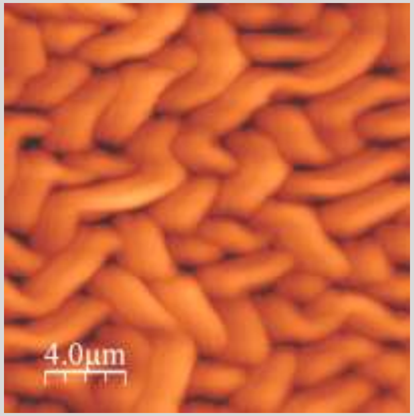
Pulsed Plasma Polymerization of Nanocellulose / Maleic Anhydride:

Parameter Study to Control Film Microstructure



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Overview

1 – Background : Sustainable materials design

2 – Renewable Resources: Cellulose Nanowhiskers – Preparation and Characterisation

3 – Plasma deposition of nanocomposite films

3.1 – Influence of Monomer Feed

3.2 – Influenced of Pulsed Plasma Parameters

3.3 – Metastable film morphologies

3.4 – Chemical characterisation

3.5 – Film Stability

4 – Conclusions and Outlook

Background : Sustainable materials design

Processes

Solvent-free deposition

Interface Engineering

In-situ Formation

Industrial upscaling

Flexibility

Materials

Renewables

Bio-based polymers

Wood constituents

Pulp residues

Functional Components

Natural composite Materials and

Micro- to nanoscale surface structures

Reinforcement, control of adhesion, optics, wettability, roughness, material guidance, channels, compatibility, biomimics, ...

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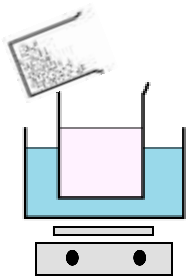
Preparation of cellulose nanowhiskers (CNW)

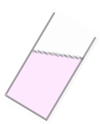
Acid Hydrolysis of Cellulose

Microcrystalline cellulose

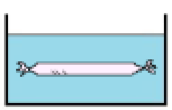
↓



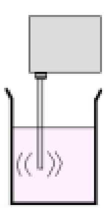
Acid hydrolysis treatment
(63% H_2SO_4)
Stirring at 45°C, 1 hour



Centrifugation
Washing

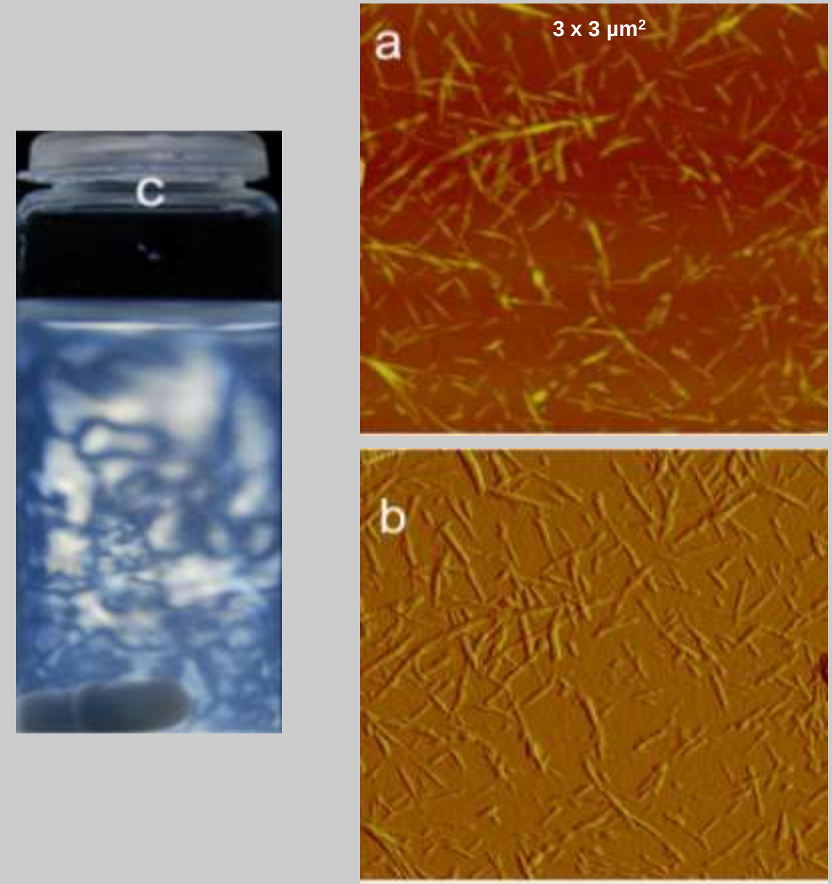


Neutralization
(dialysis to remove free acid)



