



How to use Rheology to Characterize and Formulate Nanofiber Based Materials

TAPPI Nano Division

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and**

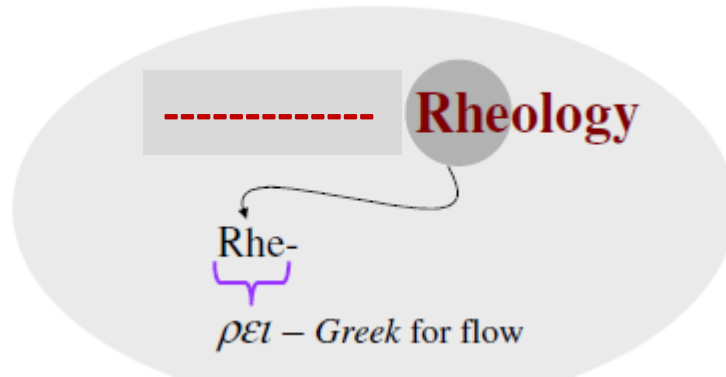
**National Institute for Nanotechnology, National Research Council of Canada
Edmonton, Alberta Canada**

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Outline

- What is and why rheology?
- Rheological terms
- What and how to measure?
- Cellulose Nanocrystals (CNC)
- Cellulose Nanofibers (CNF)

What is rheology ?



*Rheology = the study of
deformation and flow.*

Fill in the blank:

- Polymer melt
- Polymer solution
- Suspension
- Food
- Ink
- Paint
- Glacier
- Cement mixture
- NANOCELLULOSE suspensions

For scientists, engineers and laymen, rheology is observations or expressions of how the stress in a material or force applied to a material is related to deformation (change of shape) of the material.

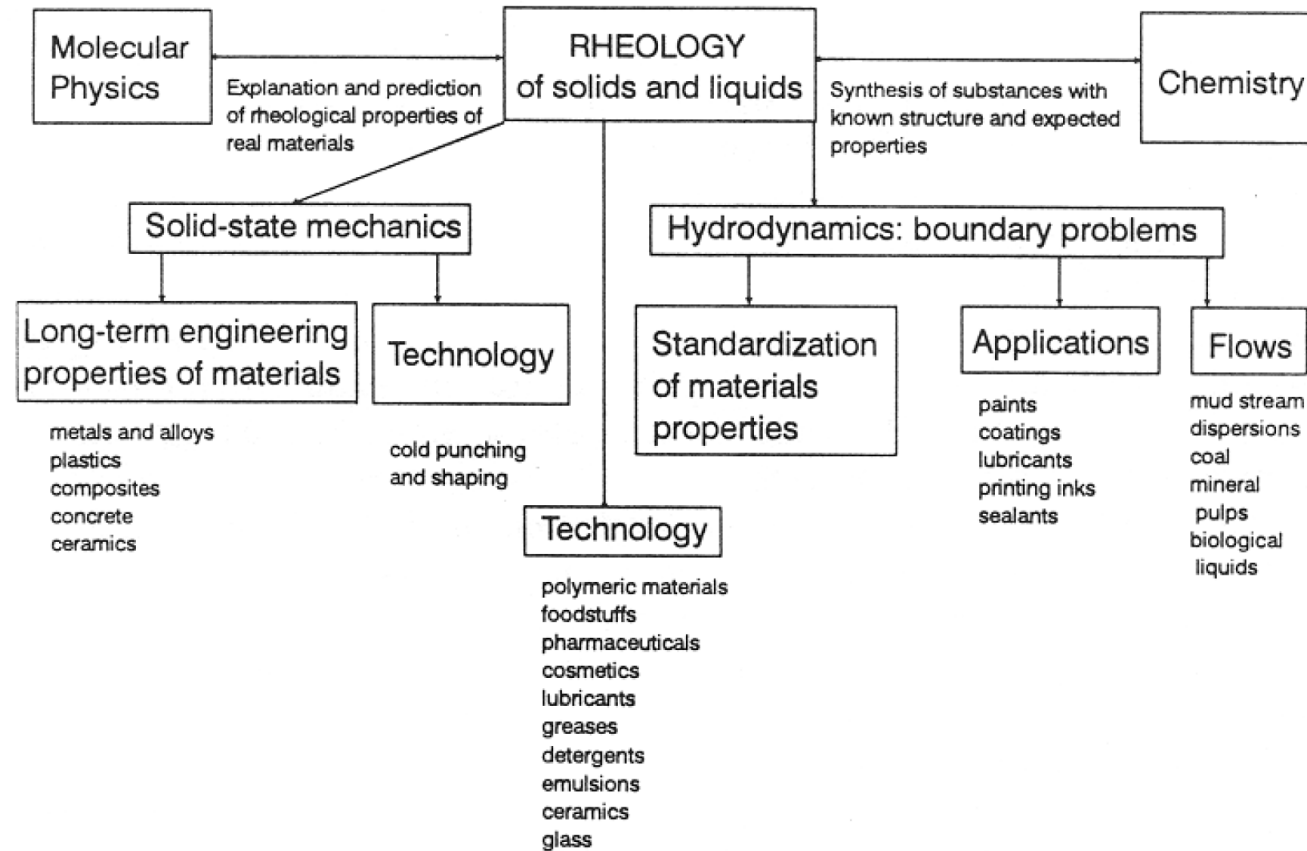
Rheology Explains Behavior

- **Drop onto a concrete floor four objects:**
 - a gum eraser
 - a cube of halite
 - a ball of soft clay
 - one cm³ of honey
- **When they fall, they behave the same by following the Newton's Second Law ($F = mg$)**
- ***Their difference is when they reach the ground:***
 - The eraser rebounds and bounces (**elastic**)
 - The clay flattens and sticks to the floor (**ductile**)
 - The halite fractures and fragments scatter (**brittle**)
 - The honey slowly spreads on the floor (**viscous**)

Why rheology?

- Predict the field performance of the material
- Understand physical properties of the materials and interactions among components

Rheology and its place among other sciences and applied problems

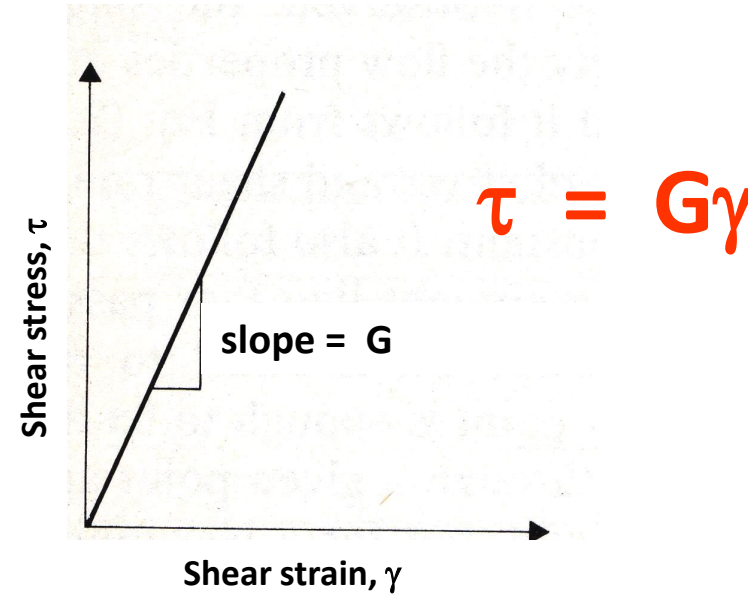
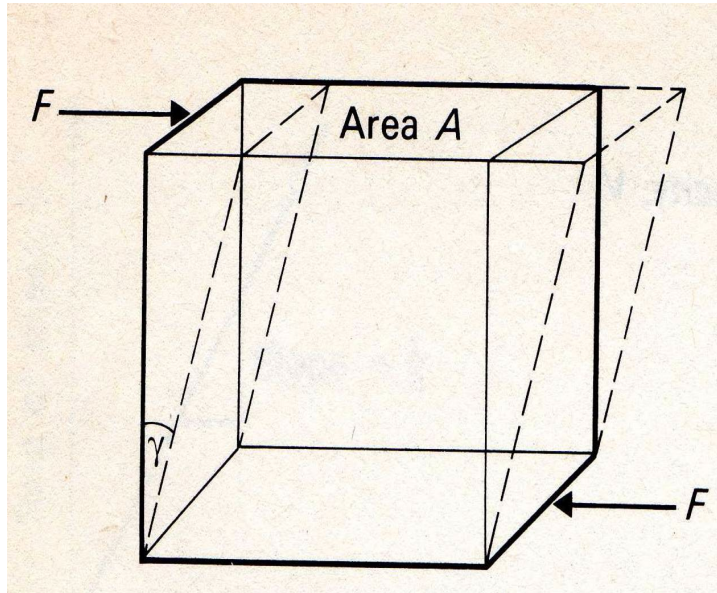


From: A. Ya. Malkin, Rheology Fundamentals, ChemTec Publishing

Material Parameters

- **Rheology depends on:**
 - **Extrinsic** (external) conditions such as:
 - **P, T, t**, chemistry of the environment
 - **Intrinsic** (internal) material properties such as:
 - Nanocellulose dimensions, surface properties, concentration, continuous phase

Hooke's Law for a Material under Shear Deformation



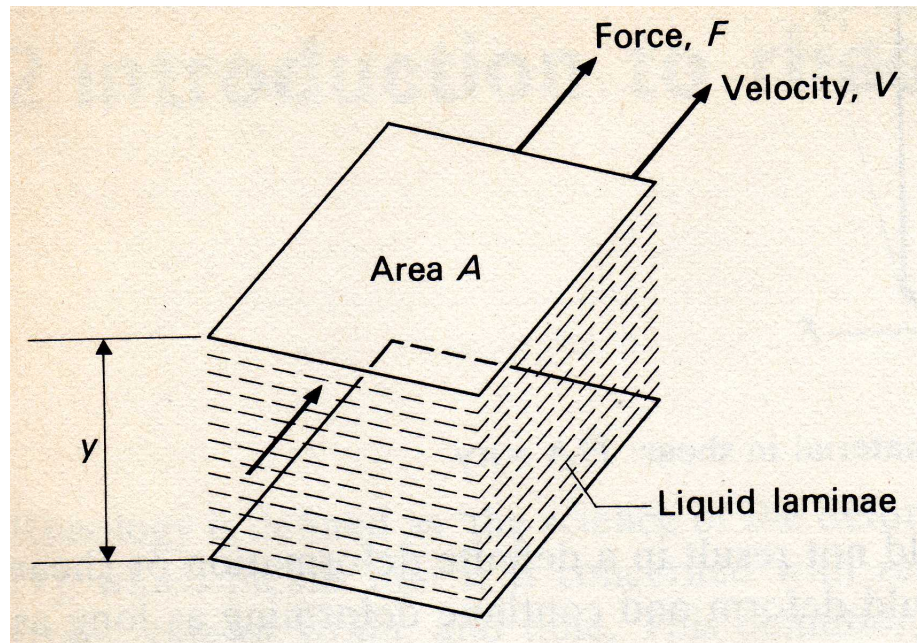
Consider a rectangular prism that is deformed by the application of equal and opposite forces, F , applied tangentially to opposite faces of the prism, each of area, A .

