π or π-cation interactions between the sp2-hybridised carbon and the cation component of the ionic liquid. The presence of highly electron-withdrawing fluorine atoms in the anion can enhance this interaction by making the cation electron-deficient and thus more inclined to interact with the electron-rich graphite surface.[32] However, [BF4]− or [FP6]− anions have been reported to not dissolve cellulose due to their inability to coordinate the hydroxyl groups in cellulose.[33] As such, those are not suitable ionic liquids for cellulose spinning, and a trade-off exists between optimizing the solvent for nanocarbon dispersion and cellulose dissolution. As another alternative, Gabryś et al. have demonstrated an approach of first dispersing GO in DMF before mixing with a spinnable ionic liquid.[9]

Here, all the studied dopes were spinnable continuously with a draw ratio of up to at least 8. The most facile to spin was the solution with 5% of GO. This also produced the fiber that looked the most uniformly black by eye. Because of the superior spinnability and visibly better additive distribution, this fiber was selected for further analysis.

3.2. Synergistic effect of additive and temperature on carbonization
The transmission electron micrographs of the precursor fibers spun with 5% of GO without or with drawing (Figure 3b, c, respectively) show that the GO – seen as dark domains in the images – is unevenly distributed across the fiber cross-section. Due to the aggregation of the additive, the cellulose alignment during spinning may have been compromised, as discussed below. Moreover, the observed GO arrangement may hinder the templating effect that the GO can have during carbonization, as it limits the shared surface area between graphite and cellulose. Nevertheless, it has been shown that, in PAN precursors, GO was able to induce templating even in regions where GO particles were not observably present.\textsuperscript{[5]} As such, GO may still affect the cellulose-based carbon fiber development beneficially, even with an aggregated dispersion.

For studying the effect of the GO additive on carbonization, fibers with a draw ratio of 4 (diameter ~9-12 μm as measured by micrometer) were selected, as that was easily spinnable with different additive contents, and the ensuing fibers produced a sufficient carbon yield that allowed practical handling of the fiber pieces after carbonization. Figure 4a shows an example of azimuthally averaged radial X-ray diffraction (XRD) spectra obtained from the samples, in this case, from fibers with 5% of GO before the carbonization (in blue) or after it at 800 °C (in purple) or 900 °C (in green). In addition, the azimuthal scan for the same fibers is provided in Figure S6a.

These spectra represent the qualitative changes that occurred upon carbonization, not only in GO5% but also in the GO2% fiber as well as the reference fiber with cellulose only. Prior to carbonization (Figure 4a, in blue), the spectrum shows the typical diffraction peaks for cellulose II at scattering angles of ~12°, ~20° and ~22° arising from crystal lattices (1–10), (110) and (020), respectively.\textsuperscript{[34,35]} After carbonization (Figure 4a, in purple or green), the spectrum changes form, featuring peaks at ~25° for carbon lattice (002) and ~44° for (10) - i.e., overlap of (100) and (101)\textsuperscript{[36]} - as shown before for carbonized pitch\textsuperscript{[36]} and carbon black.\textsuperscript{[37]}
The ratio between the crystalline and amorphous contribution to the diffracted intensity was used to calculate the crystallinity index, following Equation (3), and Scherrer equation to estimate the crystal dimensions - lateral size $La$ based on (10) band and stacking height $Lc$ based on (002) peak, according to Equation (4). The obtained crystallinity indices are shown in Figure 4b and crystal dimensions in Figure 4c-d. As seen in Figure 4b, the crystallinity increased with both carbonization temperature and GO content in the precursor. This implies that the inclusion of GO in the precursor fibers has a positive influence on the crystallinity of the ensuing carbon fiber, though it is unsure whether this is because of the contribution of the GO’s own crystallinity or because of its possible templating effect on cellulose. Previously, crystallinity of carbonized cellulose has been shown to grow nearly linearly with temperature.\cite{38} Besides, templating effect by GO on cellulose has been observed with a higher carbonization
temperature of 1000 °C. Observing templated graphitization would probably require even higher temperatures of 1500-3000 °C where cellulose typically graphitizes. As such, treatment at higher temperature may be needed to fully confirm the impact of the graphitic additive.

