Modelling NFC suspensions for pilot scale

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Outline

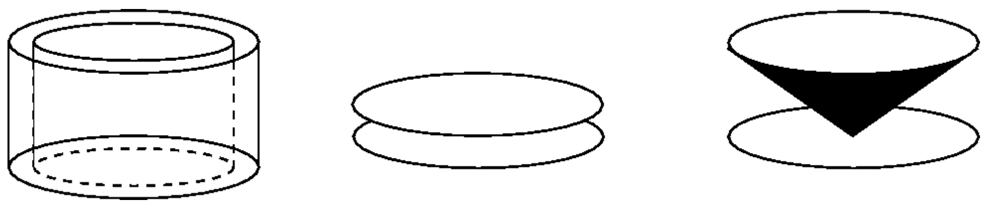
- Introduction
  - Motivation
  - Experimental background
- Introduction to rheological models
- Continuum level modelling using population balances
  - Viscous model responses and rheological characterization
- Standard models of rheology
  - Viscoelastic responses and rheometry
- Mixing processes and rheology
- Final words

Aims, Goals, and Means

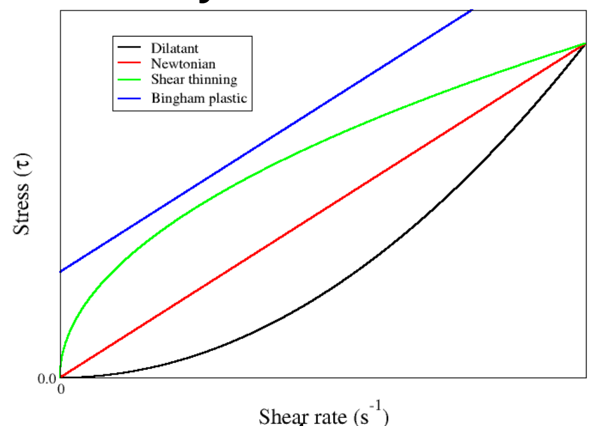
- Understanding the rheology of NFC suspensions
  - Containing only NFC
  - Multiple components – Fillers, NFC, fibers
- This boils down to:
  - Developing suitable models
  - Understanding experimental data
    - Intense collaboration
- Finding some guidelines for characterization and application of NFC
- Rheology of complex fluids is an active basic science field on its own!

Rheology and rheometers

- Rheology studies the relation of stress and strain [rate]
  - Stress or strain can be induced, and the other is measured
- Need for extremely sensitive stress and strain measurements
  - Rotational rheometers are often used

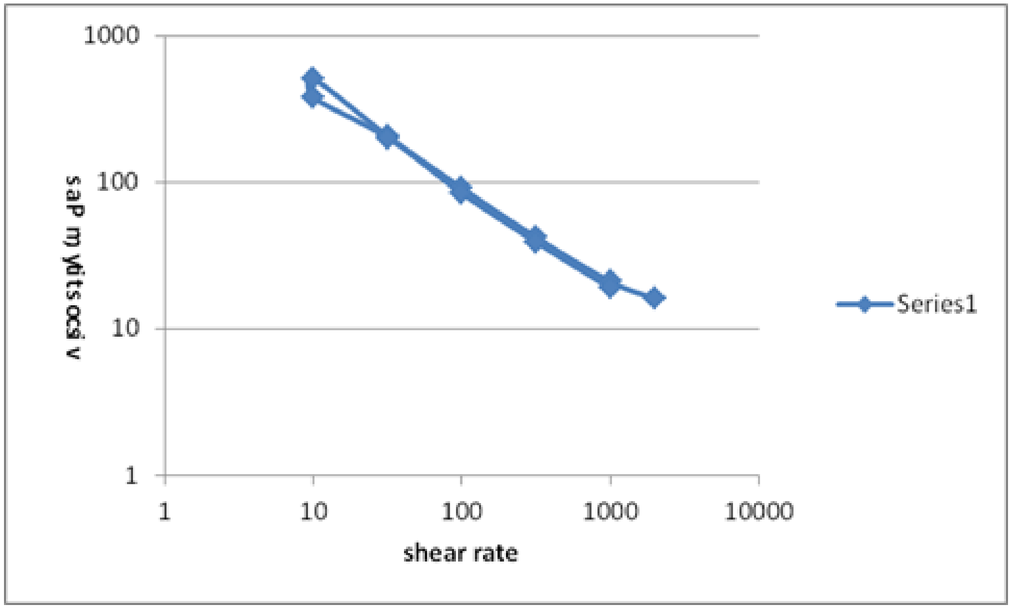


- In the rotational case, the torque and angular velocity are the main observables
- “Standard” techniques in engineering