The prism will be deformed in the manner shown, under the shear stress of

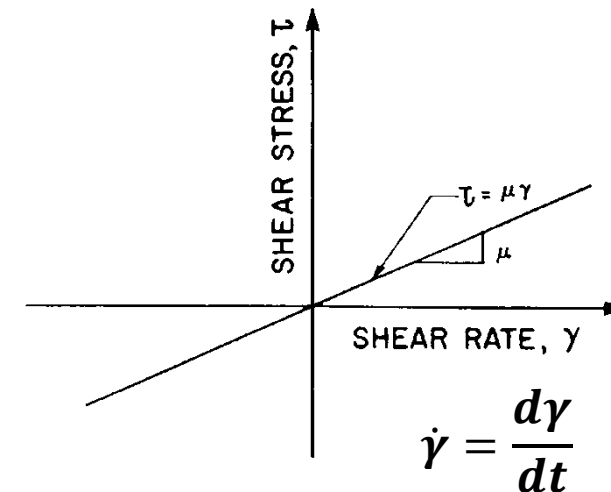
$$\tau = F/A$$

Newton's Law of Viscous Flow

- Consider a similar experiment (as described in the previous slide to establish Hooke's Law) for a “*rectangular prism*” made of a simple liquid.



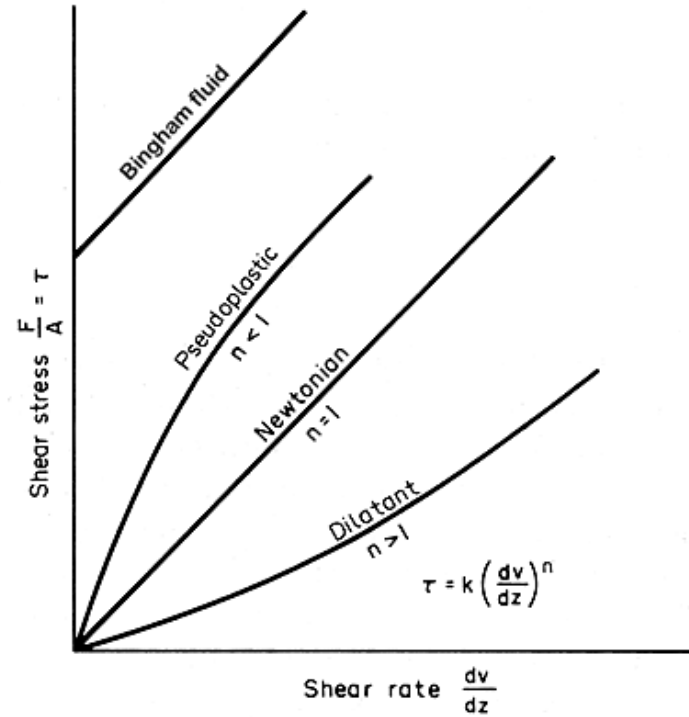
Shear rate = V/y



Viscous Flow

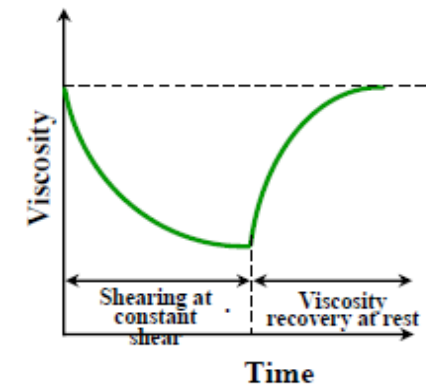
- The application of a particular shear stress will not result in a definite deformation (i.e. shear strain), but the liquid will deform and continue deforming as long as the shear stress is applied.
- This continuous increase will occur no matter how small the applied shear stress, τ , but the rate at which this occurs will depend very much on τ .
- In its simplest form (Newtonian liquid), the rate of deformation is directly proportional to the applied shear stress.

Types of Flow



- Newtonian Fluid
 - Non-Newtonian Fluids
 - Bingham Fluid
 - Shear Thickening Fluid
 - Shear Thinning Fluid
 - Thixotropic Fluid
- (closest resemblance to cement paste)

Thixotropy

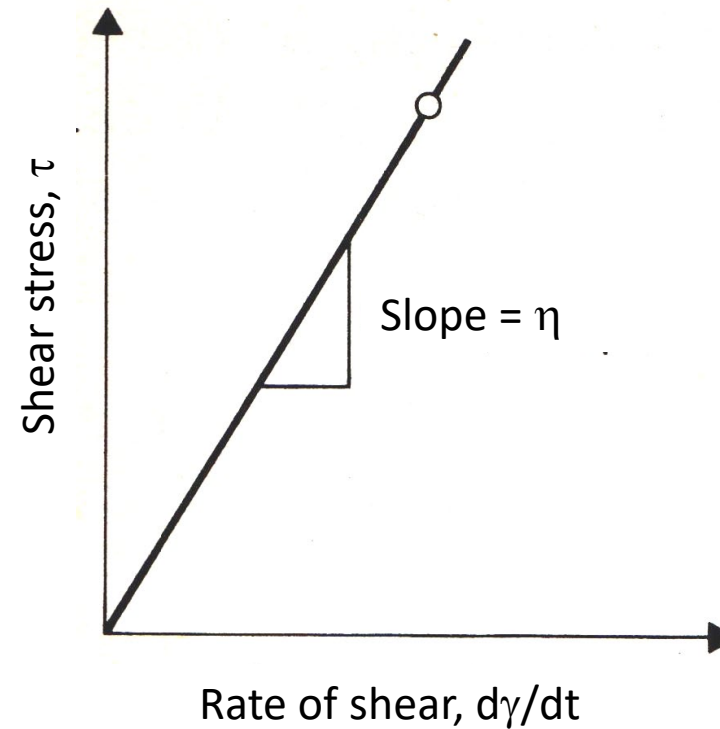


Newtonian Fluid

When the fluid flows regardless of how much it is being stressed, we have a Newtonian Fluid.

$$\tau = \eta \dot{\gamma}$$

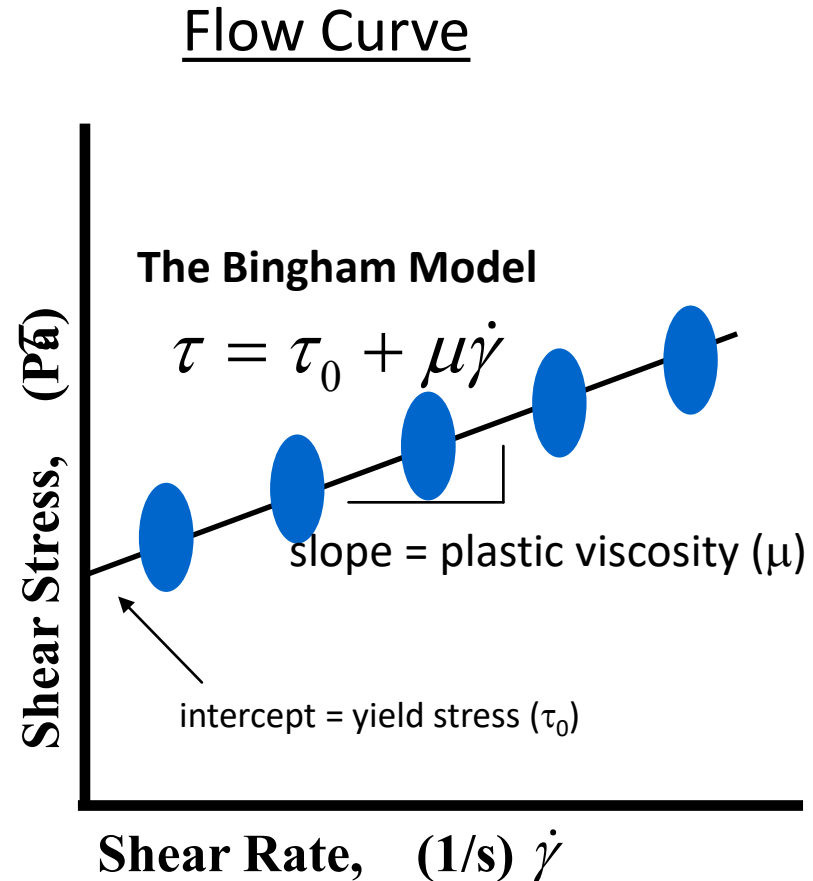
$$\dot{\gamma} = \frac{d\gamma}{dt}$$



Bingham Fluid

- A Bingham fluid acts as a rigid body at low shear stress and flows like a viscous fluid at high shear.
- Past the critical shear, it behaves as a Newtonian Fluid - there is a linear relationship between shear stress and shear rate.

$$\tau = \tau_0 + \eta \dot{\gamma}$$



$$\dot{\gamma} = \frac{d\gamma}{dt}$$

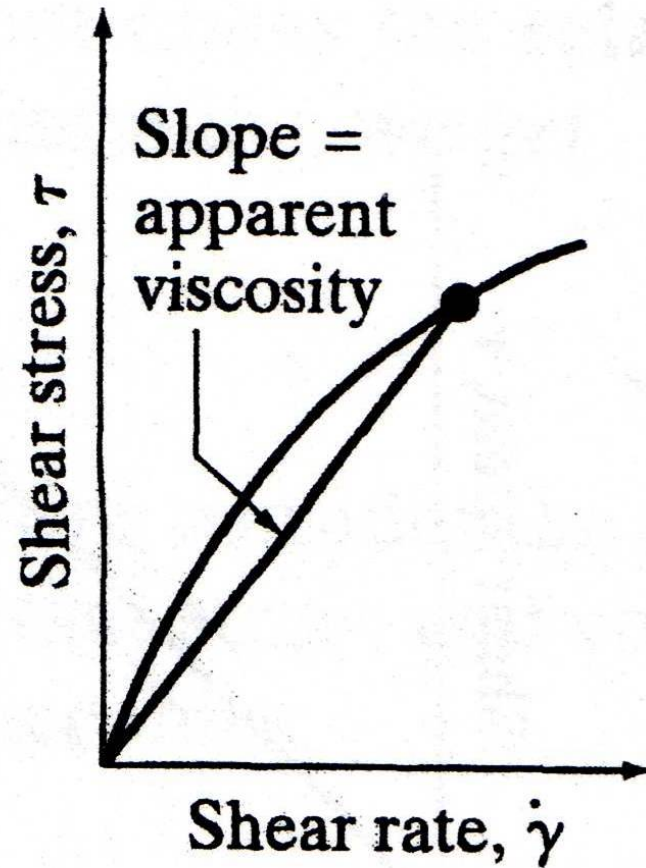
Shear Thinning

- This type of liquid displays a decrease in the viscosity with an increase in the shear rate.

