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Shear and extensional rheology of aqueous suspensions of cellulose nanofibrils for biopolymer-assisted filament spinning

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Abbreviations: CNF, cellulose nanofibrils; CA, cellulose acetate; GG, guar gum; CaBER, capillary breakup extensional rheometry; HCF, hyperbolic contraction flow; SAOS; small amplitude oscillatory shear; LVR, linear viscoelastic region.

ABSTRACT

The shear and extensional rheology of aqueous suspensions of cellulose nanofibrils (CNF) were investigated under dynamic and steady flow fields. The results were compared to those for two biopolymer solutions, cellulose acetate, CA, and guar gum, GG. Wet-spinning experiments were conducted for each system and the outcome related to the respective rheological profile. The spinnability of the system correlated with strong Newtonian and viscous responses under shear as well as long breakup time in capillary breakup experiments. CA solution was the most spinnable, also displaying the strongest Newtonian liquid behavior and the longest capillary breakup time. In contrast, the most shear-thinning and elastic CNF suspension showed instant capillary breakup and was considerably less spinnable. This is due to the limited entanglement between the rigid cellulose fibrils. In order to enable continuous wet-spinning of CNF without filament breakup, GG and CA were used as carrier components in coaxial spinning. The shear and extensional rheology of the system is discussed considering both as supporting polymers.

KEYWORDS

Nanocellulose; cellulose nanofibrils; shear; extension; wet spinning; hydrogels

INTRODUCTION

The flow behavior of biopolymer solutions and colloidal suspensions influences heavily their processability into materials that reflect their intrinsic properties. Cellulose, as the most ubiquitous polymer in nature, forms structures in plants that make possible water conduction and nutrient storage while realizing a superb mechanical integrity. In plants, an assembly of several polymer chains forms the so-called elementary fibrils, in which cellulose is partly crystallized. From these

building blocks, a highly hierarchical and multidimensional system is generated, comprising microfibrils and macroscopic fibers. Following the opposite process, top-down deconstruction of the fiber cell walls yields cellulose nanofibrils (CNF) with lateral dimensions in the nanoscale and lengths that reach several micrometers.

The cellulose crystallites in CNF exhibit a remarkable axial strength, a property that has been exploited in the design of reinforced composites and other structures [1–4]. On one hand, though, CNF are difficult to disperse in nonpolar media [5] while, on the other hand, their aqueous suspensions gel at a relatively low concentration, displaying complex flow properties. The yield stress and shear-thinning behavior of CNF hydrogels are suitable for formulation of foodstuffs, cosmetics, paints and the like. However, the same flow properties that make these systems attractive pose challenges when processing CNF into solid materials, for example, by filament spinning and 3D printing.

CNF rheology has been extensively studied under shear flow, as reviewed previously [6,7]. Aqueous suspensions of CNF form gels with a storage modulus (G') that is an order of magnitude higher than the loss modulus (G'') [8–15]. Typically, G' scales exponentially with CNF concentration (exponent between 2-5), as seen in the experimental values shown in Figure S1a and the respective scaling exponential factors in Table S1, Supporting Information. The flow profile, as defined by the Ostwald-de Waele power law (Equation 1), also shows scaling behavior with concentration for the consistency index K (see Figure S1b and Table S1, Supporting Information):

$$\eta = K\dot{\gamma}^{n-1}, \quad (1)$$

where η is apparent viscosity, $\dot{\gamma}$ is shear rate and K and n are the consistency and flow behavior indices, respectively. CNF suspensions exhibit strong shear-thinning, with a typically small n , between 0.1-0.3 [16–18], which increases with the CNF surface charge at concentrations

~ 0.7 wt.% or below [19,20]. K tends to grow exponentially with concentration (exponent ~ 3), similarly to G' , reflecting the increased fibrillar crowding as the solid fraction increases. The development of K and G' with CNF concentration is discussed in more detail in the Supporting Information.

Compared to the apparent steady-shear viscosity, the complex viscosity measured under small amplitude oscillatory shear (SAOS) has been shown to be an order of magnitude higher when the shear rate (s^{-1}) and angular frequency (rad/s) are equated [9,16]. This implies a deviation from the Cox-Merz rule, which predicts equal viscosity measured under both steady and oscillatory conditions [21]. This deviation has been explained by the formation of a water-rich and fibril-depleted boundary layer in the vicinity of the walls of the given measuring unit, which causes a lowering of the apparent viscosity recorded under steady shear [16].

Wall depletion effects have been shown to be especially relevant for CNF under conditions of low surface charge [22], large fibril diameter [17], low shear rate [23], small geometry gap and high ionic strength [24]. The fibril-depleted layer thickens with increasing flow velocity [25] and dilution [26]. During SAOS, wall depletion is not expected to occur, making the complex viscosity data to reflect more realistically the structural changes in the bulk of the CNF suspension. In contrast, CNF suspensions are often exposed to steady flows during processing through confined spaces, such as tubing, slits and dies, where wall depletion most probably occurs, as is the case of the steady flow conditions in a rheometer. As such, steady shear rheometry may reflect better the behavior of CNF for practical uses.

Several authors have studied the structure of CNF under shear through various imaging approaches [18,23–25,27–30]. Complex flow properties have been described, such as shear-

induced flocculation [18,24,27], wall-slip and shear banding [15,25,30]. Herein, we expand the analysis of CNF shear flow in the colloidal scale by using polarized imaging.

In addition to shear, CNF can be subjected to extensional flow fields during processes like extrusion, coating, spinning, drawing or swallowing. To our knowledge, despite its practical importance, extensional rheology of CNF has only been studied by Moberg et al. [20], who concluded that the apparent extensional viscosity decreased with increasing extension rate and CNF dilution, similarly to the apparent shear viscosity. A plateau in extensional viscosity at high extension rates was speculated but not enough data were acquired for confirmation. More importantly, the suspensions used by Moberg et al. were rather diluted (< 1 wt.%), limiting any conclusion relevant to filament spinning, which requires higher concentrations. This is one of our considerations in the discussion presented here. In addition, we note the work of Dimic-Misic et al., who examined via capillary breakup the extensional rheology for mixtures of CNF, carboxymethyl cellulose and pigment particles [31]. The capillary breakup was found to accelerate in the presence of CNF, which blocked the bridging flocculation induced by carboxymethyl cellulose on the pigment particles.

In this study, we characterized CNF suspensions under shear and extensional flow, in both dynamic and steady conditions and correlate the extensional viscosity with the extension rate and the suspension concentration. Firstly, shear rheological characterization was performed under dynamic conditions by applying SAOS (Figure 1a). Secondly, steady shear was applied in order to obtain the apparent viscosity under steady conditions (Figure 1b). Thirdly, extensional rheology was studied via “capillary breakup extensional rheometry” (CaBER, Figure 1c), which was used as a dynamic method to access the extensional rheology (though, with no control of the extension rate). Instead of a controlled sinusoidal pattern (as applies to SAOS), the variation of the extension

rate in the case of CaBER was taken to follow the dynamics of the capillary breakup process. Finally, the apparent extensional viscosity was measured under steady extension conditions via hyperbolic contraction flow (HCF, Figure 1d).