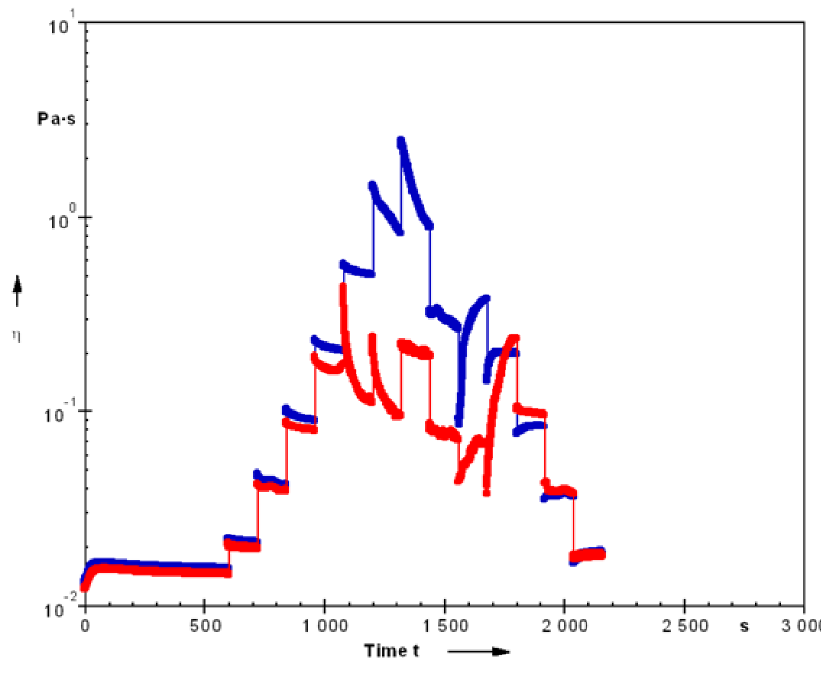


Experimental Rheology of NFC

- The standard "steady state" flow curve



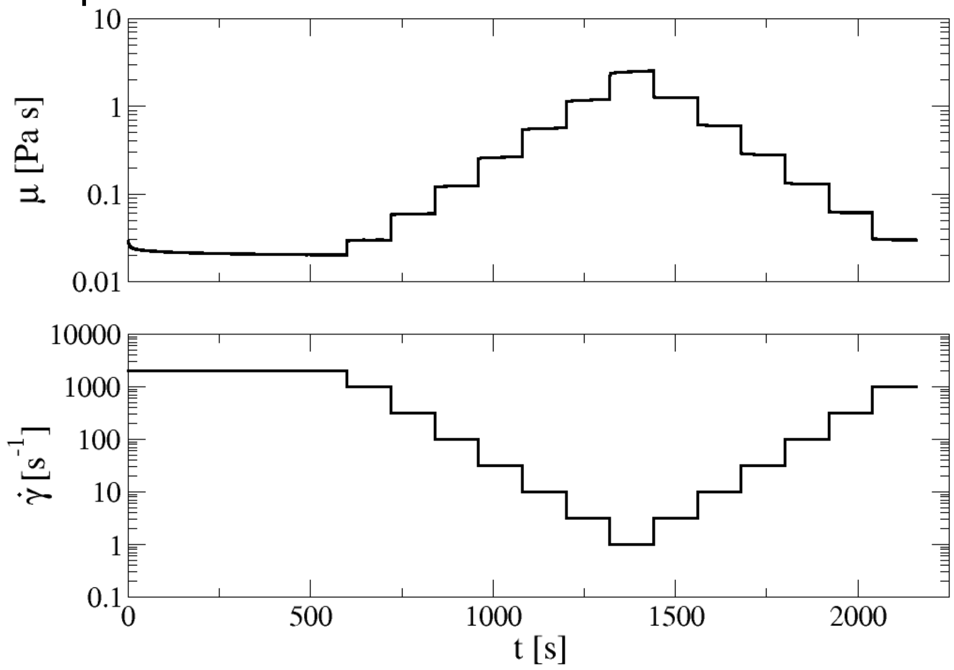
- The corresponding time-dependent data



- The "steady state" is clearly not the Steady State
- The transients are not behaving as expected for shear thinning suspensions
- Increasing the wall roughness somewhat helps the situation (right hand side figure, blue line).

Experimental Rheology of NFC

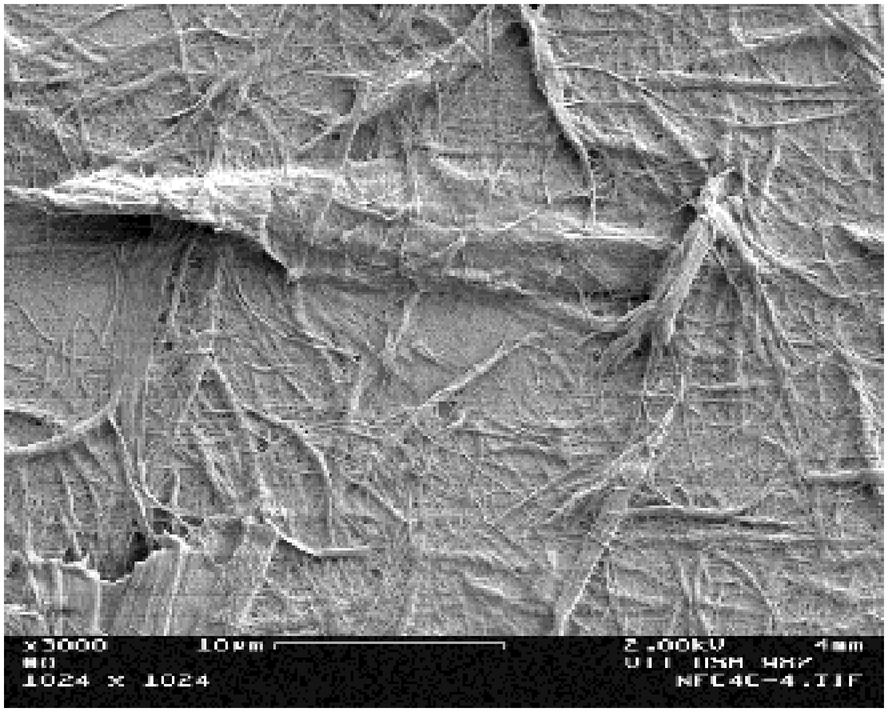
- The pre-treatment influences also the rheological behavior
  - Time dependent data for TEMPO oxidized NFC