$$\tau = A(\dot{\gamma})^m$$

where, $m < 1$

$$\dot{\gamma} = \frac{d\gamma}{dt}$$



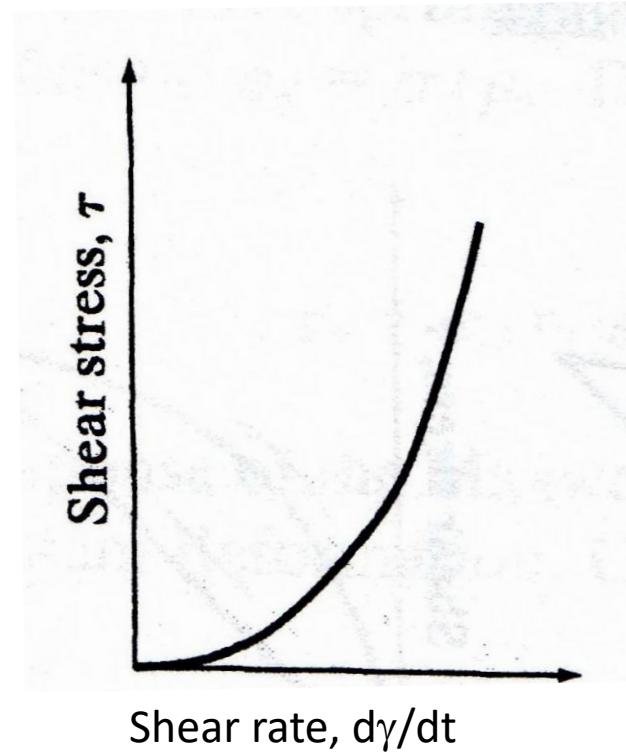
Shear Thickening

- Such fluids (also called dilatant fluids) exhibit an increase in viscosity with an increase in the shear strain rate.

$$\tau = A(\dot{\gamma})^m$$

where, $m > 1$

$$\dot{\gamma} = \frac{d\gamma}{dt}$$

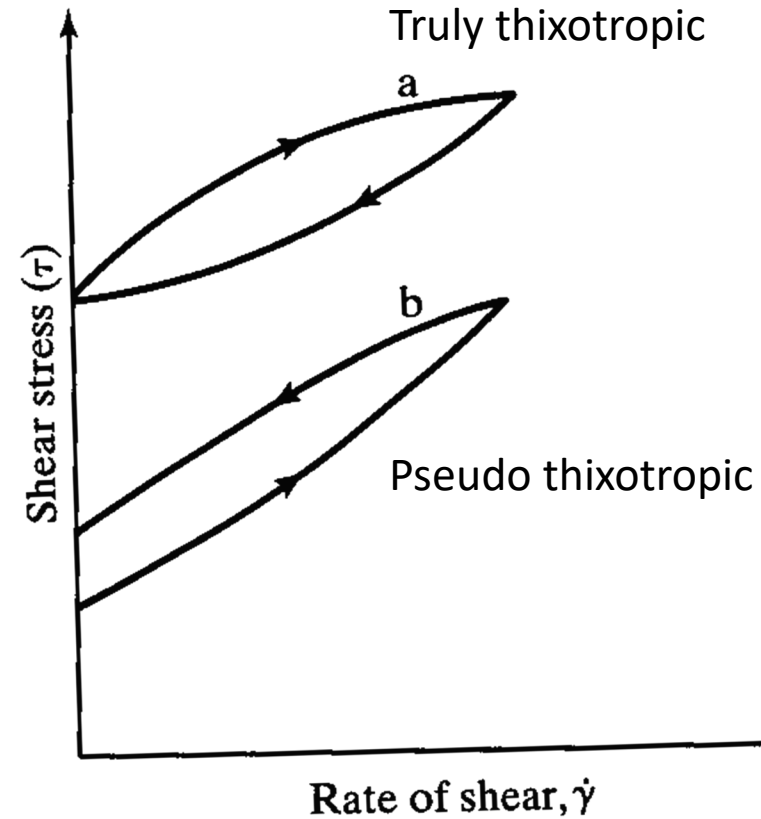
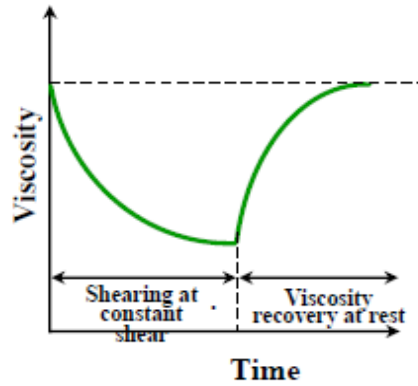


Thixotropic Fluid ...(1)

- A fluid which exhibits a drop in viscosity with time under a constant shear strain rate is said to be thixotropic.
- The viscosity undergoes a gradual recovery when the shear stress is removed.
- A truly thixotropic fluid will exhibit a completely reversible behaviour.
- A pseudo thixotropic fluid does not completely return to its original state of yield stress.

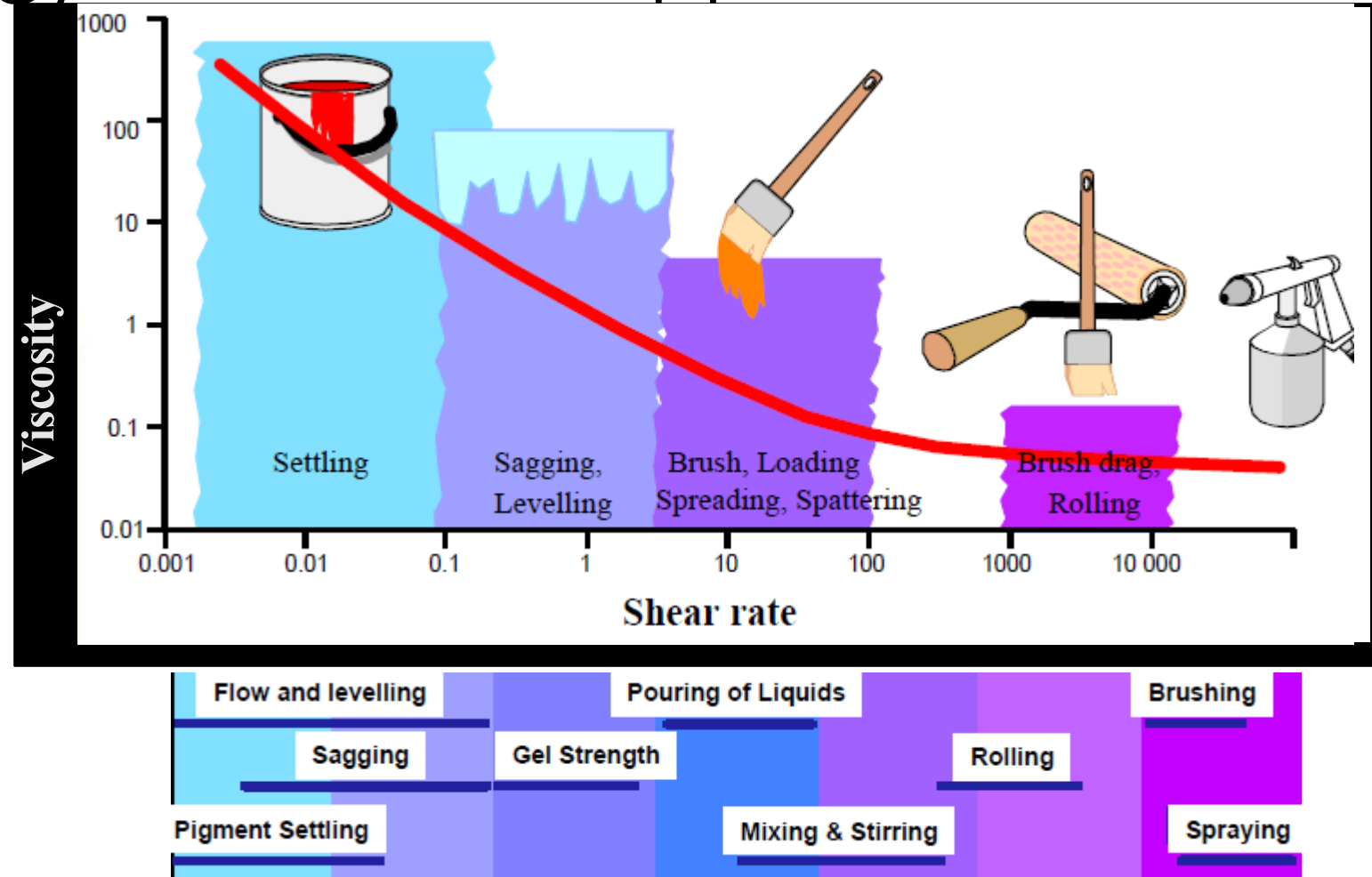
Thixotropic Fluid ...(2)