Re-dispersion by
ultrasonication

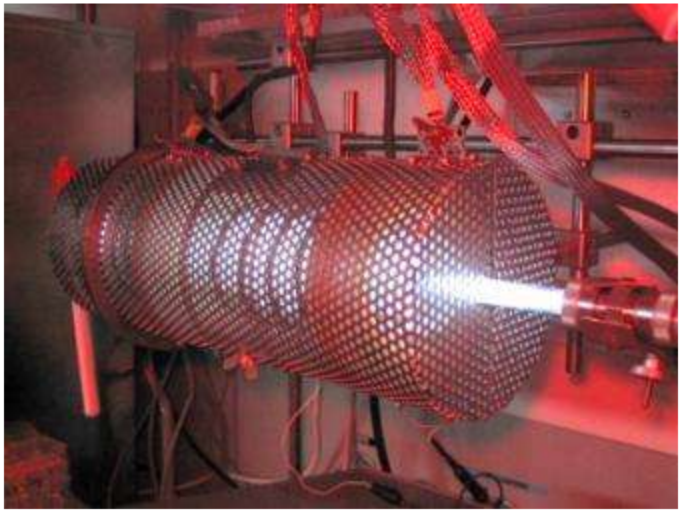
Bondeson et al., Cellulose 13 (2006), 171



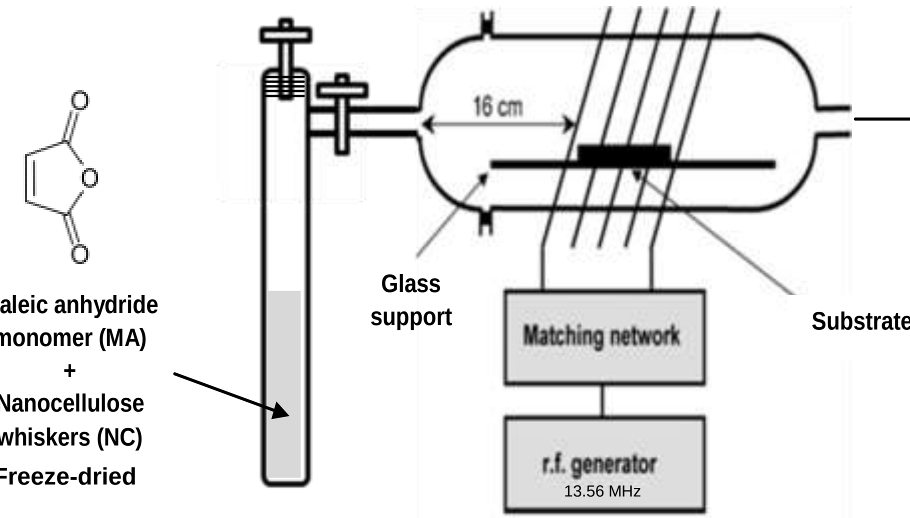
Diameters 4 to12 nm **Length 200 – 500 nm**

Pulsed Plasma Polymerisation

Maleic Anhydride pulsed plasma polymer



Diameter: 6 cm   Volume: 680 cm^3



Inductive coupling cold plasma

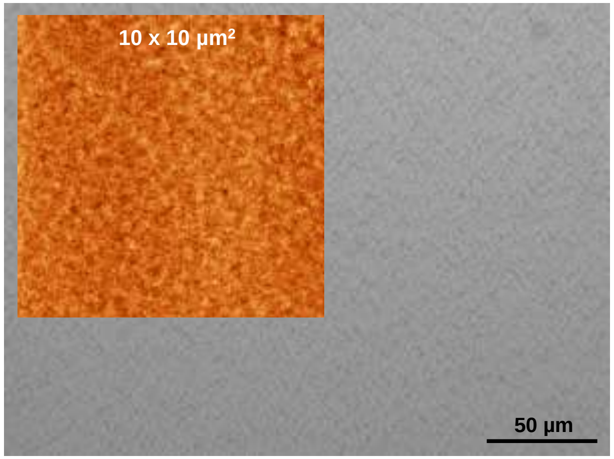
Plasma Parameters

- Monomer vapour: 0.1 to 0.2 mbar or 0.2 to 0.4 mbar
- Monomer mixtures: pure MA, pure CNW, or MA + 50, 200 wt.-% CNW
- Constant flow rate: 1.6 10^{-9} kg/s
- Constant time: 30 min
- Power: 10 W to 60 W
- Duty Cycle DC = $t_{on} / (t_{on} + t_{off})$ = 2%, 25%, 50%, 100%