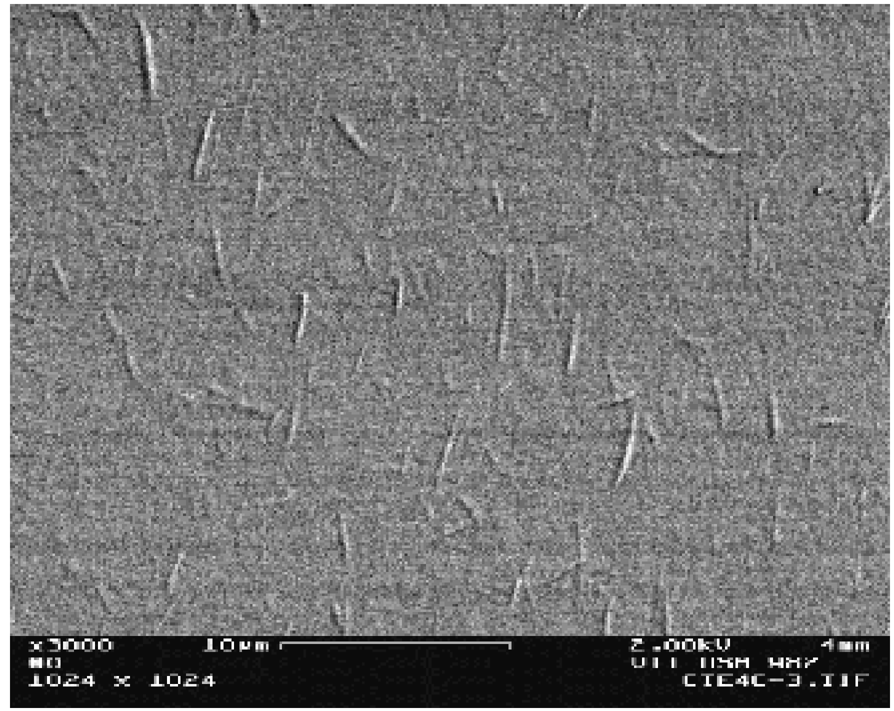
- Less “noise”
- Transients behave smoothly and as expected for shear thinning fluid

Experimental rheology

- The difference in the rheology might be related to the particle size distribution



NFC CTP



NFC TE CTP

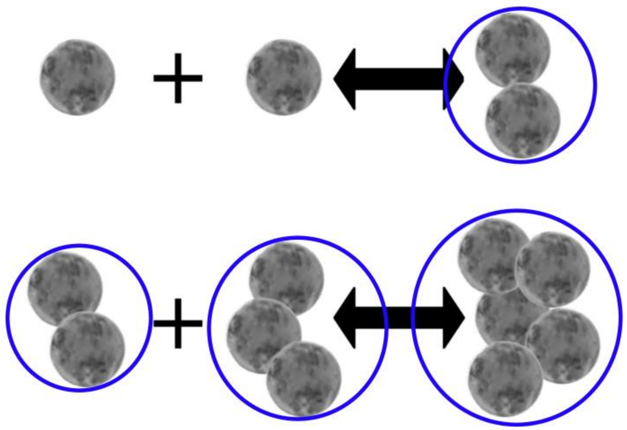
Rheological Models

- Three types of continuum level models, increasing complexity (and computational burden)
  - Phenomenological models – Such as the Herschel-Bulkley
    - Describes the “steady state”
  - Indirect structural – Lambda models based on evolution of abstract structural quantities
    - Transient as well as steady state
  - Direct structural – Based on physical properties of the system
    - Outputs real physical quantities – Here the size distribution of the flocs

Population Balances - Rheology

- The approach is computes the aggregate size distribution based on the number of collisions

$$\frac{dn_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} k^{(a)}(i-j,j)n_{i-j}n_j - \sum_{j=1}^{\infty} k^{(a)}(i,j)n_j - k^{(b)}(i)n_i + \sum_{j=i+1}^{\infty} \beta(i,j)k^{(b)}(j)n_j$$

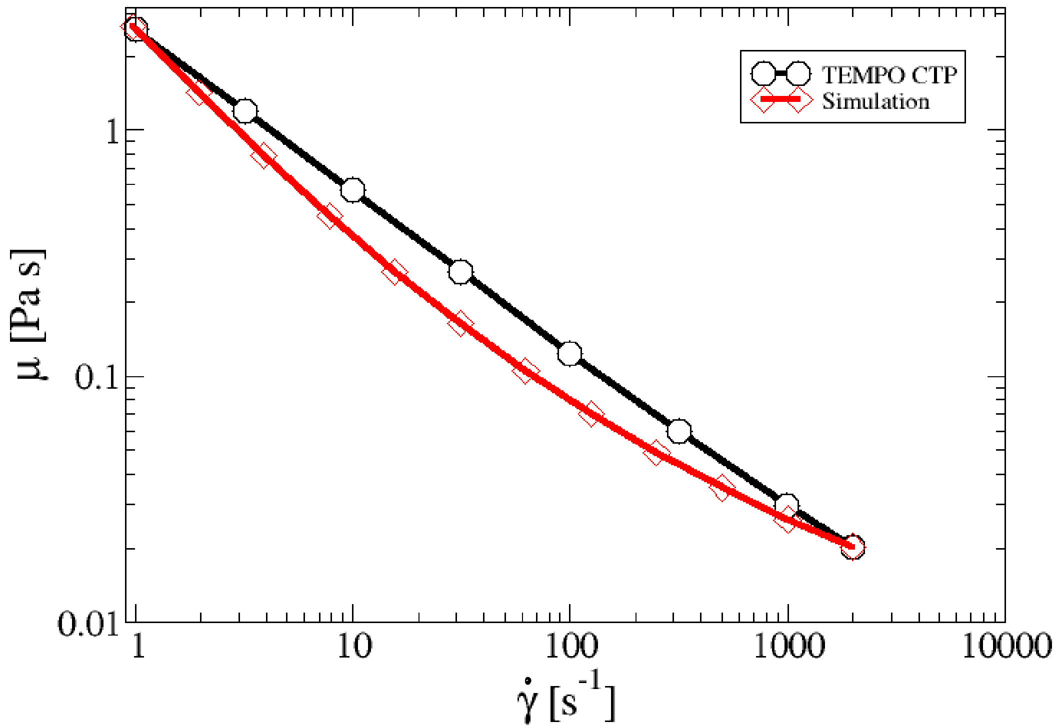


- The aggregate size distribution is connected to the intrinsic viscosity by a constitutive equation – effective volume fraction as the state variable

