



agefpi

Nanocellulose: Rheology and Applications

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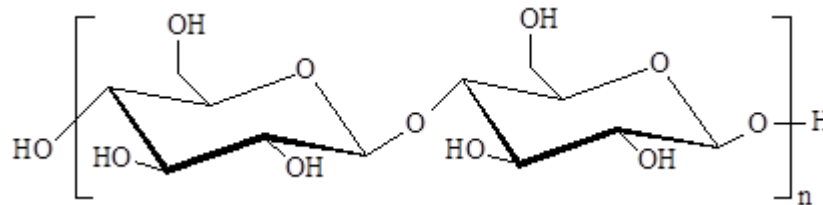
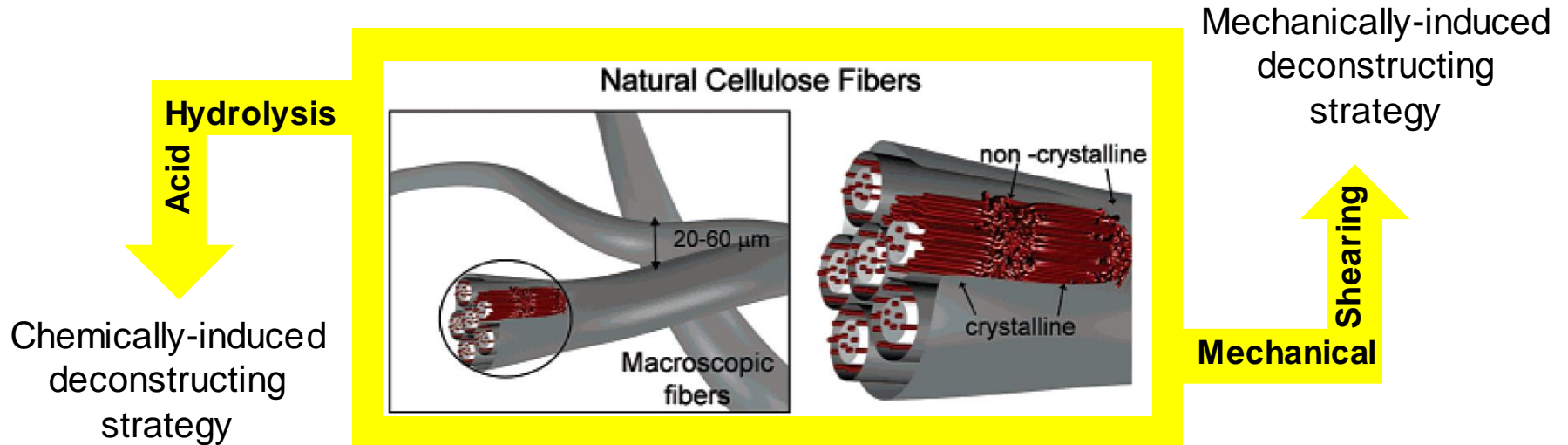


Nordic Rheology Conference,
Gothenburg, August 21-23, 2019

Outlines

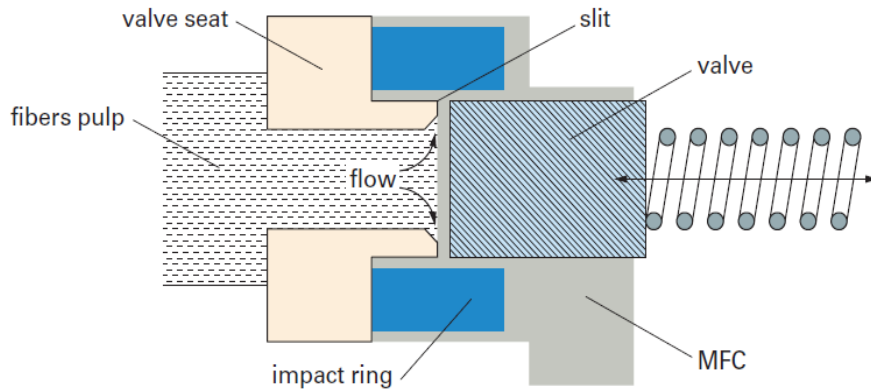
- Cellulose nanomaterials
- Dynamic rheological behavior
- Rheology of aqueous suspensions
- Birefringence/chiral nematic behavior
- Solid state rheology of cellulose/polymer nanocomposites
 - ☑ What can we learn from the storage modulus?
 - ☑ What can we learn from the loss angle?

Cellulose Nanomaterials

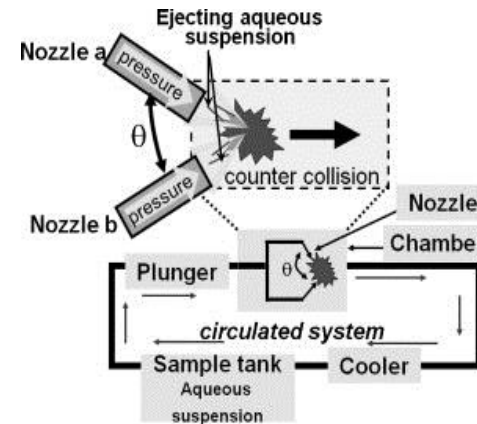


Mechanically-induced deconstructing strategy

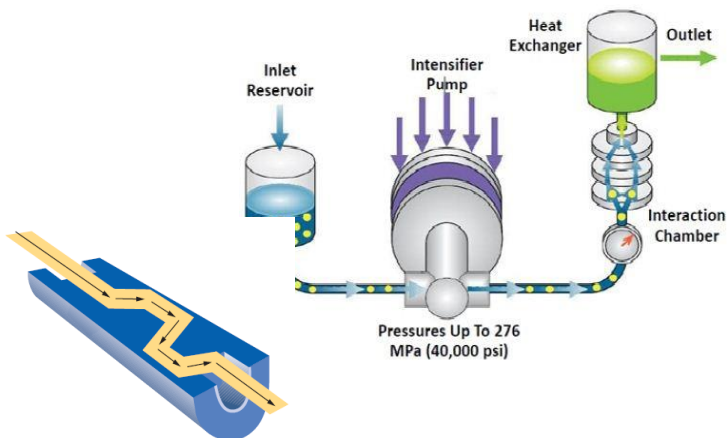
Homogenizer



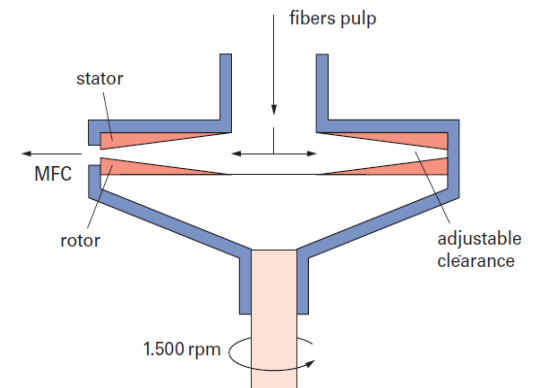
Aqueous counter collision



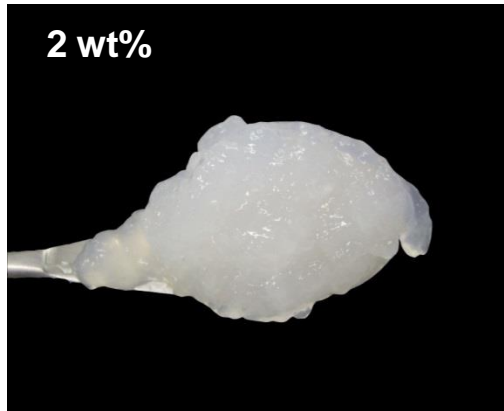
Microfluidizer (Microfluidics Inc., USA)



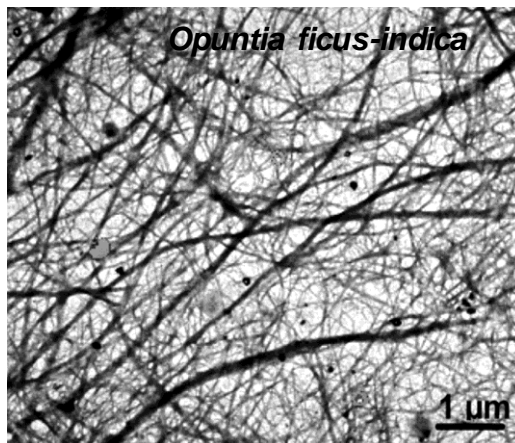
Ultra-fine friction grinder Masuko Supermasscolloider



Cellulose Nanofibrils



Lavoine et al., *Carbohydr. Polym.* **2012**, 90, 735-764



Malainine et al., *Compos. Sci. Technol.* **2005**, 65, 1520-1526

Stability in water due to residual hemicelluloses
Viscous gel with shear-thinning behavior

High energy demand

30,000 kWh/ton (Nakagaito and Yano, 2004)

70,000 kWh/ton (Eriksen et al, 2008)

→ **necessity of a pretreatment**

enzymatic hydrolysis

Carboxymethylation

TEMPO-catalyzed oxidation pretreatment

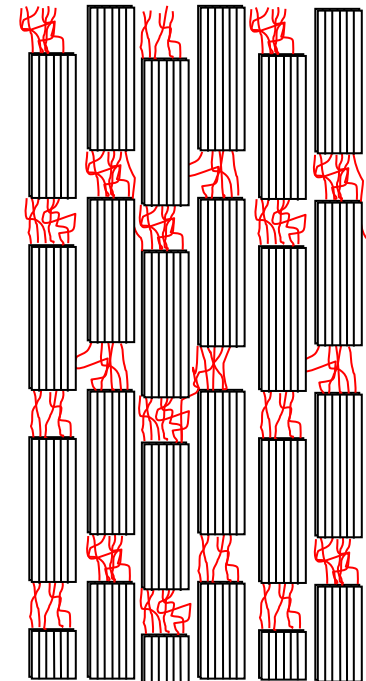
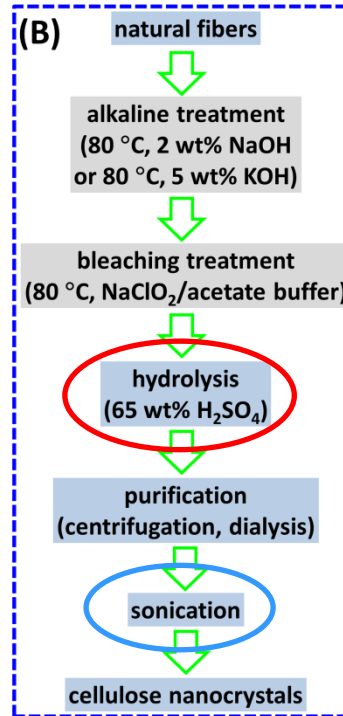
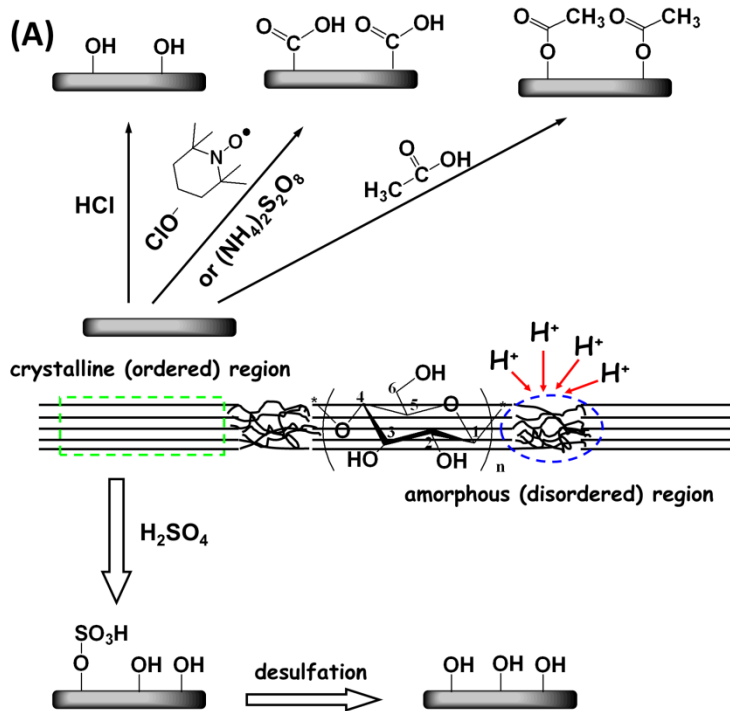
Cryocrushing

Width ~ 2-100 nm

Length ?