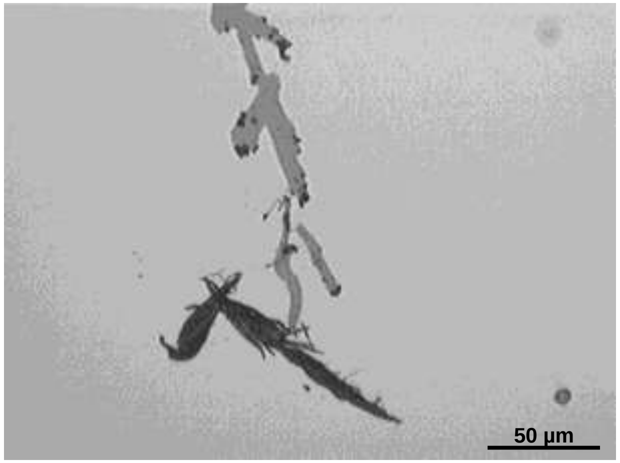
Deposition of Nanocomposite Films

Influence of MA monomer/nanowhiskers feed on morphology

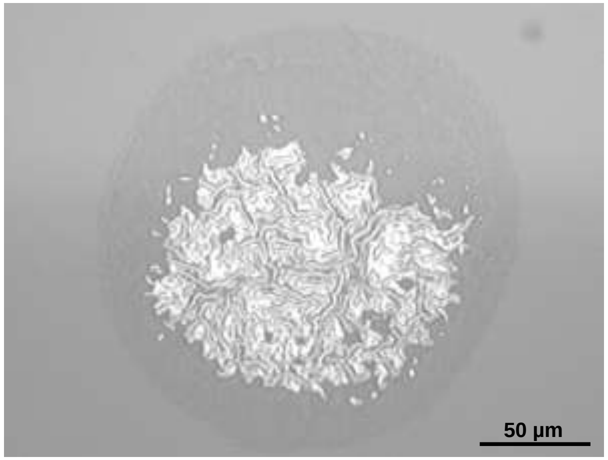
(a) **Pure maleic anhydride (MA) polymer**



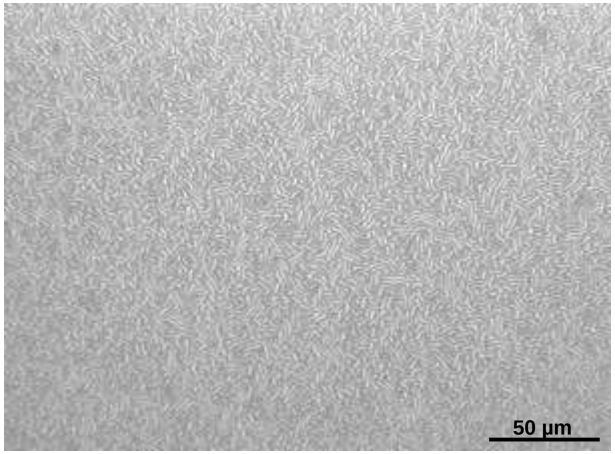
(b) **Pure CNW**



(c) **MA + 50 wt.-% CNW**



(d) **MA + 200 wt.-% CNW**



P_p = 20 W, *DC* = 2 %

Formation of metastable nano-composite film by dewetting (shrinkage) and solidification phenomena :

- Pure MA : thin film 20 nm (45°)
- 50 wt.-% CNW : dewetting and dimensional instability by film shrinkage into droplets
- 200 wt.-% CNW: fully covering interface Pattern (20°)
- Pure CNW: abrasion

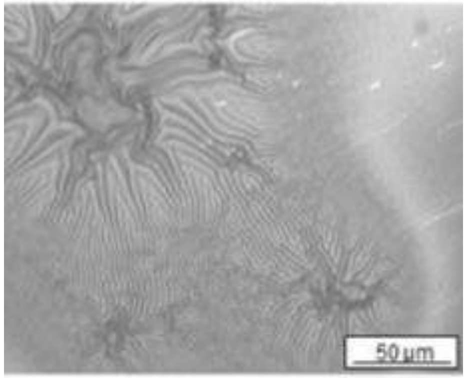
Deposition of Nanocomposite Films

Influence of plasma deposition parameters on morphology

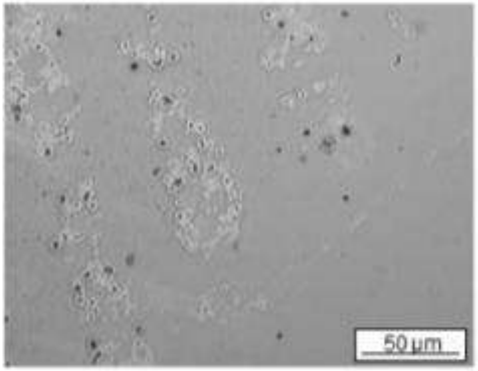
DC up to 100%: some thicker films that only develop locally