- The collision rates for various processes can be used depending on the process of interest
- The state of aggregation is connected to the rheology by the effective jammed volume fraction through a constitutive equation

Viscous responses – Flow curves

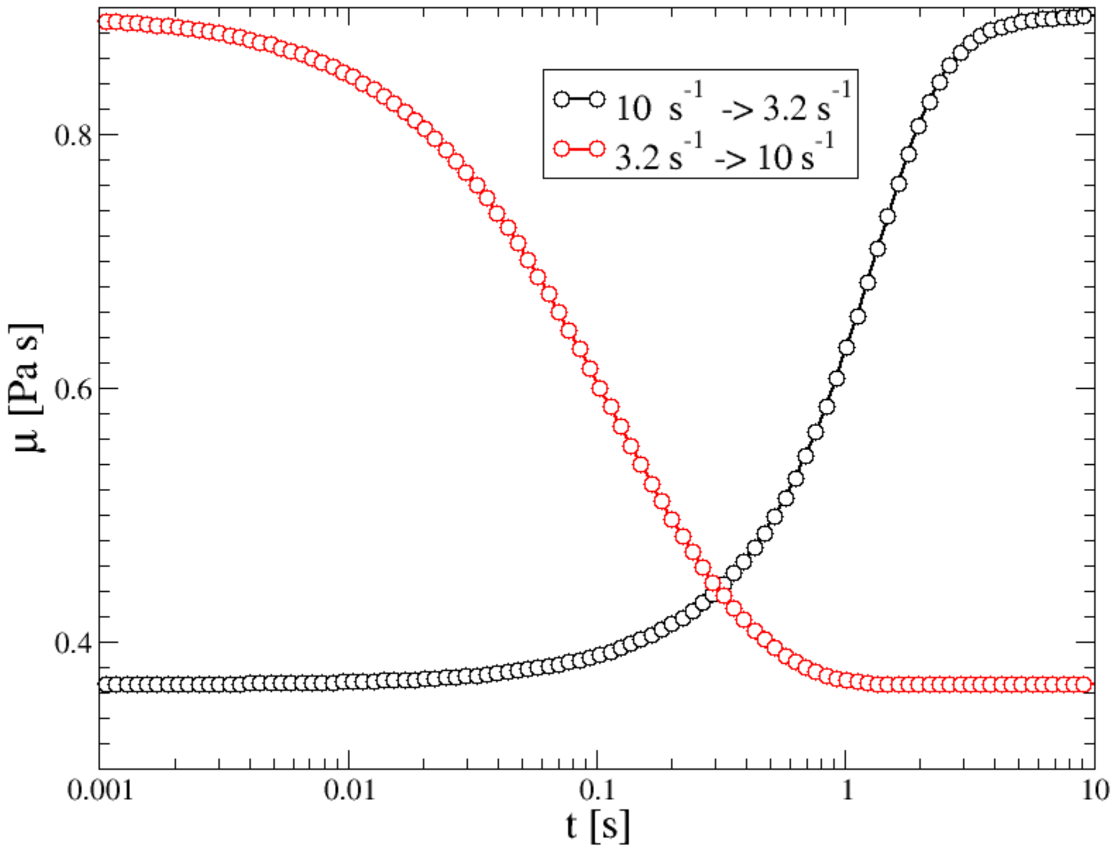
- The intrinsic flow curve of the model can be approximated using the apparent flow curve from the experiments



- The power-law scaling of the viscosity against shear rate very likely relates to the experimental geometry as explained in the following slides

Viscous responses – Shear ramps

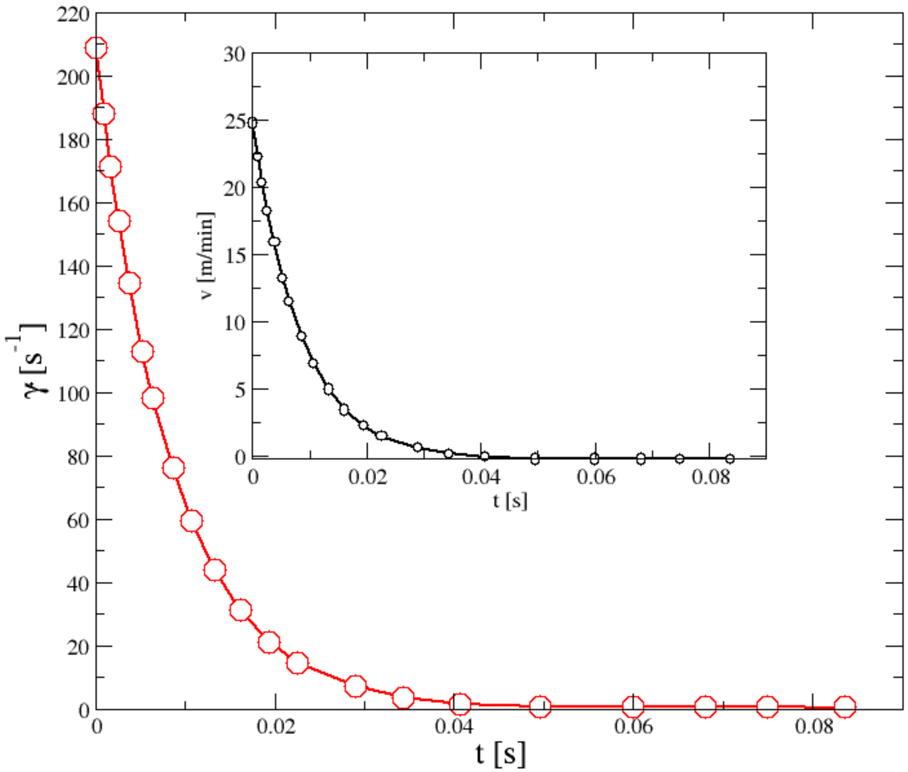
- The viscous model responds to the shear steps similarly to the TEMPO oxidized NFC in the experiments