Chemically-induced Deconstructing Strategy



Stability in water due to surface sulfate groups

Width ~ few nm
Length ~ few 100 nm



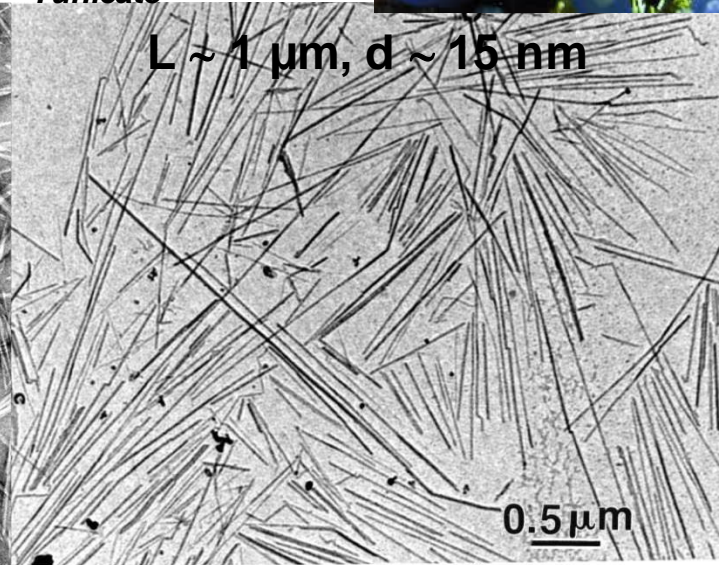
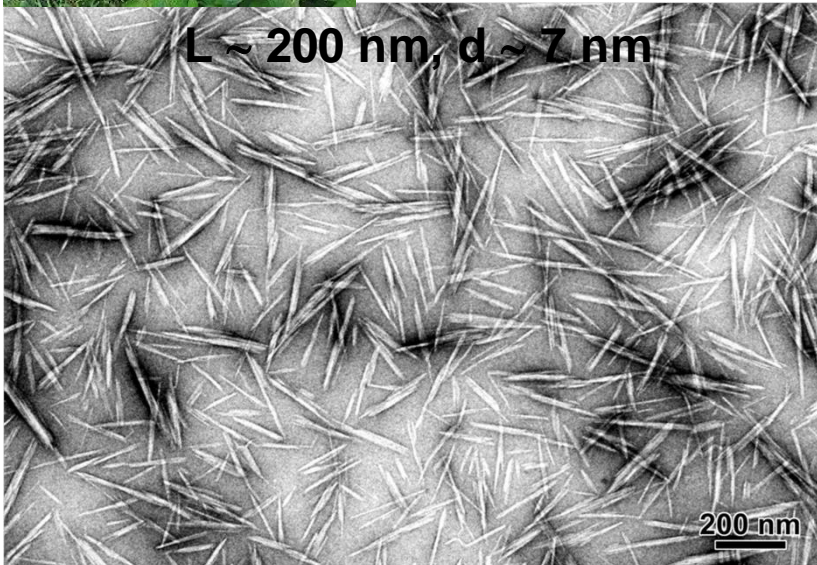
Cellulose Nanocrystals



Ramie fibers



Tunicate



Habibi et al., *J. Mater. Chem.* **2008**, 18, 5002-5010

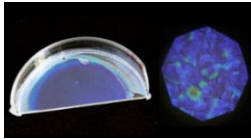
Anglès and Dufresne, *Macromolecules* **2000**,
33, 8344-8353

Applications of Cellulose Nanomaterials

Coatings



Films



Biomedical



Emulsions



Adhesives



Energy



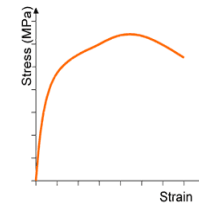
Inks/printing



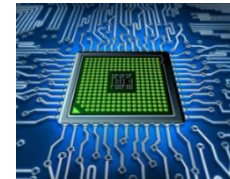
Pulp & paper



Composites



Electronics



Filtration



Textiles



Cosmetics



Food industry



Packaging



Construction



Dynamic Rheological Behavior

Can be applied over a broad range of viscosity (solid/liquid)

Useful for observing the viscoelastic nature of the material

An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured

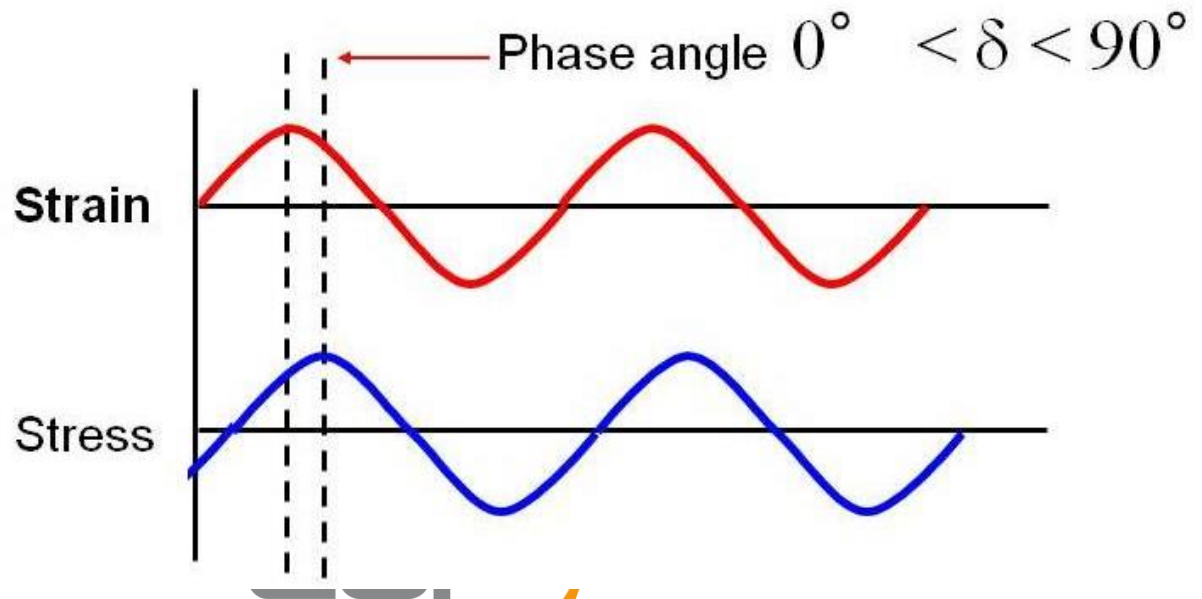
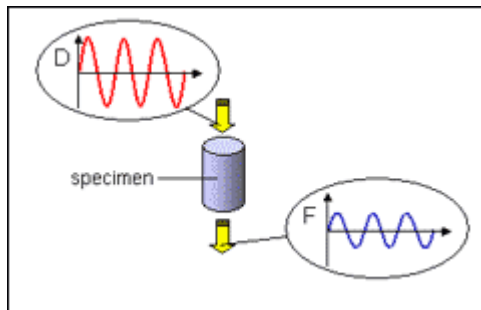
The stiffness of the sample can be determined, and the sample modulus can be calculated

By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material

Dynamic Rheological Behavior

By applying a stress that varies sinusoidally with time, a viscoelastic material will respond with a sinusoidal strain for low stress amplitude

This strain is out of phase with the applied stress, by the phase angle δ (phase lag due to the excess time necessary for molecular motions and relaxations to occur)



Dynamic Rheological Behavior

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$

$$\sigma = \sigma_0 \sin(\omega t)$$

$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

ω = angular frequency

$$\sigma = \underbrace{\sigma_0 \cos\delta}_{\text{in-phase component}} \sin(\omega t) + \underbrace{\sigma_0 \sin\delta}_{\text{out-of-phase component}} \cos(\omega t)$$

in-phase component

out-of-phase component

$$\sigma = \varepsilon_0 E' \sin(\omega t) + \varepsilon_0 E'' \cos(\omega t)$$

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos\delta = \text{in-phase modulus}$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin\delta = \text{out-of-phase modulus}$$

Dynamic Rheological Behavior

$$\sigma^* = \sigma_0 \exp i(\omega t + \delta)$$

$$\varepsilon^* = \varepsilon_0 \exp (i\omega t)$$

$$E^* = \frac{\sigma^*}{\varepsilon^*} = \frac{\sigma_0}{\varepsilon_0} e^{i\delta} = \frac{\sigma_0}{\varepsilon_0} (\cos\delta + i\sin\delta) = E' + iE''$$

E' = storage modulus (describes ability of material to store potential energy and release it upon deformation) → stiffness ~ Young's modulus

E'' = loss modulus (associated with energy dissipation in the form of heat upon deformation) → internal friction ~ molecular motions, relaxation processes

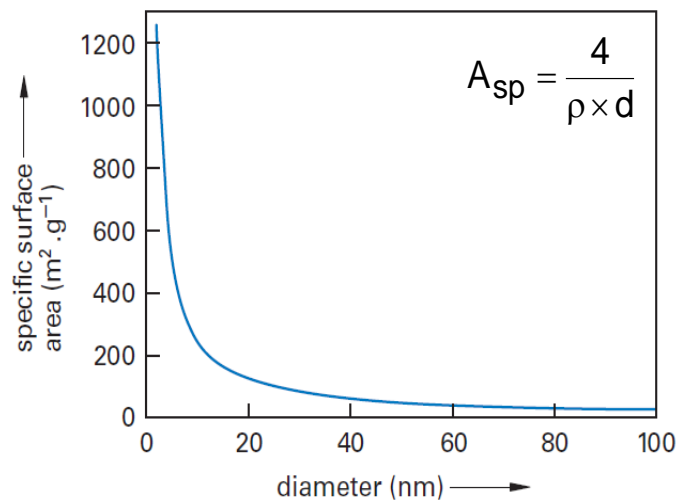
$$\tan \delta = E''/E' = \text{tangent of the phase angle}$$

DYNAMIC PROPERTIES PROVIDE INFORMATION AT THE MOLECULAR LEVEL TO UNDERSTAND THE MACROSCOPIC MECHANICAL BEHAVIOR

Applications of Cellulose Nanomaterials

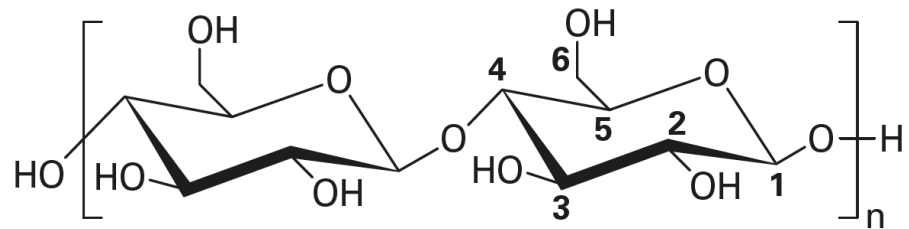
Important features of cellulose nanomaterials for use as rheology-modifier

High specific area



Dufresne, *Nanocellulose* 2017, 2nd Ed., Berlin/
Boston: Walter de Gruyter GmbH & Co KG

High density of surface OH groups



Strong interaction with polar liquid when in suspension

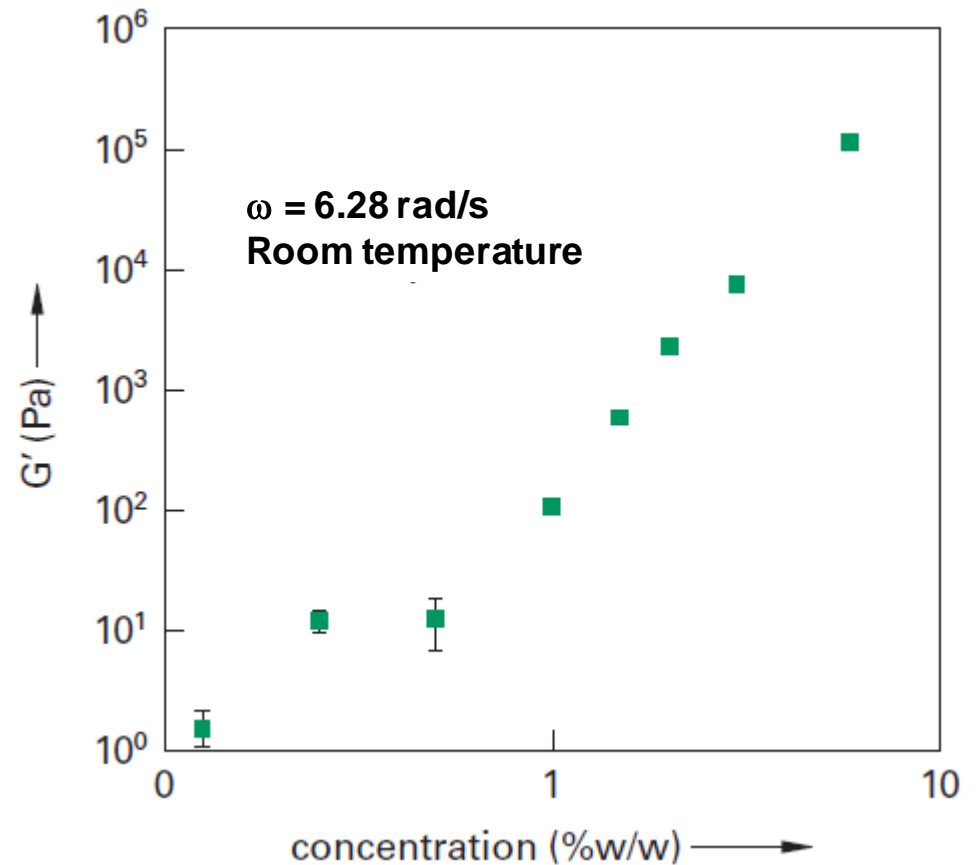
Impact of Concentration



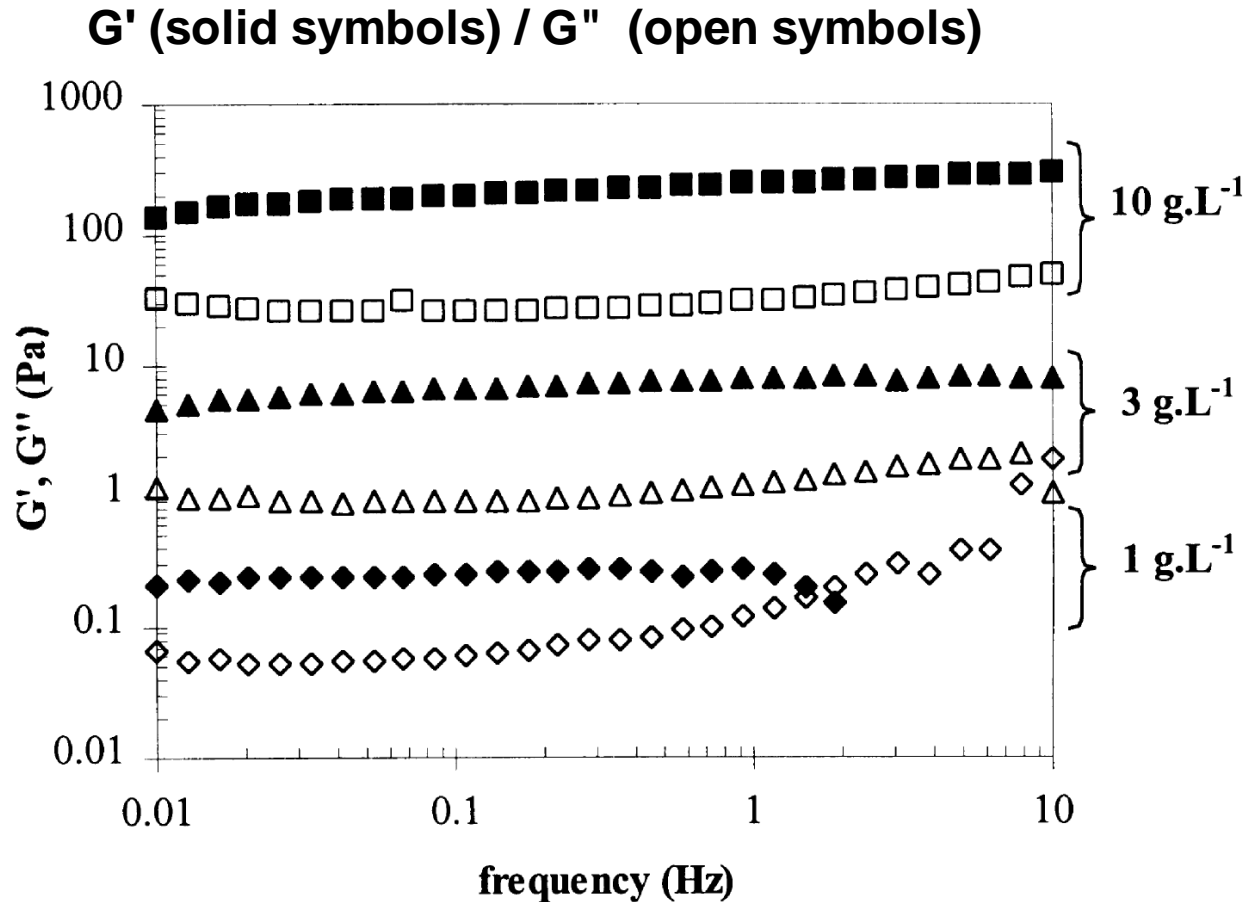
Lavoine et al., *Carbohydr. Polym.*
2012, 90, 735-764