Thixotropy



$$\dot{\gamma} = \frac{d\gamma}{dt}$$

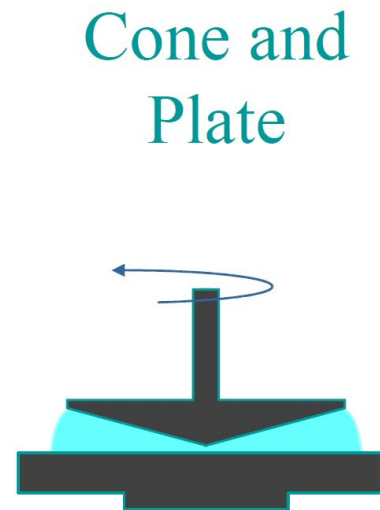
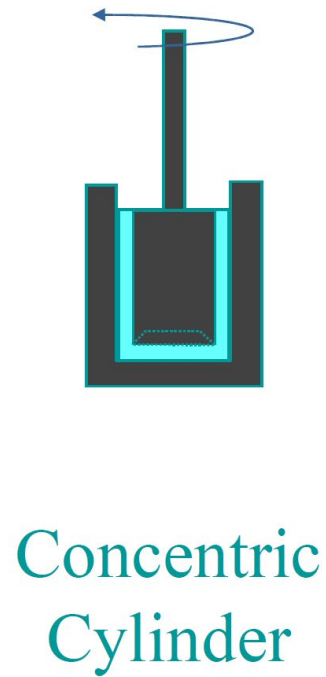
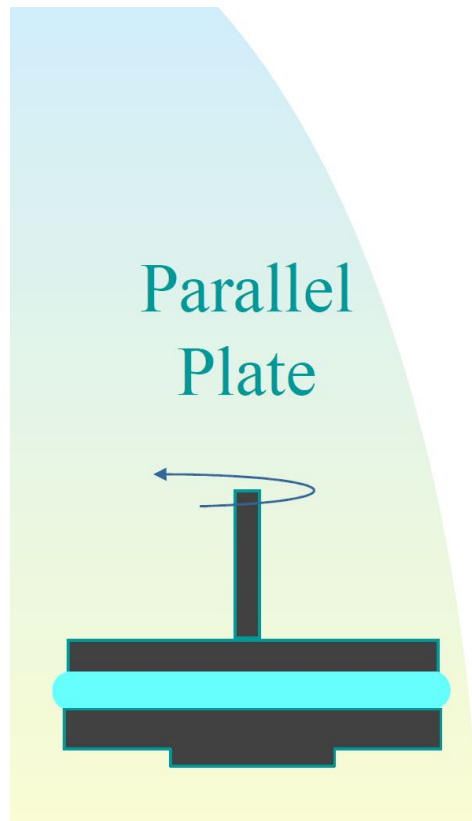
Rheology Profile and Applications



Shear rates of some familiar materials and processes

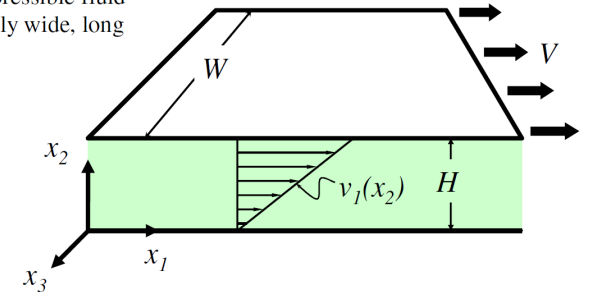
Situation	Typical range of shear rates (s^{-1})	Application
Sedimentation of fine powders in a suspending liquid	$10^{-6} - 10^{-4}$	Medicines, paints
Levelling due to surface tension	$10^{-2} - 10^{-1}$	Paints, printing inks
Draining under gravity	$10^{-1} - 10^1$	Paints, printing inks
TABLE 2.2 Shear rates typical of some familiar materials and processes		
Extruders		
Chewing and swallowing	$10^1 - 10^2$	Foods
Dip coating	$10^1 - 10^2$	Paints, confectionary
Mixing and stirring	$10^1 - 10^3$	Manufacturing liquids
Pipe flow	$10^0 - 10^3$	Pumping, Blood flow
Spraying and brushing	$10^3 - 10^4$	Spray-drying, painting, fuel atomization
Rubbing	$10^4 - 10^5$	Application of creams and lotions to the skin
Milling pigments in fluid bases	$10^3 - 10^5$	Paints, printing inks
High speed coating	$10^5 - 10^6$	Paper
Lubrication	$10^3 - 10^7$	Gasoline engines

Common rotational viscometers (rheometers)



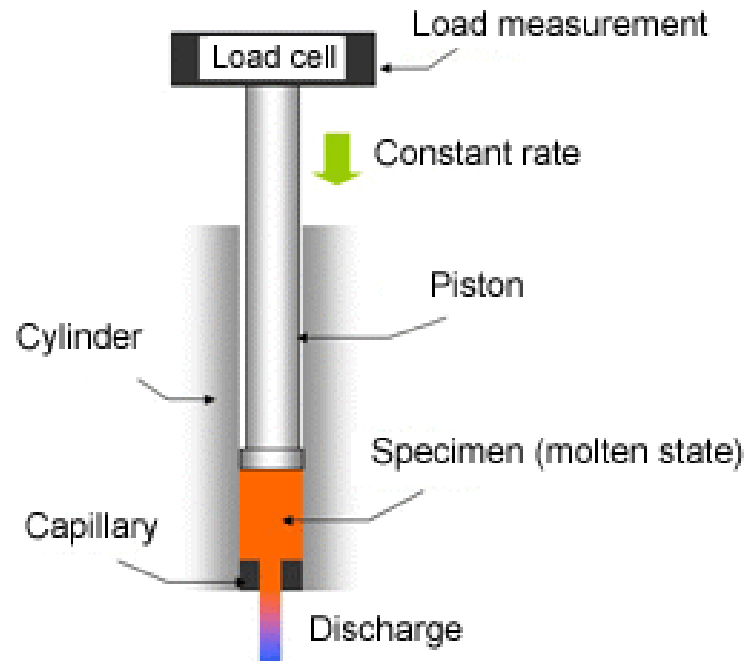
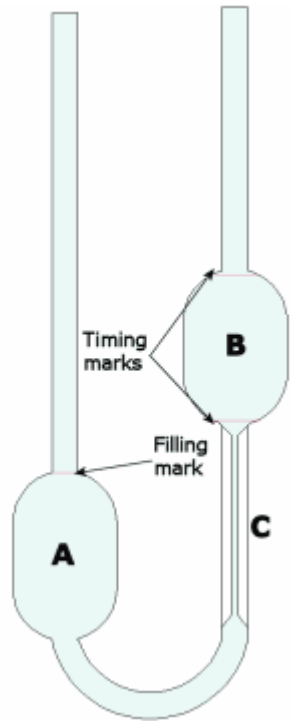
EXAMPLE: Drag flow between infinite parallel plates

- steady state
- incompressible fluid
- infinitely wide, long



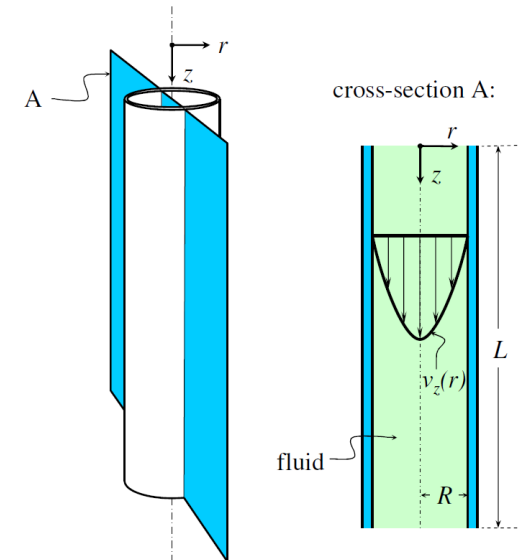
From Morrison Rheology Notes

Capillary and piston viscometers



EXAMPLE: Poiseuille flow in a tube

- Steady state
- incompressible fluid
- long tube



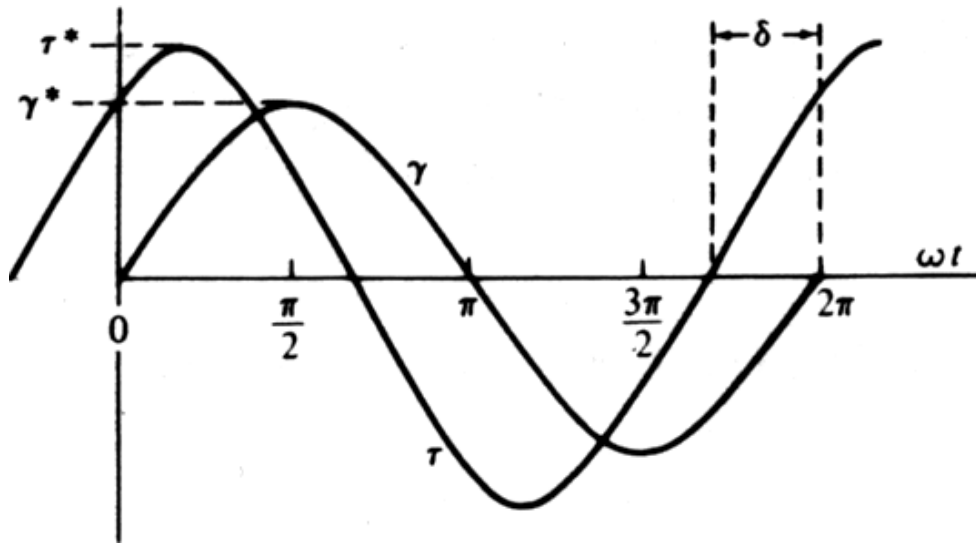
From Morrison Rheology Notes

Shear Oscillatory Measurements

- Measured using rotational rheometers (strain or stress controlled), with cone-and-plate or parallel plate fixtures in the dynamic oscillatory mode.
 - Stress sweeps: To identify linear viscoelasticity region. Very sensitive to branching and presence of fillers.
 - Temperature sweeps: To identify temperature stability, degradation, crosslinking
 - Frequency sweeps: Useful to detect structure of the material, viscous vs. elastic behaviour etc.
 - Stress relaxation: To detect the relaxation modulus as a function of time.
- Oscillatory measurements can also be performed on solid samples (i.e. rubber, polymers in the solid state) using DMA (Dynamic Mechanical Analyzer) instruments.
 - Temperature sweeps are commonly used to identify glass transition temperatures, and damping properties ($\tan\delta$) of the solid samples.