- No viscosity overshoots

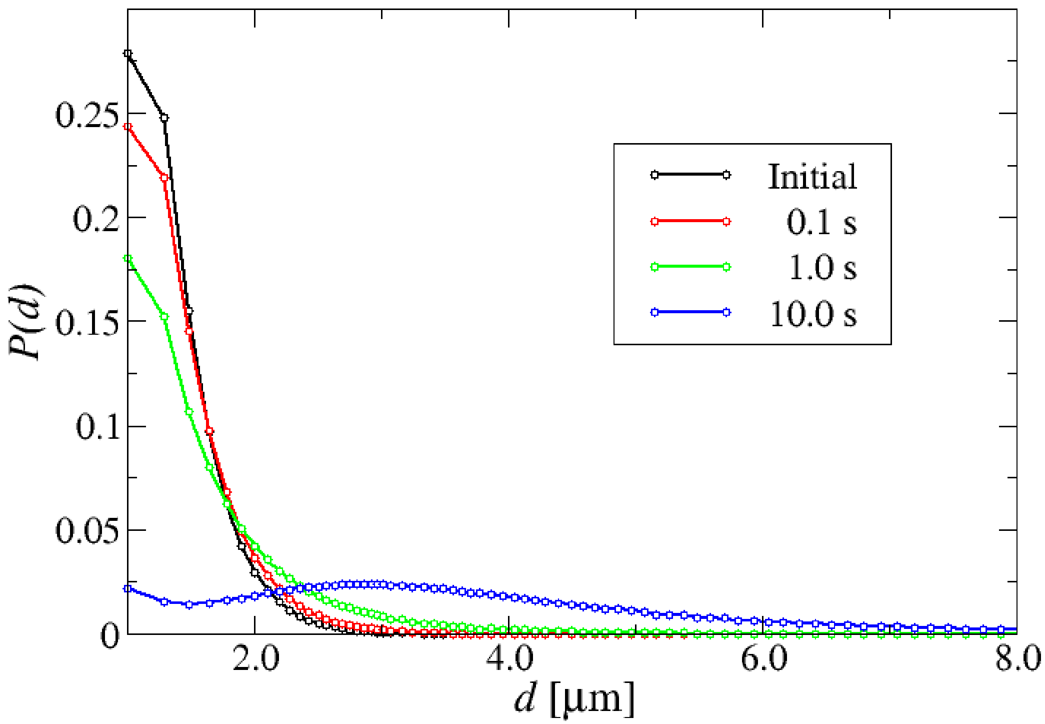
Can we say something about formation?

Typical velocity difference induced shear when spraying the slurry on the wire



Lindström and Uesaka (2008)

The floc size evolution of the TEMPO NFC under such shear



Viscous responses – Simulations

- The rheometer geometry can be taken into account by coupling the rheological model to a flow model
- Here, the flow field of a Couette rheometer is applied

$$\dot{\gamma}(r) = \frac{\Omega_B - \Omega_A}{\left[\int_{R_A}^{R_b} \frac{1}{r^3 \mu(r)} dr\right]} \cdot \frac{1}{r^2 \mu(r)}$$

- Advantages: Simple analytical solution exists – What such rheometer is measuring is easy to understand compared to more complicated geometries

Viscous responses – What does a rheometer measure

- A rotational rheometer measures the torque and the angular velocity with extremely high accuracy
- The stress is obtained in a straight-forward way

$$\sigma = A \cdot F = A \cdot \frac{T}{r}$$

- The shear rate is computed assuming a Newtonian, linear shear rate profile

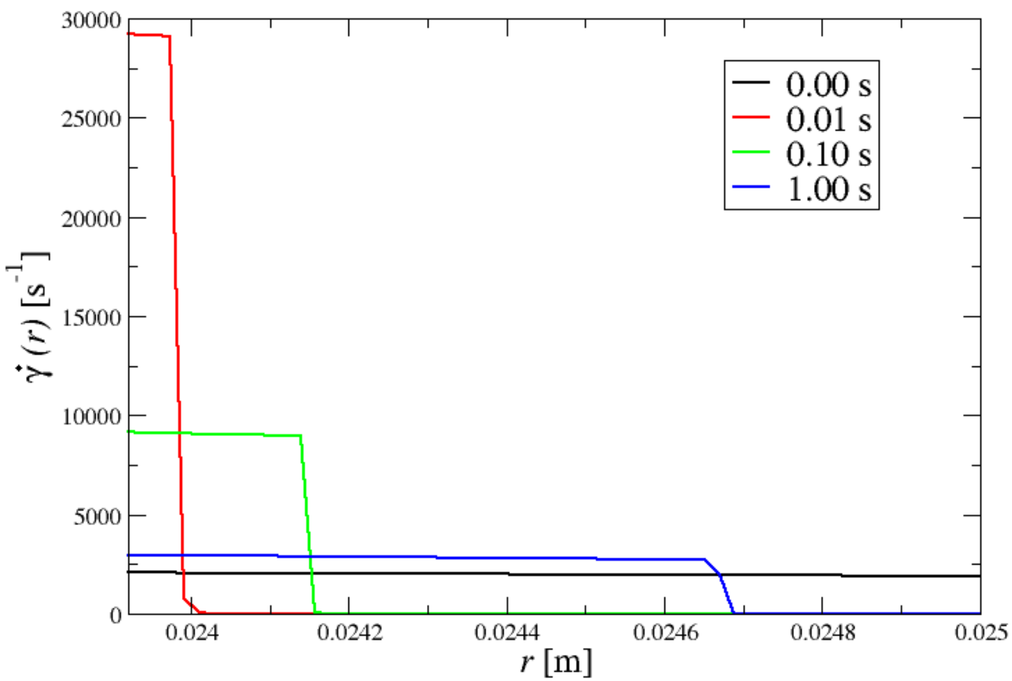
$$\dot{\gamma}(R_A) = (\Omega_B - \Omega_A) \cdot \frac{R_B^2}{R_B^2 - R_A^2}$$

