

Effect of carbon nanomaterials on the rheology and spinnability of cellulose solutions in ionic liquid

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ABSTRACT

Hybrid spinning dopes were prepared by mixing different carbon nanomaterials with cellulose solutions in ionic liquid. The viscoelastic behaviours of the obtained dopes were analysed and the spinnability and electrical conductivity of the ensuing fibres tested. Graphene oxide and carbon nanotubes could increase both the viscosity and the elastic behaviour of the dopes. When the graphene was exfoliated from graphite, it even made the dope fully gel-like and thus unspinnable. The results show that nanocarbon can be incorporated in cellulosic fibres by using hybrid dopes for spinning, though without sufficient percolation to enable electrical conductivity.

INTRODUCTION

Incorporation of carbon nanomaterials in cellulosic fibres has several potential benefits, such as adding reinforcement, electrical conductivity and a graphitic templating effect when the fibres are used as carbon fibre precursors.^{1,2} In certain cases, specifically cellulosic fibres spun from solutions in ionic liquids, the dope solvent can even have a synergistic effect on both dissolving cellulose and dispersing the carbon material.

The ability of ionic liquids to aid carbon nanomaterial dispersion has been shown previously through graphite exfoliation via ultrasonication³ as well as electrochemically in ionic liquid containing electrolytes.^{4,5} Furthermore, carbon nanotubes⁶ and graphene oxide⁷ have been used as additives

in regenerated cellulose fibres spun from solutions in ionic liquids.

However, the effect of the type of the nanocarbon additive on the rheology and spinnability of the cellulose-carbon hybrid dopes has not been specifically addressed. Herein, hybrid dopes were prepared by replacing part of the cellulose in spinning dopes with different types of carbon additives. The rheology and spinnability of the dopes were analysed in order to determine the most feasible ways to blend nanocarbon into cellulosic fibres.

EXPERIMENTAL

Sample preparation

Ground graphene oxide (GO) flakes, single-walled carbon nanotubes (CNT, refluxed for 4h at 120 °C in 1:1 vol:vol mixture of 2 M HNO₃ and 1 M H₂SO₄ for purification/oxidation) or 1 mm x 1 mm pieces of graphite were mixed with [DBNH][OAc] (prepared as reported previously⁸) at a concentration of 0.7 wt%. The mixture was sonicated for 30 min at 80 °C in a bath sonicator (for GO and CNT) or with a tip sonicator, using 15 s pulses (amplitude 20-30 W) at 30 s intervals, total sonication time 1h (for graphite to induce exfoliation). Subsequently, ground cellulose was added to the suspension to attain a total solids content of 13 wt% (additive concentration 5 wt% out of total solids). The mixtures were kneaded at 80 °C at a reduced pressure of 8-40 mbar for 2h.

The ensuing cellulose solutions with dispersed carbon additives were sonicated again for 30 min at 80 °C and filtered at the same temperature through a metal filter mesh with 5 µm absolute fineness. The obtained dopes were formed into the shapes needed for further experiments, wrapped air-tight in plastic and parafilm and refrigerated. A control sample without additive was prepared similarly (dissolving 13 wt% of cellulose in [DBNH][OAc]), only omitting the sonication steps.

Characterisation

The quality of the dispersion at different stages of dope preparation was assessed at 80 °C with Axio Zeiss A1 optical microscope equipped with a heating stage.

The shear rheological properties of the dope were analysed 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 dissolved cellulose 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).

Based on the data for storage and loss moduli, loss tangent $\tan \delta$ (i.e., measure of viscous nature) was calculated according to Eq. 1:

$$\tan \delta = \frac{G''}{G'}, \quad (1)$$

where G' and G'' are storage and loss modulus, respectively.

The zero shear viscosity η_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 η^* as a function of

angular frequency ω was fitted with the Cross model:

$$\eta^* = \frac{\eta_0^* - \eta_\infty^*}{1 + (K\omega)^m} + \eta_\infty^*, \quad (2)$$

where η_∞^* is limiting complex viscosity when ω approaches infinity, K is the cross constant (i.e., time constant describing the onset of shear-thinning) and m is the shear thinning index.

Dope spinnability was examined using a custom-made dry-jet wet-spinning line described previously.⁹ The dope was placed in the spinning cylinder and heated to 85 °C (for GO), 72 °C (for CNT) or 70 °C (reference without additive). The melted dope was extruded at a volumetric speed of 0.015 cm³/min 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. 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 electrical conductivities of the obtained filaments were measured with BS1704 multimeter.