Dynamic (Oscillatory) Rheometry

In the general case when the sample is deformed sinusoidally, as a response the stress will also oscillate sinusoidally at the same frequency, but in general will be shifted by a phase angle δ with respect to the strain wave. The phase angle will depend on the nature of the material (viscous, elastic or viscoelastic)



➤ Input

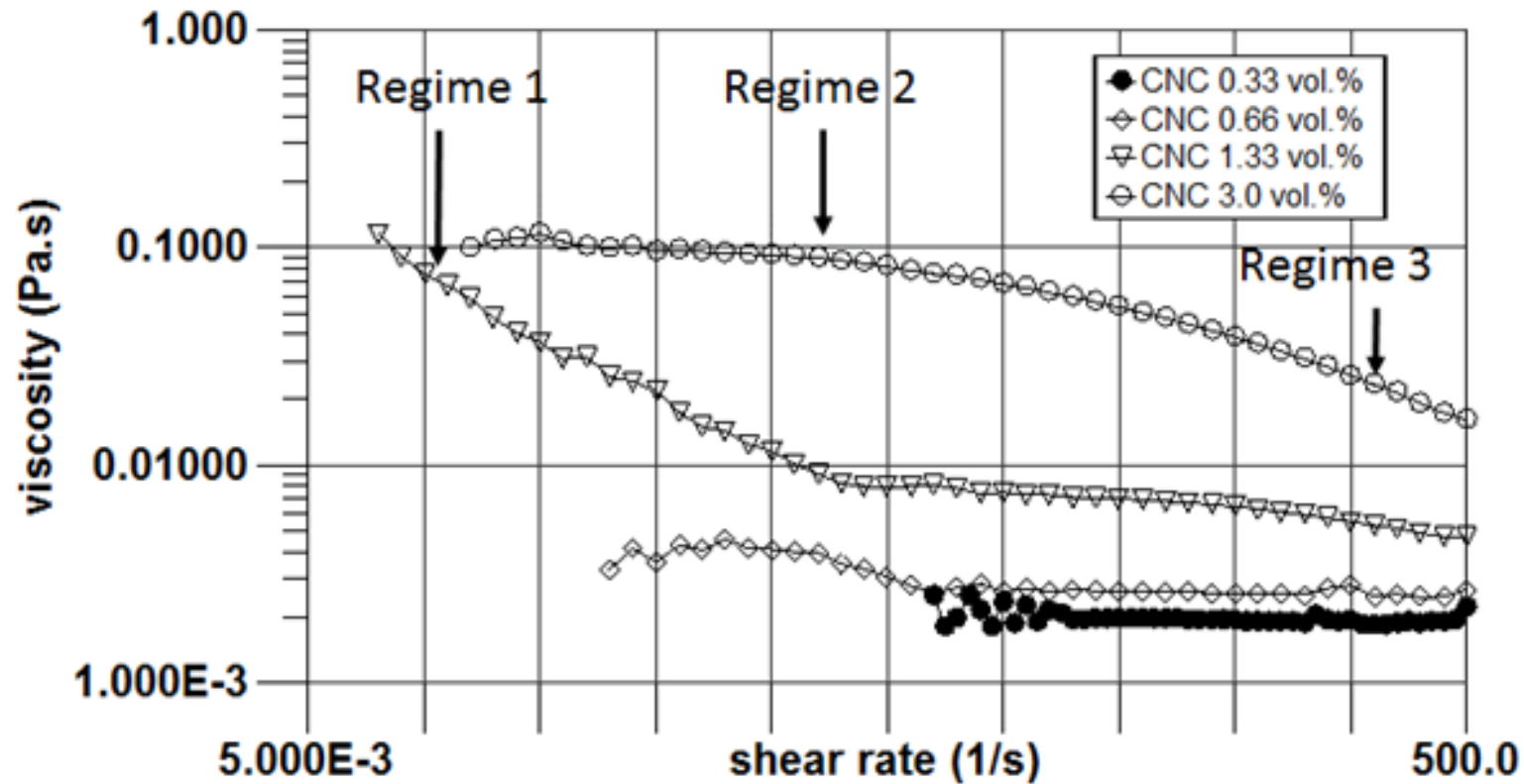
$$\gamma = \gamma_0 \sin(\omega t)$$

➤ Response

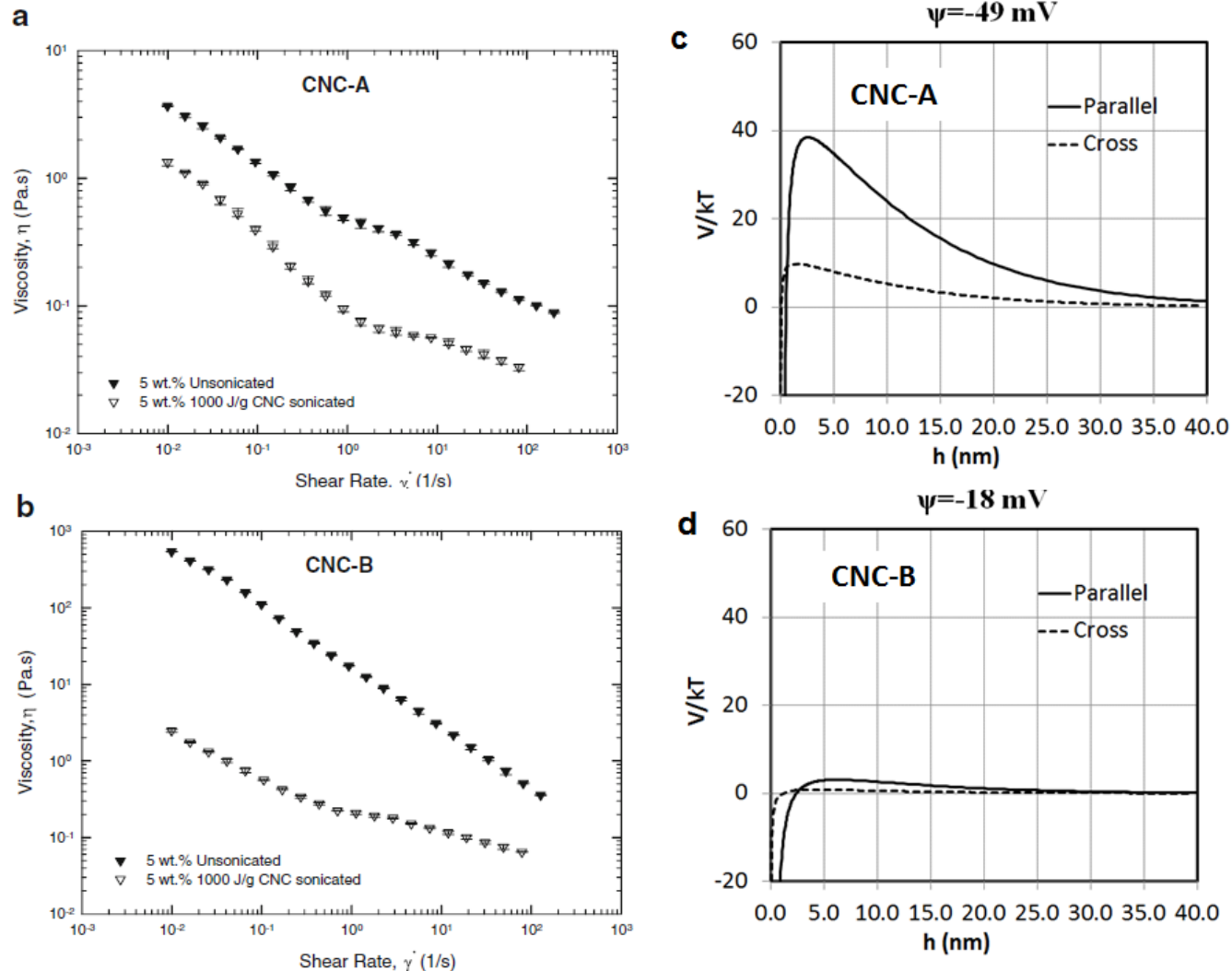
$$\tau = \tau_0 \sin(\omega t + \delta)$$

where $0^\circ < \delta < 90^\circ$

Steady state shear viscosities of CNC with L/D=12 at 0.33vol%



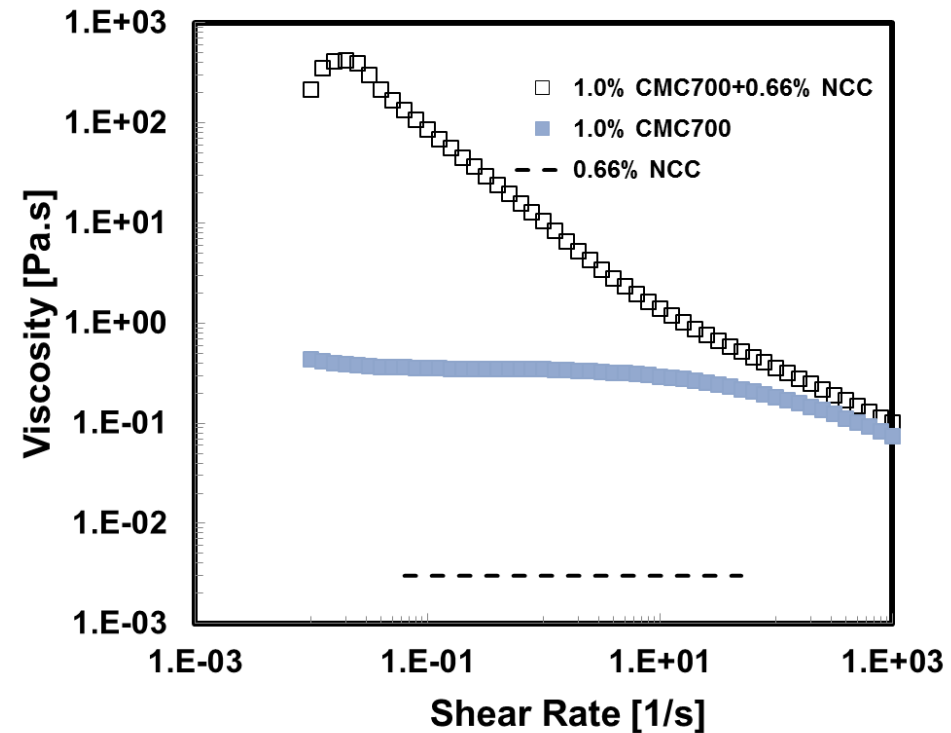
CNC surface charge effect on viscosity



- Viscosity vs. shear rate plots of: CNC-A (a); CNC-B (b) before and after sonication; Interaction energy (V/kT) between CNC rods in parallel and cross orientations vs particle-particle distance (h): CNC-A (a); CNC-b (b). V/kT calculations performed for particle diameter (d) = 7nm; length (L) = 100 nm; Hamaker constant (A_{123}) = 1.20×10^{-20} J.; Debye Length (κ^{-1}) = 9.68 nm; Zeta potentials (ζ) are given on each plot. (a and b reprinted with permission from Ref. [15]. Copyright 2013 Springer).