Comparison between the crystal sizes (Figure 4c, d) shows that the crystallites were approx. 50% smaller in both dimensions when incorporated in fibers than in plain ground GO flakes, even though the carbon present in fibers GO2% and GO5% can be expected to largely originate from the additive, as cellulose is more prone to degradation upon heating than GO. Likewise, the interlayer spacing $d_{002}$ was wider in fiber samples than in ground GO flakes (Figure S6d). These findings suggest that the fiber preparation - including steps like sonication of the GO in ionic liquid and filtration - impacts the crystallinity of the GO in a way that leads to smaller and less densely packed crystallites in the resulting carbon fiber. In addition, since the reference fiber carbonized from plain cellulose has a larger $d_{002}$ of ~4 Å whereas GO alone has ~3.5 Å (Figure S6d), the cellulose-based carbon present in the carbonized hybrid fibers may contribute to increasing the average $d_{002}$.

The impact of carbonization temperature on the size of the crystallites (i.e., aromatic clusters) was minor (Figure 4c, d), as expected, since the crystal size has been shown to not significantly grow at the temperatures studied here, even for anthracene that graphitizes more effectively than cellulose. Nevertheless, when increasing the carbonization temperature, the aromatic clusters slightly expanded in the lateral direction ($L_a$ increased, Figure 4c) but diminished in stacking height ($L_c$ decreased, Figure 4d). This indicates that, as the carbonization progresses, the crystalline clusters grow more easily along the basal plane rather than developing larger stacks, which is seen as an increase in $L_a$ but stagnancy in the growth of $L_c$. Similar effect has been observed at the same temperatures for pitch fibers. Kim et al. reported that a carbonization temperature above 1400 °C was necessary to increase $L_c$. Moreover, Emmerich reported growth in $L_c$ through crystal coalescence in the stacking direction after 1000-1200 °C. A similar temperature may be needed to enhance $L_c$ in carbon fibers based on cellulose-GO hybrid precursors, too.

$L_c$ became even lower when GO content in the precursor fiber was increased, possibly because the additive disturbed the alignment of the cellulose during spinning, which is seen as decreasing Herman’s orientation parameter of the precursor fiber as a function of GO content.
(Figure S6b). When the cellulose chains in the fiber are arranged in more disorder, there are even less opportunities for crystallites to grow through stacking of adjacent layers. The decreasing orientation with GO content can be explained by the aggregated distribution of the GO in the dope (Figure 1d, inset) and in the fiber (Figure 3b, c).

Figure S6a shows that the crystallites had a preferential orientation along the fiber direction, as the azimuthal integration of the XRD data shows peaks at 0° and 180°. The orientation of the carbon crystallites originates from the alignment of the cellulose crystallites created during the spinning process.\[42\] However, a large portion of the alignment was lost during the carbonization, as the azimuthal peaks turned wider. This can be quantified as a decrease in Herman’s orientation parameter from >0.7 before carbonization to <0.4 after it (Figure S6b). This deterioration of the orientation parameter could probably be mitigated by applying drawing during the carbonization.

Figure 5a shows examples of Raman spectra (normalized for better visibility of different spectra together) that were used to calculate the ratio between the intensities of the D and G bands (at ~1300 cm\(^{-1}\) and ~1600 cm\(^{-1}\), respectively) shown in Figure 5b. Both bands arise from sp2-hybridised carbon, while the D band is specifically associated with a disordered structure of it.\[4,38,29\] In disordered carbons (such as carbonized cellulose), the D:G peak intensity ratio correlates with the extent of the in-plane aromatic cluster (D:G ratio proportional to the square of \(L_a\)), whereas in ordered carbons (such as graphite or GO), the D:G ratio indicates the extent of disorder,\[43\] along with the width of the D peak (Figure S7a).\[44\] In the ordered regime, D:G is inversely proportional to \(L_a\) according to the Tuinstra-Koenig relation.\[43,45\]

Comparison between the cellulosic samples (no GO) shows that the D:G ratio increased with temperature (Figure 5b). Considering that this material is expected to behave as disordered carbon, the finding indicates that raising the carbonization temperature expanded the area of the aromatic clusters. This aligns with the subtle increase in the \(L_a\) of cellulose-based carbon with temperature, as measured with XRD (Figure 4c).
In contrast, when GO was included (samples GO2% and GO5%), D:G ratio decreased with temperature (Figure 5b), even though \( La \) kept its rising trend with temperature (Figure 4c). In addition, raising the temperature narrowed the D and G peaks (Figure S7), which is associated with reducing disorder. These results imply that the additive-containing fibers may behave as ordered carbon; i.e., their \( La \) is proportional to D:G peak intensity ratio, following the Tuinstra-Koenig relation. This is reasonable considering that, assumedly, the carbon included in these fibers originates largely from well ordered GO, which is less prone to degradation during heating than cellulose. Furthermore, the templating effect of GO may cause even the cellulose to carbonize into a form that behaves like orderly carbon.