Figure 1. Schematic illustration of the rheological characterization methods used in this study: (a) small amplitude oscillatory shear (SAOS); (b) steady shear; (c) capillary breakup extensional rheometry (CaBER) and (d) hyperbolic contraction flow (HCF). (e) Photograph of continuous core-shell wet-spinning of CNF and CA with CNF colored purple.

Importantly, the results of our work were factored to understand CNF wet-spinning, a process that is effective in aligning the nanofibrils extruded through a narrow nozzle into an anti-solvent that coagulates them into a filament which may be subjected to drawing. Unfortunately, so far, this process has been challenging for high throughput operation and optimization [32,33]. In particular, the CNF filaments in the wet state suffer from frequent breakage, preventing continuous

spinnability. To overcome this limitation, careful control of the rheology of the CNF suspension is required, considering both the shear and extensional flows present during wet-spinning.

In the course of our work on CNF spinning, it was found that the use of a carrier polymer, in a coaxial configuration, made possible the formation of continuous filaments [34]. We found that cellulose acetate (CA) and guar gum (GG) were effective for this purpose, while allowing control of filament properties by their inherent differences in hydrophilicity and solvency. Therefore, here we compare the rheology of aqueous suspensions of CNF with that of aqueous solutions of GG as well as organic solutions of CA (degree of substitution, DS ~2.5). While GG solutions form only weak filaments on their own, they are effective as CNF carrier or supporting solution during spinning [34]. Spinning exposes the semiflexible random coil conformation of water-dissolved GG [35] to a combination of shear and extensional flows, like CNF. Previously, the extensional rheology of GG systems has been considered in filament stretching and breakup [36,37]. Unfortunately, under these conditions, the extensional flow field is unsteady, introducing uncertainties in determination of the apparent extensional viscosity. We propose HCF to arrive close to a steady state in extensional flow at low strain rates and to reveal, together with CaBER at high rates, the behavior of GG solutions relevant to coaxial spinning.

In contrast to GG, CA is suitable for wet-spinning from an organic solvent, such as acetone, under the right solution conditions [38], and it has been used to enhance nanocellulose spinnability when mixed in the formulation [39–41]. The shear rheology of both CA solutions [41–44] and its blends with other components [45] have been reported. As such, we discuss the key rheological aspects that facilitate spinnability of CA solutions compared to the more challenging CNF suspensions.

Finally, we capitalize on the rheological characteristics of CNF, CA and GG by employing them in coaxial spinning toward a core-shell configuration (see Supplementary Video). Owing to the supporting effect of the shell material (GG or CA), this approach allowed continuous wet-spinning and drawing of CNF. For this purpose, we selected concentrations of GG and CA as low as possible (1 wt.% and 15 wt.%, respectively) but concentrated enough to enable continuous core-shell spinning. Given the distinctive solubility of each carrier polymer (water and acetone, respectively), they required the use of different anti-solvents. For instance, organic solvents, such as acetone, were suitable anti-solvents for CNF and GG, whereas water was used for CA. The effect of the anti-solvent selection is discussed more in depth in an accompanying report [34].

MATERIALS AND METHODS

Materials. Bleached hardwood kraft fibers were supplied by Metsä Fibre's mill at Äänekoski, Finland. The fibers were refined and fluidized for six passes through a high-pressure microfluidizer (Microfluidics M110P, US) at a concentration of 2 wt.% or 1.5 wt.% in deionized water. In addition, a sample with a concentration of 1 wt.% was prepared by dilution of the 2 wt.% suspension. Also, a batch of the refined fibers was TEMPO-oxidized up to a carboxylate content of 0.6 mmol/g before fluidization for one pass. The preparation of both types of CNF (CNF and TEMPO-oxidized CNF) is described in more detail in a previous report [9].

Cellulose acetate (CA) with DS ~2.5 and an average M_n of 30000 was purchased from Sigma Aldrich and used as a 15 wt.% solution in acetone (Sigma Aldrich). Guar gum (GG) has a typical molecular weight in the range of 1-3 millions [36,46–48] and comprises galactose residues substituted on a linear mannan backbone with a mannose-galactose ratio of 1.6-1.8 [49]. It was obtained from Sigma Aldrich and used as a 1 wt.% solution in deionized water. Before use, the GG solution was stirred at high speed and long enough for the sample to foam and warm up to

approximately 40 °C (10-20 min). After this, the solution was mixed in vacuum for 10 min to reduce the amount of air bubbles. The GG solution was used within one day following this procedure.

Density and surface tension. The density and surface tension of the samples were determined for later use in the extensional viscosity (CaBER) study. For CNF, the surface tension was measured at a concentration of 1 wt.% (the concentration used in CaBER). A density of 1000 kg/m³ was assumed for CNF and GG dispersions. The density of CA solution (830 kg/m³) was measured by weighing 10 ml of the solution. The surface tensions of the fluids were determined by the pendant drop method, using a CAM optical contact angle and surface tension meter (KSV Instruments, Finland). A drop of each sample was suspended in air and imaged at room temperature and at a relative humidity of 63%. The images were used to compute the surface tension with CAM2008 software. Five test repetitions were performed for each sample.

Shear rheometry. The shear rheological behavior of CNF, GG and CA dispersions was analyzed with an MCR 300 stress-controlled rheometer (Anton Paar, Austria), using bob-cup geometry (bob diameter 27 mm, smooth surfaces) with a gap of 1 mm at a temperature of 23 °C. A schematic illustration of the setup is presented in Figure 1a, b. The cup was covered with a lid to prevent the evaporation of the solvent. Firstly, the linear viscoelastic region was identified by amplitude sweeps at an angular frequency of 10 rad/s. After a hold period of five minutes, the mechanical spectrum was obtained via SAOS, at angular frequencies ranging from 100 to 0.04 rad/s with a strain amplitude of 0.1% (within the linear viscoelastic region for all the samples). After this, the samples were held for five minutes prior to applying a steady shear sweep from 0.01 to 1000 s⁻¹ in order to monitor the apparent viscosity under steady shear. For CNF, each measurement was repeated separately, changing the specimen in between. Since the obtained data

remained similar with this procedure, it was concluded that one specimen was sufficient for conducting all the three experiments, provided that a waiting time of five minutes was allowed between each measurement.

The flow curves were fitted using Ostwald-de Waele power law (Equation 1). The parameters acquired from steady shear experiments were used to calculate the shear stress during HCF experiment, as explained below. In the case of SAOS experiments, η was replaced with complex viscosity and $\dot{\gamma}$ with angular frequency in Equation 1. In the case of GG, the data were fitted only at shear rates $> 1 \text{ s}^{-1}$, corresponding to the onset of shear thinning. For CNF and CA, the whole range of shear rates was considered, from 0.01 to 1000 s^{-1} . As discussed above, it should be noted that the data obtained for CNF was probably influenced by wall depletion effects, as described earlier [16,17,22,24–26,30].