Rod Shaped Cellulose Nanocrystals

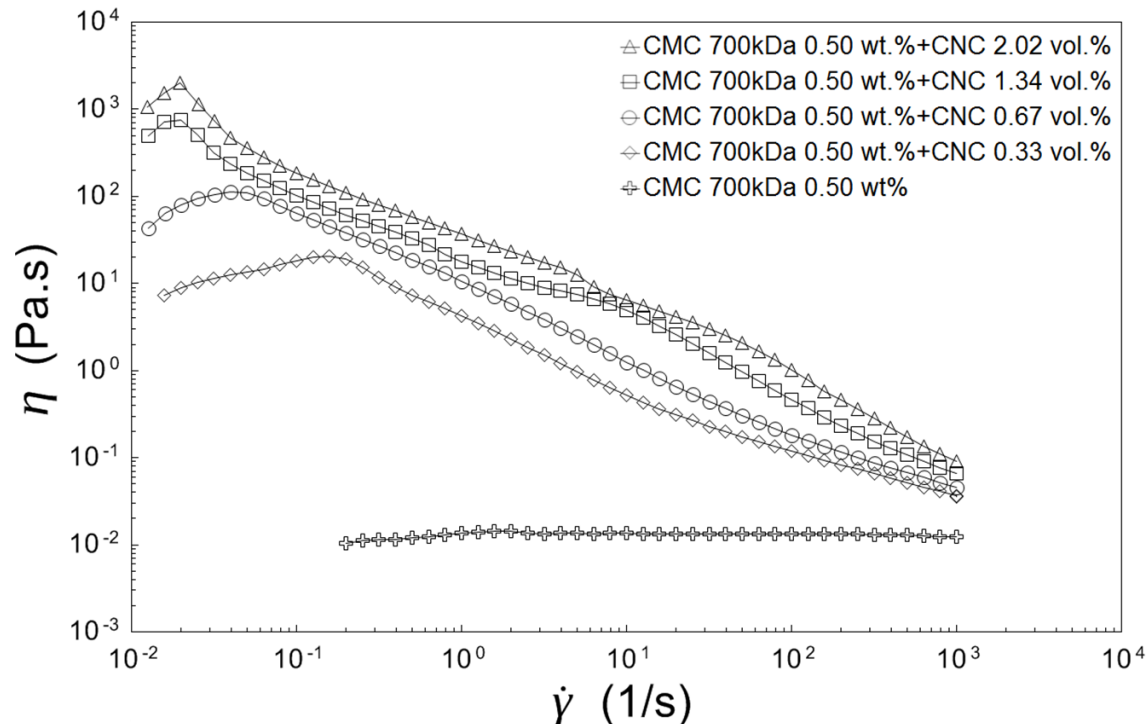
- CNC is not a thickener in diluted and semi-diluted concentrations
- However CNC (in semi dilute concentration range) at least 500 time enhances non-Newtonian characteristics of certain semi-dilute water soluble polymers.
- Commercial potentials:
 - Use of CNC at low concentrations
 - Use as a rheology modifier in coatings, personal care, drilling fluids, and other functional fluids



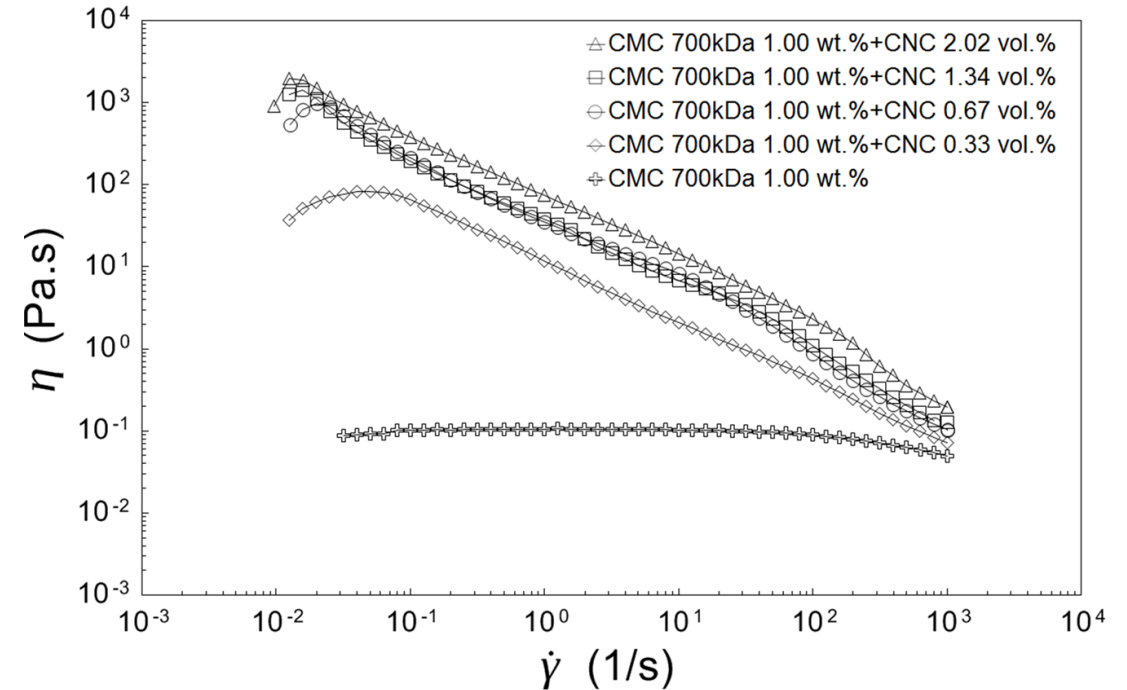
Boluk and Zhao, US Patent 8,105,430 B2
Boluk et. al Langmuir, 28:6114-6123 (2012)

Shear viscosities of CNC in a) 0.5 % ; b) 1.0 % CMC solutions

$T = 25^{\circ}\text{C}$



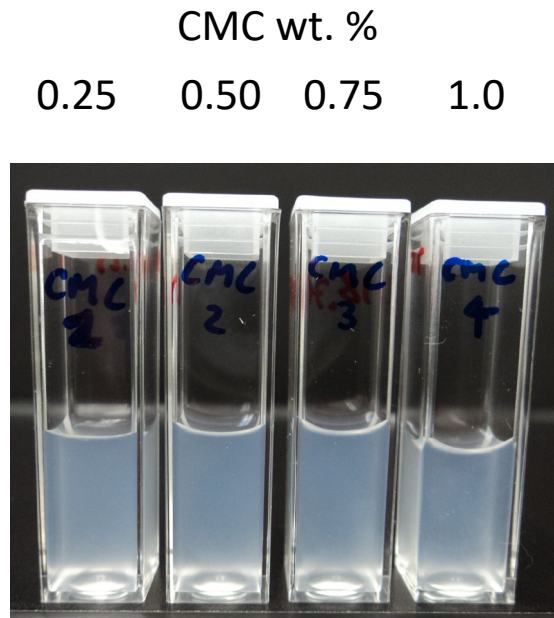
(a)



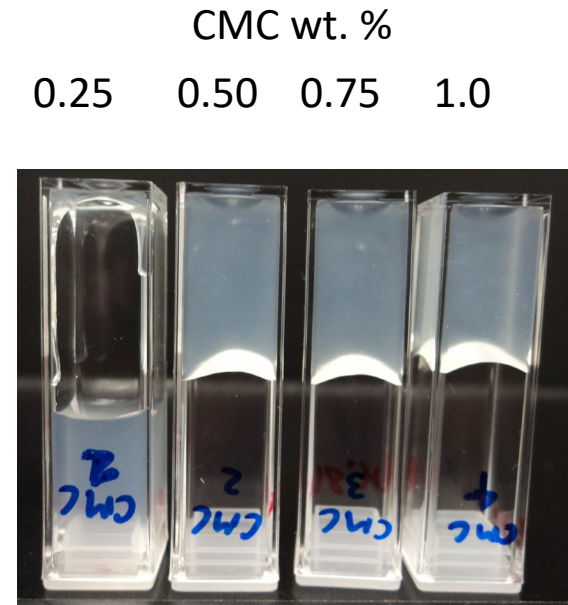
(b)

Oguzlu, Hale, Christophe Danumah, and Yaman Boluk. "The role of dilute and semi-dilute cellulose nanocrystal (CNC) suspensions on the rheology of carboxymethyl cellulose (CMC) solutions." *The Canadian Journal of Chemical Engineering* 94.10 (2016): 1841-1847.

0.33 vol.% CNC suspension in CMC (700 kDa) solutions.



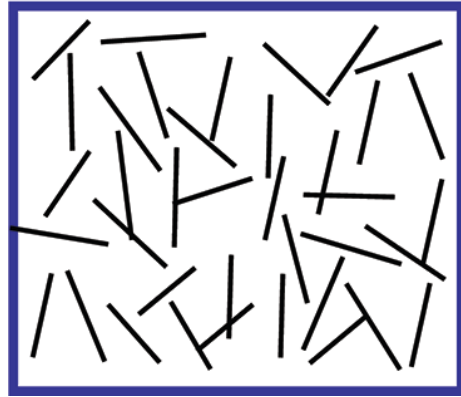
(a)



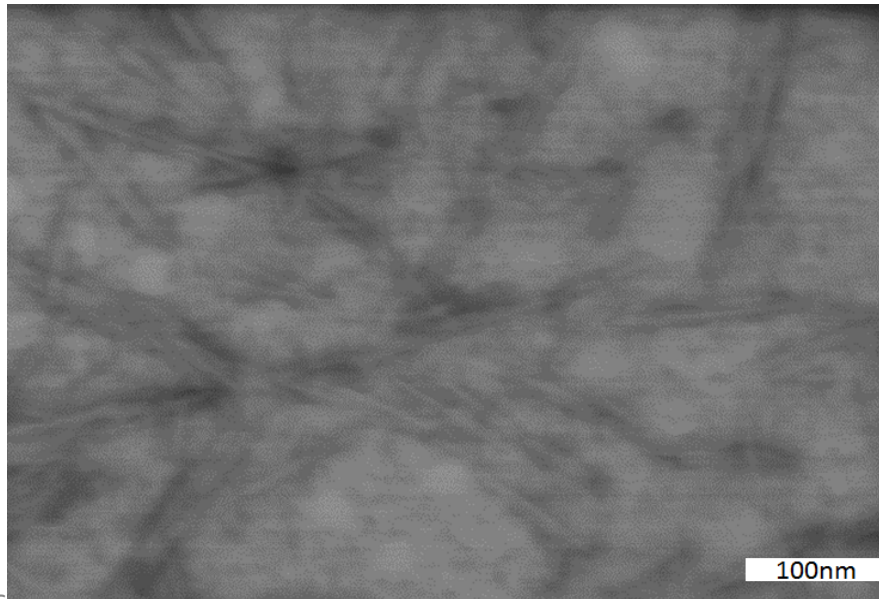
(b)

CNC Structure of Polymer Solutions

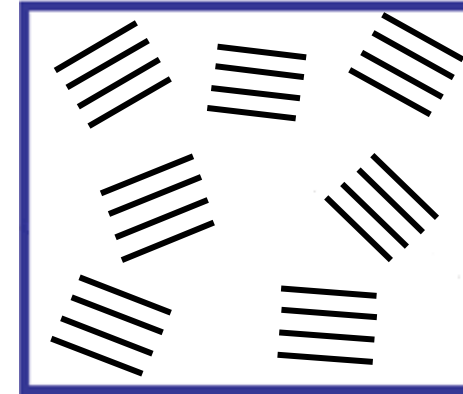
without the presence of non-adsorbing polymer



