Gel point in CNC dispersion from FT Rheology

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ABSTRACT

A non-linear analysis via Fourier-Transform Rheology (FT-Rheology) and Large Amplitude Oscillatory Shear (LAOS) of cellulose nanocrystals (CNC) dispersions is presented. Dynamic frequency and strain sweep measurements were performed for different CNC concentrations with various parameters ($\omega, \gamma$). The relevance of nonlinear material rheological parameters on flow-field-CNC interactions are initially investigated. This preliminary analysis is mainly formed on the magnitude of the stress response nonlinearities. Dependence of concentration on phase transition in CNC while applying strain was investigated. A comparison between the linear viscoelastic dynamic moduli and nonlinearities a steep increase in nonlinear response around the gel point.

INTRODUCTION

Cellulose is one of the most abundant natural resource on earth with wide presence in wood, plants, tunicates, algae, bacteria.\textsuperscript{14} Cellulose nanocrystals (CNC) are stiff, highly crystalline and rod like shaped cellulose structures obtained by removing the amorphous part of cellulose nanofibrils through acid-catalysed hydrolysis.\textsuperscript{1} CNC in aqueous suspensions can behave as a liquid crystalline or gel-like depending on the concentration, CNC dimensions, ionic strength and type of counter-ion.\textsuperscript{7} The interest in nanocellulose is generally motivated by its wide occurrence and possibility of new applications. It is one of the main reasons for understanding the effect of process structur-
lar frequency of the excitation. However, in the case of a nonlinear viscoelastic shear stress, the output is non-sinusoidal which will lead to higher harmonics in the corresponding Fourier spectra in addition to fundamental intensity $I_1$. The principle is detailed elsewhere, e.g.\textsuperscript{2,4,9,16} The higher harmonics can be used to quantify the nonlinear material response. Higher harmonics are typically detected also in the small amplitude oscillatory shear (SAOS), however, they are the result of instrumentation noise.\textsuperscript{2} With increasing strain amplitude, nonlinearities are detectable at higher shear strain amplitude and increase in medium amplitude oscillatory shear (MAOS) region at $I_{3/1} \propto \gamma_0^2$ or above that region at large amplitude oscillatory shear (LAOS). Consequent, a nonlinear coefficient from Fourier-Transform Rheology can be defined as (intrinsic nonlinearity).\textsuperscript{5}

$$Q \equiv \frac{I_{3/1}}{\gamma_0^2}.$$  

(1)

The zero-strain limit of the $Q$-parameter therefore is

$$Q_0 = \lim_{\gamma \to 0} Q(\gamma)$$  

(2)

The magnitude of this intrinsic nonlinearity can be evaluated for any complex fluids.\textsuperscript{6,8} A visual inspection of the nonlinear response can be performed using elastic and viscous Lissajous-Bowditch diagrams. A linear viscoelastic response is represented by elliptic shaped diagrams. A nonlinear viscoelastic response due to distorted signal (non-sinusoidal) results in distorted (non-elliptic) signatures.\textsuperscript{8}

EXPERIMENTAL

Aqueous suspensions of juvenile CNC were obtained by the acid hydrolysis $H_2SO_4$ of microcrystalline cellulose using a procedure outlined by Hasani et al.\textsuperscript{3} Deionized water (Millipore Milli-Q Purification System) was used to obtain following concentrations: 1 wt%, 1.5 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%. The suspensions were stirred by sonicator to ensure homogeneity. Directly before measurements, suspensions were treated in ultrasonic bath for 15 min. Rheological behavior of CNC suspensions depends on pretreatment (e.g. applied ultrasound energy, standing time).\textsuperscript{11,14} Thus, the same procedure was performed before each measurement.

