Roll-to-roll Coating of Cellulose Nanofiber Suspensions

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Introduction

Micro- and nanoscale cellulosic fiber materials have recently been intensively studied for potential uses in various applications. Examples include use as rheology modifier, emulsifier, strength additive in paper and composites, absorbent, cell growth matrix, aero gel, transparent "nanopaper", membrane filter and barrier coating or film. The coating applications have been motivated by the high oxygen and grease barrier of the nanocellulosic films. However, most research so far has been limited to small, batch-produced samples. Reports on continuous processing into films or coatings, which is required for large-scale low cost production, are few. Similarly, high deformation rate rheology of nanocellulose, which is relevant for high speed coating operations, has not been reported. The current work aims at understanding cellulose nanofiber (CNF) suspension rheology at high shear rates and demonstrates roll-to-roll coating of CNF on paper with slot die geometry.

Experimental

Figure 1 shows electron micrographs of mechanically produced cellulose nanofibers (also known as microfibrillated cellulose) used in the current work. Without chemical or enzymatic pre-treatment, the fibril diameter varies greatly, from less than 100 nm to microns, and the length can reach tens of microns. With, e.g., TEMPO-mediated oxidation or acid hydrolysis prior to defibrillation much smaller sized nanocellulose can be produced. CNF suspensions are typically gel-like, and demonstrate very high viscosities and yield stress already at low solids concentrations, as exemplified to the right in Figure 1. The high viscosity, the large amount of water to be dried and water absorption into paper during coating challenge the CNF coating on paper.

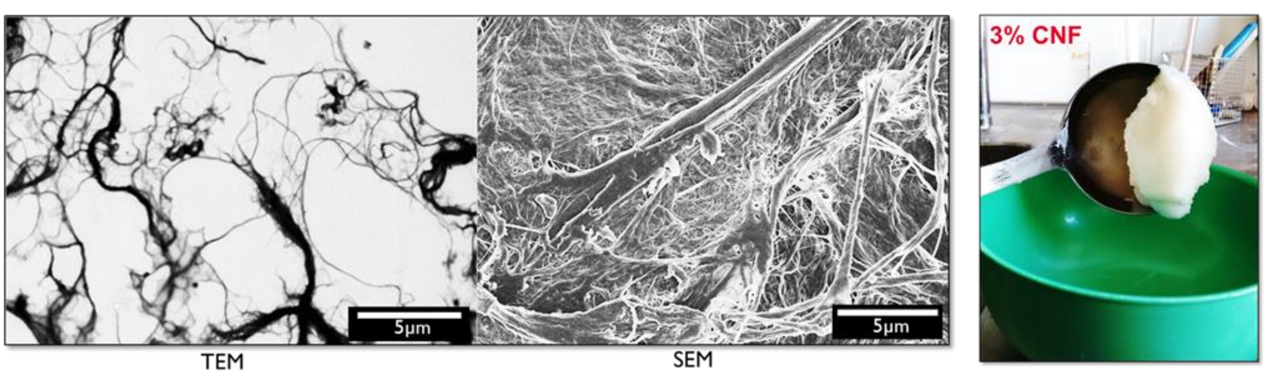

Figure 1. Mechanically produced cellulose nanofibers (University of Maine).

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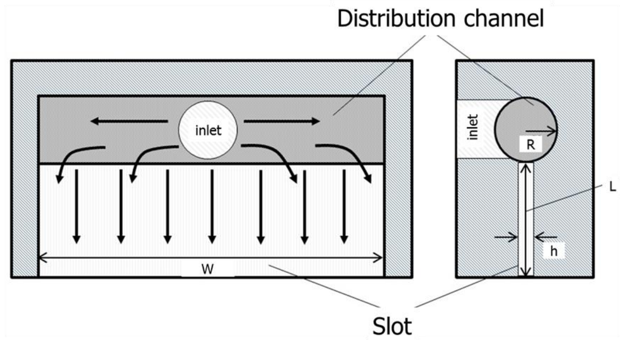


Newtonian Flow:

$$\Delta P_{slot} = \frac{12\eta LQ}{Wh^3}$$
$$\sigma_w = \frac{-\Delta P}{L}\frac{h}{2}$$
$$\dot{\gamma}_w = \frac{6Q}{Wh^2}$$
$$\eta = \frac{\sigma_w}{\dot{\gamma}_w} = \frac{-\Delta P}{L}\frac{Wh^3}{12Q}$$