Applications

Food, cosmetic, pharmaceutical industries

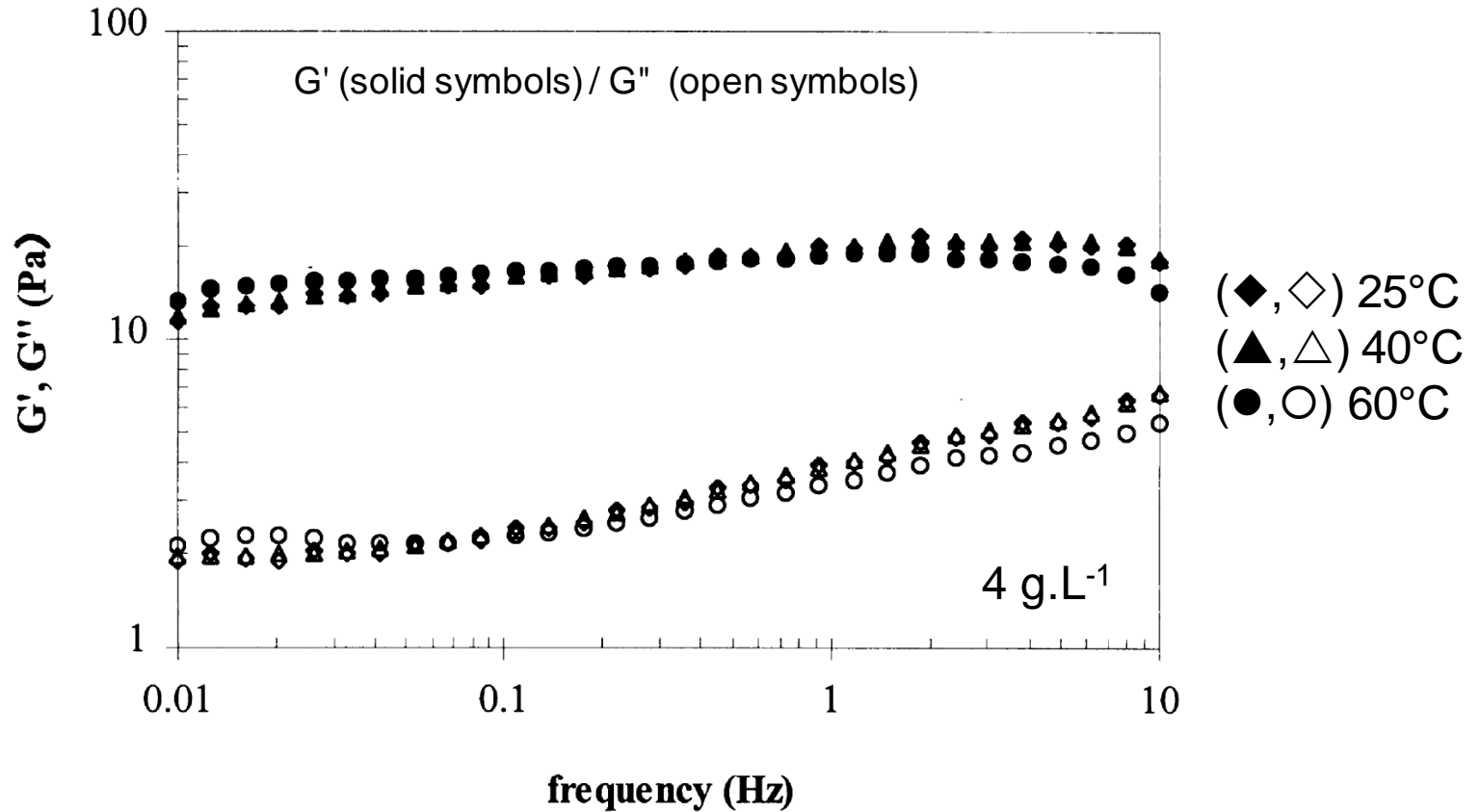


Impact of Concentration

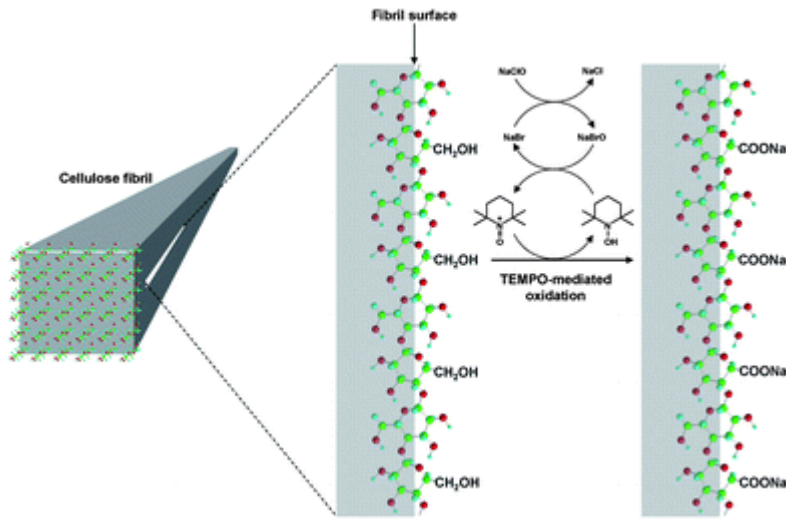


$G' > G''$ a physical network is formed due to mechanical entanglements between nanofibrils

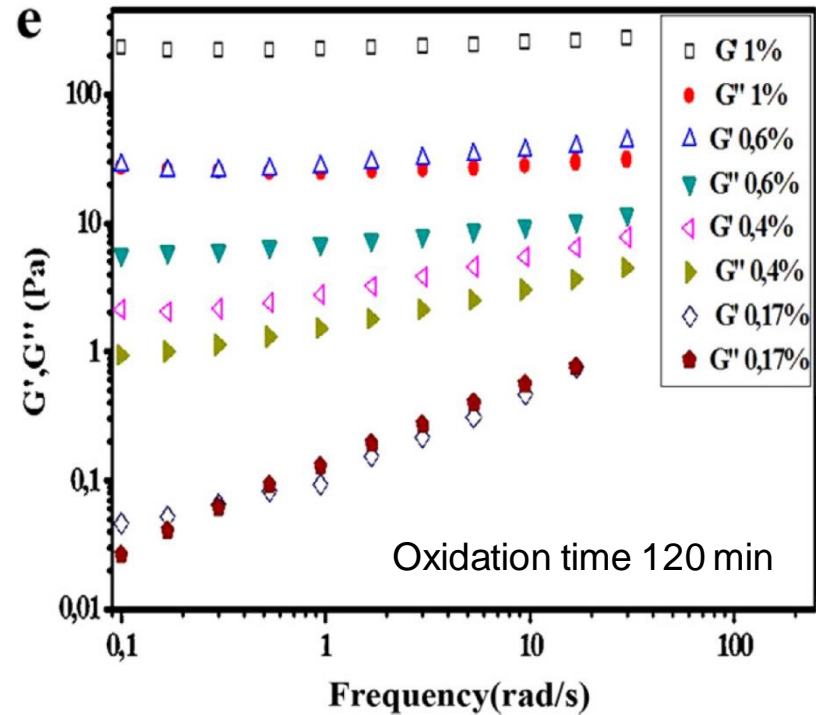
Impact of Temperature



Impact of Oxidation



Schematic model for the oxidation of C6 primary hydroxyls on native cellulose nanofibrils surface to C6 carboxylate groups using the TEMPO/NaBr/NaClO system



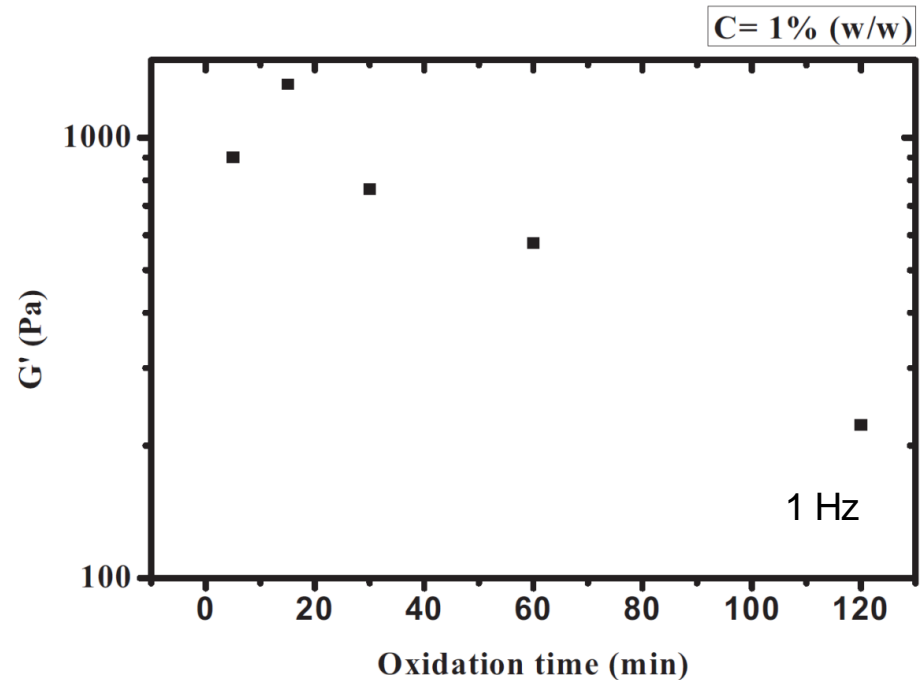
1 Hz

Okita et al., *Biomacromolecules* **2010**,
11, 1696-1700

Benhamou et al., *Carbohydr. Polym.*
2014, 99, 74-83

Impact of Oxidation

Reaction Time (min)	COONa Content ($\mu\text{mol.g}^{-1}$)	DP
0	177	650
5	221	500
15	265	390
30	442	215
60	575	130
120	774	100

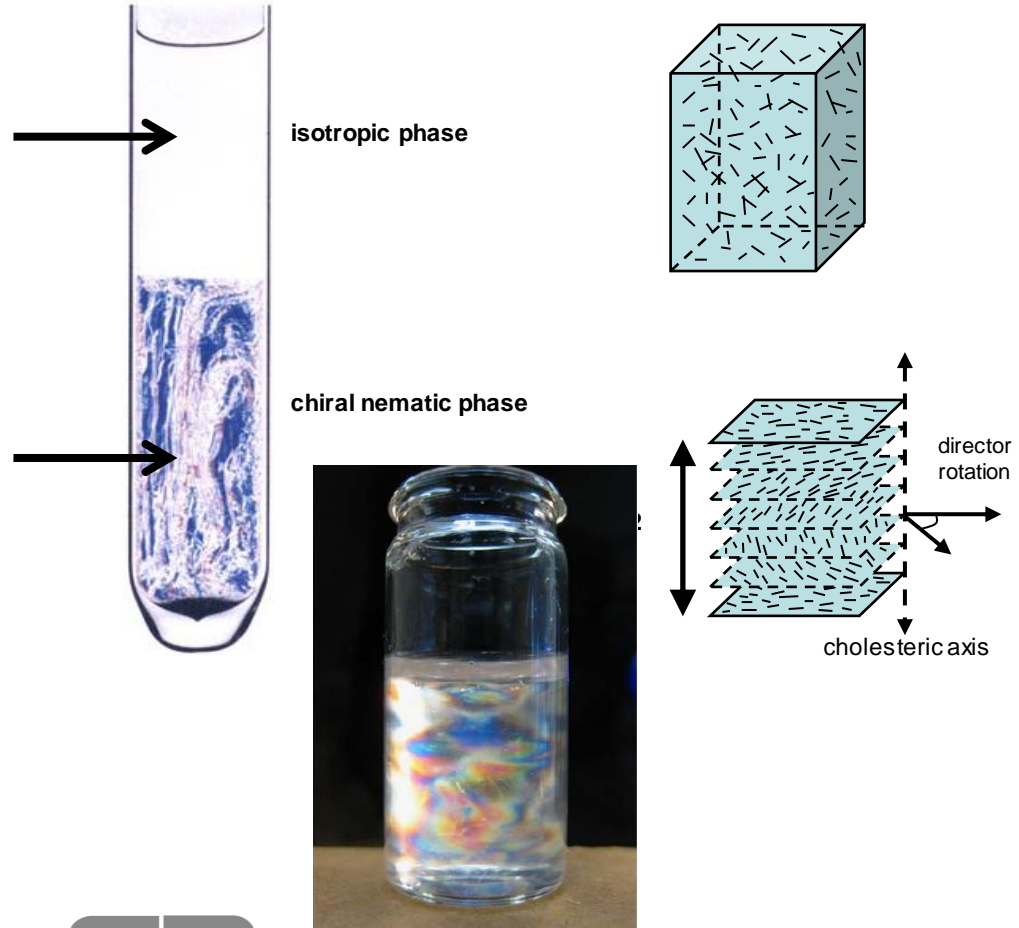


Increase in CNF surface charge → stronger immobilization of surrounding water molecules
→ higher gel stiffness
Decrease of CNF length → lower gel stiffness

