Effect of shear and extensional viscosities on wet-spinning of cellulose nanofibril hydrogels

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ABSTRACT

Rheology of cellulose nanofibrils (CNF) was analysed under both shear and extensional flows. These results were connected with the observed possibilities to prepare filaments from CNF via wet-spinning. Sufficiently high shear viscosity, storage modulus, loss modulus and extensional viscosity were discovered as potential predictors for spinnability in the studied wet-spinning system. Filaments could be spun with lengths up to approximately 20 cm, when using CNF dopes with the rheological parameters at the appropriate level. This limitation in length is proposed to originate from the flow characteristics of CNF hydrogel differing from those of a more typical polymer solution conventionally used for wet-spinning.

INTRODUCTION

Cellulose nanofibrils (CNF) are regarded as a high-potential material for a variety of future applications combining high mechanical performance with functionality and biodegradability.[1-5] However, their usage in commercial scale applications is challenging due to their limited processability. Enabling the processing of CNF in large batches and preferably using conventional machinery with minimal upgrades requires understanding about the behaviour of CNF hydrogels in flow fields. While several studies analyse CNF under shear flow,[6-8] only few reports concern CNF in extensional flow field,[9,10] even though several industrial processes involve both types of flow.

Herein, we examine the rheology of CNF in both shear and extensional flow fields and connect the results to CNF processability. For this purpose, we employ wet-spinning as an example of a conventional industrial process that can be applied on CNF, as reviewed earlier.[11,12] In addition to a platform for studying the flow of CNF in a practical setting, wet-spinning also serves as a route to obtain a solid filament consisting of CNF with preferred alignment along the filament axis. The resulting dry and structurally optimised filament could act as a practical form to transport CNF and expose it to further processing, such as filament winding or impregnation to create composite structures.

EXPERIMENTAL

CNF was prepared from unmodified bleached birch fibres and spun into filaments as described in our previous report.[13] This report already established the range of solids contents (from 1-2% up to 7-10%) that allows for spinning of > 5 cm long filaments from unmodified CNF in the studied system. In order to study more closely the lower limit, CNF hydrogels were prepared with solids contents of both 1% and 2% in deionised water.

Apparent and complex viscosities as well as storage and loss moduli were measured for the CNF hydrogels under shear with MCR 300 rheometer (Anton Paar, Austria). Serrated plate-plate geometry (diameter 25 mm) was used with a gap of 1 mm. Extensional viscosity was measured for both hydrogels via hyperbolic contraction flow (HCF).[9,14,15] The hydrogel was pressed through a channel contracting from a diameter of 20 mm to 1.56 mm over a distance of 15 mm in a hyperbolic shape. The extensional viscosity calculated based on the monitoring of the pressing force, as described earlier.[9,14,15] For the more diluted hydrogel (solids content 1%), extensional viscosity was also measured with HAAKE capillary break-up extensional rheometer (CaBER, Thermo Scientific, USA). The hydrogel was stretched between plates with a diameter of 6 mm from an initial separation of 1.99 mm up to a final separation of 8.98 mm. The thinning of the capillary formed by the sample between the plates was monitored and extensional viscosity calculated as explained previously.[16] All rheological measurements were performed at room temperature.

RESULTS AND DISCUSSION

Fig. 1a shows a Cox-Merz plot acquired with shear rheometry for CNF hydrogels with solids contents of 1% and 2%. Clearly, at both solids contents, CNF hydrogel has an approximately ten times higher complex viscosity than apparent viscosity under steady shear, if shear rate equates with angular frequency. This signifies a deviation from Cox-Merz rule, which would predict similar values for apparent and complex viscosity at similar values of shear rate and angular frequency.

Fig. 1b displays the storage modulus (G') and loss modulus (G'') as a function of angular frequency for each hydrogel. At both solids contents, CNF hydrogel has a damping factor (G''/G') of approximately 0.17. This denotes that both hydrogels have dominantly elastic (solid-like) behaviour at the studied range of angular frequency.