RESULTS AND DISCUSSION

Optical micrographs of the dopes are presented in Fig. 1. As seen in this figure, all the additives are dispersed as aggregates with a wide size distribution. In the case of exfoliated graphite (Fig. 1c), though, the dope appears almost completely black, which implies that the additive forms a more connected network than GO (Fig. 1a) or CNT (Fig. 1b).

This observation was supported by the oscillatory rheological measurements (Fig. 2). Especially at low angular frequencies and high temperatures, all the additives decrease the loss tangent; i.e., they make the viscoelastic behaviour of the solution more elastic (solid-like) and less viscous (liquid-like). This implies that the additives

and/or their interaction with cellulose contributed to the elasticity of the solution more than cellulose alone.

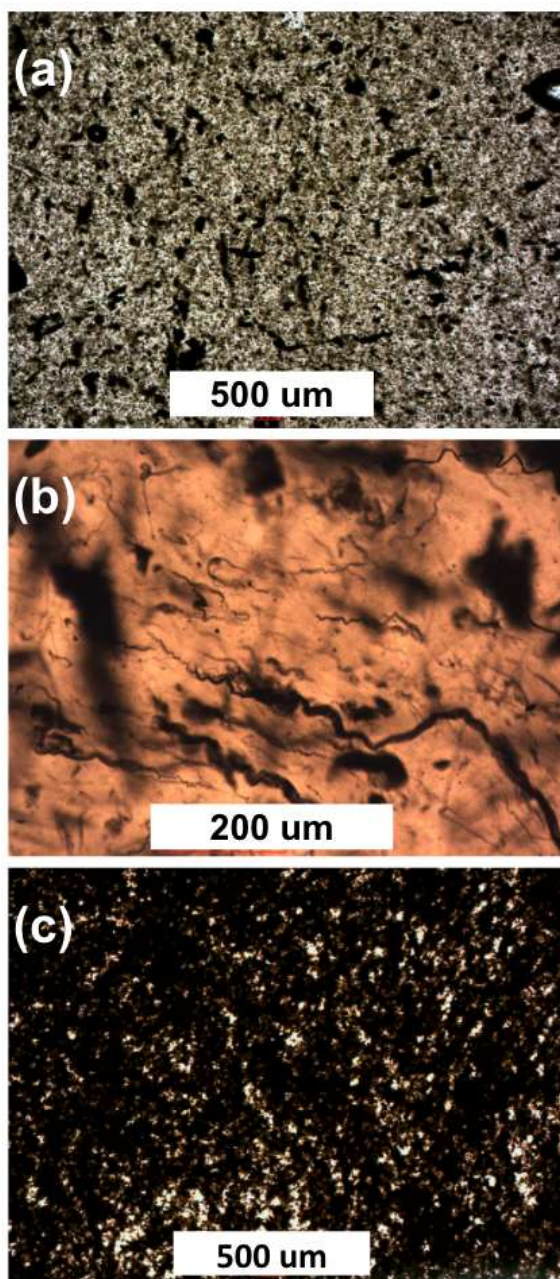


Figure 1. Optical micrographs of cellulose in ionic liquid with GO (a), CNT (b) and exfoliated graphite (c).