Birefringence – Chiral Nematic Behavior

A CNC suspension in water at low concentrations forms a clear stable isotropic fluid

At higher concentrations the CNCs self-align to form a chiral nematic liquid crystalline phase in equilibrium with isotropic phase



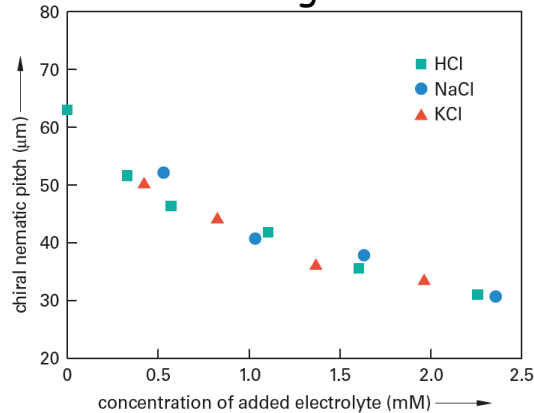
Marchessault et al., *Nature* **1959**, 184, 632-633

Revol et al., *Int. J. Biol. Macromol.* **1992**, 14, 170-172

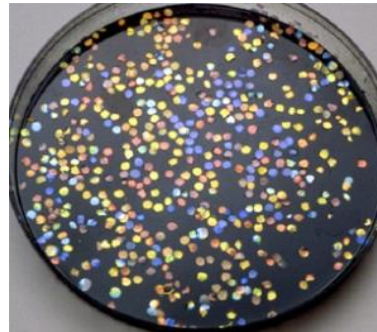
Birefringence – Chiral Nematic Behavior

$$\lambda = n P \sin \theta$$

(P controlled through ionic strength, T, concentration, exposure to magnetic field and US treatment)



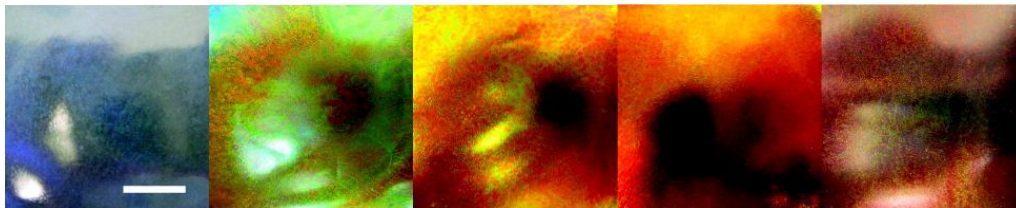
Slow evaporation produces semi-translucent films that retain the self-assembled chiral nematic liquid crystalline order formed in the suspension



Mixture of confettis cut from CNC films prepared with different NaCl concentrations, thus giving different reflection wavelengths

Dong et al., *Langmuir* **1996**, 12, 2076-2082

Revol et al., *US Patent* 5,629,055, 1997



CNC films produced from suspensions treated with increasing applied ultrasonic energy (0, 250, 700, 1800, and 7200 J/g CNC) from left to right
Scale marker = 1 cm

Beck et al., *Biomacromolecules* **2011**, 12, 167-172

Applications

Security papers

UV or IR reflective barriers



Applications of Cellulose Nanomaterials

Important features of cellulose nanomaterials for use as reinforcement for polymeric matrices

High specific surface area ($\sim 100 \text{ m}^2.\text{g}^{-1}$)

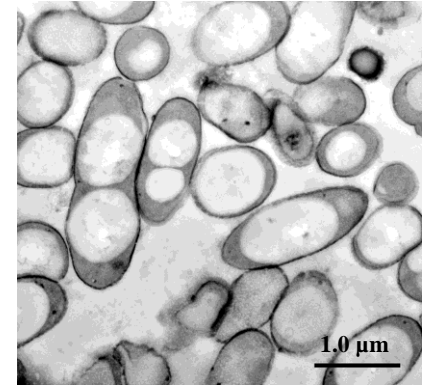
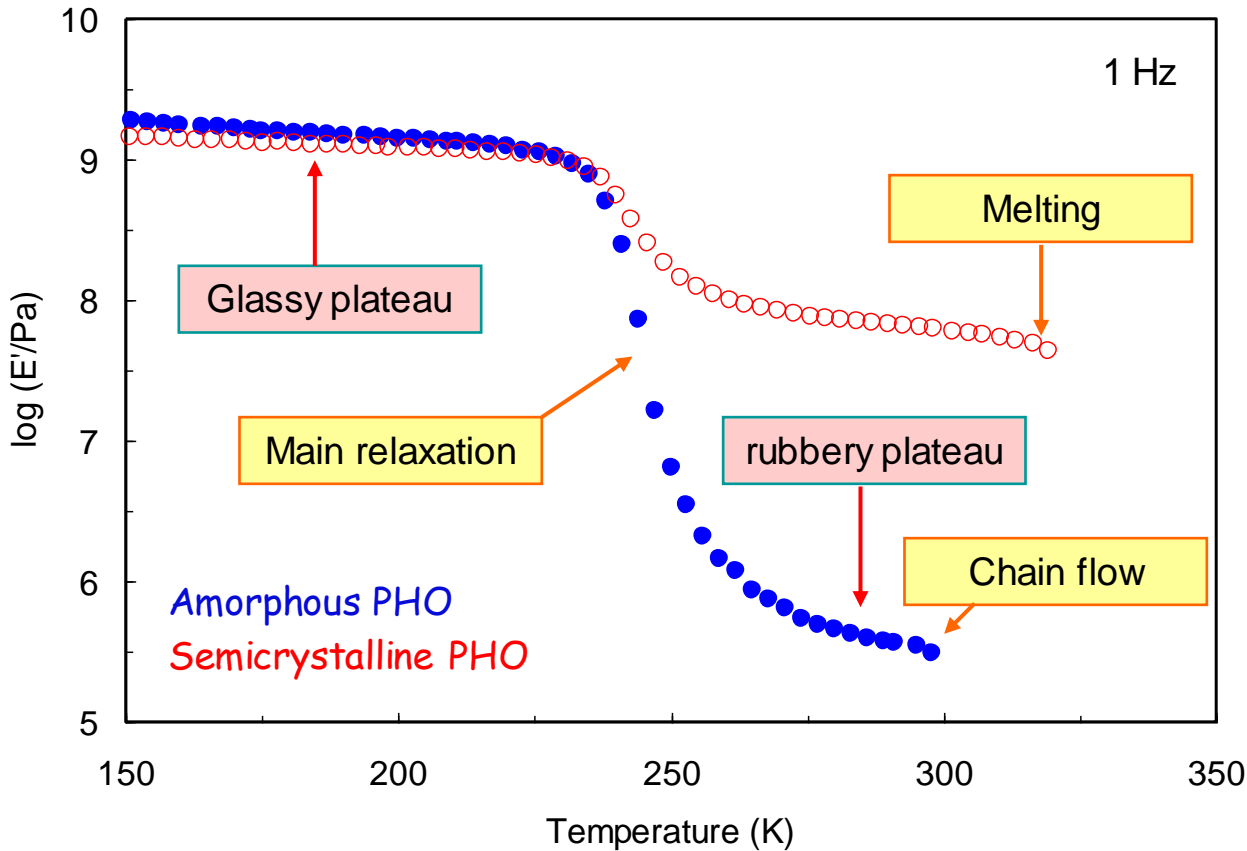
High aspect ratio

High modulus/strength ($E = 130/100 \text{ GPa}$ for CNC/CNF)

Lightweight (density = 1.5 g.cm^{-3})

Surface functionalization

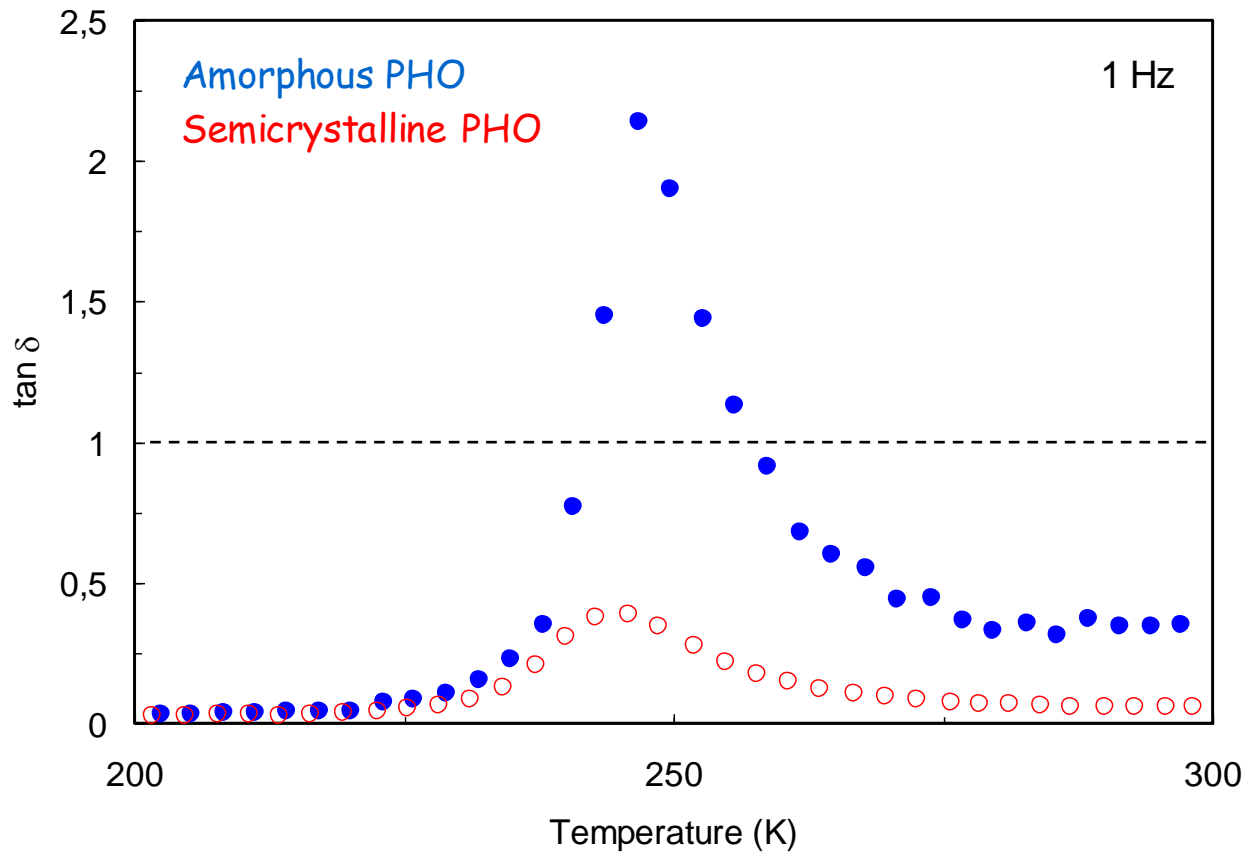
Solid State Rheology



Semicrystalline polymer

- (i) rubbery modulus known to depend on χ_c (filler)
- (ii) flow = melting (physical crosslinks)

Solid State Rheology



Max $\tan \delta$ (T_α)

- (i) number of mobile units
- (ii) magnitude of modulus drop

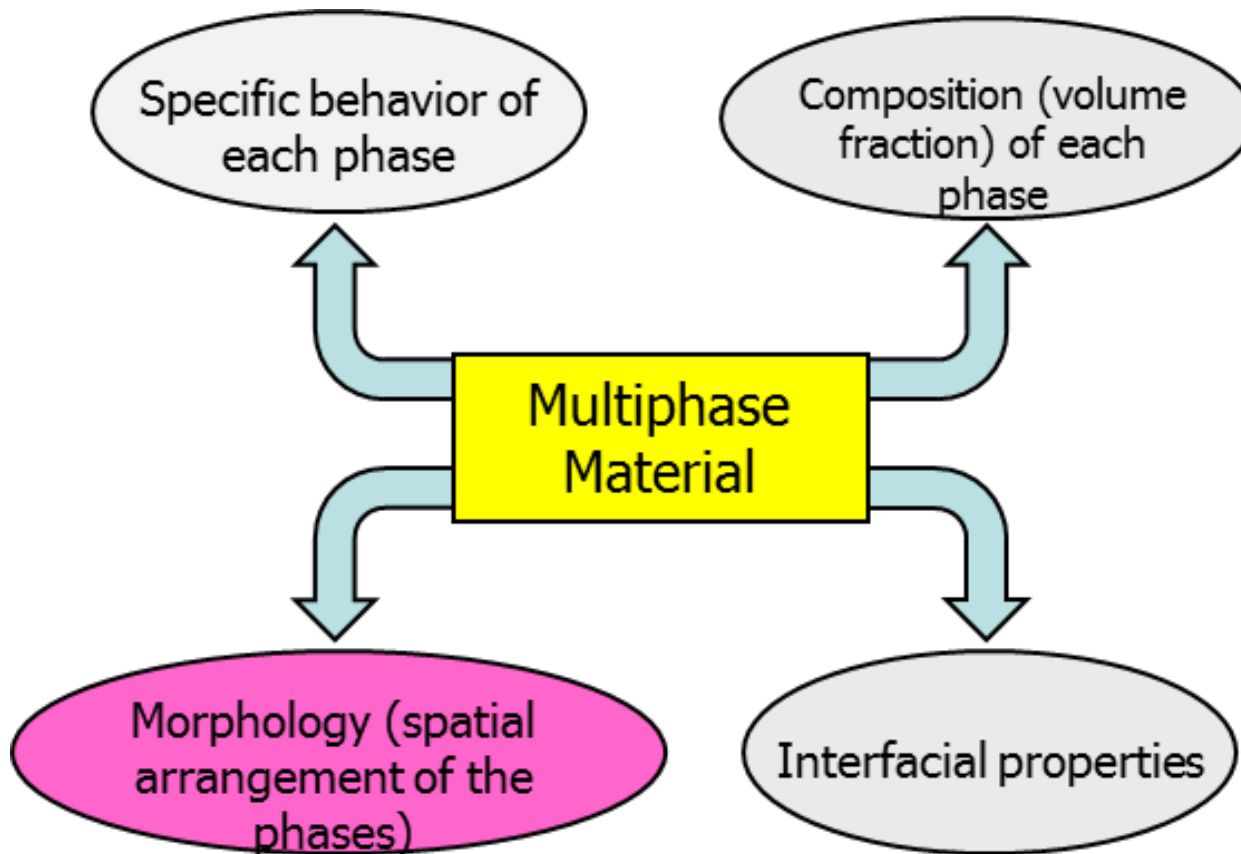
Transition vs. Relaxation

Transition = change from one physical state to another
1st order : melting, crystallization
~ 2nd order : glass-rubber transition