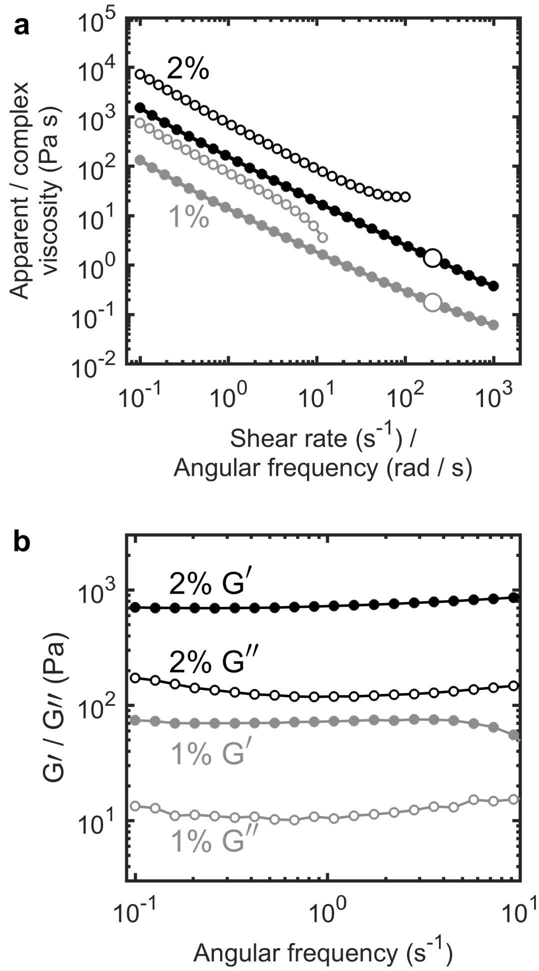

Figure 1. a) Apparent viscosity as a function of shear rate (filled symbols) and complex viscosity as a function of angular frequency (empty symbols) for CNF hydrogels with solids contents 2% (black) and 1% (grey). Enlargened symbols signify the approximate shear rate applied in the studied spinning system. b) Storage and loss moduli as a function of angular frequency for both CNF hydrogels.

Both the deviation from Cox-Merz rule and persistently dominant elastic behaviour represent characteristics that distinguish a CNF hydrogel from a typical polymer solution that wet-spinning processes are conventionally applied to. Possibly, the exceptional flow characteristics cause the limitations observed for CNF hydrogels in spinning experiments: even using the more spinnable solids content of 2% results in limited filament length between 5-20 cm. With a solids content of 1%, only filament sections shorter than 5 cm can be spun. Moreover, neither hydrogel allows for drawing during the spinning.

When raising CNF solids content from 1% to 2%, the clearest rheological change appears to be an elevation in shear viscosity (Fig. 1a), storage and loss moduli (Fig. 1b) as well as extensional viscosity (Fig. 2). Apparent shear viscosity was even measured at the same shear rate applied in the studied spinning system (Fig. 1a, enlarged symbols). These results show that the increase of the apparent viscosity from 0.2 to 1.4 Pa s correlated with improved spinnability at an approximate shear rate of 200 s^{-1}. In the case of storage and loss moduli (Fig. 1b) and extensional viscosity (Fig. 2), general increase in the level can be associated with the possibility to spin longer filament sections. For example, when CNF solids content is augmented from 1% to 2%, spinnability increases as described above, while storage modulus increases from almost 100 to almost 1000 Pa and loss modulus from about 10 to more than 100 Pa at the studied angular frequencies.

The extensional viscosity measurements with HCF and CaBER (Fig. 2, filled and empty symbols, respectively) both display a similar extension-thinning trend. Note that the results obtained via CaBER appear significantly lower than expected based on extrapolation of the HCF results. Moreover, CaBER covered only a narrow range of high extension rates. This is due to the extremely fast break-up of the capillary formed by CNF hydrogel in the beginning of a CaBER experiment. HCF can, therefore, be considered as a more reliable technique for CNF extensional rheometry, especially when simulating wet-spinning. Essentially, HCF channel mimics the conditions inside a wet-spinning nozzle more closely than the CaBER experiment, which relies on the sample forming a capillary in air.

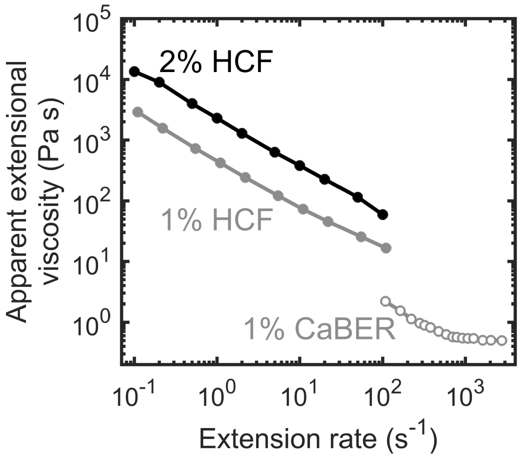

Figure 2. Apparent extensional viscosity of CNF hydrogels with solids contents 2% (black) and 1% (grey) measured with HCF (filled symbols) and, for the more diluted hydrogel, also with CaBER (empty symbols).

Comparing the HCF results for CNF (solids content 1%) to those reported earlier for microfibrillated cellulose (solids content 0.95%), a close to similar extensional viscosity in the order of thousands of Pa s is observed at a low extension rate below 0.3 s^{-1}.[9] In contrast, when the extension rate increases above 0.3 s^{-1}, CNF extensional viscosity decreases more heavily than that of microfibrillated cellulose. Presumably, both fibril types align under extensional flow towards the flow direction. This restructuring facilitates further extension; *i.e.*, decreases the extensional viscosity. In the case of CNF, the higher fibril aspect ratio could cause the fibril alignment to have a more powerful impact on the hydrogel viscosity (*i.e.*, stronger shear-thinning).

CONCLUSIONS

Increasing the solids content of a CNF hydrogel from 1% to 2% was found to increase the length of filaments that could be wet-spun from the hydrogel. This enhanced spinnability correlated with elevated shear viscosity, storage modulus, loss modulus and extensional viscosity. Potentially, measurement of these rheological parameters could be used as predictors for the spinnability of a CNF hydrogel. Further work will be necessary to determine the relations between the parameters and spinnability in alternative systems as well.

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