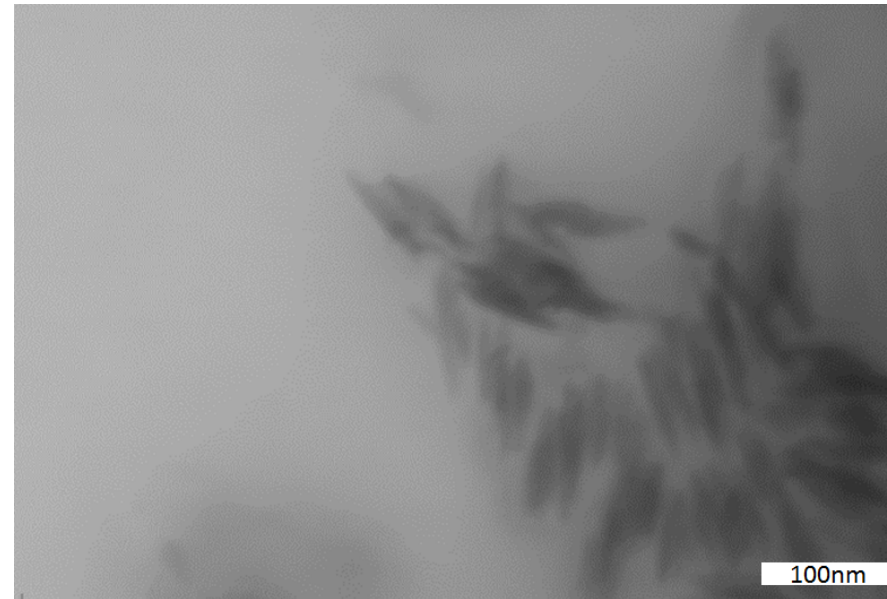
PEO-CNC



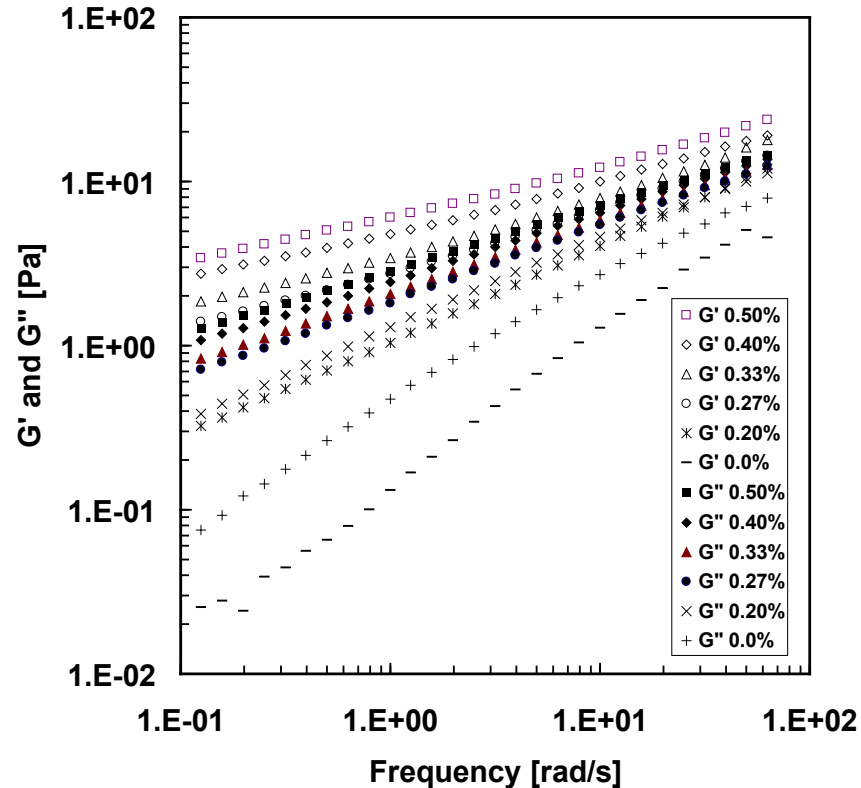
with the presence of depleted non-adsorbing polymer.



CMC-CNC

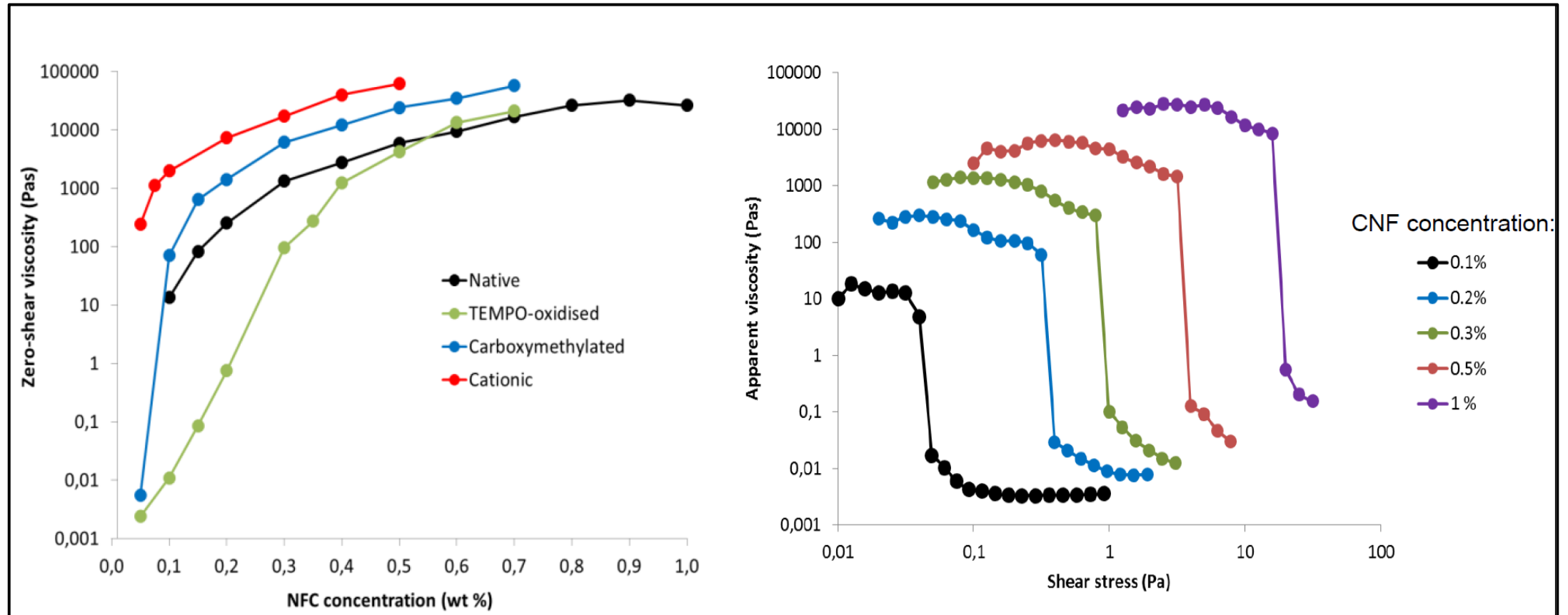


Oscillation measurements of CNC in HEC solutions



$G'(\omega)$ and $G''(\omega)$ of CNC suspensions in 1.0% (wt) HEC solutions.

Flow behavior of CNF depends on the grade and concentration



From Webinar, May 27, 2015, Pia Qvintus & Heli Kangas, VTT Technical Research Centre of Finland Ltd.

Oscillation measurements of CNF suspensions

Lasseuguette, Elsa, Denis Roux, and Yoshiharu Nishiyama.
"Rheological properties of microfibrillar suspension of TEMPO-oxidized pulp." *Cellulose* 15.3 (2008): 425-433.