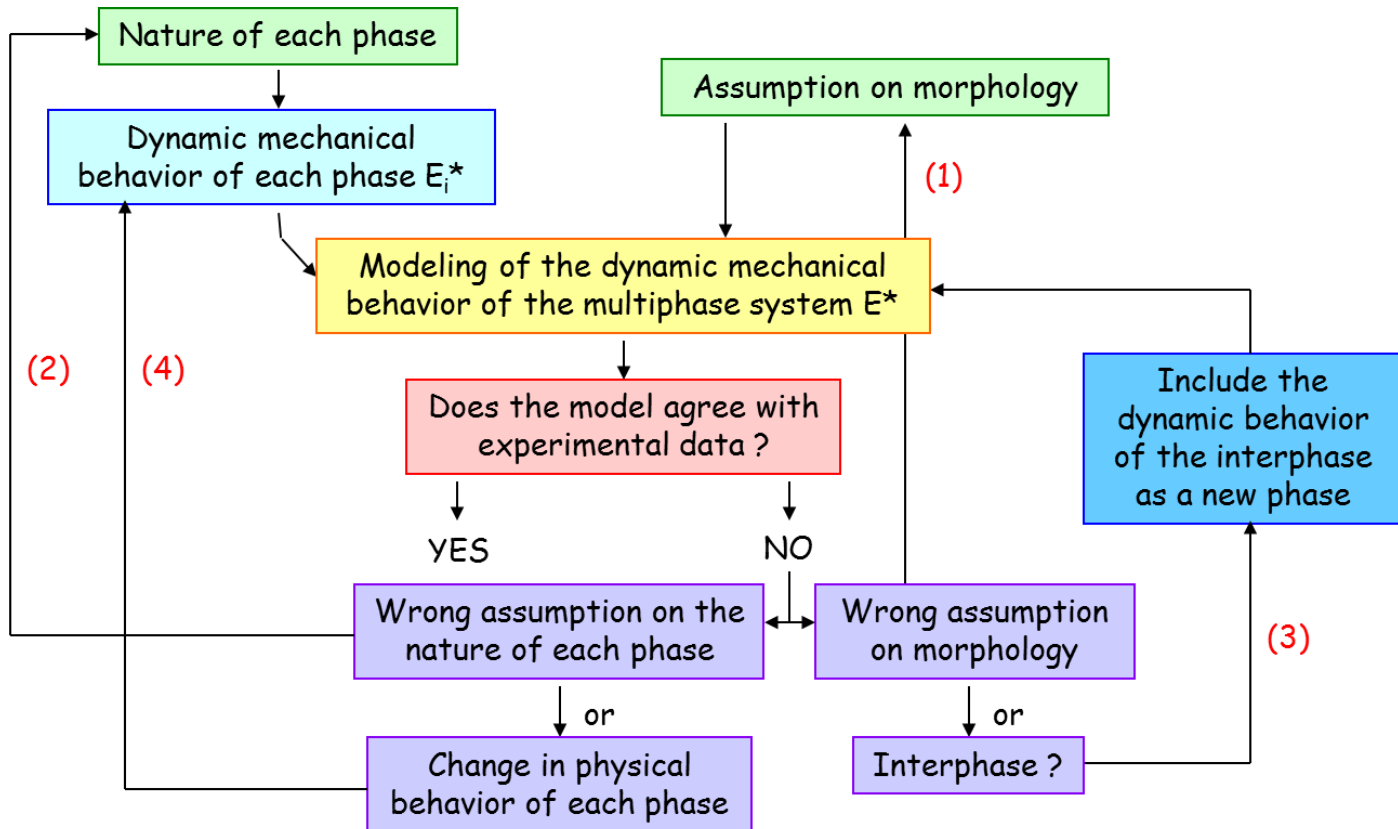
Relaxation = reversible and detectable phenomenon
resulting from a change of molecular mobility
Main relaxation associated to T_g
Secondary relaxations (lateral groups, crankshaft)



Properties of Multiphase Materials



Flow-chart for the Study of Multiphase Materials

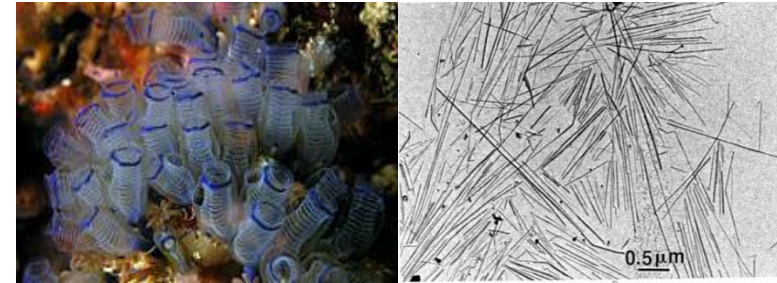
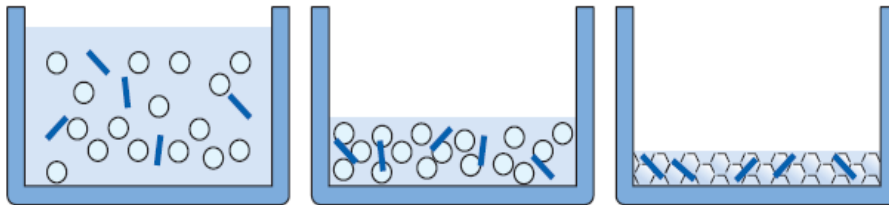


- (1) Morphology (2) Chemical composition of each phase (3) Interphase between main phases
 (4) Possible change in physical properties of each phase

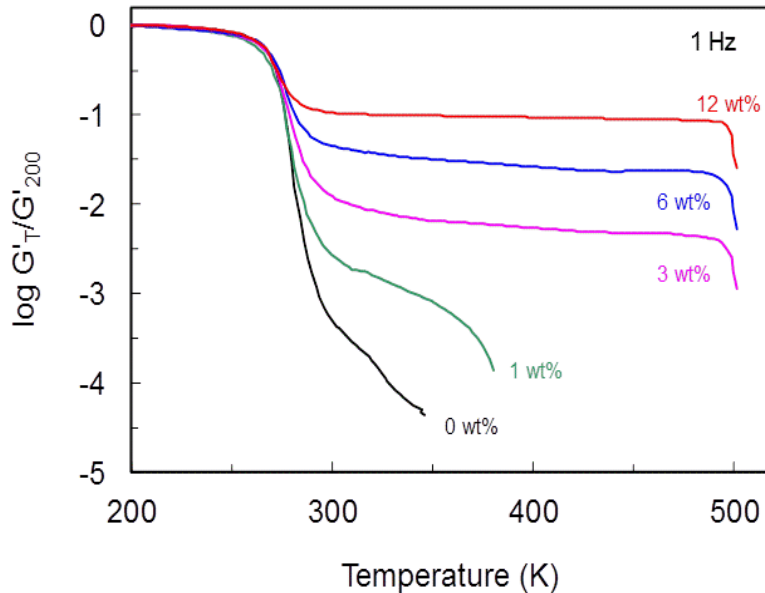
Rheology of Cellulose/Polymer Nanocomposites

Tunicin CNC/poly(S-co-BuA) latex

water evaporation ($T > T_g$) → particle coalescence
→ nanocomposite film



$L \sim 1 \mu\text{m}$, $d \sim 15 \text{ nm}$
 $L/d \sim 67$

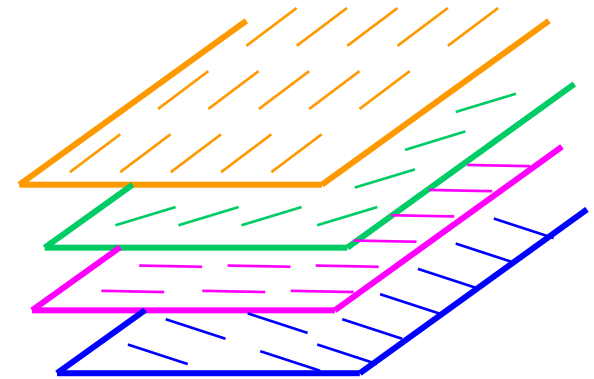
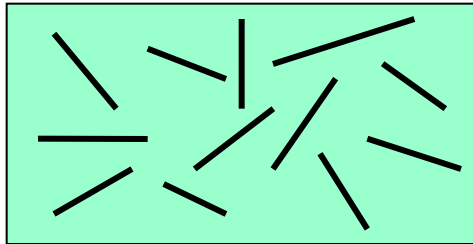


High reinforcing effect at $T > T_g$

Thermal stabilization up to 500 K ($\phi_R > 1\text{wt}\%$)
(degradation of cellulose)

Morphology

Mean Field Approach: Halpin-Kardos



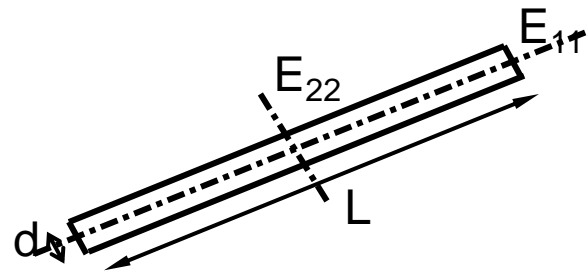
$$E_c = f(E_{ii}, G_{12}, \nu_{12}, \nu_{21})$$

$$\frac{E_{ii}}{E_m} = \frac{(1 + \xi_{iif}\phi_f)E_{iif} + \xi_{ii}(1 - \phi_f)E_m}{(1 - \phi_f)E_{iif} + (\xi_{ii} + \phi_f)E_m} \quad (i = 1, 2)$$

$$\frac{G_{12}}{G_m} = \frac{(1 + \phi_f)G_f + (1 - \phi_f)G_m}{(1 - \phi_f)G_f + (1 + \phi_f)G_m}$$

filler geometry : $\xi_{11} = 2 \times \frac{L}{d}$ $\xi_{22} = 2 \times \frac{e}{d} = 2$

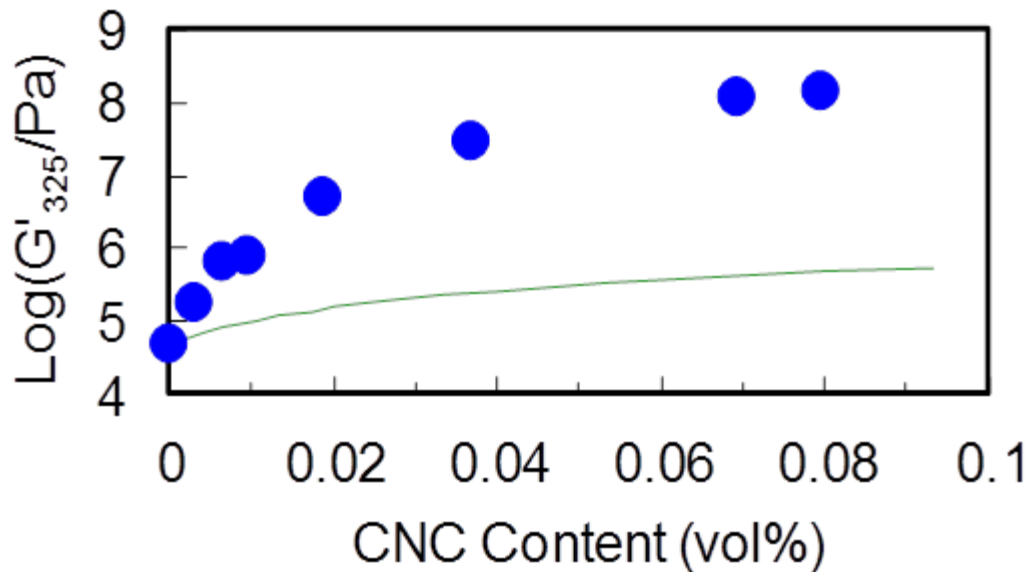
filler volume fraction : ϕ_f
 mechanical anisotropy : E_{iif}



no interaction between fibers

Morphology

Mean Field Approach: Halpin-Kardos



$L/d = 67$ (TEM)

$\nu_m = 0.5$ (rubbery matrix)

$G_m = 0.1$ (experimental data)

$\nu_f = 0.3$ (crystalline cellulose)

$E_{11f} = 150$ GPa (theoretical data)

$E_{22f} = 15$ GPa (theoretical data)