Power up to 60 W: degradation of the polymer film and only local deposits

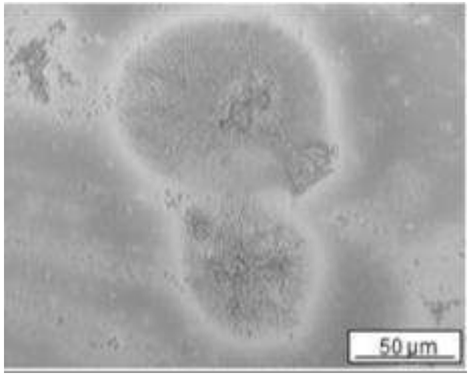
Narrow range of processing parameters for nanocomposite film is mainly determined by MA stability



P_p = 20 W, DC = 50%



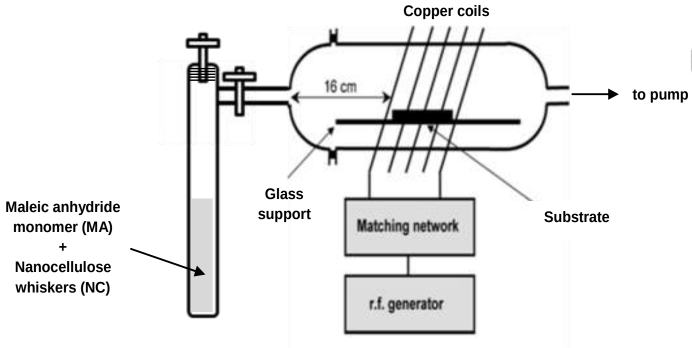
P_p = 20 W, DC = 100 %

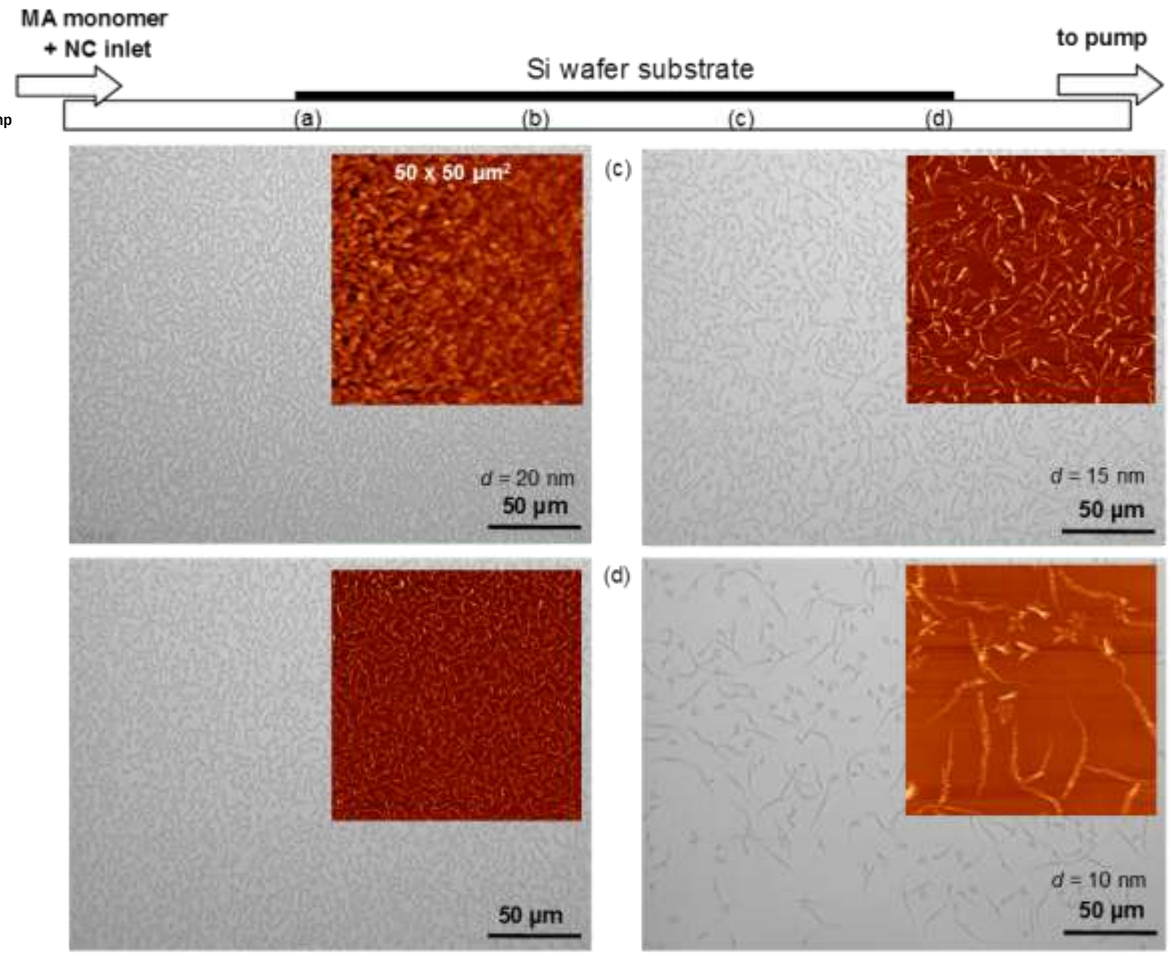


P_p = 60 W, DC = 2%

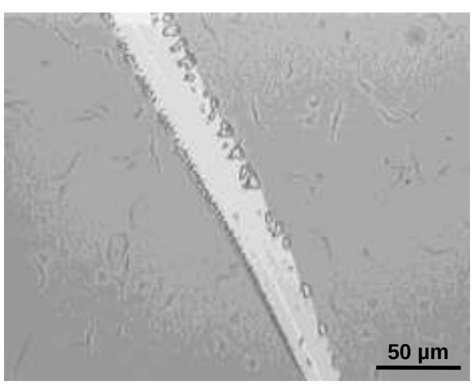
Deposition of Nanocomposite Films

Influence of plasma deposition parameters on morphology :