Non-Newtonian Flow:

$$\dot{\gamma} = \left(\frac{2Q}{Wh^2}\right)\left(2+\frac{1}{n}\right)$$
$$\eta_a = \frac{\sigma_w}{\dot{\gamma}} = \frac{-\Delta P}{L}\frac{Wh^3}{4Q\left(2+\frac{1}{n}\right)}$$

Kinetic Energy Correction:

$$P_{kE} = \frac{27 f \rho Q^2}{35 h^2 W^2}$$

Rabinowitch Correction:

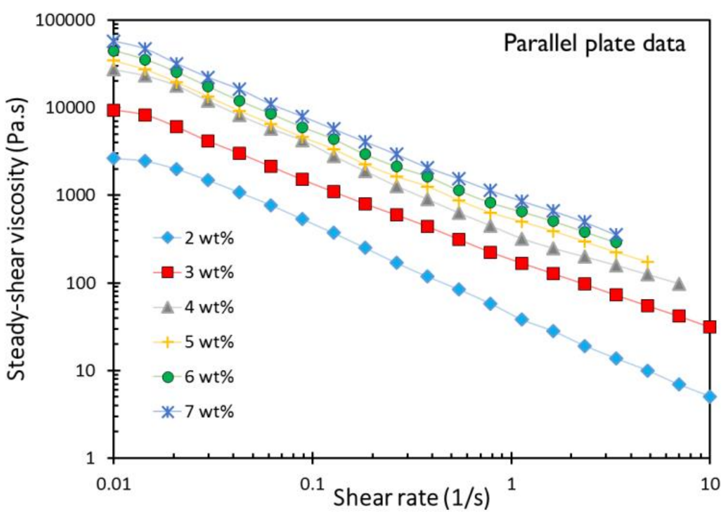
$$n = \frac{d[log(\sigma_w)]}{d[log(6Q/Wh^2)]}$$

Figure 2. Slot geometry and equations to calculate viscosity.

Due to experimental problems, viscosity of CNF suspensions has usually been reported only for very low shear rates, typically up to 100 s^{-1}. Sample ejection from the measurement gap, potentially due to repeated shear, is a common problem when measuring with rotational viscometers. In order to reach higher shear rates, the current work utilizes slot rheometry with a simple custom-built slot die shown in Figure 2. By measuring the inlet pressure and the outflow, the viscosity of the test material can be calculated with well-known equations for narrow gap flow. Corrections to account for fluid acceleration, slot end/exit effects and non-Newtonian behavior can be applied in a manner similar to capillary viscometry.

Results

Figure 3 plots steady-shear viscosity of CNF at different concentrations measured with parallel plate geometry at low shear rates. Besides the high viscosity and its concentration dependence, the highly shear-thinning behavior with a power law index of ca. 0.1 is apparent. With slot geometry, it is possible to reach high deformation rates, as shown in Figure 4, which plots the apparent viscosity of 3% CNF suspension over 6 decades of shear rate. The viscosity from the boundary-driven parallel plate devices at low shear rates



$$\eta = k\dot{\gamma}^{n-1}$$

Solids content (wt%)	K (Pa.s^n)	n
2	46.1	0.04
3	199.7	0.15
4	432.1	0.09
5	577.9	0.12
6	729.5	0.11
7	959.2	0.11

Figure 3. Steady-state viscosity of CNF suspension and power law fits to the data.

