Rheology of concentrated suspensions of cellulose nanofibrils

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in collaboration with

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and
J.-L. Putaux, Université de Grenoble Alpes – CNRS – CERMAV for some TEM images

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Cellulose nanofibrils (NFC)?

Morphology and physico-chemical properties of NFC depend on both the cellulose source (wood, annual plant) and the extraction process.

Moon, 2008
For which applications?

Films/Nanopapers\(^1\)
Mechanical & barrier properties

NFC suspensions
(2%)

Cosmetics\(^3\)
Thickening agent

Paper coating\(^2\)
Barrier properties

Inks and paints\(^3\)
Film-forming properties

Composites\(^4\)
Reinforcement nanofibres

Few experimental studies to understand and model the rheology of NFC suspensions

(2) Lavoine et al. *Carbohydrate Polymers*, 90, 735-764, 2012
(4) Sehaqui et al., *Soft Matter*, 2011
Objectives

1. Extraction of NFC using chemical and mechanical treatments

2. Microstructure of NFC suspensions

3. Shear rheology of cellulose nanofibril water suspensions
   - macroscopic scale
   - mesoscopic scale
   - microscopic scale

4. Micromechanical approach to describe the yield stress of NFC suspensions
Materials and methods
Extraction of NFC suspensions

3 extraction methods

- **Eucalyptus fibres**
  - Refining (1.7%, 6h)
  - Grinding (70 cycles, 2500 rpm)
  - Mechanical NFC

- **Enzymes**
  - Enzymes\(^1\)
    - (Cellulase, pH 5, 2h)
  - Grinding (70 cycles, 2500 rpm)
  - Enzymatic NFC

- **TEMPO**\(^2\)
  - TEMPO\(^2\)
    - (NaClO/NaBr, pH 10, 3h)
  - Grinding (70 cycles, 2500 rpm)
  - TEMPO NFC

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Shear rheometry

Plate-plate rheometer (MCR 301, Anton Paar)
- diameter 25 mm, gap 1 mm, $T = 20^\circ$C
- suspensions homogenised at 10 000 rpm for 30 s
- shear stress $\tau$ measured:
  - (i) log ramp: $\dot{\gamma} \in [1000 \text{ to } 0.1 \text{ s}^{-1}]$ in 300 s
  - (ii) quasi-static: $\dot{\gamma} \in [1000 \text{ to } 0.01 \text{ s}^{-1}]$ in 3000 s
Shear rheometry

In collaboration with C. Perge, M.-A. Fardin, S. Manneville, ENS Lyon

Couette rheometer (ARG2, TA Instruments) ultrasonic velocimetry\textsuperscript{1,2}

- inner cylinder 23 mm, gap 2 mm, height 60 mm
- high-frequency ultrasonic velocimetry system
- suspensions pre-sheared at 1000 s\textsuperscript{-1} for 60 s
- $\tau$ measured in the steady state for $\dot{\gamma}$ between 1 and 100 s\textsuperscript{-1}

Morphology of NFC
Morphology of NFC

3 classes of size for mechanical and enzymatic NFC’s
- partially fibrillated fibres \( (d \approx 20 \, \mu m \text{ and } l \approx 250 \, \mu m) \)
- intermediate elements \( (d > 100 \, nm \text{ and } l \approx 10 \, \mu m) \)
- small elements \( (d \approx 30 \, nm \text{ and } l \approx 5 \, \mu m) \)

2 classes of size for TEMPO NFC
- partially fibrillated fibres \( (d \approx 25 \, \mu m \text{ and } l \approx 600 \, \mu m) \)
- elementary fibrils \( (d \approx 5 \, nm \text{ and } l \approx 2.5 \, \mu m) \)

Precise quantification of the microstructure difficult to achieve
Shear rheology of NFC suspensions
Macroscale rheology

Transient and steady flow curves

- **Yield stress fluid at low** $\dot{\gamma}$
- **Shear thinning behaviour at high** $\dot{\gamma}$
- **Complex evolution between 1 and 100 s$^{-1}$**