For TEMPO-oxidized CNF, only a steady shear sweep was applied from 1 to 1000 s^{-1} at 23°C . This was performed with MCR 302 stress-controlled rheometer (Anton Paar, Austria), using parallel plate geometry with a gap of 1 mm, a smooth metallic top plate and a transparent bottom plate. The sample was illuminated with LED light, which passed first through a polarizer, then through the sample, again through the sample after reflection from the top plate and finally through an analyzer rotated at 90° with respect to the polarizer. The transmitted light was detected in order to visualize the birefringence in the sample under flow.

Capillary breakup extensional rheometry (CaBER). The apparent extensional viscosity of the samples was measured with a HAAKE capillary breakup extensional rheometer (Thermo Scientific, USA) operated at room temperature. The sample was loaded between plates with a diameter of 6 mm and initial separation of 1.99 mm (initial aspect ratio 0.66). The upper plate moved rapidly in the upward direction to reach a separation of 8.98 mm (final aspect ratio 2.99),

stretching the sample into a capillary (Figure 1c). The device monitored the diameter of the capillary being formed. For aqueous CNF and GG, one minute was allowed for the sample to relax after loading before the measurement. For CA, no relaxation time was applied in order to prevent excess evaporation of the solvent (acetone). However, in this case, the evaporation probably influenced the results during the CaBER experiment, nonetheless. Thus, the reported data should not be used for quantitative interpretation but rather for qualitative comparison with the other samples.

For each sample, CaBER measurement was repeated at least five times and a representative dataset selected for analysis. The extent of gravitational effects on the CaBER results can be estimated by calculating the Bond number, Bo , as a function of the capillary diameter, r_{cap} [50]:

$$Bo(t) = \frac{\rho g r_{cap}^2(t)}{\Gamma}, \quad (2)$$

where ρ is density, g is the gravitational acceleration, and Γ is the surface tension. Gravitational effects can be considered negligible for $Bo < 0.2$ [50].

Assuming an axially symmetrical fluid capillary, Hencky strain ε (i.e., true extensional strain) in the capillary can be calculated by

$$\varepsilon = \int_{L_0}^{L_{cap}} \frac{dL}{L} = \ln \frac{L_{cap}}{L_0} = 2 \ln \frac{r_0}{r_{cap}}, \quad (3)$$

where L_0 and r_0 are the capillary length and radius in the beginning of the thinning, respectively. L_{cap} is the hypothetical length of the capillary during thinning, assuming constant capillary volume. Thus, L_{cap} and r_{cap}^2 are inversely proportional. In reality, though, the capillary length remains constant and the sample volume drains into the reservoirs attached to each CaBER plate (Figure 1c). The CaBER extension rate $\dot{\varepsilon}_{CaBER}$ in the fluid is determined as the time derivative of the Hencky strain [50]

$$\dot{\epsilon}_{CaBER} = -\frac{2}{r_{cap}} \frac{dr_{cap}}{dt}. \quad (4)$$

The obtained data for CaBER extension rate was used to identify the development of the CaBER apparent extensional viscosity η_{CaBER} , henceforth referred to as CaBER viscosity. This was calculated based on a force balance between the stress created by capillary forces Γ / r_{cap} and the corresponding viscous stress in the material ($\eta_{CaBER} \dot{\epsilon}_{CaBER}$) [50]

$$\eta_{CaBER} = \frac{\Gamma}{r_{cap} \dot{\epsilon}_{CaBER}}. \quad (5)$$

The data for capillary diameter and CaBER extension rate were smoothed using locally weighted linear regression for CA and GG and moving average of five points for CNF. The different smoothing methods were necessary because of the different number of data points collected due to the significantly faster CNF capillary breakup compared to those for CA and GG. The extension-thinning sections observed in the curves for the CaBER viscosity as a function of CaBER extension rate were fitted using Ostwald-de Waele power law (Equation 1, replacing η with η_{CaBER} and $\dot{\gamma}$ with $\dot{\epsilon}_{CaBER}$).

Hyperbolic contraction flow (HCF). In addition to CaBER, apparent extensional viscosities of the samples were measured via HCF [51,52]. In contrast to CaBER, where extension rate changes along with the capillary diameter, HCF exposes the fluid to an assumedly constant extension rate, allowing the flow to achieve a nearly steady state. It should be noted, though, that fully steady flow may not be attained even in HCF, due to the influence of the wall depletion effects [16,17,22,24–26,30] and thixotropy [6,10,12,18,19,22] of CNF suspensions.

To conduct the experiment, the sample was loaded in a cylinder with a diameter of 20 mm (Figure 1d). The cylinder ended in a die contracting from 20 mm to 1.56 mm over a distance of 15 mm in a hyperbolic shape. The pressure drop was measured over the die at varying speeds of

the piston (corresponding to varying flow rate). Before recording the pressure drop, the reading was allowed to stabilize. Each data point was repeated three times and their average reported.

During the extrusion through the hyperbolic die, the shear stress σ_{shear} is expressed as [51,52]

$$\sigma_{shear} = \frac{4H \left(3 + \frac{1}{n}\right)^n \left(\frac{K}{\pi}\right)^n Q^n \left(\frac{1}{R_0^{3n+1}}\right) \left(\left(\frac{R_0^2}{R_1^2}\right)^{\frac{3n+3}{2}} - 1\right)}{(3n+3) \left(\frac{R_0^2}{R_1^2} - 1\right)}, \quad (6)$$

where R_0 , R_1 and H are initial radius, end radius and length of the hyperbolic die, respectively, and Q is the volumetric flow rate. The pressure drop contribution caused by extensional stress σ_{ext} is

$$\sigma_{ext} = \Delta P_{meas} - \sigma_{shear}, \quad (7)$$

where ΔP_{meas} is the measured pressure drop. HCF apparent extensional viscosity (hereafter: HCF viscosity) can be calculated from extensional stress (Equation 7) and HCF extension rate. For a power law fluid flowing in a die with a hyperbolic shape, HCF extension rate $\dot{\epsilon}_{HCF}$ is [52]

$$\dot{\epsilon}_{HCF} = \frac{3n+1}{n+1} \frac{Q}{\pi} \frac{R_1^{-2} - R_0^{-2}}{H}. \quad (8)$$

Combination of Equations 7 and 8 provides the HCF viscosity η_{HCF}

$$\eta_{HCF} = \frac{\sigma_{ext}}{\dot{\epsilon}_{HCF}}, \quad (9)$$

The obtained curves for the HCF viscosity as a function of HCF extension rate were fitted using Ostwald-de Waele power law (Equation 1, replacing η with η_{HCF} and $\dot{\gamma}$ with $\dot{\epsilon}_{HCF}$).