As such, even though the dope preparation and spinning processes somewhat impaired the crystallinity and crystal dimensions of the carbon fibers made of GO-containing precursors in comparison to plain, heated GO, as discussed above, the nature of the carbon material stayed as ordered. However, the effect could not be confirmed by comparison to plain graphene, as it showed negligible variation in both D:G ratio (Figure 5b) and \( La \) (Figure 4c) with temperature.

Previously, \( La \) of \( \sim 20 \text{ Å} \) has been reported as the transition between the disordered and ordered regimes of carbon. Here, all the samples had \( La \) larger than that (Figure 4c), which supports the conclusion that the graphene-containing fibers can behave as ordered carbon. Even though the reference fiber would have \( La > 20 \text{ Å} \) as well, cellulose carbonized at the studied temperatures has been typically described as disordered, and thus it is still preferable to expect it to behave as such.
Considering the upward trend with temperature in crystallinity and La (Figure 4b, c) as well as the downward trend in D:G ratio and D peak width (Figure 5b, S6a), which can be associated with reducing disorder in the case of the graphene-containing fibers, even larger temperatures could bring about even more benefits from the graphitic template. Additionally, including drawing during carbonization could enhance the fiber development by compacting it. Moreover, even a smaller amount of additive could probably be sufficient if dispersed more uniformly in the fiber structure.

Finally, when comparing the data for unheated graphene (Figure 5b, in blue, GO only as well as non-carbonized GO2% and GO5%, where the D and G peaks originate solely from GO), D:G ratio can be seen to rise when increasing amount of GO is mixed with cellulose. Apparently, during the fiber preparation, as the GO is sonicated in ionic liquid, kneaded with cellulose, filtered, refrigerated and spun into fiber, it loses some of its original crystal order. This correlates, as could be expected, with the findings that the mixing of cellulose and GO also disturbs the cellulose alignment in the precursor fiber (Figure S6b) and slightly decreases the ensuing carbon crystal stacking height (Figure 4d). Nevertheless, the carbonization compensates for this effect, especially in the case of the GO5% fiber (Figure 5b), and could even outperform it at higher temperatures if the same trend continues.

4. Conclusions

Hybrid spinning dopes were prepared out of cellulose mixed with 2% or 5% of GO or CNT. Addition of GO clearly thickened the dope and increased its elastic nature in comparison to pure cellulose solution, while CNT only made the dope moderately more elastic. The dopes were spun into precursor fibers that were carbonized at 800 or 900 °C.

XRD measurements showed that raising carbonization temperature increased the crystallinity and crystal size in lateral dimension. When adding GO to the precursors, the behavior of the ensuing carbon fiber changed from disordered (Raman D:G peak intensity ratio increasing with crystal growth) to ordered (D:G ratio inversely proportional to lateral crystal size). This was seen also as a slight decrease in \( d_{002} \) with GO content. However, the inclusion of the additive also disturbed the cellulose alignment in the precursor fiber and slightly decreased the ensuing carbon crystallite size in stacking dimension. As such, the additive has a dual effect on the carbon fiber formation.
Further work is needed to expose the fibers to higher temperatures and drawing during the carbonization to further enhance the effects of the added GO. Moreover, a more uniform dispersion of the additive may improve the cellulose alignment during spinning and thus mitigate the adverse effects of GO and make its beneficial effects accessible with a minimal amount of additive. Finally, carbonization at sufficiently high temperatures could validate if the nanocarbon additive can function as a template for graphitization.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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References
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Effect of graphitic additives on the rheology of cellulose solutions for the preparation of templated carbon fiber precursors

This study demonstrates the preparation of hybrid fibers out of cellulose and carbon nanomaterials in ionic liquid, including analysis of their rheological properties, which strongly influence their spinning process. Carbon nanotubes are shown to only subtly thicken the dispersion, while graphene oxide can interact more strongly with cellulose and produce a more rigid network.
Supporting Information

Effect of graphitic additives on the rheology of cellulose solutions for the preparation of templated carbon fiber precursors

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This supporting information contains supplementary discussion on

- FTIR spectroscopy
- Lattice spacing based on XRD
- Heat-induced reduction of GO

as well as 7 figures:

1. FTIR spectra of the studied carbon additives
2. Loss tangent as a function of angular frequency
3. Complex viscosity as a function of angular frequency
4. Zero shear viscosity as a function of the inverse temperature and flow activation energy calculated based on it
5. Optical micrographs of additives in ionic liquid
6. Supplementary XRD data
7. G and D peak widths based on Raman spectra
Supplementary discussion: Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared (FTIR) spectra of the nanocarbon additives were recorded using a PerkinElmer Spectrum Two FTIR spectrometer. 8 scans were averaged with a resolution of 16 cm$^{-1}$. According to the FTIR spectra shown in Figure S1, the peaks associated with oxidized groups in GO (such as C=O stretching at 1705 cm$^{-1}$ as well as C-O stretching and/or O-H deformation at ~1030 cm$^{-1}$) are missing from the spectrum of CNT, even after the purification treatment. In fact, the CNT spectrum stays rather unaltered by the treatment, which implies that the purification did not induce oxidation or other chemical modification on the CNT surface. As such, the surface chemistries of the applied carbon additives (GO and purified CNT) are different, GO more similar to cellulose.