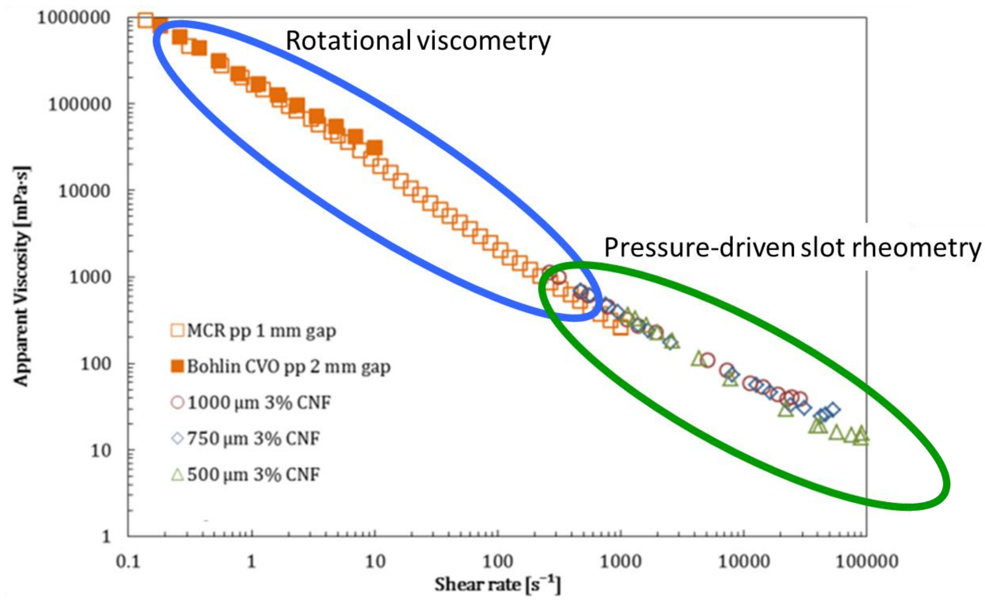


Figure 4. Apparent viscosity of CNF suspension with parallel plate and slot geometries.

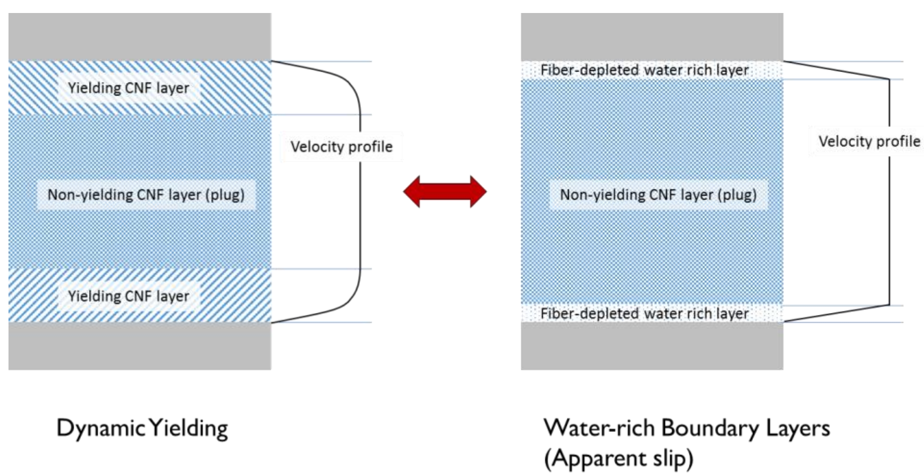


Figure 5. Alternative mechanisms for apparent shear-thinning behavior in slot flow of CNF.

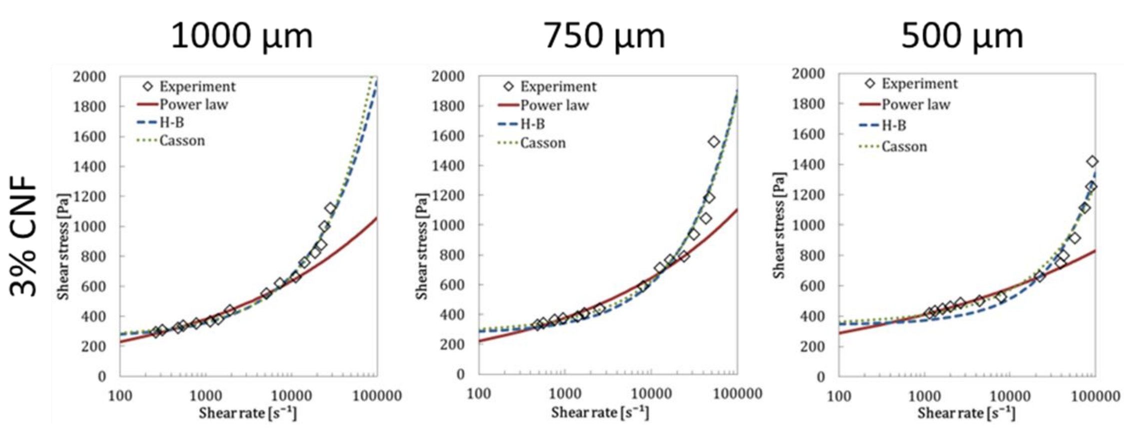


Figure 6. Power law, Herschel-Bulkley and Casson fits to slot rheometry data.