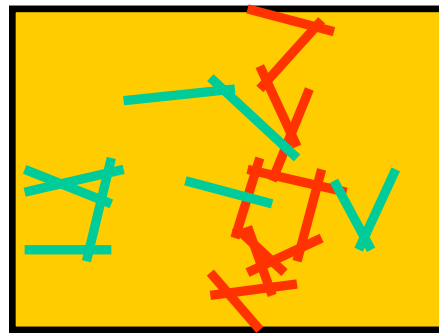
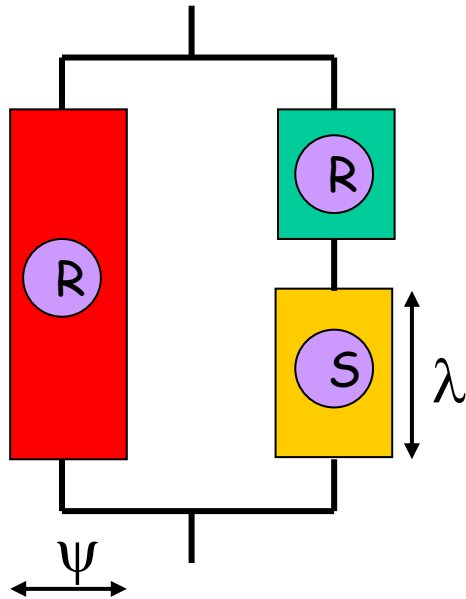
$G_f = 5$ GPa (theoretical data)

Experimental data much higher than the prediction by a mean-field mechanical model

CNCs act as fibers much longer than expected from geometrical observation

Morphology

Percolation Approach: Takayanagi Model



percolating whiskers network :
 $E_R = 15 \text{ GPa} \rightarrow G_R = 5 \text{ GPa}$

$$G = \frac{(1 - 2\psi + \psi\phi_R)G_S G_R + (1 - \phi_R)\psi G_R^2}{(1 - \phi_R)G_R + (\nu_R - \psi)G_S}$$

if $G_R \gg G_S \Rightarrow G = \psi G_R$

$$\psi = 0 \quad \text{for } \phi_R < \phi_{Rc}$$

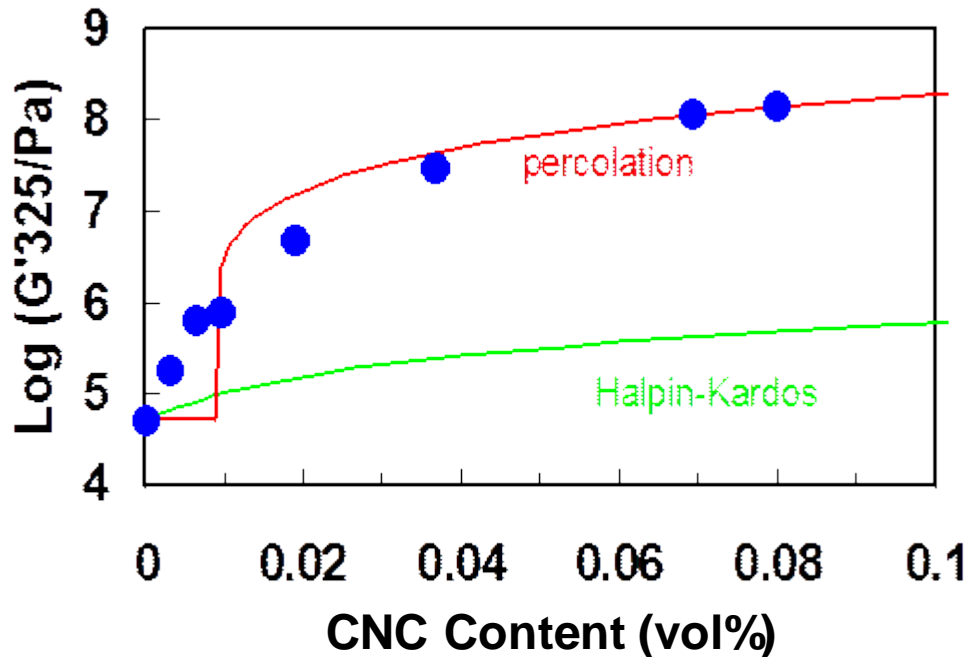
$$\psi = \phi_R \left(\frac{\phi_R - \phi_{Rc}}{1 - \phi_{Rc}} \right)^b \quad \text{for } \phi_R \geq \phi_{Rc}$$

$$L/d = 67 \rightarrow \phi_{Rc} = 1\%$$

$$b = 0.4 \text{ (3D system)}$$

- ψ = volume fraction of the percolating rigid phase
- ϕ_R = volume fraction of filler
- ϕ_{Rc} = critical volume fraction at the percolation threshold
- b = critical exponent
- G_R = modulus of the percolating CNC network

Morphology



Good agreement between experimental and predicted data



Strong interactions between CNCs (H-bonding forces)
→ formation of a rigid cellulose CNC network for $\phi_R > \phi_{RC}$

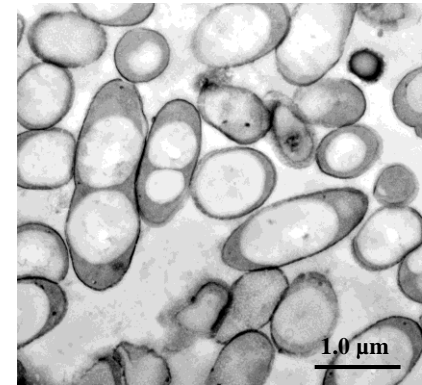
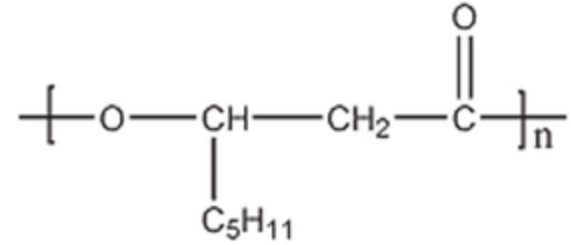
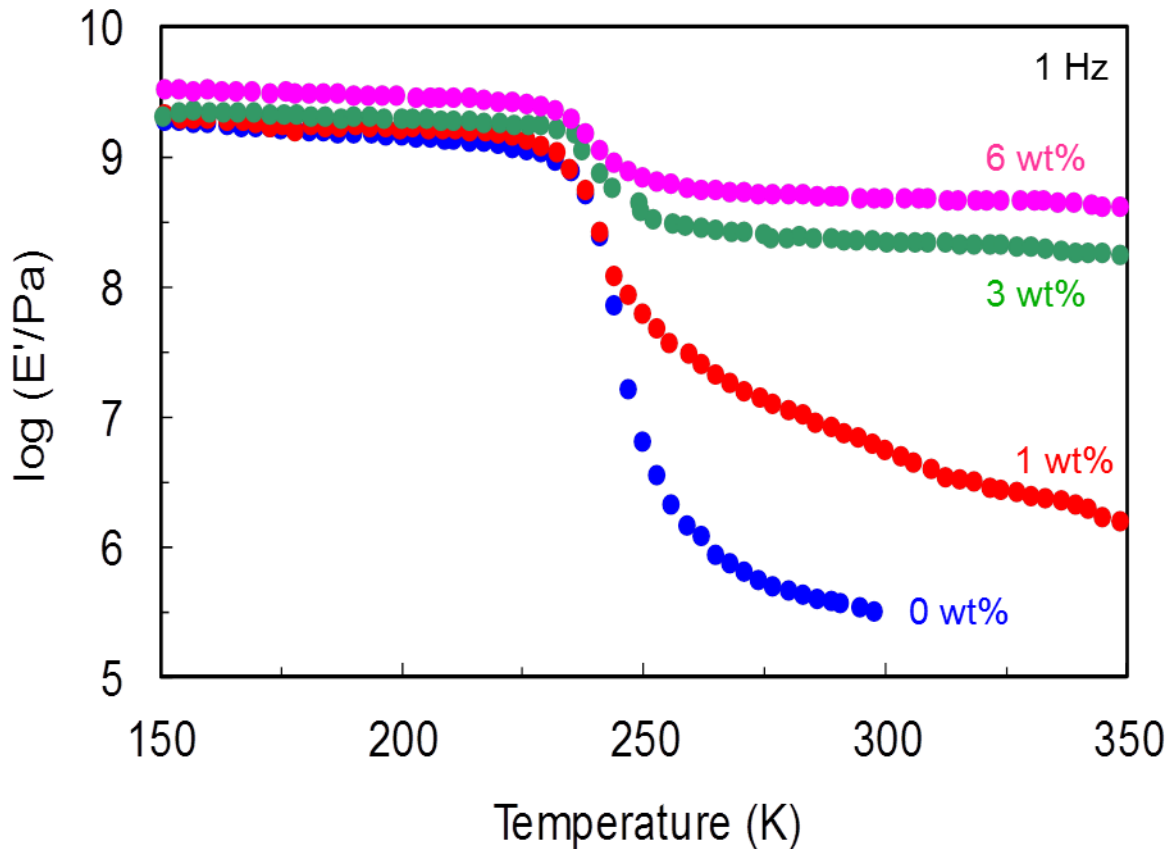
Mechanical percolation effect

- ➔ High reinforcing effect
- ➔ Thermal stabilization of the composite modulus
(water evaporation = slow process)

Favier et al., *Polym. Adv. Technol.*, 1995, 6, 351-355

Interphase

Tunicin CNC/amorphous PHO latex



Dufresne and Samain,
Macromolecules **1998**, 31, 6426-6433

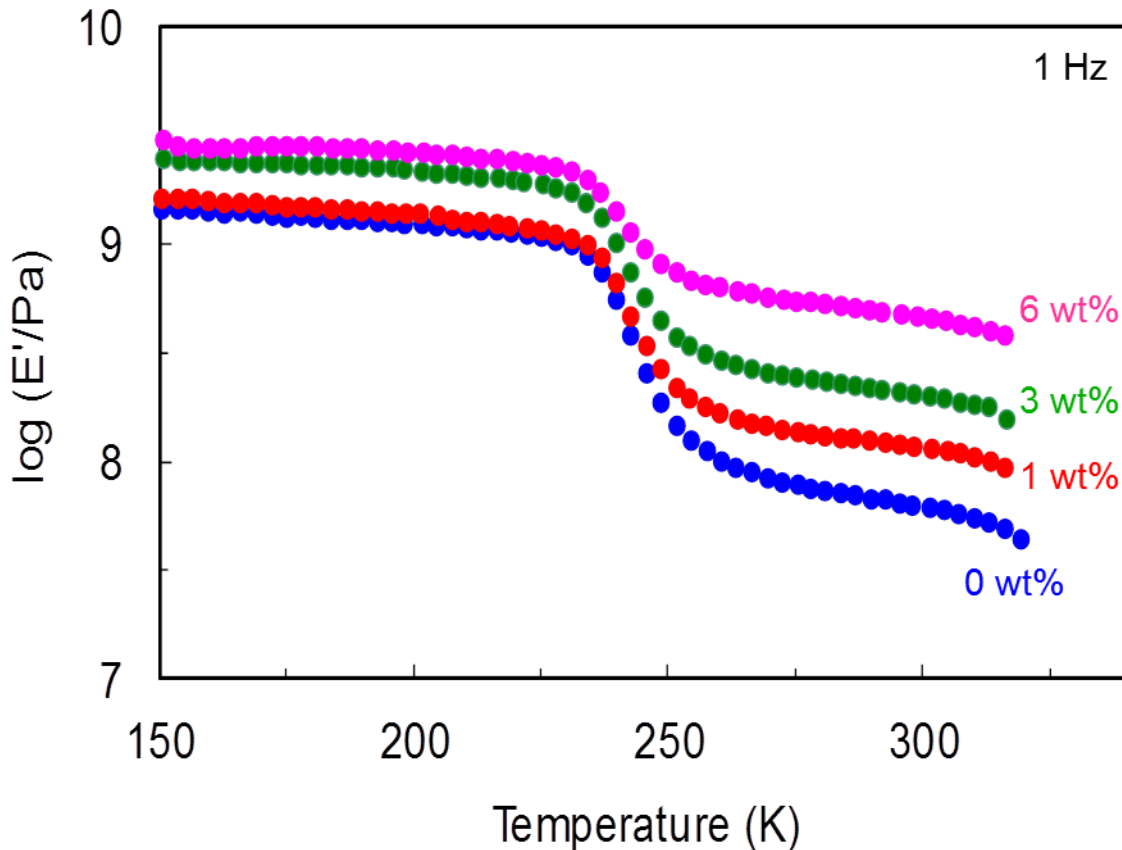
Percolation

Dufresne, *Compos. Interfaces*
2000, 7, 53-67



Interphase

Tunicin CNC/semicrystalline PHO latex

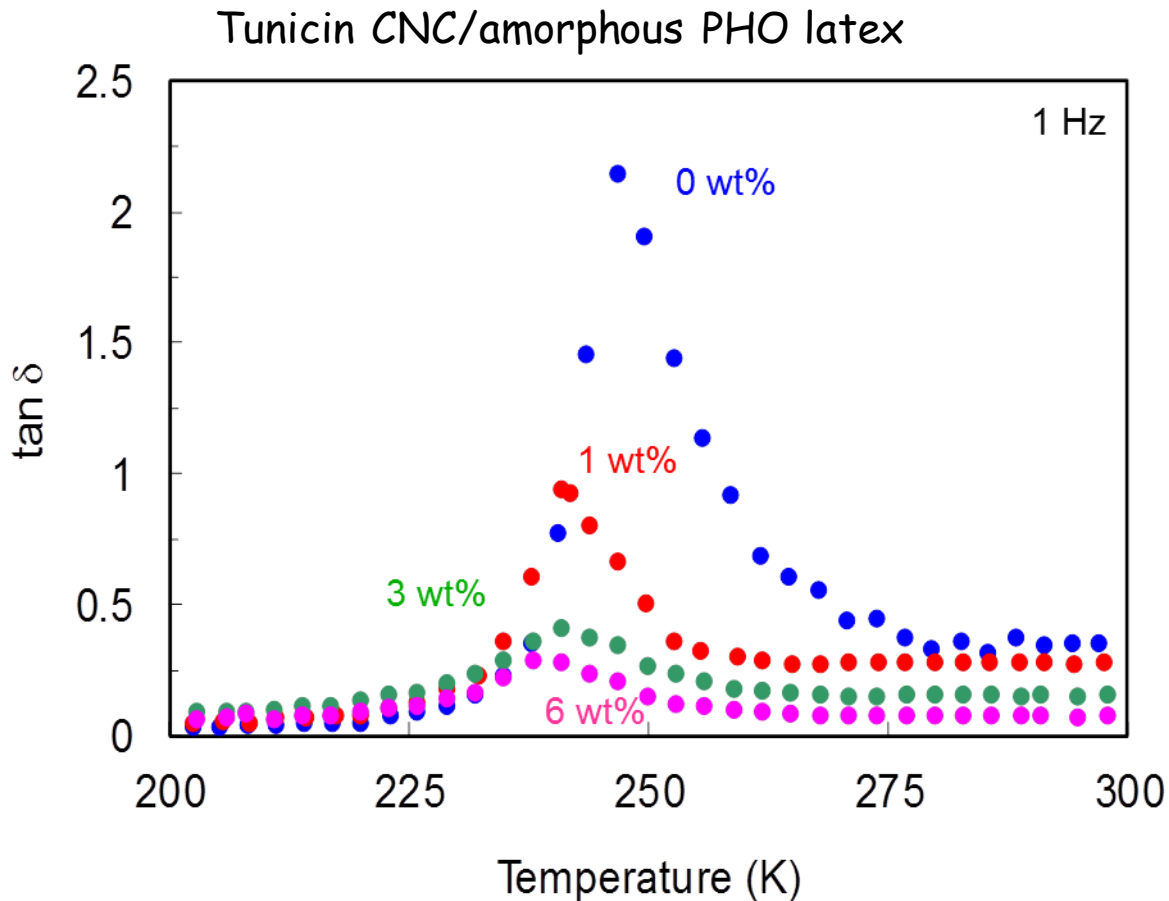


Global behavior similar except lower relative modulus increase

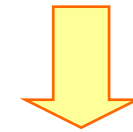
Crystalline domains = filler + physical crosslinks