- Medium vacuum monomer pressure 0.2 to 0.4 mbar
- Control of substrate position
- Confirmation by scratch test



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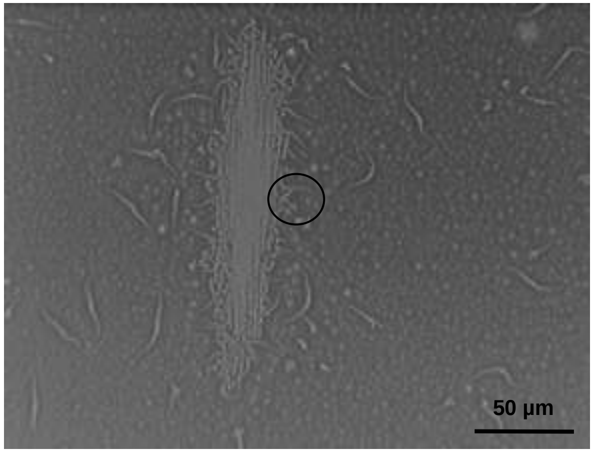
Mechanisms of metastable composite formation

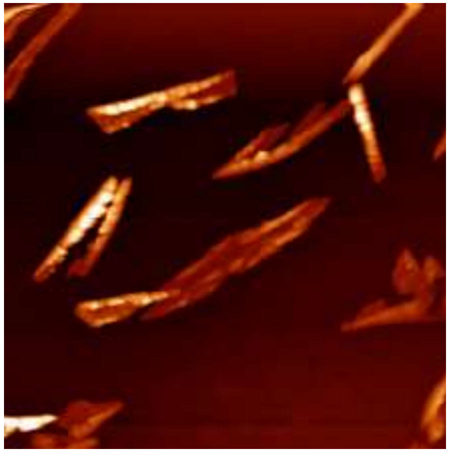
1. Fibrous CNW depositions

Defibrillation

Freeze-dried CNW are compacted and powdery aggregates likely defibrillate into single fibers while carried in the monomer gas stream. MA = dispersant.