Nonlinear oscillatory shear tests were performed on an Anton Paar MCR 702 TwinDrive rheometer (Graz, Austria) in strain controlled mode (separate mode-transducer) using a parallel plate geometry of ($2R =$) 50 mm in diameter, with 1 mm gap. The frequency sweep tests were performed in counter oscillation. All experiments were performed at 23 °C. Relaxation time was 300 s. In this presented study, elastic ($\sigma(t)/\sigma_{max}$ vs. $\gamma(t)/\gamma_0$) and viscous ($\sigma(t)/\sigma_{max}$ vs. $\dot{\gamma}(t)/\dot{\gamma}_0$) Lissajous-Bowditch diagrams were used for visual inspection of the nonlinearities, whereas the quantitative data analysis was performed in the framework of Fourier-transform rheology analysis.\textsuperscript{15} Strain sweep measurements were performed within a strain range from 0.01 to 1500 % at following frequencies: 0.6 Hz, 1 Hz, 2 Hz and 4 Hz for each suspension. Frequency sweep measurements were...
carried out over an angular frequency range from 600 to 0.001 rad/s, with constant strain 0.3%.

The nonlinear analysis of the shear stress output signal was performed in the framework of Fourier-Transform analysis.

RESULTS AND DISCUSSION

Dynamic strain sweep measurements with constant frequency $\omega = 2$ rad/s and increasing strain amplitude were performed to determine storage and loss modulus ($G', G''$) of unmodified CNC suspensions (Fig. 1). From the linear viscoelastic data, the 1 wt% suspension exhibited rheological liquid crystal fluid behavior ($G'' > G'$). At 1.5 wt% concentration appears gel-point which is more clear detectable at 2 wt%, where storage and loss modulus are equal ($G' \cong G''$). The suspensions above 2 wt% (3-5 wt%) showed a cross-over after which the $G' > G''$. They are confirmed as a rheological gels. A similar qualitative concentration dependence applies to the complex viscosity (Fig. 2). It is observed a significant increase of the complex viscosity $|\eta^*|$ above 2 wt% unmodified CNC suspension, meaning above the gel-point. This is quite important, because $|\eta^*|$ increases above the gel point whereas $Q_0$ increases at the

gel point.

The nonlinear material response expressed by the third relative higher harmonic, $I_{3/1}$, from dynamic strain sweeps for different concentrations of CNC suspensions, $\omega = 2$ rad/s.

![Figure 3. Third relative higher harmonic, $I_{3/1}$, from dynamic strain sweeps for different concentrations of CNC suspensions, $\omega = 2$ rad/s.](image)

![Figure 2. Complex viscosity functions, $|\eta^*|$ ($\omega, \phi$) from linear viscoelastic frequency sweep measurements.](image)
Figure 4. Lissajous-Bowditch diagrams for unmodified CNC suspensions for selected $\omega$=0.6, 1, 4 rad/s for (a,d)1 wt% (below gel-point), (b,e) 1.5 wt% (gel-point), (c,f) 5 wt% (above gel-point) compiled in Pipkin diagrams. Top row, (a)-(c) represent the Elastic Lissajous-Bowditch diagrams and bottom one, (d)-(f), represent viscous Lissajous-Bowditch diagrams.
SUMMARY AND CONCLUSIONS

Rheology is an essential tool for characterization of suspension flow dynamics. In particular, nonlinear viscoelastic analysis from oscillatory shear tests have the potential to provide novel insights into the flow-field - CNC interactions, particularly in the framework of surface modification of CNC and their self-organization. In this pre-study, several concentrations of aqueous CNC dispersions were examined mainly using Fourier-transform rheology. Dynamic strain sweep measurements showed dependence of the suspension concentration on its form and transition around the gel-point. Correspondingly, the magnitude of the nonlinear shear stress distortions as quantified by the zero-strain nonlinearity, $Q_0$, exhibited a steep increase around the gel point. Furthermore, a visual examination of elastic and viscous Lissajous-Bowditch diagrams reveal significant qualitative changes between CNC concentrations below and above gel-point. Further work will focus on surface treated CNC suspensions and further insights into the nonlinear behavior of the dispersions will be sought by expanding the scope of the nonlinear analysis.
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REFERENCES