Theoretical extensional viscosity. For Newtonian fluids, the extensional viscosity can be calculated by assuming a Trouton ratio of three [53]. As such, the theoretical extensional viscosity η_{theory} was obtained based on apparent shear viscosity η_{shear}

$$\eta_{theory} = 3\eta_{shear}. \quad (10)$$

Wet-spinning. The suitability of the samples for wet-spinning was compared by extrusion, at a constant rate, into an anti-solvent: either acetone (for CNF and GG) or water (for CA). Firstly, single-component filaments were produced from each precursor. In the case of CNF and GG, the system was allowed to coagulate in the anti-solvent bath for approximately five minutes. The CNF suspension underwent frequent breakup and the filaments spun thereof were collected as segments that were dried by fixing both of their ends. In the case of GG, a continuous filament was collected and dried on a winder. CA filament coagulated fast enough for immediate collection on the drying winder after proceeding 26 cm in the bath. Secondly, core-shell filaments were spun by extruding simultaneously two components through a coaxial needle. CNF was extruded through the inner section (core) and either GG or CA were used as the outer component (shell). Notably, both types of combinations could be spun continuously. Herein, the bicomponent filaments are labelled with names that include first the core and then the shell component; e.g., CNF-CA refers to CNF core with a CA shell. In the case of CNF-CA filaments, the CNF concentration was 1 wt.% and water was used as anti-solvent (coagulation). In the case of CNF-GG filaments, the CNF concentration was 1.5 wt.% and acetone was used for coagulation. The spinning conditions are summarized in the Supporting Information (Tables S2 and S3) and a video of the core-shell wet-spinning process is included in the Supplementary Material.

RESULTS AND DISCUSSION

Rigid colloids form stiffer and more brittle networks than flexible polymers. The storage and loss moduli (G' and G'') for CNF at given concentrations were measured under SAOS (Figure 2a). The G' values were similar to those reported previously for CNF (Figure S1a, Supporting

Information). G' at an angular frequency of 6.28 rad/s (frequency 1 s⁻¹) scaled with concentration C following a power law:

$$G' = 69C^{4.6} \quad (11)$$

The power law exponent of 4.6 is at the higher end of the range of published values; however, note that our value was obtained from a limited range of concentrations (three levels). Similar exponents for G' have been reported by Jowkarderis et al. [54] and can be calculated based on the data by Nechyporchuk et al. [15] and Li et al. [55]. However, other authors have observed a weaker sensitivity of G' to CNF concentration (Table S1, Supporting Information).

The CNF formed viscoelastic hydrogels with a predominantly elastic behavior at all the concentrations and angular frequencies tested, with $G' > G''$; i.e., loss tangent $\tan \delta (= G''/G')$ lower than unity (~ 0.12) (Figure 2b). Values similar [12,27,56] or higher [8,57] have been reported elsewhere. Also, an increase in loss tangent up to 0.24 has been indicated at concentrations < 1 wt.% (below our conditions) owing to a stronger viscous response in diluted conditions [8].

Figure 2. (a) Storage and loss moduli G' and G'' (filled and empty symbols, respectively) as a function of angular frequency ω for CNF at varying concentration. (b) Loss tangent $\tan \delta = G''/G'$ as a function of ω for CNF and GG. Note the overlap of CNF profiles at different concentrations (blue triangle down – 1%; purple square – 1.5%; dark grey triangle up – 2%). (c) G' and G'' as a function of ω for GG and CA. G' of CA was too low for reliable measurement. (d) Schematic illustration of CNF and GG in aqueous and CA in organic medium, not drawn to scale.

While CNF and GG are entirely different systems (colloidal fibril suspension versus solution), it is worth exploring their rheology in light of their intended use in coaxial spinning. For the GG solution, viscous behavior prevailed at angular frequencies < 6 rad/s, while the elastic contribution became dominant at higher frequencies (Figure 2b, c, green spheres). The crossover point for G' and G'' was similar to that reported before [36]. This transition highlights the profoundly different rheological nature of GG compared to that of CNF, the latter of which lacks a regime with predominant viscous behavior, mostly owing to the stiffness of the colloidal fibrils illustrated in Figure 2d.

Distinctively, the CA solution displayed a strongly viscous behavior: G' was too low for accurate measurement (Figure 2c), making irrelevant the calculation of the loss tangent (Figure 2b). Noting that CA and GG are linear polymers, this behavior originates from the low molecular weight of CA compared that of GG. In solution, the long GG chains entangle, which enhances the elastic response at high angular frequencies. The short CA chains exist as rather distinct coils with minimal interaction with each other. Figure 2d provides a schematic illustration of the macromolecules in relation to the colloidal cellulose fibrils.

The colloidal cellulose nanofibrils (CNF) are significantly more rigid than GG or CA, which exist in solution as individual polymer chains that tend to coil, depending on the solvency, electrolyte concentration and temperature (Figure 2d). The implications of their distinctive differences are highlighted in an oscillatory strain sweep (Figure S2, Supporting Information). For CNF, the linear viscoelastic region (LVR, i.e., G' and G'' independent of strain amplitude) ends at a critical strain amplitude of $\sim 0.2\%$, in agreement with previous observations [22,30,57,58]. For TEMPO-oxidized or carboxymethylated CNF, the LVR region is typically wider than for the less charged CNF, with a critical strain close to 1% [15,30,56] or even 10% [59]. Curiously, when freed

from residual hemicelluloses and lignin, CNF has an exceptionally wide LVR (critical strain > 10%) combined with a relatively lower G' (Figure S1a, Supporting Information) [14].

Here, the critical strain (~0.2%) of the CNF hydrogels is two decades lower than that for dissolved GG (~20%, Figure S2, Supporting Information). Before reaching the critical strain, CNF suspensions have higher G' than the GG solution (Table 1). For CA, the LVR spans over the whole range of strain amplitudes, given its extremely low storage modulus. This implies the absence of network structuring that otherwise would break under shear. These observations highlight the role of the high rigidity of the cellulose fibrils in contrast to the dissolved GG and CA polymers (Figure 2d). As the fibrils are unlikely to coil, they are subjected to volume exclusion effects and formation of nodes, thus establishing a volume-spanning network with a high G' . However, as these node-like contacts are weaker than entanglements found between the more flexible polymers, the network is easily disturbed by deformation.

The recorded critical strains correspond to critical stresses presented in Table 1 along with the G' at LVR. In the case of CNF, the critical stress provides an estimation of the yield stress [59]. The critical stresses determined for CNF are similar [12] or lower [16,17,25,26,54,59] than the yield stresses measured previously for CNF suspensions. Notably, the measured yield stress depends heavily not only on the type of CNF but also on the detailed experimental conditions. Nevertheless, the results highlight the increase of the CNF network strength with concentration, similarly to the network stiffness measured by G' (Figure 2a). Markedly, the critical stress of CNF remains below that of GG, implying that a dissolved polymer system has more ductility than a network of rigid fibrils, even though not reaching as high G' values.

A related effect has been discovered earlier when comparing rigid and flexible nanofibrils prepared from whey protein isolate [60]. The rigid fibrils, akin to CNF, have a higher storage

modulus that collapses at a smaller strain, while the flexible ones form an entangled structure, like GG, with a lower but more sustained storage modulus [60]. The “brittleness” of the CNF structure can be beneficial in applications requiring a fluid not only to form a structure but also to flow easily, such as in extrusion/injection systems.

Table 1. G' at LVR, critical stress, power law parameters K and n (Equation 1) as well as surface tension Γ of the different systems studied.