- How linear is the shear rate profile, then?

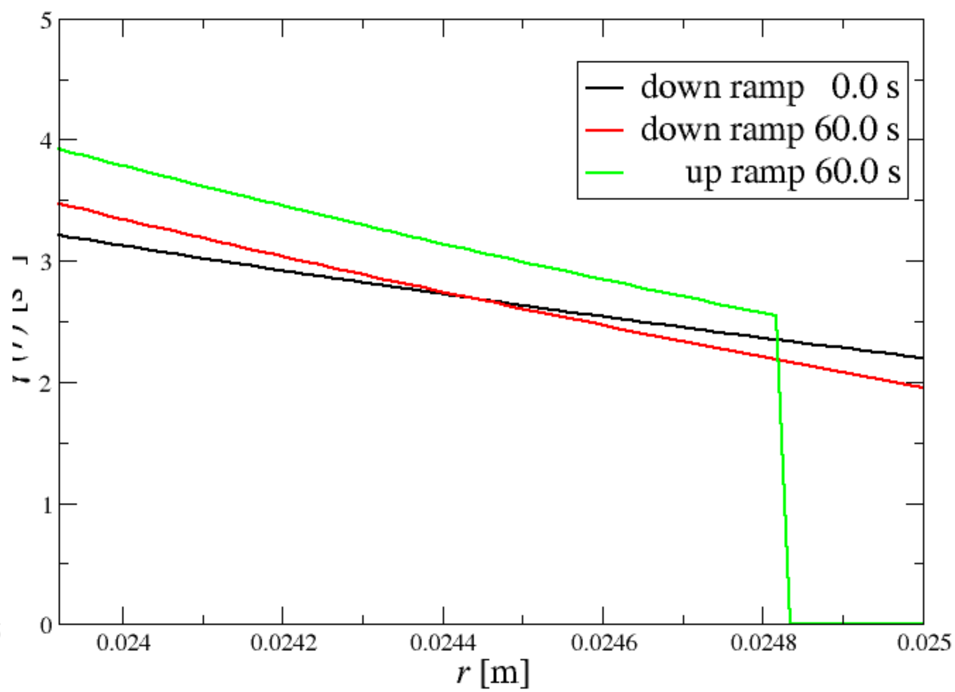
Viscous models – NFC

- The model shear rate profiles in a small gap Couette during shear ramp, 60 s point time

Over-edge shear rate 2000 s^{-1}

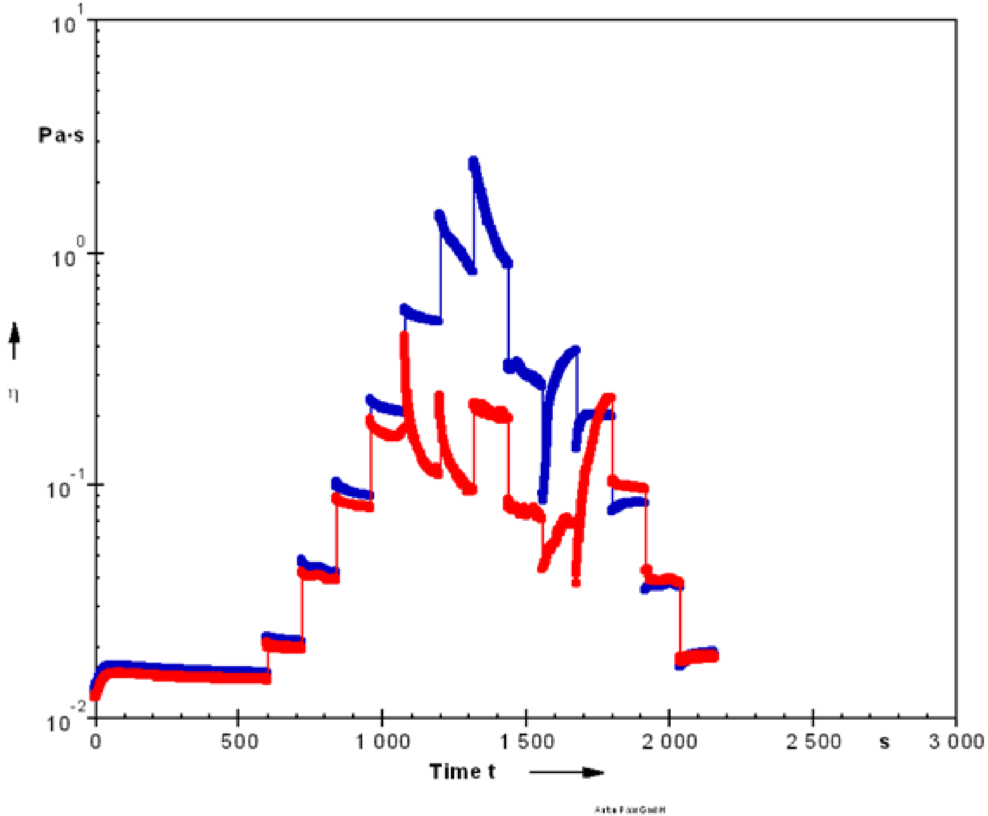


Over-edge shear rate 2.7 s^{-1}



- Answer: The quality of the measurement depends on the shear rate, time, and sample history…. Thixotropy!