agrees reasonably with that from the slot geometry at high shear rates. The three different used slot gaps, 500 µm, 750 µm and 1000 µm give the same result. Noteworthy is the extension of the apparent shear thinning to high shear rates, where the viscosity approaches 10 mPas. The shear-thinning can be explained by dynamic yield behavior, where a non-yielding center plug is surrounded by a yielded, flowing suspension layers at the boundaries as illustrated to the left in Figure 5. Support for this can be found in Figure 6, which fits the power law, Herschel-Bulkley and Casson material models to the shear stress vs. shear rate data. Only the latter two, which include yield stress, do fit the experiments.

An alternative explanation for the apparent shear thinning can be provided by apparent slip at the boundaries (Figure 5, right). Optical coherence tomography measurements for Couette flow of nanocellulose by Haavisto et al. [*TAPPI Journal* 14 (2015):291] provides experimental evidence for existence for fiber-depleted watery boundary layers. Assuming a non-deforming center plug surrounded by water layers, the thickness of the water layer calculated for 3% CNF suspension in the current experiments varies from less than one micron up to 5 microns. While the current work cannot separate the two mechanisms causing the high apparent shear-thinning, the low flow resistance does suggest possibility of using slot die coating for processing of CNF suspensions into coatings and films.

Roll-to-roll coating of cellulose nanofiber suspension

Figure 7 shows the experimental setup for slot coating of CNF on paper. A custom-built slot die (slot width=74 mm, slot length=34 mm, slot gap=500-1000 µm, lip lengths=5 mm) is placed at three o'clock position. For a chosen slot gap, the coating process can be controlled by changing the web speed (1-30 m/min), feeding pressure (0-10 bar) and the Slot-Web Gap (SWG, 0-2000 µm). Occasional large aggregates in the CNF material forces one to use relatively large slot gaps to avoid clogging of the slot entrance. At the same time, high flow rates through the slot are needed to produce the low apparent (process) viscosity. Therefore, to obtain low coat weights at relatively low coater speeds the slot die has to be run in an unconventional mode in which part of the coating material is metered off. For well-controlled metering, it was found to be beneficial to offset the slot die (6 mm below) the center line of the backing roll. This creates a converging geometry between the paper and the slot die, which enables coat weight control by changing the SWG. The split, i.e. the percentage of CNF coated on paper vs. being metered off, is determined by the