Sample	G' (Pa) at LVR ^a	Critical stress (Pa)	K (Pa s ⁿ)	n	Γ (mN/m) ^b
CNF 1%	61	0.1	6.0 ^c or 4.4 ^d	0.19 ^c or 0.30 ^d	34.2 ± 3.9
CNF 1.5%	320	0.6	26.5 ^c or 22.5 ^d	0.19 ^c or 0.25 ^d	n.a. ^e
CNF 2%	610	1.2	56.5 ^c or 52.5 ^d	0.21 ^c or 0.24 ^d	n.a. ^e
GG	16	3	7.8 ^f	0.3 ^f	60.0 ± 0.3
CA	n.a. ^e	n.a. ^e	1.0 ^c	1.0 ^c	24.0 ± 1.4

^aLinear viscoelastic region, angular frequency 10 rad/s, strain amplitude 0.1%, values based on oscillatory strain sweep (Figure S2, Supporting Information)

^bError margins defined as the standard deviation divided by the square root of the sample size (5 specimens)

^cDetermined at 0.01-1000 s⁻¹ shear rate (full range)

^dDetermined at 18.9-1000 s⁻¹ shear rate (true shear-thinning range)

^eNot reported since CaBER measurement was not possible

^f K and n determined at 1-1000 s⁻¹ shear rate (shear-thinning regime)

^gNot measured because G' too low for sufficient resolution

Wall depletion and restructuring cause apparent shear-thinning. The behavior of CNF under steady flow is shown with the apparent viscosity η plotted against shear rate (Figure 3a,

filled symbols). Over the whole range studied and for all the tested concentrations, CNF appeared shear-thinning. Interestingly, stronger shear-thinning seemed to occur at shear rates $< 1 \text{ s}^{-1}$. In this regime, even the shear stress declined with shear rate (Figure S4, Supporting Information), which is associated with shear banding [61,62]. This phenomenon has been also shown experimentally for CNF [18,30]. In addition, wall depletion has been shown to dominate over bulk restructuring of CNF suspensions under low shear rates [23]. Therefore, the strong shear-thinning behavior mostly originates from shear banding and wall depletion rather than the reorganization of the fibrils in the suspension. Essentially, at shear rates $< 1 \text{ s}^{-1}$, CNF undergoes plug flow and the measured apparent viscosity describes the friction between the plug and the wall instead of actual viscosity of the hydrogel.

In order to experimentally confirm the plug flow at low shear and structuring of CNF at high shear, CNF suspensions were monitored *in-situ* between crossed polarizers (Figure 3c). Colored areas are indicative of a birefringent structure that is oriented at an angle with respect to the crossed polarizers. CNF may be birefringent (i.e., turn the polarization direction of light) when the fibrils are in unidirectional alignment. For example, at a shear rate of 1000 s^{-1} , when fibrils are oriented tangentially with respect to the system geometry, a Maltese cross pattern is observed: areas where fibrils align parallel to either polarizer appear dark and areas where fibrils align at a 45° angle appear bright. In our experiments, we used translucent hydrogels of TEMPO-oxidized CNF, which facilitated the imaging.

Figure 3. Cox-Merz plots (apparent viscosity as a function of shear rate with complex viscosity as a function of angular frequency) for (a) CNF with varying concentration (blue triangle down: 1 wt.%, purple square: 1.5 wt.%, dark grey triangle up: 2 wt.%) as well as (b) CA and GG. The

filled symbols correspond to the apparent viscosity η and the open ones indicate the complex viscosity $|\eta^*|$. (c) Flow curve of TEMPO-oxidized CNF with associated images observed between crossed polarizers (directions indicated by arrows).

At rest or under low shear, CNF appeared randomly oriented, with local birefringent areas (Figure 3c). These might be macroscopic CNF agglomerates with an internally aligned arrangement. At a shear rate of 48 s^{-1} , the birefringent areas became larger, though remaining still in a mutually nearly random orientation (no clear Maltese cross was observed). It is possible that shear induces an increase in floc size and broadening of their size distribution, as observed earlier through imaging at shear rates of $\sim 10 \text{ s}^{-1}$ [18,27] and $\sim 5 \text{ s}^{-1}$ [24].

As the shear rate approached 100 s^{-1} , the cellulose nanofibrils started to orient along the shear direction (Figure 3c). Firstly, a cross pattern started to emerge close to the periphery of the plate, where the shear first reaches the critical level required for restructuring the CNF in the bulk suspension [23]. As the shear sweep proceeded, the whole sample became sheared enough to show birefringence (Figure 3c). Similar development could be seen at both concentrations (1 and 2 wt.%), though the more concentrated hydrogel produced a more intensive signal.

Our results are in line with the observations of Saarinen et al. [23] who indicated a decrease in floc size above the yield stress of a CNF suspension ($\sim 20 \text{ Pa}$). Despite the differences in suspension type and measurement geometry, tangential alignment occurred at a nearly similar shear stress according to polarized imaging ($\sim 40 \text{ Pa}$, Figure 3c). The apparent shear-thinning at shear rates $< 40 \text{ Pa}$ is, therefore, mostly produced by wall depletion rather than CNF restructuring.

In the case of GG, similarly to the SAOS results discussed above, a transition ensued from a Newtonian plateau at shear rates $< 1 \text{ s}^{-1}$ to shear-thinning regime at higher rates (Figure 3b, green

spheres), as reported earlier [36]. After the onset of the shear-thinning, though, GG followed a similar pattern as that of CNF at the same concentration: apparent viscosity decreased from ~ 1 Pa s to ~ 0.1 Pa s while shear rate accelerated from 1 to 1000 s^{-1} . Conversely, CA exhibited a rheological behavior close to that of a Newtonian fluid with a constant apparent viscosity of ~ 1 Pa s, over the whole shear rate range considered (Figure 3b, red diamonds). This is in part due to the lack of interactions between the low molecular weight CA chains. CA with similar degree of substitution but slightly higher molecular weight undergoes shear-thinning at concentrations > 25 wt.% [41]. Power law parameters (Table 1) were calculated based on Ostwald-de Waele power law fit of the steady shear data for each sample (Figure S3, Supporting Information).

As the apparent viscosity measured for CNF is unreliable due to the effects of wall depletion at low shear rates, the fitting was also performed for CNF using only the data at shear rates $> 18\text{ s}^{-1}$. The sensitivity of the parameters in the selected range increased with decreasing CNF concentration. At 1 wt.%, n was 55% and K 27% lower when the high shear rates were fitted to the power law rather than whole measured range. This discrepancy highlights the critical influence of wall depletion and shear banding on the flow behavior of CNF hydrogels and emphasizes the need to exert caution when interpreting related rheological data.