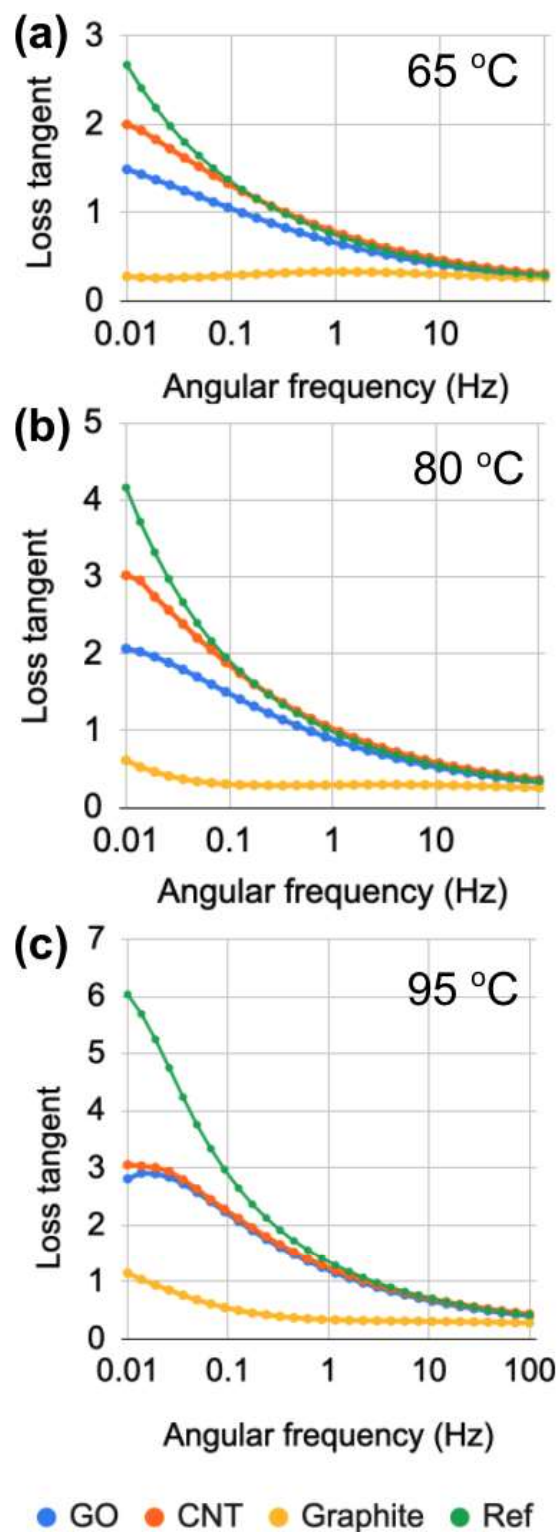


Figure 2. Loss tangent as a function of angular frequency for dopes with GO, CNT, graphite and no additive at 65 °C (a), 80 °C (b) and 95 °C (d).