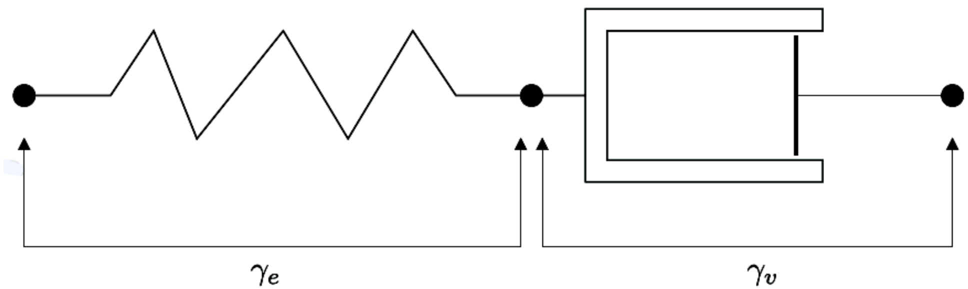
The viscosity overshoots of enzymatically pre-treated NFC



- The viscosity overshoots during the transients were not seen with the viscous model – What about the elastic effects?

Viscoelastic models

- Lots of variants, base types Kelvin-Voigt and Maxwell models
- Here: a simple Maxwell type dashpot-spring model



$$\sigma = \mu\dot{\gamma} - \frac{\mu}{G}\dot{\sigma}$$

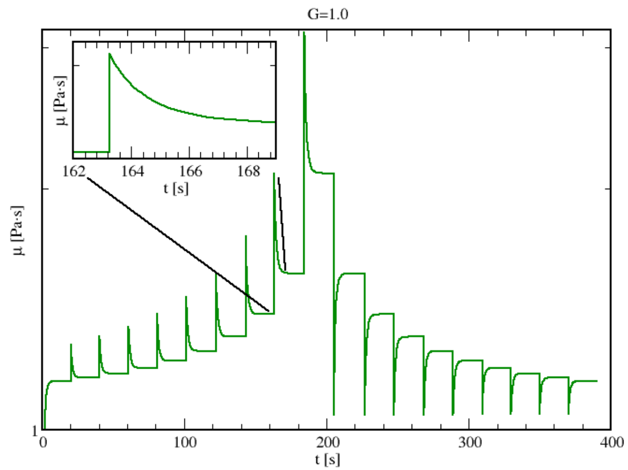
- Viscous stress evolves with a structural parameter

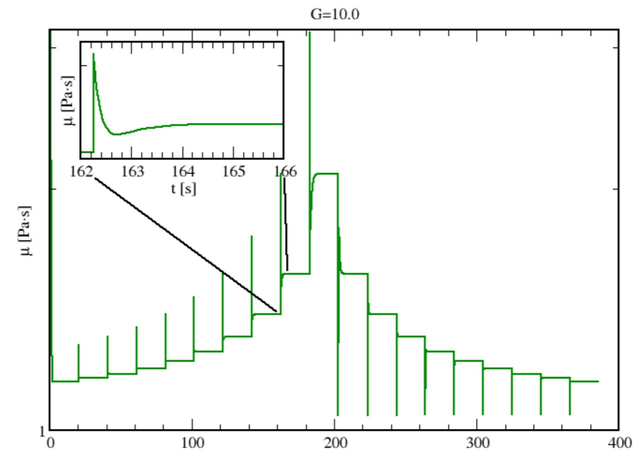
$$\begin{aligned} \frac{d\lambda}{dt} &= \frac{1}{k_1} - k_2\dot{\gamma}\lambda \\ \mu(\lambda) &= \mu_0\left(1 + k_3\lambda^n\right) \end{aligned}$$

- Stress in the system divides to two components: elastic and viscous stresses, both which have equal value but different shear

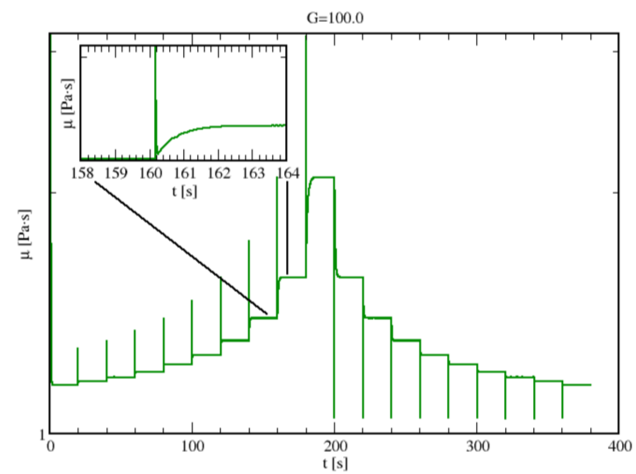
Viscoelastic effects

- The viscosity reported by the device in an experiment can be computed in the simulations by the Newtonian assumption





- The viscoelastic response shows similar “viscosity overshoots” as the experiments for enzymatically pre-treated NFC
- The overshoots are related to small elastic constant of the suspension



Viscoelastic effects – What did we learn?