From the oscillatory shear data, the complex viscosity $|\eta^*|$ was plotted together with the apparent viscosity η under steady shear (Figure 3a, b). The complex viscosity of CNF remained a decade higher than the apparent viscosity at all shear rates or angular frequencies measured (Figure 3a). This agrees with earlier findings about CNF complex viscosity that deviates from the apparent viscosity under steady shear, by an order of magnitude [9,16]. The low apparent viscosity is likely a consequence of the shear-induced migration of the fibrils from the walls towards the center of the testing geometry, leaving behind a water-rich, low-viscosity boundary layer [16]. Moreover,

the steady shear flow curves of CNF include a plateau between 1 and 10 s⁻¹, which is not observed in the complex viscosity curve. This plateau has been explained by shear-induced structural changes in the CNF network [10,12,58]. Indeed, increased floc size and broadened floc size distribution have been indicated in the plateau regime [27,63]. Apparently, wall depletion and floc clustering effects occur only under steady shear and not upon SAOS performed within the linear viscoelastic region.

The deviation between steady shear and complex viscosities has been observed for GG, too, though only at high shear rates and angular frequencies [36]. According to Figure 3b, the apparent and complex viscosity of GG overlapped throughout the measured range of angular frequency. This signifies that GG follows the Cox-Merz rule [21], typical of polymers without significant long-range interactions [64]. In the case of CA, the complex viscosity was slightly higher than the apparent steady shear viscosity (Figure 3b). This implies that CA undergoes a given change in solution structure under steady shear but not under oscillation within the LVR. Possibly, this relates to the molecular associations in CA solutions [65] enabled by hydrogen bonding between the unsubstituted hydroxyl groups [66]. Hypothetically, SAOS allows for the presence of more associations and thus somewhat higher viscosity.

Long relaxation time inhibits restructuring under fast extension. The development of the fluid capillary with time in a CaBER experiment with CNF (concentration 1 wt.%), GG and CA is shown in Figure 4a, b. The capillary diameter of CNF decreased extremely fast compared to the other samples. In fact, the capillary broke up too fast to allow detection for the concentrated CNF hydrogels. This can be beneficial in fluid products that are poured or extruded through air. Often, easy breakup of the fluid stream is desired in the end of the process, without the formation of a

lingering fluid capillary. Figure 4c displays the visual differences in capillary formation while pouring the tested fluids.

Figure 4. (a) Fluid capillary diameter r_{cap} as a function of time during the CaBER experiment. (b) Normalized capillary diameter against normalized time. Black symbols at large diameters for the GG sample correspond to unreliable data obtained with a bond number > 0.2 . (c) Photographs of CNF hydrogel (left), GG solution (middle) and CA solution (right) poured from a spoon.

The instant capillary breakup of the CNF hydrogel also possibly indicates that too short a time elapsed for a proper capillary to form and axial stresses to relax, after the separation of the CaBER plates. In this case, the data for CNF may be unreliable, as Equation 5 assumes that no axial stress

prevails in the capillary [67]. Moreover, the behavior of CNF is likely influenced by the pre-stretching conditions present during the opening of the plates before the onset of the capillary thinning, as observed earlier for fluids deviating from homogeneous polymer solutions [68]. As such, the CaBER results for CNF presented here should be taken only as an indication of the relative behavior, to highlight the difference in CNF extensional rheology compared to that of the dissolved polymer systems. For example, the plot of the normalized CNF capillary diameter as a function of normalized time (Figure 4b) has a distinct shape, suggesting a different mechanism of capillary breakup.

The GG capillary took almost 300 ms to break; i.e., more than double the time reported by Torres et al. for a 1 wt.% solution [36]. On the other hand, Bourbon et al. measured a breakup time as long as 1 s at a similar concentration [37]. Ostensibly, CaBER method is very sensitive to the specific properties of the GG solution, such as molecular weight, polydispersity, dissolution method and possible presence of impurities, among others. In the case of CA solution, the capillary breakup is expected to be critically influenced by evaporation of the acetone used as the solvent. Due to this uncertainty, only CNF and GG are included in the following analysis of extensional rheology. For reference, corresponding data obtained for CA is included in the Supporting Information (Figure S5, Table S5).

CaBER extension rate (Equation 4) and CaBER viscosity (Equation 5) are plotted as a function of time in Figure 5. In the plots, distinct extensional flow regimes are identified, as shown previously [50,69] (see data highlighted in dark colors). In the first regime, the data is unreliable because of gravitational effects. This regime (Figure 5b) is characterized by $Bo > 0.2$ (Equation 2). In the case of CNF, the capillary was thin enough for $Bo < 0.2$ (i.e., negligible gravitational effects occurring) throughout the whole thinning.

Figure 5. CaBER extension rate $\dot{\epsilon}_{\text{CaBER}}$ (grey, left axis) and CaBER viscosity η_{CaBER} (colored, right axis) as a function of time during CaBER experiment for (a) CNF and (b) GG. Dark colors and roman numerals highlight the detectable extensional flow regimes.

In the second regime, the diameter decreases approximately linearly, implying a nearly Newtonian behavior (Equations 4 and 5), as the polymers or fibrils have not (yet) started to significantly orient. Meanwhile, the extension rate increases proportionally to the inverse of the

diameter (Equation 4). The third flow regime is characterized by a rapid decrease in diameter, which raises the extension rate quickly, thus forcing the polymer chains to uncoil and/or disentangle and orient along the capillary axis. This phenomenon is observed as a decrease in apparent extensional viscosity. Following, in the fourth region, elastic stresses start to dominate over the viscous ones, extension rate plateaus and extensional viscosity increases again.

CNF appeared to remain in the second regime (II) throughout the whole CaBER experiment (Figure 5a). This is probably related to the capillary breakup occurring faster than the relaxation time of the CNF hydrogel under extensional flow. This conclusion is supported by a previous estimation of the timescale for CNF alignment upon extension, ~ 0.31 s [70]. This implies that CNF might deviate from the Newtonian behavior if the suspension was allowed enough time to reach a steady state under a constant extension rate, before measuring each data point. This can be approached at lower extension rates by HCF, as will be discussed below.

GG experienced not only a Newtonian plateau (regime II) but also extensional thinning (regime III) and a short, predominantly elastic response right before breakup (regime IV, Figure 5b). As such, this solution first dissipates the energy applied by low extension rates, via continuous formation of new coils and/or entanglements (regime II), but then starts to restructure when the extension rate increases from dozen to > 100 s⁻¹ (regime III). These findings agree with shear rheometry, which indicates the need for sufficient shear to start orienting the GG polymer chains (Figure 3b, green spheres). In the fourth regime (IV), the extension rate is presumably too high to allow time for chains to disentangle and orient. Instead, the chains start opposing the extensional flow, which is seen as a brief increase in apparent extensional viscosity.

The same flow regimes are highlighted when plotting the CaBER viscosity as a function of Hencky strain (Figure 6c). At Hencky strains between 1.7-3.0, the CaBER viscosity of GG

remained approximately steady (regime II) before a peak that contained regime III. Torres et al. described nearly similar behavior for GG at Hencky strains below 6, with CaBER viscosity also stabilizing at somewhat below 10 Pa s [36]. However, they reported no peak close to breakup. Moreover, only Hencky strains up to 6 were involved [36], whereas here, the peak occurs at a Hencky strain of 6.5. Besides the main peak, smaller peaks are seen at lower Hencky strains. This can be interpreted as a sign of a multimodal system featuring several floc sizes. Similarly, bimodal systems have been shown to produce two peaks of apparent extensional viscosity as a function of Hencky strain [31]. However, further studies on the dispersion structure would be necessary to confirm this hypothesis.