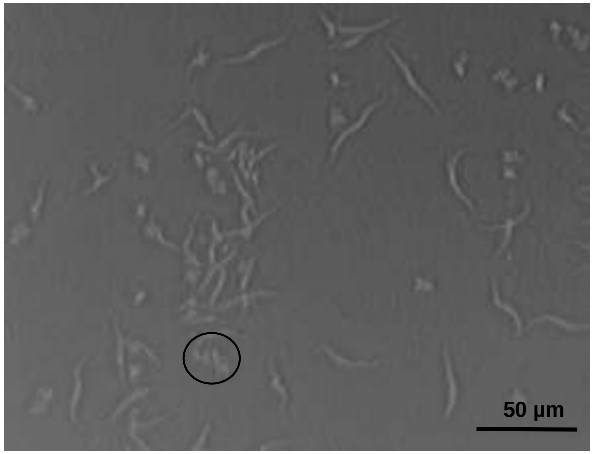


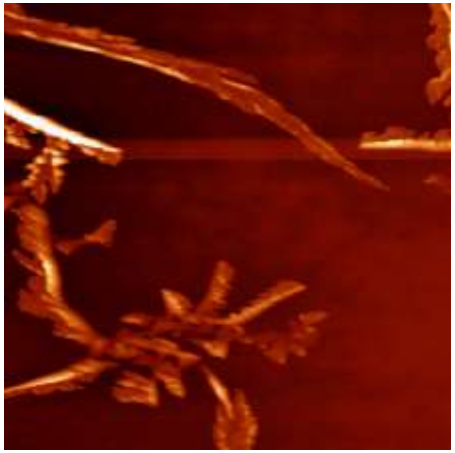
10 x 10 µm²



Crystallisation

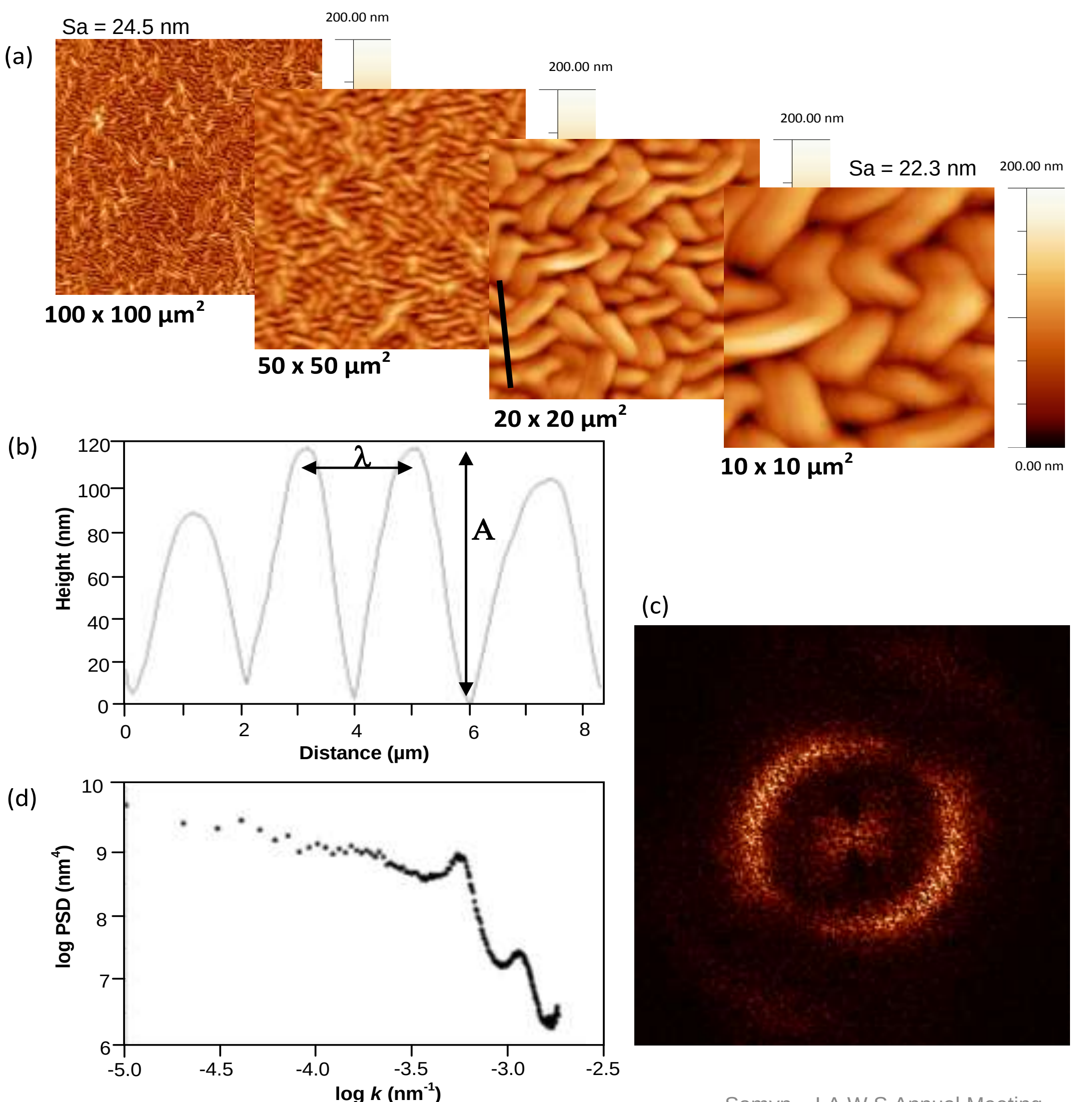
Elementary nanofibrils aggregate into secondary nanofibrils via lateral co-crystallization: small nano-crystallites further coagulate into nanofibrillar bund-les, lamellas, bands or layers.