Modulus decreases irreremediably ~ 320 K (melting) regardless filler content

Interphase



Magnitude of relaxation process decreases with CNC content

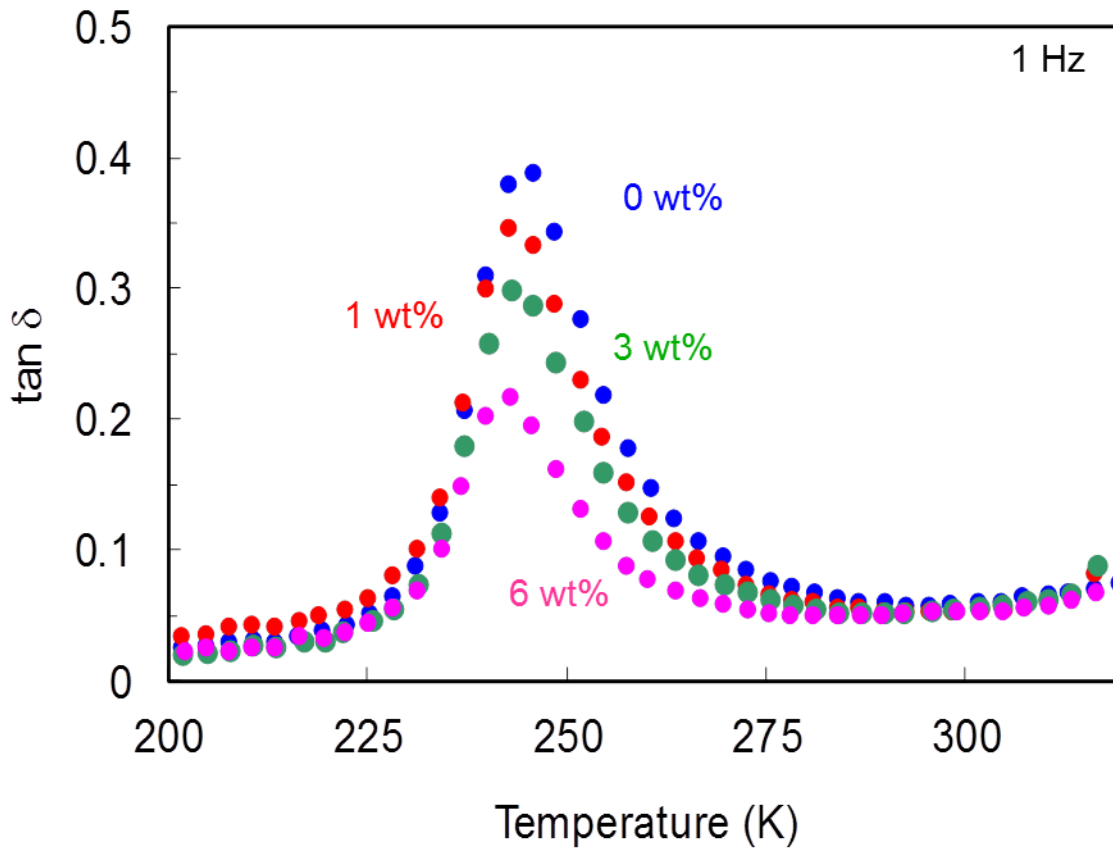


- (i) number of mobile units
- (ii) magnitude of modulus drop
- (iii) interfacial effect

Dufresne, *Compos. Interfaces*
2000, 7, 53-67

Interphase

Tunicin CNC/semicrystalline PHO latex



Similar observations

Dufresne, *Compos. Interfaces*
2000, 7, 53-67

Interphase – Loss Angle

Main characteristics deduced from the relaxation process displayed through the maximum of the loss angle

Temperature position = linked to T_g and to the magnitude of the modulus drop (mechanical coupling effect)

Width = representative of the size distribution of mobile entities participating to the relaxation process and distribution of relaxation times

Magnitude = related to the magnitude of the modulus drop and depends upon both the number of mobile entities and their contribution to the compliance

Interphase – Loss Angle

Matrix	CNC Content (wt%)	T_{α} (K)	L_{α} (K)	I_{α}
Amorphous PHO	0	247	14	2.14
	1	241	16	0.938
	3	241	25	0.404
	6	240	21	0.290
Semicrystalline PHO	0	246	20	0.388
	1	243	19	0.346
	3	243	19	0.300
	6	243	20	0.216

Temperature position (T_{α})

Half-height width (L_{α})

Magnitude (I_{α}) of the α relaxation process

Interphase – Loss Angle

Matrix	CNC (wt%)	T_α (K)	L_α (K)	I_α
Am. PHO	0	247	14	2.14
	1	241	16	0.938
	3	241	25	0.404
	6	240	21	0.290
SC PHO	0	246	20	0.388
	1	243	19	0.346
	3	243	19	0.300
	6	243	20	0.216

Shift of T_α towards lower temperatures with increasing CNC content



mechanical coupling effect

Temperature position (T_α)

Half-height width (L_α)

Magnitude (I_α) of the α relaxation process

Interphase – Loss Angle

Matrix	CNC (wt%)	T_{α} (K)	L_{α} (K)	I_{α}
Am. PHO	0	247	14	2.14
	1	241	16	0.938
	3	241	25	0.404
	6	240	21	0.290
SC PHO	0	246	20	0.388
	1	243	19	0.346
	3	243	19	0.300
	6	243	20	0.216

Increase of L_{α} with crystallinity



coexistence of crystalline and amorphous chains (broader distribution of τ)

Temperature position (T_{α})

Half-height width (L_{α})

Magnitude (I_{α}) of the α relaxation process

Interphase – Loss Angle

Matrix	CNC (wt%)	T_{α} (K)	L_{α} (K)	I_{α}
Am. PHO	0	247	14	2.14
	1	241	16	0.938
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	6	240	21	0.290
SC PHO	0	246	20	0.388
	1	243	19	0.346
	3	243	19	0.300
	6	243	20	0.216

Increase of L_{α} with CNC content
for amorphous PHO



modification of mobility of
amorphous PHO

Temperature position (T_{α})

Half-height width (L_{α})

Magnitude (I_{α}) of the α relaxation process

Interphase – Loss Angle

Matrix	CNC (wt%)	T_α (K)	L_α (K)	I_α
Am. PHO	0	247	14	2.14
	1	241	16	0.938
	3	241	25	0.404
	6	240	21	0.290
SC PHO	0	246	20	0.388
	1	243	19	0.346
	3	243	19	0.300
	6	243	20	0.216

Decrease of I_α with CNC content



- decreasing number of mobile units
- possible chain adsorption
- dependence on the modulus drop

Temperature position (T_α)

Half-height width (L_α)

Magnitude (I_α) of the α relaxation process

Interphase – Loss Angle

Specific surface of tunicin CNC $\sim 170 \text{ m}^2.\text{g}^{-1}$

→ Interfacial effects are expected to be important

Yim *et al.*, 1973

$$\frac{I_{\alpha C}}{I_{\alpha M}} = 1 - v_R \left(1 + \frac{\Delta R}{R_o} \right)^2 \left(1 + \frac{2\Delta R}{L} \right)$$

adsorption :
effective filler
volume fraction

+

Dufresne, 2000

$$\frac{I_{\alpha C}(\text{cal})}{I_{\alpha C}(\text{exp})} = \left(1 + \frac{\Delta R}{R_o} \right)^2 \left(1 + \frac{2\Delta R}{L} \right)$$

mechanical
coupling effect

$I_{\alpha C}$ = magnitude of loss angle for composite

$I_{\alpha M}$ = magnitude of loss angle for matrix

v_R = volume fraction of filler

R_o, L = radius, length of fiber

ΔR = thickness of interphase

Interphase – Loss Angle

Modeling the viscoelastic behavior with the percolation approach

$$E_C^* = \frac{aE_S^* E_R + bE_R^2}{cE_S^* + dE_R} = E_C' + iE_C''$$

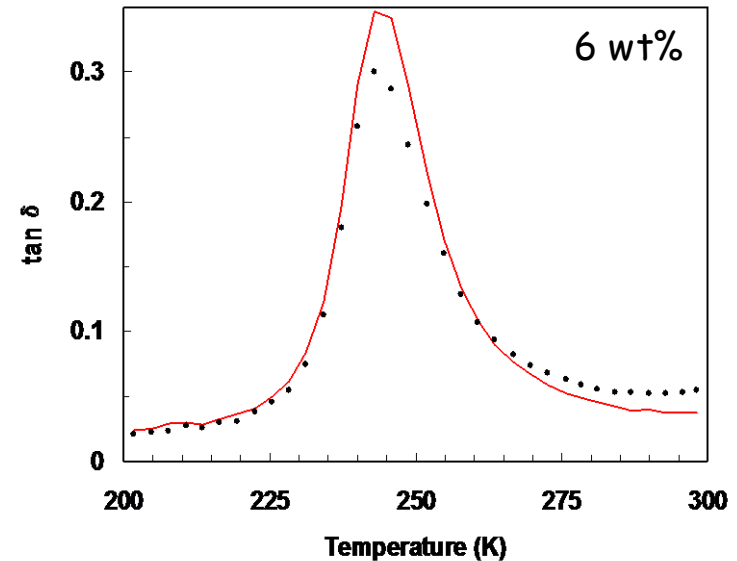
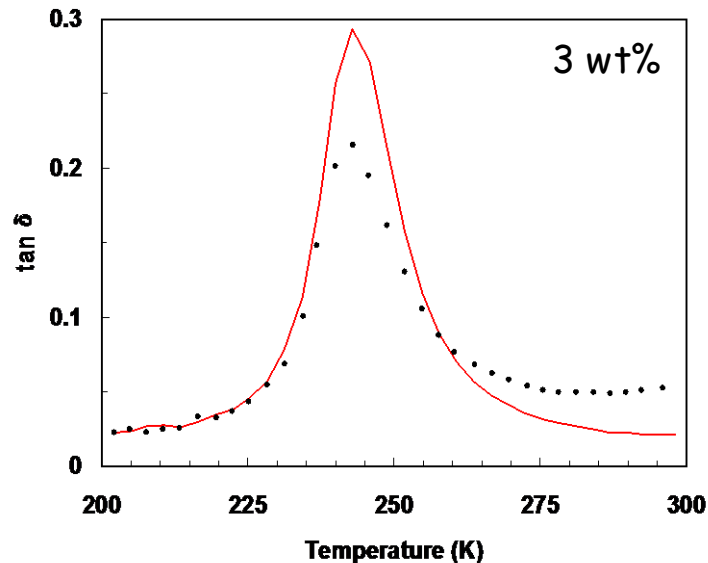
$$\begin{aligned} a &= 1 - 2\psi + \psi v_R \\ b &= (1 - v_R)\psi \\ c &= v_R - \psi \\ d &= 1 - v_R \end{aligned}$$

$$E_C' = \frac{AC + BD}{C^2 + D^2} E_R \quad E_C'' = \frac{BC - AD}{C^2 + D^2} E_R$$

$$\begin{aligned} A &= aE_S' + bE_R \\ B &= aE_S'' \\ C &= cE_S' + dE_R \\ D &= cE_S'' \end{aligned}$$