Steady extension conditions allow time for restructuring. The apparent extensional viscosity of CNF and GG is plotted against extension rate in Figure 6a, b, respectively, measured under both dynamic (CaBER, filled symbols) and approximately steady (HCF, empty symbols) extensional flow, as well as calculated (Equation 10, x symbols for GG during Newtonian flow regime). Essentially, HCF allowed for measurements at low extension rates ($< 100 \text{ s}^{-1}$) and CaBER at high rates ($> 10 \text{ s}^{-1}$). In fact, no method is available for extensional rheometry at high extension rates and under steady conditions. Both HCF and the extension-thinning sections of the CaBER results were fitted to the Ostwald-de Waele power law (Figure S3b, d, Supporting Information). The obtained power law parameters are compiled in Table S4 (Supporting Information) and plotted as a function of CNF concentration in Figure 6d, together with corresponding values calculated based on shear rheometry as well as the data reported by Moberg et al. [20]

Figure 6. Apparent extensional viscosity η_e as a function of extension rate for (a) CNF and (b) GG. Empty symbols refer to HCF, filled symbols to CaBER data and x symbols to theoretical values based on apparent shear viscosity (Equation 10). The enlarged symbols indicate the extension rates applied on CNF and the corresponding HCF viscosities during core-shell wet-spinning with CA: a triangle for a draw ratio of 5 and a square for a draw ratio of 9 (Table S3, Supporting Information). (c) CaBER viscosity η_{CaBER} as a function of Hencky strain for CNF (blue) and GG (green). Flow regimes are highlighted in dark colors and labels. (d) Power law consistency index (K , purple dashed line) and flow behavior index (n , cyan solid line) as a function of CNF

concentration: squares – present study; triangles – Ref. [20]; empty symbols – extension (HCF); filled symbols – shear.

As hypothesized above, the HCF and CaBER results deviate remarkably for CNF (Figure 6a). At a concentration of 1 wt.%, CaBER results imply a low and almost steady viscosity (K of 11 and n of 0.7) while HCF suggests extensional thinning (n of 0.3) with a higher K of 403 (Table S4, Figure 6d). The combination of the HCF and CaBER plots suggests that the extensional thinning would continue up to an extension rate of 100 s^{-1} . At higher rates, the extensional viscosity would drop heavily and plateau. However, more probably, this observation is related to the different characteristics of the measurement techniques. Since HCF allows the flow to reach an approximately steady state at each studied extension rate, it records the properties of the CNF suspension assumedly after relaxation. In contrast, CaBER records data immediately in the dynamic state, representing the properties of the suspension without time to relax.

For CNF, n stays nearly constant as a function of concentration, while K appears to grow following a power law equation (Figure 6d, Table S4):

$$K = 382C^{2.4} \quad (12)$$

This trend matches rather closely with that derived from the shear flow results (Figure 6d), though K appears somewhat less sensitive to concentration in extensional flow in comparison to shear (growth exponents 2.4, Equation 12, and 3.3, Table S1 of the Supporting Information, respectively). Thinning occurs to an approximately similar extent under both shear and extension, possibly slightly less under extensional flow, as HCF provides a slightly higher n than shear rheometry (Figure 6d).

As the most significant difference between shear and HCF results, the K values acquired via HCF are more than a decade higher than those obtained via shear rheometry. This corresponds to extensional viscosity staying at a more than a decade higher level than shear viscosity, as can be concluded by comparing Figure 6a and Figure 3a. This finding highlights the deviation of CNF extensional and shear viscosities from the Trouton ratio (Equation 10), as is typical for non-Newtonian fluids. The same applies to GG with K (measured by both shear and HCF) on the same level as that for CNF at a similar concentration (Table S4).

It should be noted that the HCF extension rate and viscosity reported for the CNF hydrogels were calculated using the power law parameters obtained from the full shear flow curves (shear rates 0.01-1000 s⁻¹). This range was selected in order to include the shear rates equivalent to the extension rates applied in HCF, even though the lower end of this range is heavily influenced by wall depletion observed as shear stress declining with shear rate (Figure S4). Table 2 presents the sensitivity of the HCF-based power law parameters to the respective parameters resolved under shear at different shear rate ranges. Following the trend observed under shear, K becomes increasingly sensitive to the underlying shear rate range upon dilution of the CNF hydrogel. Likewise, n is influenced by the range only at concentrations <2 wt.%. Nevertheless, the discrepancies are smaller than those between the respective parameters from shear experiments (Table 1).

For GG (Figure 6b), CaBER indicates a more marked extensional thinning than HCF, with n of 0.1 and 0.5, respectively (Table S4, Supporting Information). This might originate from the insufficient time for the solution to adjust to the extension rate generated in CaBER. As the extension history affects the sample at any particular extension rate, the restructuring of the solution (detected as decreasing CaBER viscosity) might be exaggerated. Nevertheless, both

CaBER and HCF provide an approximately similar K (Table S4, Supporting Information), which implies that the extension-thinning profile from CaBER could be interpreted as a continuation of the HCF flow curve at higher extension rates. Furthermore, the shape of the CaBER flow curve for GG resembles that obtained from theory and HCF together. As the main difference, CaBER estimates the Newtonian plateau lower (~ 10 Pa s) and the extension-thinning region to start later (extension rates > 10 s $^{-1}$) than expected based on theory (plateau at ~ 30 Pa s with extension rates < 1 s $^{-1}$; i.e., outside of the shear-thinning region in Figure 3b).

Table 2. Power law parameters K and n (Equation 1) measured through HCF using respective parameters defined under shear flow at indicated shear rate ranges.

CNF concentration	Shear rate range 0.01-1000 s $^{-1}$		Shear rate range 18.9-1000 s $^{-1}$		Difference	
	K (Pa s n) from HCF	n from HCF	K (Pa s n) from HCF	n from HCF	K (Pa s n) from HCF	n from HCF
1 wt. %	402.6	0.26	328.7	0.24	18.3%	7.7%
1.5 wt. %	890.6	0.26	814.1	0.24	8.6%	9.1%
2 wt. %	2153.5	0.22	2032.1	0.22	5.6%	0.0%

While the dynamic conditions during CaBER result in very different results for CNF and GG, under steady extension in HCF, they both show a similar pattern at the same concentration of 1 wt. %: as the extension rate increases from 1 to 100 s $^{-1}$, the apparent extensional viscosity decreases from hundreds to dozens (Figure 6a, b). This development corresponds to K of a few hundreds and n of 0.3 for CNF or 0.5 for GG (Table S4, Supporting Information). The observed similarity for CNF and GG behavior in HCF compares with some common phenomena under steady shear: at a concentration of 1 wt. %, the apparent viscosity decreases from below 10 to below

0.1 Pa s as shear rate increases from 1 to 1000 s⁻¹ (Figure 3a, b), as corroborated by the close power law parameters (Table 1).