Mechanisms of metastable composite formation

2. Pattern formation by buckling



Wavelength analysis versus properties

$$\lambda = 2\pi d \left[\frac{(1-\nu_f^2)E_s}{3(1-\nu_s^2)E_f} \right]^{1/3}$$

$\lambda = 1.8 \pm 0.2$ µm, $d = A = 100 \pm 10$ nm

e.g. $E_s = 150$ GPa, $\nu_s = 0.25$, $\nu_f = 0.32$

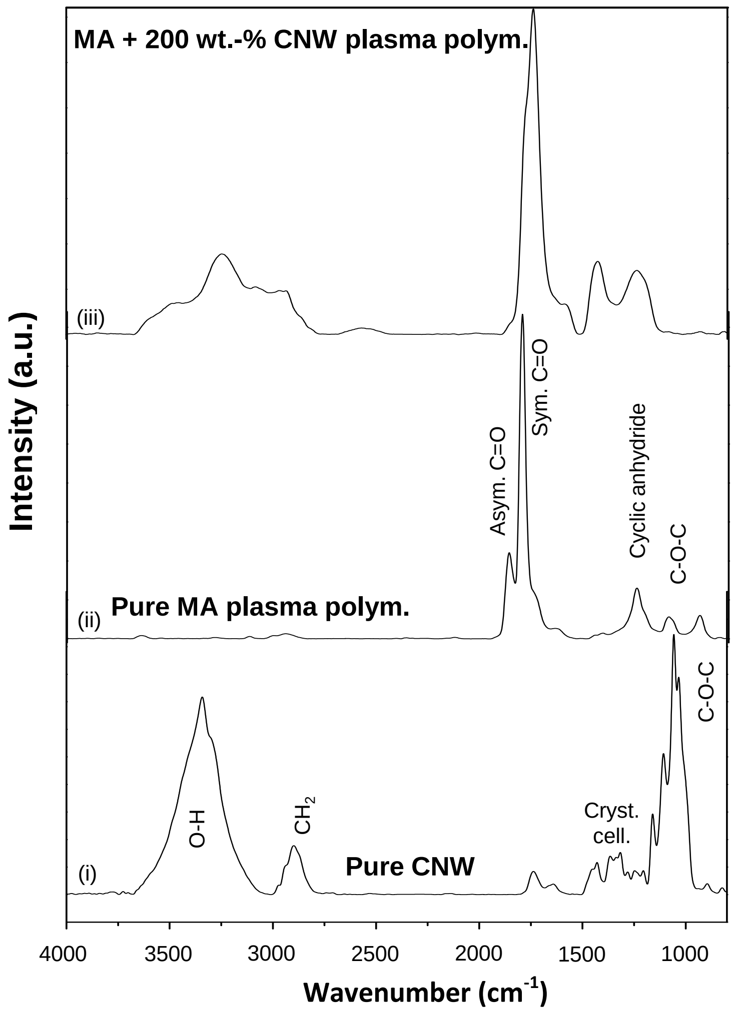
$E_f = 1.66$ GPa

Comparable to nanocomposite films made from layer-by-layer deposition.

Cranston et al. *Biomacromolecules* **2011**, in press.

Chemical characterisation

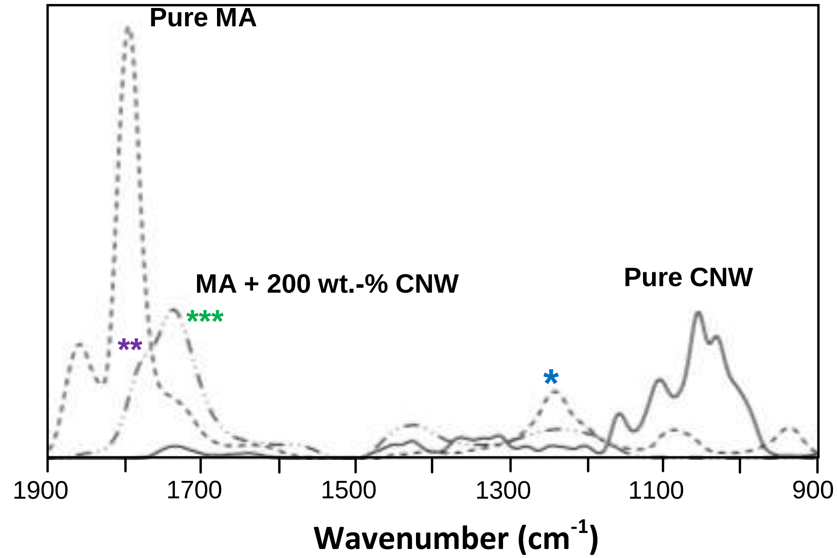
FTIR (P = 20 W, DC = 2 %)