Herschel-Bulkley fluids

\[ \tau = \tau_0 + \mu_0 \dot{\gamma}^n \]
Macroscale rheology

Evolution of $\tau_0$, $\mu_0$, $n$ as a function of the NFC volume fraction $\Phi$

- Power law evolution for $\tau_0$ (1.9 < exponent < 2.7)$^{(1)}$
- Quadratic evolutions for $\mu_0$ with $\Phi$ (NFC’s slenderness)
- Non linearity: high concentration regimes
- Intensification of the shear thinning behaviour ($n \downarrow$) with $\Phi$
- The HB parameters highlight the influence of the extraction processes

$\tau = \tau_0 + \mu_0 \gamma^n$

$^{(1)}$ Varanasi et al., Cellulose, 20, 1885–1896, 2013
Mesoscale rheology – Homogeneity of NFC suspensions?

Example of enzymatic NFC suspensions

\[ \dot{\gamma} = 0 \text{ s}^{-1} \quad \dot{\gamma} = 100 \text{ s}^{-1} \quad \dot{\gamma} = 1000 \text{ s}^{-1} \]

- Mechanical and enzymatic NFC are flocculated suspensions\(^1\,^2\)
- Disintegration of flocs with \(\dot{\gamma}\)

NFC TEMPO

![Image of NFC TEMPO suspensions at different shear rates]

**Detailed study on stable TEMPO NFC suspensions**

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(1) Saarikoski et al. *Cellulose*, 1-13, 2012
Mesoscale rheology – Homogeneity of flows?

Orthoradial velocity profiles measured by shear-velocimetry

TEMPO NFC (1%)

- Wall slipping
- Nonlinearities (Shear banding)

NFC TEMPO 1%

Log ramp steady-state
Review of results

- Heterogeneity of NFC suspensions (flocculated suspensions)
- Heterogeneity of TEMPO NFC flows (wall slipping and shear banding)

Low influence of the strain-rate on the yield stress $\tau_0$:

$\tau_0 = 5.10^6 \phi^{2.7}$

Micromechanical modelling for the yield stress

Varanasi et al., Cellulose, 20, 1885–1896, 2013
Micromechanical modelling of the yield stress of TEMPO NFC suspensions
Expression of the macroscopic bulk stress tensor

General expression:

\[ \sigma = -p\delta + 2\mu D + \sigma^h + \sigma^{col} \]

At low shear rates \( \dot{\gamma} \)

Colloid forces are predominant

\[ \sigma \approx -p\delta + \sigma^{col} \]

Expression of \( \sigma^{col} \)
**Expression of the macroscale colloidal stress tensor** \( \sigma^{col} \)

**Existence of sheared zones of finite size**

In these zones, suspensions flow because forces are important enough to displace NFC from their equilibrium distance at rest \( \bar{H}_{eq} \)

\[
\sigma^{col} = \frac{n\bar{z}}{2} \sum_{b \in B} \bar{\xi}_b \otimes f^{col}_b
\]

- \( n \) : number of NFCs per unit of volume
- \( \bar{z} \) : mean NFC coordination number

TEM image obtained in coll. with J.-L. Putaux, CERMAV
Expression of the shear component $\tau_0$

The shear component $\tau_0$ measured during low-strain shear tests can thus be written as follows:

$$\tau_0 \propto \frac{n\bar{Z}}{2} \xi^c f^c$$

Mean colloidal force

Microstructural parameters

Estimation of microstructural parameters $(n, \bar{Z}, \xi^c)$? from
- geometry of NFC $(\bar{d}, \bar{l})$
- NFC volume fraction $(\Phi)$
- interparticle distance $(H)$
- orientation of NFC $(\varphi)$
Estimation of microstructural parameters

\[ \tau_0 \propto \frac{n \bar{Z}}{2} \xi_c f_c \]