- The fact that viscous and elastic stresses are impossible to separate in the experiment produces “viscosity” overshoots in the experimental data
  - They are impossible to get rid of in any practical measurement

- They have nothing what so ever to do with the suspension viscosity and are related to the Newtonian assumption used in rheometers to approximate the viscosity

- Such effect has no influence in the experiment if the elastic modulus is high compared to the viscous dissipation

NFC Mixtures

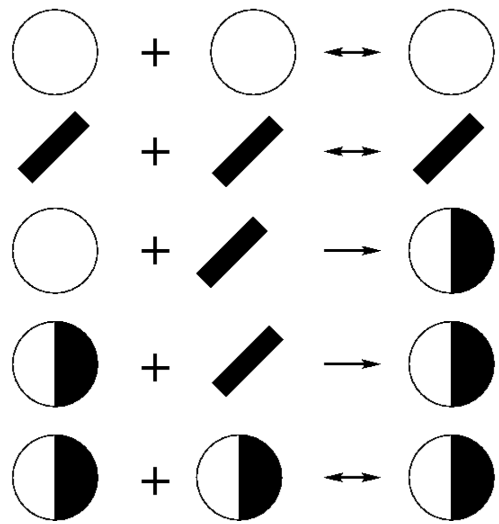
- In practice the NFC ends up being mixed with both fillers and fibers
- What are the implications of such simple models for the mixing of NFC with fibers and fillers?

Particle mixing – Population Balances

- The approach: Multicomponent Population Balances
- The same principles hold as for the one species model

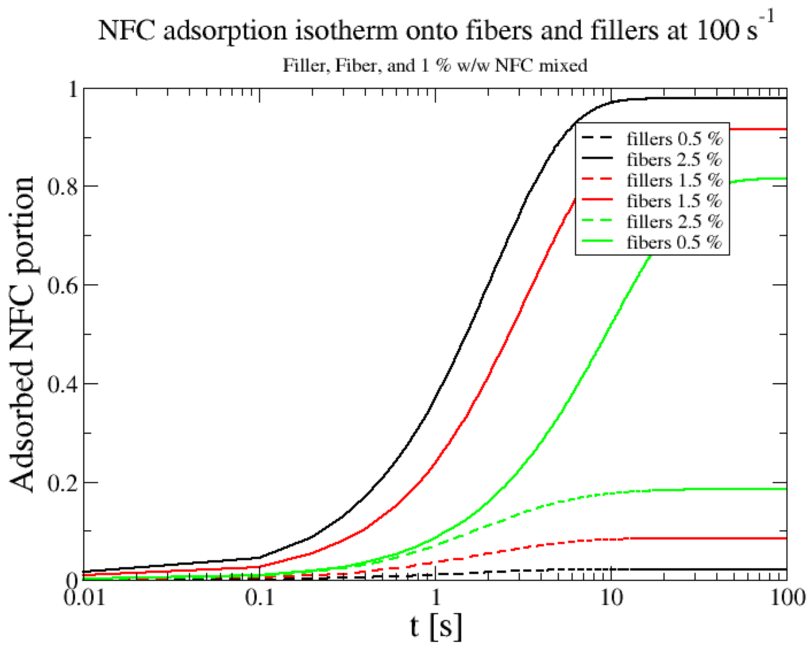
- Add distribution cross-terms between the NFC, filler, and fiber distributions

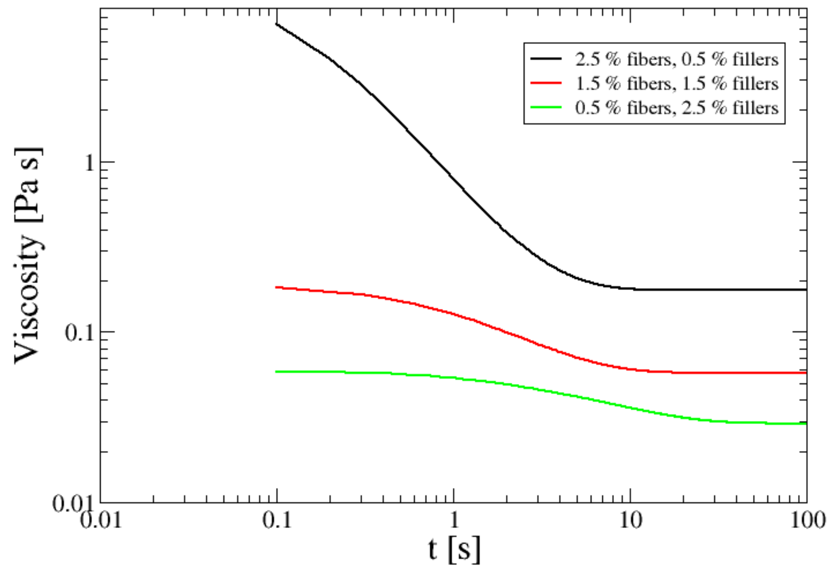
- Correct the collision rates using the effective surface areas for each species



- Figure: Population Balance equations for two components

Mixing – Results





If chemical interactions between the species are neglected

- NFC mixes with fibers rather than fillers because of their larger surface area
- Increasing filler content improves (of course) the mixing between the fillers and NFC
- NFC flocculates into large aggregates, since the collision rate is highest inside the NFC distribution

Summary

- Rheology of NFC suspensions was studied using computational continuum mechanics methods
- Explanations for the transient flow viscosity overshoots, and power-law scaling of the viscosity with shear rate was obtained
- The “noise” in the viscosity levels of enzymatically pre-treated NFC remains unsolved: possible explanations can relate to any combination of wall slip, elastic backward flow, and too short gaps (for the wide size distribution)
- Mixing of NFC was simulated, based on their relative surface area
    - NFC prefers to flocculate
    - Mixes better with fibers than fillers
    - The relative portions can be used to adjust the mixing

Acknowledgement

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