The generic rheological patterns for CNF and GG, which share some analogies, even if partially, highlights the potential suitability of CNF for functions where GG is employed, such as thickening. Unlike GG solution, CNF hydrogel experiences both shear and extension-thinning behavior already at a strain rates below 1 s⁻¹. This is likely enabled by the brittleness of the CNF gel network discussed above. Furthermore, the CNF gel thins somewhat more markedly than the GG solution, as shown by slightly lower values of n (Tables I and S4 of the Supporting Information). As such, CNF can outperform GG in applications requiring gel-like consistencies with thinning already at low shear and extension rates. Currently, galactomannans are usually combined with other components, such as xanthan gum, when a gel-like texture is required; e.g., in food applications [46]. CNF represent a promising alternative, as they have already been shown to improve the texture and thermal stability of food products [71–77]. Furthermore, CNF and GG have been shown to have a synergistic effect on emulsion stabilization [78]. For oil-drilling operations, CNF have been introduced as an alternative to GG as an additive to treatment fluid [79–81], demonstrating stronger resistance to thermal aging than GG [82].

CNF wet-spinning requires proper rheological parametrization and/or a supporting material. The processability of CNF was analyzed by testing its suitability as a precursor for wet-spinning. The results are discussed thoroughly in the Supporting Information. In summary, the findings suggest that a $G' > 400$ Pa and K at least in the order of dozens or thousands (measured under steady shear or HCF, respectively) are required from a CNF hydrogel to allow wet-spinning and filament recovery. These criteria can be regarded as indicators of sufficient interfibrillar interactions to hold a filament structure together. Herein, the criteria were fulfilled and filaments

were successfully recovered from CNF spinning at concentrations of 1.5 and 2 wt.% using acetone as coagulation bath. Even at these conditions, though, CNF filaments could only be recovered in < 30 cm sections.

When enclosed by a shell formed by the easily spinnable CA solution, CNF could be spun continuously, as an essentially infinitely long filament, which could also be drawn, already at a concentration of 1 wt.% (Figure 1e). A video of the continuous spinning process is included in the Supplementary Material and an image of the cross-section of the ensuing core-shell filament is shown in Figure S6 (Supporting Information). Likewise, GG was effective in supporting continuous spinning of CNF, though the bicomponent CNF-GG filament could not be drawn (Table S6, Supporting Information). Similar pattern applies to the neat CA and GG filaments: only the former could be drawn even though both allowed for continuous filament production. The superior drawability of CA agrees with its longest capillary breakup time compared to the other samples (Figure 4a).

In conclusion, comparing the spinnability of dispersions with different characteristics, stronger Newtonian and viscous responses as well as long capillary breakup time correlated with enhanced spinnability (Table S6, Supporting Information). Probably, these rheological features serve as indicators of sufficient flexibility of the dissolved polymers to form entanglements that attach together into a ductile structure during filament formation. This was supported by oscillatory strain sweep results (Figure S2, Supporting Information): spinnability increased with increasing critical stress (Table 1), which provides an estimation for the ductility of the fibril/polymer dispersion.

CONCLUSIONS

The shear and extensional flow behavior of CNF suspensions as well as those of GG and CA solutions were characterized in both dynamic and steady flow conditions. Through steady shear rheometry, a shear-thinning behavior was noted in CNF, following a power law $\eta = K \dot{\gamma}^{-0.8}$, where K scales with concentration C according to power law $K = 6.3 C^{3.3}$. Polarized imaging of the flow confirmed that the shear-thinning at shear rates $< 100 \text{ s}^{-1}$ was caused mainly by wall depletion, whereas at $> 100 \text{ s}^{-1}$ alignment of the CNF took place in the direction of the shear. SAOS indicated a gel-like behavior with a power law relationship between storage modulus and CNF concentration, as expected, though with a rather high power law exponent (4.6). In contrast, the polymer solutions displayed a more liquid-like behavior, especially the CA solution, which essentially shows no elastic contribution.

Under the extensional flow created in a hyperbolic die, the apparent extensional viscosity η_{HCF} of CNF declined with extension rate ϵ_{HCF} according to a power law ($\eta_{HCF} \approx K \epsilon_{HCF}^{0.7}$), where K scales exponentially with fibril concentration C according to $K \approx 382 C^{2.4}$. This development resembles that of steady shear viscosity, though the K values were two orders of magnitude higher, highlighting the deviation from Trouton ratio. Lower and more stable apparent extensional viscosity was noted in CaBER experiments, indicating the strong influence of the structural relaxation of the CNF suspension, as the relaxation is allowed to a larger extent in HCF than during CaBER. Similarly, CaBER and HCF results deviated for the GG solution, also highlighting the influence of the extent of relaxation in the case of dissolved polymers. Importantly, the capillary breakup of the GG and CA solutions took place significantly slower than that of the CNF suspension, which is beneficial for wet-spinning.

Comparison of CNF results with those of dissolved biopolymers (GG and CA) indicated that the rigidity of the colloidal fibrils induced the formation of stiff and brittle gels. They are in contrast

to the more liquid-like structures of the flexible dissolved polymer chains. The enhanced flexibility of GG and CA were shown to be beneficial for wet-spinning, as the limited entanglement ability between CNF could only hold together short filaments spun from concentrated CNF (> 1 wt.%). In contrast, GG and CA could be wet-spun continuously. When CA or GG was used to support CNF spinning in a coaxial configuration, continuous spinning of CNF was possible. CA was more effective than GG as a polymer carrier for CNF spinning.

Overall, the results indicate that the rheology of CNF, related to fibril entanglement, needs to be adjusted to improve processability, in this study illustrated by wet-spinning. Regarding other types of processes, CNF hydrogel displayed a very similar rheological response to GG under both shear and extensional flows, at a similar concentration of 1 wt.% and at strain rates above the onset of shear-thinning in GG. This indicates that CNF could act as an alternative to GG for enhanced performance in related functions, such as thickening, when a gel-like texture is required with both shear and extension-thinning at a wide range of strain rates.

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APPENDIX

Supporting Information. Further literature analysis concerning CNF rheology; strain amplitude sweep data; power-law fitting of rheological data; specification of the wet-spinning conditions; data and discussion related to the extensional rheology of CA; analysis of the wet-spinning results.

DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. The data will be made available upon request.

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Shear and extensional rheology of aqueous suspensions of cellulose nanofibrils for biopolymer-assisted filament spinning

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Highlights for

Shear and extensional rheology of aqueous suspensions of cellulose nanofibrils for biopolymer-assisted filament spinning

- The shear threshold required for flow-assisted reorganization of cellulose nanofibrils was determined through polarized light imaging.
- Extensional rheology of cellulose nanofibrils hydrogels as well as guar gum and cellulose acetate solutions was analyzed.
- Rheological properties of the studied biopolymers were connected with their behavior during wet-spinning.
- Continuous wet-spinning of cellulose nanofibrils was demonstrated in a core-shell configuration with an assisting biopolymer solution.