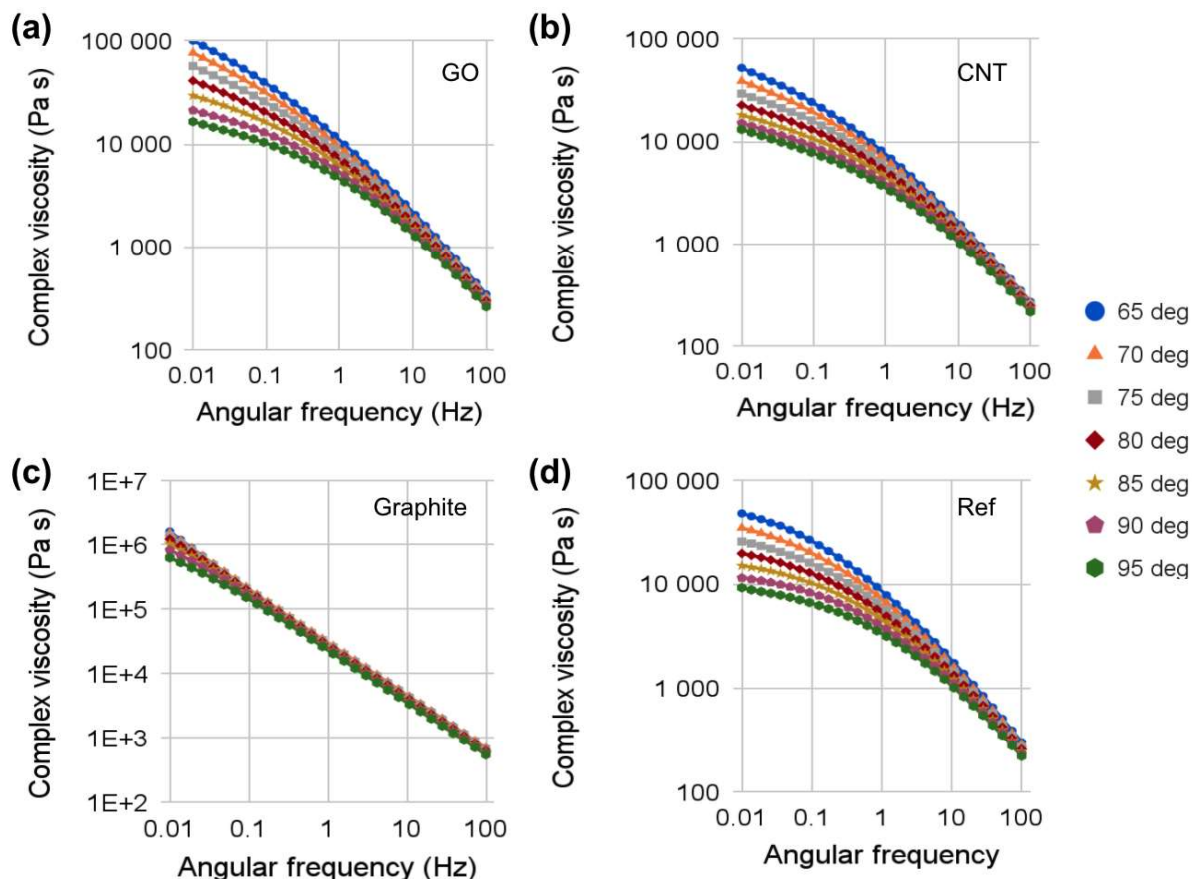


Figure 3. Complex viscosity as a function of angular frequency for dopes with GO (a), CNT (b), graphite (c) and no additive (d).

This effect was the most pronounced in the case of exfoliated graphite (Fig. 2, yellow). This sample also qualitatively felt like the most gel-like and brittle. The gel-like behaviour of this dope is highlighted also by the development of the complex viscosity as a function of angular frequency (Fig. 3c). It lacks the clear Newtonian plateau observed in other dopes (Fig. 3a, b, d) at low angular frequencies. Instead, shear-thinning occurs at an almost constant rate throughout the studied frequency range. Moreover, at higher frequencies, the complex viscosity of the graphite one is an order of magnitude higher than that of the other dopes.

Due to the excessive solid nature and viscosity, the graphite-containing dope could not be spun, as it was too thick to

even extrude through the spinneret. Also previously, too dominantly elastic behaviour has been shown to deteriorate spinnability in a different spinning setup.¹⁰ Possibly, the cellulose-graphite hybrid dope could be made spinnable by decreasing the amount of incorporated graphite. Moreover, further work is needed to confirm if the observed elastic behaviour has arisen from the graphite addition or from possible cellulose regeneration during the experiment.

For the other dopes, suitable spinning temperatures were estimated by calculating their zero shear viscosities according to Eq. 2. Spinning temperatures of 85 °C, 72 °C and 70 °C were selected for the dopes with GO, CNT and cellulose only, respectively, in order to aim their zero shear viscosities close to 40 000 Pa s during the spinning. At

these respective temperatures, all the dopes turned out spinnable up to a draw ratio of at least 10.

Interestingly, though, none of the obtained filaments was electrically conductive, even though the rheological properties suggest a sufficient level of percolation of the carbon additives to function as an elastic network. Even previously, the percolation threshold of multiwalled CNT has been reported as 0.1-0.4 wt% in CNT-epoxy nanocomposites.¹¹ In the fibres of this study, the nanocarbon content was even higher (5 wt%), as the ionic liquid of the dope has been removed.

Apparently, the dispersion of the carbon additives here was sufficient to create enough percolation for an observable rheological effect but not enough to induce electrical conductivity. Alternatively, the elasticity-enhancing effect in the dope may at least partly result from interactions between cellulose and carbon and thus happen even without the percolation of the additive. Possibly, the dispersion could be improved by increasing the sonication time and/or power as well as optimising the ionic liquid for this purpose.

Even without sufficient dispersion for electrical conductivity, the hybrid fibres can have other application areas, such as carbon fibre precursors. In the case of PAN precursors, GO has been shown to improve carbonisation via a templating effect even in regions where GO particles were not observably present,¹² which implies that even moderately even distribution of the additive can be sufficient for this application. Further work is needed to validate this.

CONCLUSIONS

These results show that cellulose-nanocarbon hybrid fibres can be spun by incorporating the carbon additive in the cellulose solution used as spinning dope. Among the studied forms of nanocarbon,

graphene oxide and carbon nanotubes were the most feasible to blend while still maintaining suitable rheological behaviour for spinning. When graphite was directly exfoliated into the ionic liquid used as cellulose solution, the solution became too viscous and its viscoelastic behaviour too strongly elastic for spinning. The fibres spun from the spinnable dopes are not conductive, probably due to insufficient percolation of the carbon additives. Nevertheless, they could have applications as advanced carbon fibre precursors, among others.

ACKNOWLEDGMENTS

This work was conducted using the facilities of Aalto University School of Chemical Engineering. Prof. Michael Hummel is acknowledged for support and discussion.

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