Figure S1. FTIR spectra of the studied carbon additives, including CNT both before and after purification with acid.

Figure S2. Loss tangent as a function of angular frequency at 65 °C (a), 80 °C (b) and 95 °C (c).
**Figure S3.** Complex viscosity as a function of angular frequency for dopes GO2\% (a), GO5\% (b), CNT2\% (c), CNT5\% (d) and no additive (e).
Figure S4. Zero shear viscosity as a function of the inverse temperature, along with its exponential fit (a) used to calculate the activation energy (b).

Figure S5. Optical micrographs of 0.7 wt% of GO (a, c / left) and non-purified CNT (b, d / right) in [DBNH][OAc] before (a, b / above) and after (c, d / below) 30 min of sonication in a bath sonicator.
Figure S6. Azimuthal integration of the radial XRD spectra of GO5% before and after carbonization at 800 or 900 °C (a). Herman’s orientation parameter derived from the azimuthal peaks for all the fiber samples (b). Lattice spacings in lateral dimension \( da \) (c) and stacking direction \( dc \) or \( d_{002} \) (d). Azimuthally averaged XRD spectra for GO5% fiber before and after carbonization at 800 or 900 °C (e). The azimuthal integrations used in (a) and (b) were obtained at a scattering angle range of 10.4°-13.2° (cellulose II 1–10 peak) for the non-carbonized fibers and 21.2°-24.0° (carbon 002 peak) for the carbonized ones. Herman’s orientation parameter \( S \) was calculated according to:

\[
S = \frac{3\langle \cos^2 \gamma \rangle - 1}{2},
\]

where \( \langle \cos^2 \gamma \rangle = 1 - 2\langle \cos^2 \phi \rangle \),

where \( \langle \cos^2 \phi \rangle = \frac{\sum_{\phi_0}^{\phi_0+\pi/2} I(\phi) \sin \phi \cos^2 \phi}{\sum_{\phi_0}^{\phi_0+\pi/2} I(\phi) \sin \phi} \),

where \( I(\phi) \) is scattered X-ray intensity at azimuthal angle \( \phi \), and \( \phi_0 \) is the azimuthal angle in the beginning of the range used for the calculation: 0, \( \pi/2 \), \( \pi \) or \( 3\pi/2 \).
**Supplementary discussion: Lattice spacing based on XRD**

Lattice spacing in the carbon fibers stayed constant at 2.1 Å in the lateral dimension with both changing temperature and GO content (Figure S6c). This is intuitive, since no significant changes were expected in the aromatic planes themselves. In the stacking direction, the interlayer spacing stayed constant with temperature but slightly decreased with GO content from 4.0 to 3.9 Å (Figure S6d), probably reflecting the increased contribution of the GO-based, more organized carbon with a tighter stacking. Considering the stacking height of 10-12 Å, an average crystalline cluster only consisted of less than three graphene layers while no clear growth was observed when changing the GO content or increasing the temperature, similar to the previous observation for pyrolyzed softwood.\(^1\)

**Supplementary discussion: Heat-induced reduction of GO**

Interestingly, heat treatment of plain GO caused changes in its radial XRD spectra (Figure S6e). After heating, the peak at a scattering angle of \(~10^\circ\), arising from the (001) plane of graphite (Figure S6e, in blue),\(^2\) shifted up to \(~26^\circ\), i.e., changed into (002) peak of graphite (Figure S6e, in purple or green). This shift is associated with the decreased spacing between graphitic planes upon the removal of carbonaceous oxygen moieties from GO surfaces.\(^3\) This transition has previously been shown to occur with heating between 150 and 200 °C.\(^3\) As such, also the GO present in the carbonized hybrid fibers can be concluded to reduce during the carbonization.

![Figure S7](image.png)

**Figure S7.** Peak widths at \(~1300\) cm\(^{-1}\) (a) and \(~1600\) cm\(^{-1}\) (b) based on Raman spectra.

**References**