- \( \xi_c \approx \bar{d} + \bar{H}_{eq} \) (mean interparticle distance)
- \( n = \frac{4 \phi}{\pi \bar{d}^2 \bar{l}} \)
- \( \bar{Z} \) can be estimated using a tube model\(^{1,2,3,4}\)

\[
\bar{Z} = \frac{4a^2 \phi}{\bar{d}^2} \left( \frac{2\bar{l}}{\pi a} \varphi_1 + \varphi_2 + 1 \right)
\]

\( \varphi_1, \varphi_2 \) are NFC orientation distribution functions

For planar isotropic orientation\(^{1,2}\) : \( \varphi_1 = \varphi_2 = \frac{2}{\pi} \)

\[
\bar{Z} = \frac{16la\phi}{\pi^2 \bar{a}^2}
\]

Estimation of the interaction radius \( a \)?

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(2) Toll, S. J. Rheol. 37, 123, 1993
(3) Giraud et al., J. Rheol., 56(3), 593, 2012
Estimation of microstructural parameters

Interaction radius $a$?

Electrostatic forces predominate

$\kappa^{-1}$ is the Debye length

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monovalent ions

$\alpha = \bar{d} + \alpha \kappa^{-1}$

Vanishing colloidal forces

$5\kappa^{-1} \approx$ thickness of the double electric layer

$\bar{Z} = \frac{16l(\bar{d} + \frac{\alpha \beta}{\sqrt{\phi}})}{\pi^2 \bar{d}^2}$

Micromechanical modeling at yield

Estimation of the yield stress $\tau_0$

$\tau_0 \propto \frac{n\bar{z}}{2} \xi^c f^c$

Fitting parameters: $\alpha=5$, $\beta=0.22$ nm, $\bar{d}=5$ nm, $\bar{l}=2.2$ $\mu$m,

- Linear dependence of $\xi^c f^c$ on the NFC volume fraction
- Very good correlation with the micromechanical approach
Estimation of microstructural parameters

\[ \tau_0 \propto \frac{n\bar{z}}{2} \xi^c f^c \]

- \(\xi^c \approx \bar{d} + \bar{H}_{eq}\) (mean interparticle distance)
- \(n = 4\phi / \pi \bar{d}^2 \bar{l}\)
- \(\bar{z}\) estimated using a tube model\textsuperscript{1,2,3,4}

Straight fibres \((\bar{d}, \bar{l})\)

\(\bar{H}_{eq}\) and \(f^c\) estimation

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(2) Toll, S. J. Rheol. 37, 123, 1993
(3) Guiraud et al., J. Rheol., 56(3), 593, 2012
Micromechanical analysis at low strain rate

Estimation of the mean interparticle distance at equilibrium

Assumption:
\[ \xi_c f_c \approx (H^{eq} + d)f^{DLVO}(H^{eq}) \]

\[ f^{DLVO} \approx f^w + f^e \]

van der Waals

\[ f^w = -\frac{Ad}{12H^2}e_n \]

electrostatic

\[ f^e = \frac{64\pi d n k T y^2 e^{-\kappa H}}{\kappa} e_n \]

Micromechanical modeling at yield

Estimation of the mean interparticle distance

\[ F = \frac{\alpha}{r^n} \]

Fitting parameters: \( \alpha = 5, \beta = 0.22 \text{ nm}, \bar{d} = 5 \text{ nm}, \bar{l} = 2.2 \text{ \mu m}, \)

Estimation the mean interparticle force

\[ f_c = \frac{\phi}{\bar{d}} \]

Volume fraction \( \phi \)

Interparticle distance (nm)

Volume fraction \( \phi \)

Mean colloidal force \( f_c (\text{pN}) \)
Conclusions

- **Extraction of cellulose microfibrils**
  - Polydisperse suspensions
  - Precise quantification of the microstructure difficult to achieve

- **Rheological behaviour**
  - Herschel-Bulkley fluids
  - Complex evolution between 1 and 100 s⁻¹
    - Heterogeneity of suspensions
    - Heterogeneity of NFC flows

- **Micromechanical modeling**
  - Estimation of $\tau_0$ from both microstructural parameters and a mean colloidal interaction force
  - The model reproduces the observed macroscopic scale trend
Thank you for your attention

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