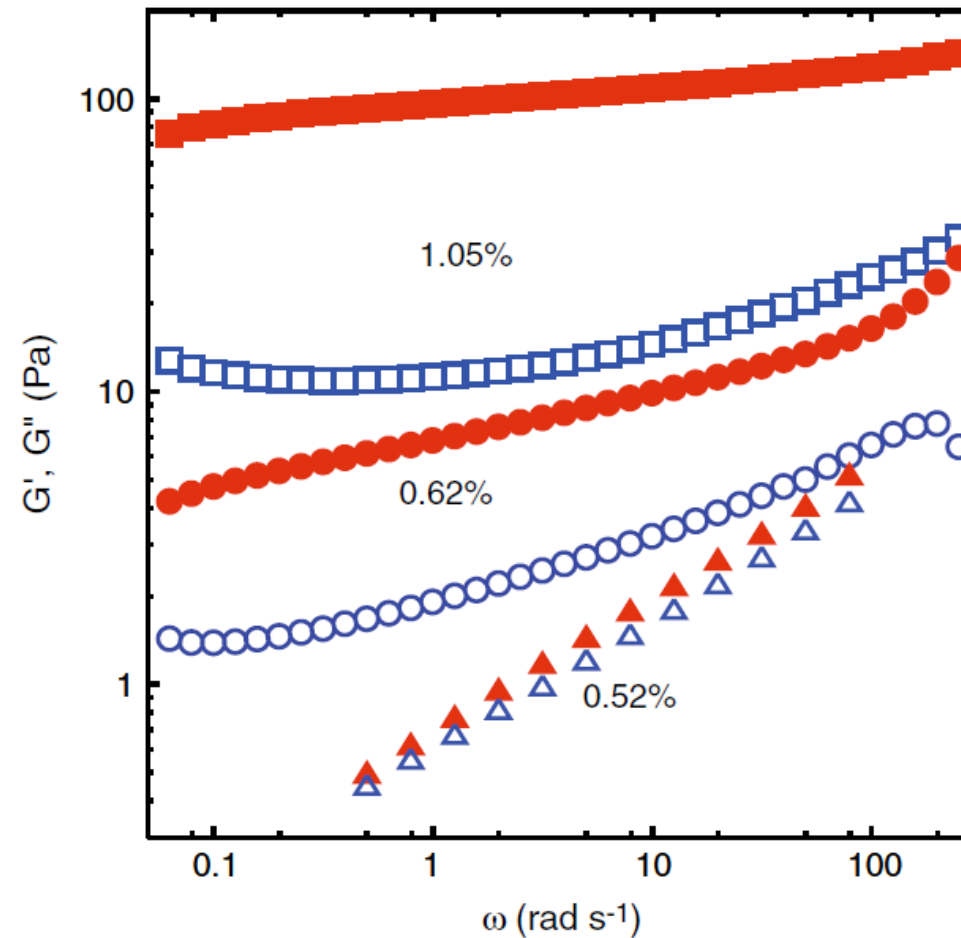
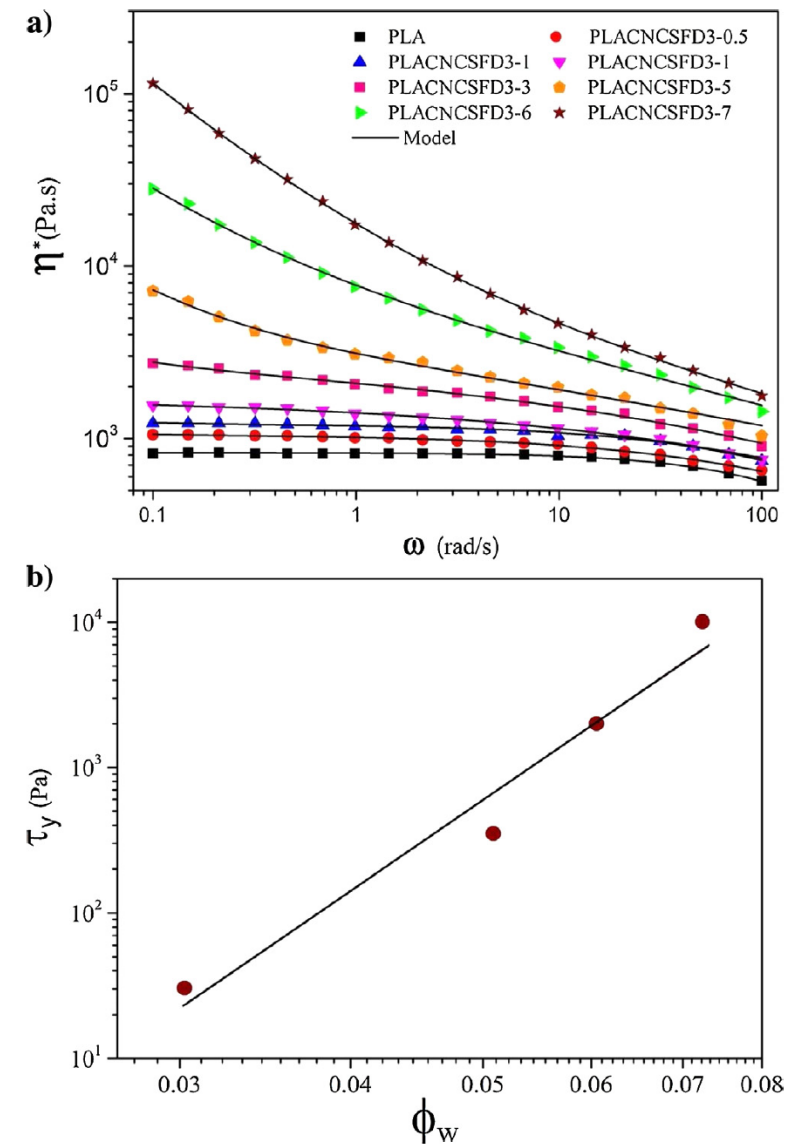


Fig. 6 Storage modulus and loss modulus of oxidized microfibril suspension as a function of angular frequency. Filled symbols correspond to G' and open symbols correspond to G''

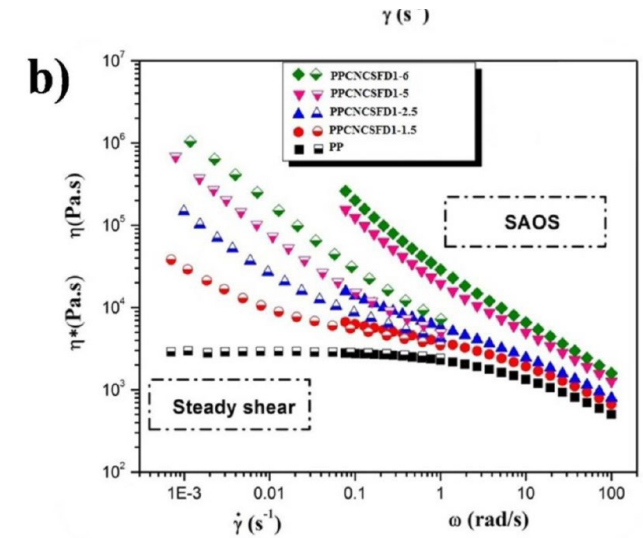
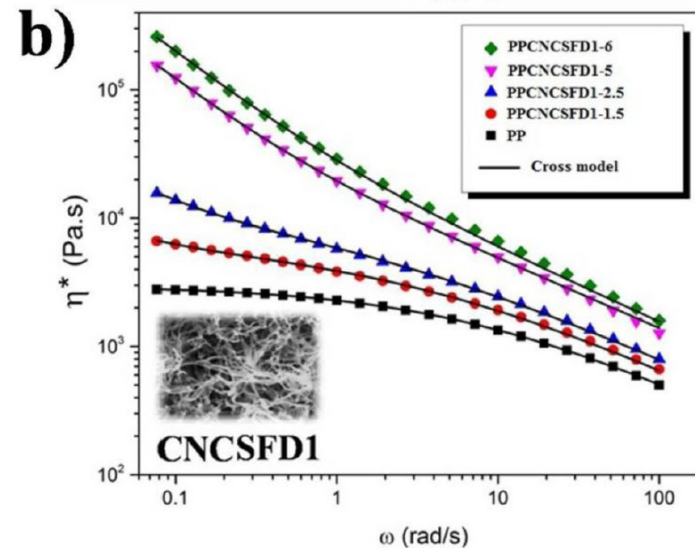
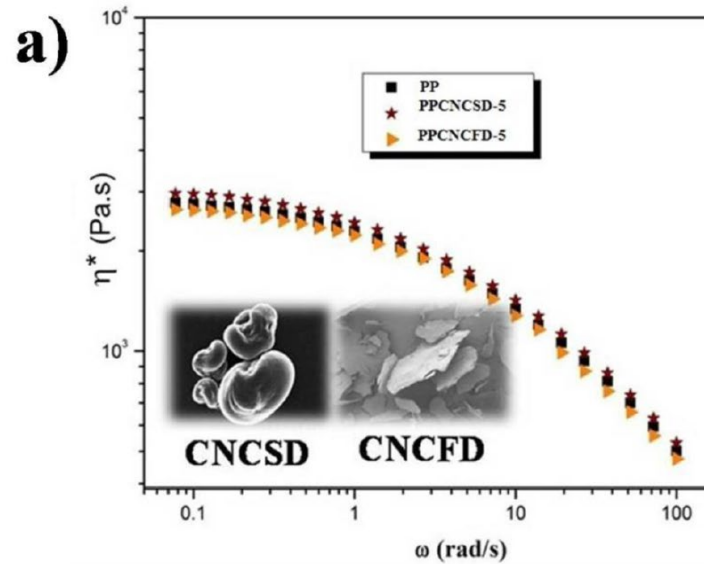
CNC in PLA melt

Kamal, Musa R., and Vahid Khoshkava. "Effect of cellulose nanocrystals (CNC) on rheological and mechanical properties and crystallization behavior of PLA/CNC nanocomposites." *Carbohydrate polymers* 123 (2015): 105-114.



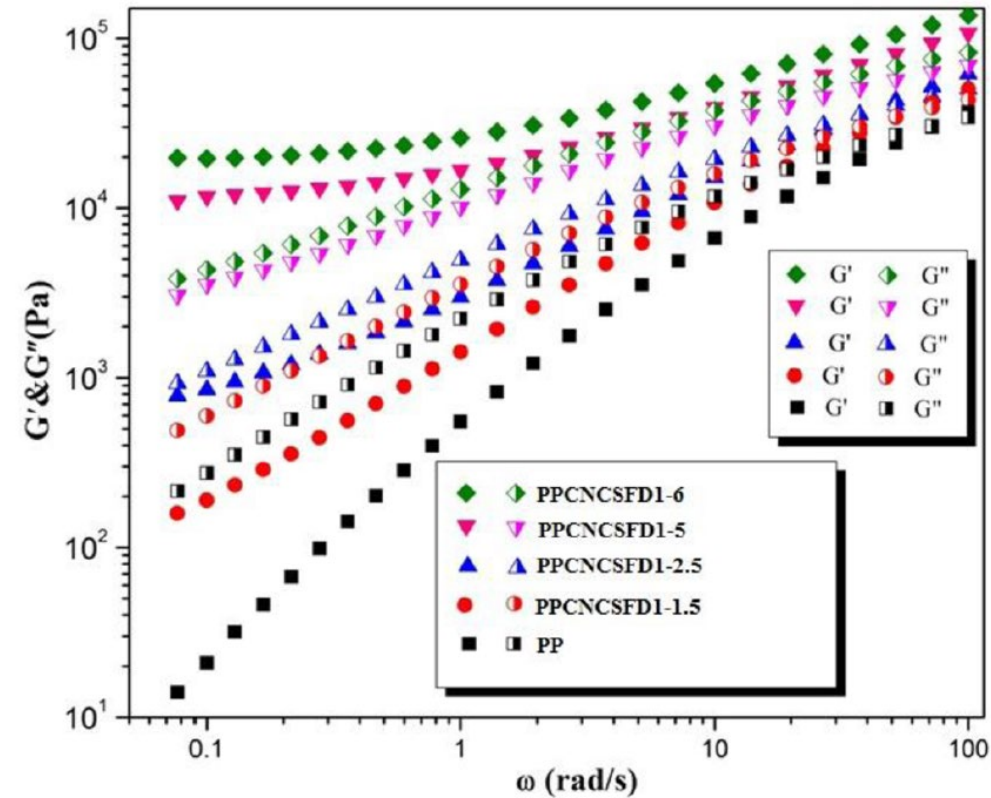
CNC in PP melt

Khoshkava, Vahid, and Musa R. Kamal.
 "Effect of cellulose nanocrystals (CNC)
 particle morphology on dispersion and
 rheological and mechanical properties
 of polypropylene/CNC
 nanocomposites." *ACS applied materials
 & interfaces* 6.11 (2014): 8146-8157.



CNC in PP melt (Oscillation test)

Khoshkava, Vahid, and Musa R. Kamal.
"Effect of cellulose nanocrystals (CNC)
particle morphology on dispersion and
rheological and mechanical properties
of polypropylene/CNC
nanocomposites." *ACS applied materials
& interfaces* 6.11 (2014): 8146-8157.



Concluding remarks

- Steady state shear viscosity measurements
- Dynamic measurements (Oscillation)
- Further things to learn
 - Elongational viscosity
 - Creep test
 - Stress relaxation
 - And more