In nanocomposite film MA + 200 wt.-% CNW:

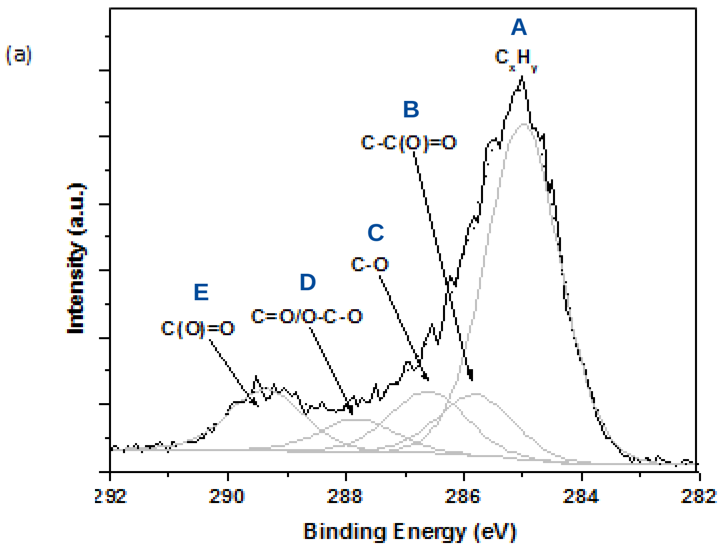
- No simple ‘addition’ of the spectra
- No clear detection of CNW in nanocomposite
- No more MA cyclic ring structures *
- Open MA ester (1781**) and acid (1735***) groups

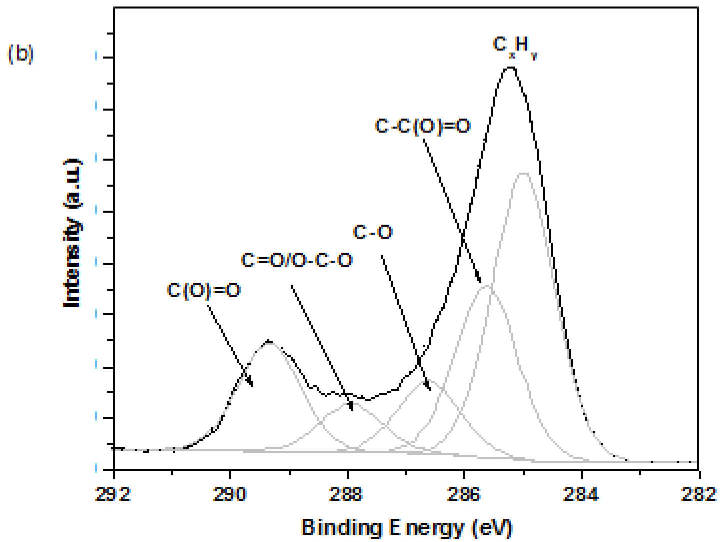
→ Esterification



Chemical characterisation

XPS





Measurement of O and C contributions:

Pure MA:

O/C = 0.43 (monomer); 0.33 (MA film);

74.78 at.-% C and 25.22 at.-% O

Fine-structure: peak area B = E

MA + 200 wt.-% CNW:

O/C = 0.32 (film)

75.95 at.-% C and 24.00 at.-% O

Fine structure: Larger peak B due to esterification; intensification of peak C (C-OH) is less than 5:1 expected for pure cellulose, indicating esterification.

Conclusion

Formation of nanocomposite films by gas-phase process, by co-deposition of cellulose nanowhiskers with maleic anhydride :

- Critical set of pulsed plasma parameters for continuous nanocomposite film determined by MA, other mechanisms include fibrillar deposits with defibrillation and crystallisation of the CNW.
- Formation of metastable films through a combination of dewetting (shrinkage) and solidification, with dimensionally stabilizing 'anchoring' points at a balanced monomer feed composition with cellulose nanowhiskers.
- Control and stabilization of the buckled film morphology depending on topography.
- Chemical interface compatibility most likely through esterification between MA and cellulose hydroxyl groups.

Outlook **Maleic anhydride is used as a model-polymer**

Surface patterning can be controlled by incorporation of renewable materials.

Acknowledgements

Thank you !

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Robert Bosch Stiftung

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