Interphase – Loss Angle

Semicrystalline PHO



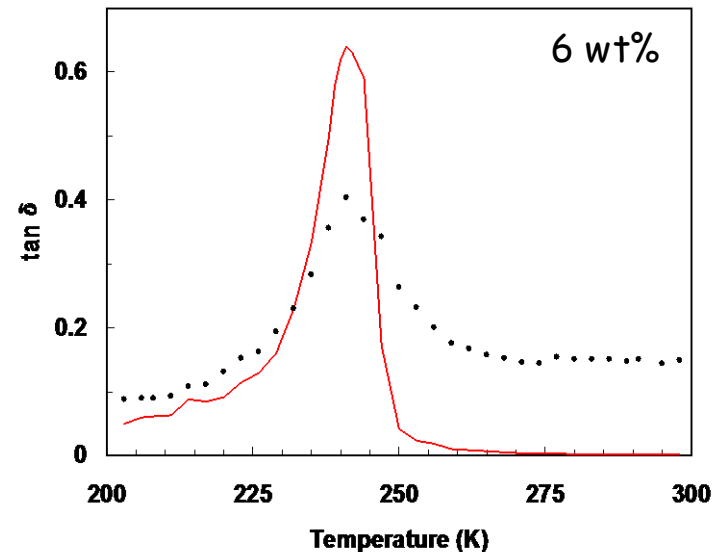
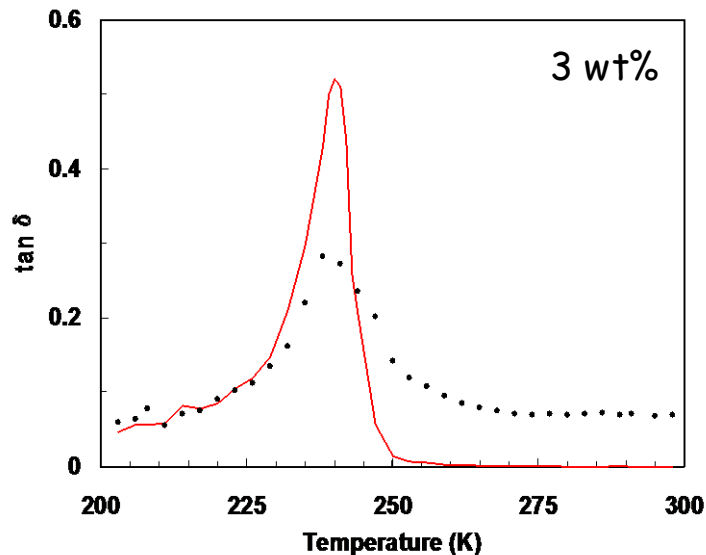
Rather good agreement between experimental and predicted values

→ the mobility of amorphous chains at the filler-matrix interface is not significantly affected

→ no direct contact between amorphous chains and CNCs

Interphase – Loss Angle

Amorphous PHO



The model fails to describe the experimental data

→ the mobility of amorphous chains at the filler-matrix interface is affected

Interphase – Loss Angle

Matrix	CNC (wt%)	T_α (K)	L_α (K)	I_α	ΔR (nm)
Am. PHO	0	247	14	2.14	—
	1	241	16	0.938	—
	3	241 [241]	25 [10]	0.404 [0.640]	3.8
	6	240 [240]	21 [9]	0.290 [0.52]	5.0
SC PHO	0	246	20	0.388	—
	1	243	19	0.346	—
	3	243 [243]	19 [18]	0.300 [0.347]	1.1
	6	243 [243]	20 [16]	0.216 [0.293]	2.4

[calculated data]

Agreement between exp. and predicted data much better for semicrystalline PHO based systems

Temperature position (T_α)

Half-height width (L_α)

Magnitude (I_α) of the α relaxation process

Dufresne, *Compos. Interfaces*
2000, 7, 53-67

Interphase – Loss Angle

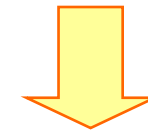
Matrix	CNC (wt%)	T α (K)	L α (K)	I α	ΔR (nm)
Am. PHO	0	247	14	2.14	—
	1	241	16	0.938	—
	3	241 [241]	25 [10]	0.404 [0.640]	3.8
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SC PHO	0	246	20	0.388	—
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	3	243 [243]	19 [18]	0.300 [0.347]	1.1
	6	243 [243]	20 [16]	0.216 [0.293]	2.4

Temperature position (T α)
 Half-height width (L α)
 Magnitude (I α) of the α relaxation process

Dufresne, *Compos. Interfaces*
 2000, 7, 53-67

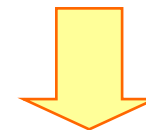


Ratio between exp. and predicted data



Thickness of interphase

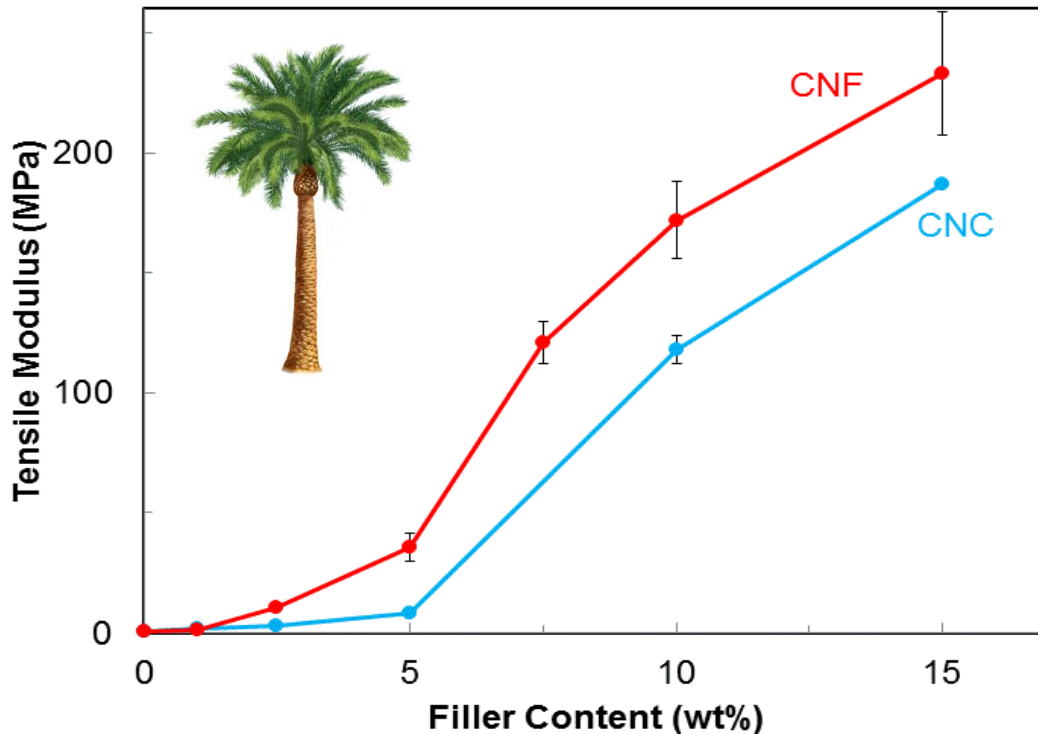
Interphase much thicker for amorphous matrix



Presence of transcrystalline layer around CNC preventing any direct contact between amorphous PHO chains and CNC

Cellulose Nanomaterials - CNC vs. CNF

Palm tree CNC-CNF/NR



Higher modulus for CNF-based nanocomposites than for CNC-based nanocomposites

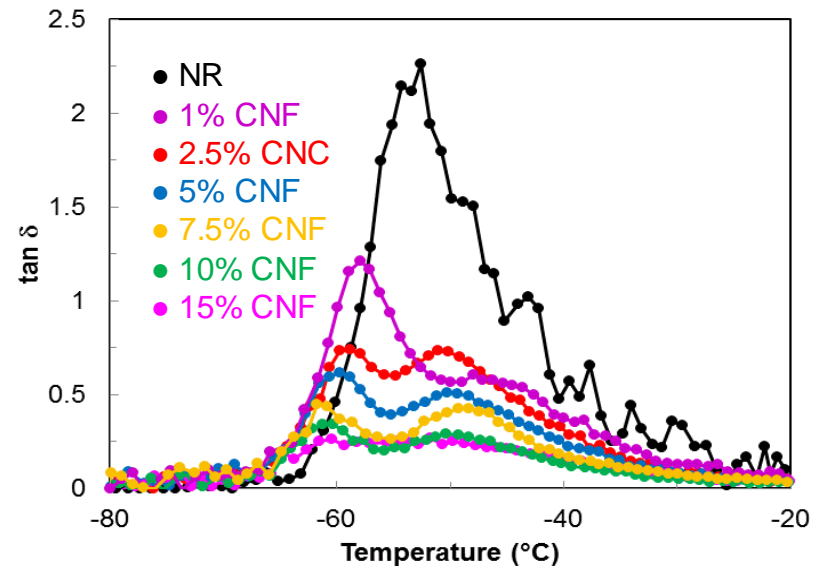
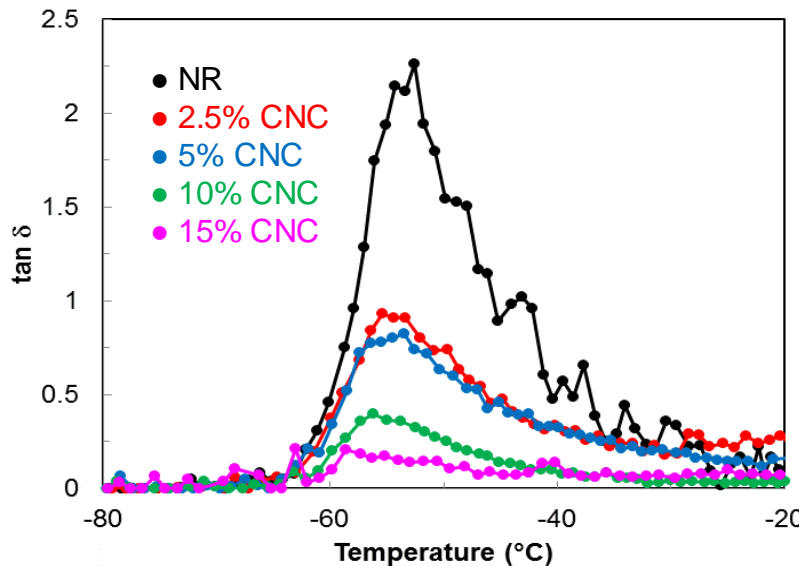
But higher modulus for CNC (130 GPa) than for CNF (100 GPa) ?

Cellulose Nanomaterials - CNC vs. CNF

- Higher aspect ratio for CNF → Connection of the nanoparticles for lower contents
- Entanglements → Stronger connection
- Residual hydrophobic compounds (lignin, extractive substances and fatty acids) at the surface of CNF → Compatibilization

Cellulose Nanomaterials - CNC vs. CNF

Residual hydrophobic compounds at the surface of CNF



Splitting of the relaxation process ascribed to strong interactions between CNF and NR : formation of an interfacial layer with restricted mobility

Conclusion

Cellulose nanomaterials strongly impact the rheological behavior of suspensions/solid nanocomposites

Gel stiffness can be accessed

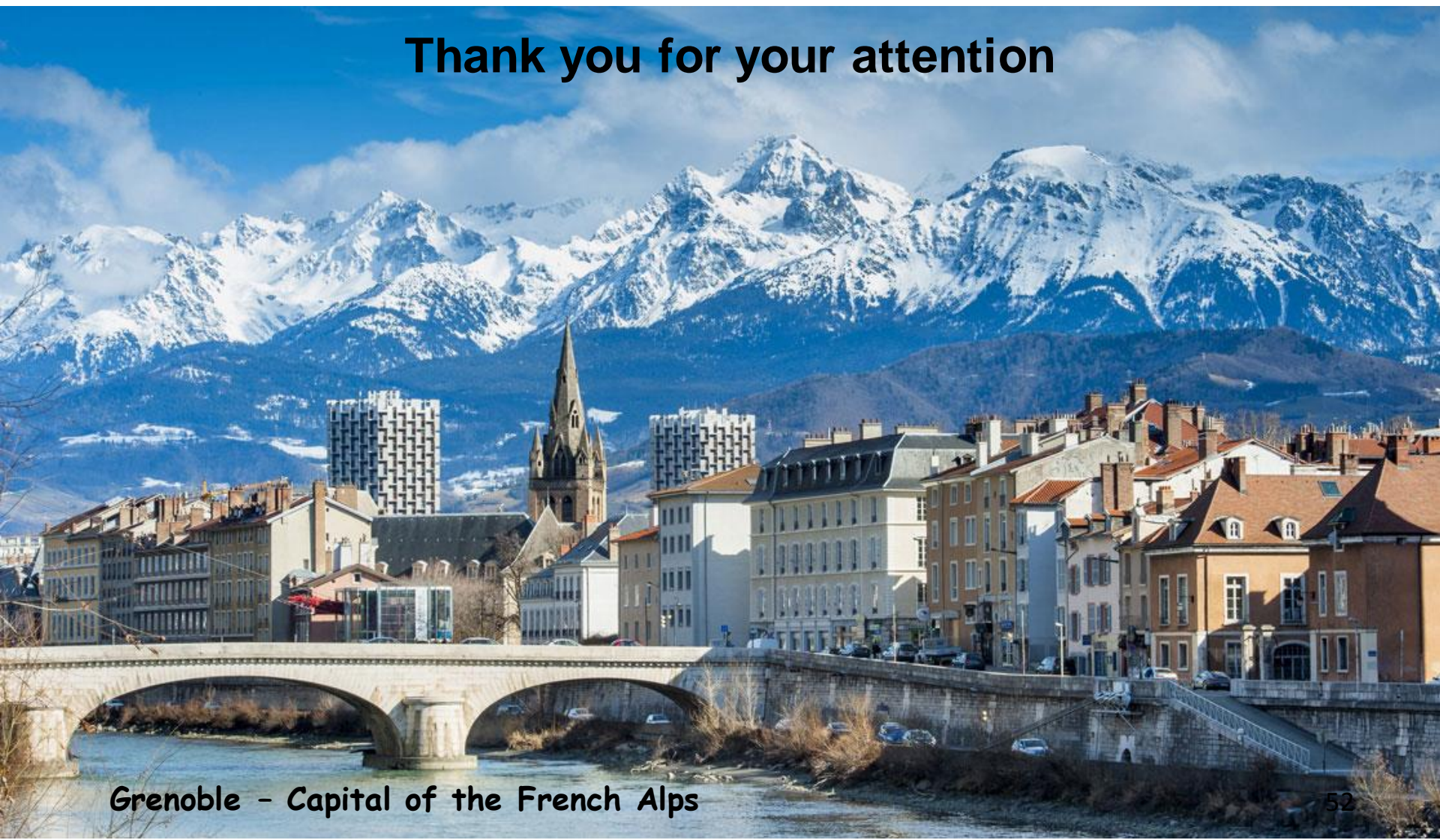
Solid state rheological characterization often used only to determine the glass-rubber transition temperature

Additional information can be obtained to characterize the microstructure/morphology and interfacial effects



agefpi

Thank you for your attention



Grenoble - Capital of the French Alps