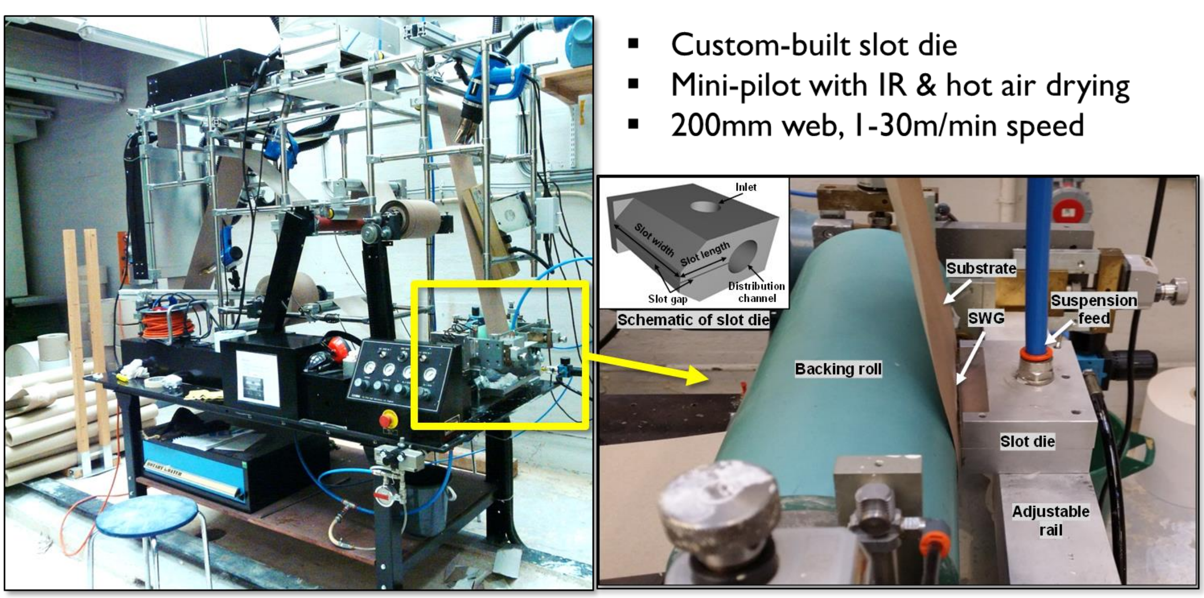


Figure 7. Experimental setup for slot coating of CNF suspension.

balance between the pressure-driven extrusion flow forcing the coating both upward and downward, and the shear-drag of the moving paper web pulling the coating along upwards. In the converging geometry the pressure-driven flow scales to the third power of the gap distance, whereas the shear drag upward is directly proportional to the inverse of the gap distance. Closing the SWG and increasing the feeding pressure both reduce the relative proportion of coating transferred to the paper, as shown in Figure 8, whereas increasing the coating speed will increase the coating amount. The possibility to control the coat weight with both the SWG and the feeding pressure is useful since the flow profile in the slot-paper gap seems to have a strong influence on the coating quality of the fibrous nanocellulose.

Concluding remarks

The current work measured high shear rate viscosity of cellulose nanofibers utilizing slot geometry. The results agree with those obtained with parallel plate devices and demonstrate that, in pressure-driven flow, the highly shear-thinning behavior observed with rotational instruments at low shear rates extends to high shear rates. The high apparent shear-thinning behavior can be explained by dynamic yielding or fiber-depleted water-rich boundary layers (apparent wall slip) controlling the flow. The highly shear-thinning process viscosity of CNF suspensions in slot flow enables roll-to-roll coating of viscous, gel-like cellulose nanofiber suspension on paper. Offset slot die placement enables easy metering with slot-to-paper gap control. Future work will analyze in detail the flow dynamics of highly shear-thinning yield stress materials in the used experimental geometry.

References

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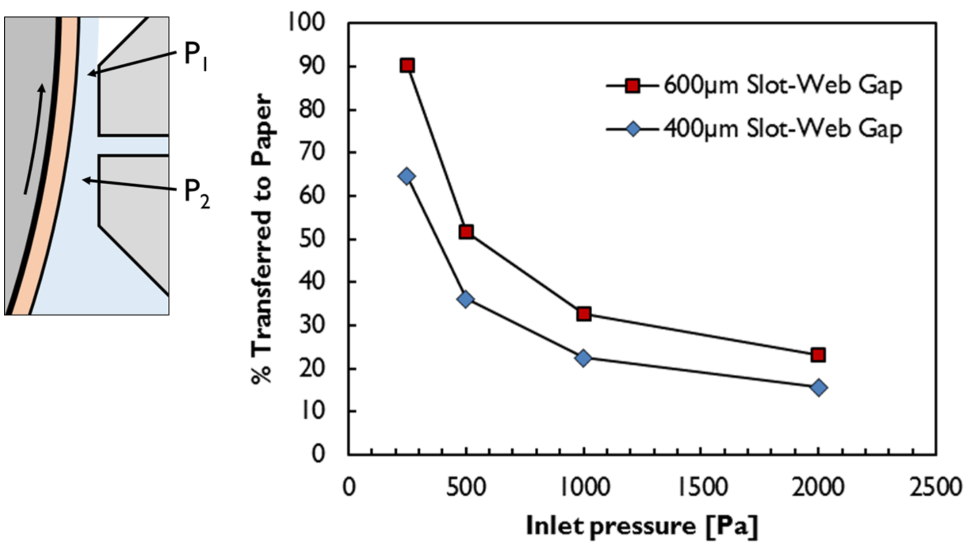

Figure 8. Geometry of the slot-paper gap, and COMSOL CFD prediction of the influence of the gap distance and inlet pressure on % coating transferred on to the paper.