Optimizing various aspects of nanocellulose film forming on steel substrate for drying studies

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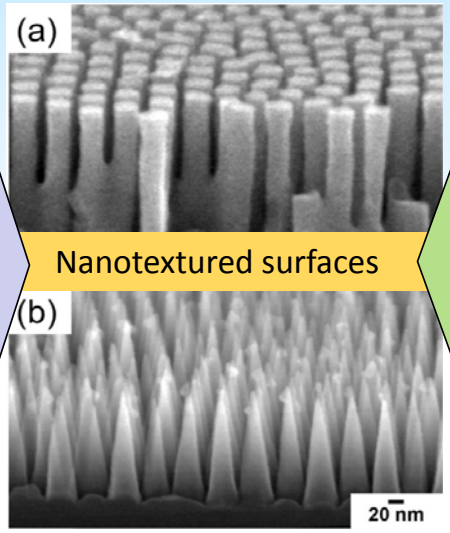
NanoTextSurf – Horizon 2020 EU project

Project partners

Are covered with structures, such as dots, fibrils, cones or holes, with smallest dimension on the nano-scale (0.1—100 nm)



Nanotextured surfaces

Have unique physical, optical, electric, or magnetic properties making them attractive for a wide range of applications such as membranes, protective textiles, friction pads and abrasive materials

NanoTextSurf project focuses on manufacturing technologies such as *cast coating, foam coating, or screen-printing* for producing these surfaces, patterns and architectures using different nano-scaled materials such as nanocellulose. The goal is to upgrade and optimize existing pilot lines, and use them to demonstrate novel nanotextured surfaces.

This work was performed at Berndorf Band Group in Austria by **Volker Uhl** and **Lukasz Krzyzanowski**

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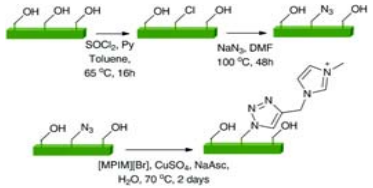
http://www.nanotextsurf.eu/

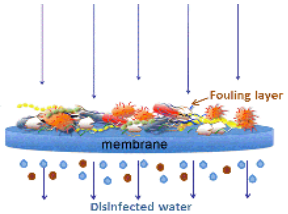
Why nanocellulose films and coatings?

Environmental benefits

Coating and film properties



Applications



Majority of these applications have been demonstrated only at the lab scale!

There is a definite need for upscaling!

Nanocellulose film manufacturing on semi-pilot scale at VTT

- Nanocellulose coated evenly on plastic film
- Controlled spreading and adhesion
- No shrinkage (adhered to plastic while drying)
- Smooth base surface replicated to the nanocellulose film
- Tunable thickness

Tammelin et al. PCT Int. Appl. (2013), WO 2013060934 A2 20130502
Mäkelä et al. Microelectronic Engineering 163 (2016) 1–6, http://dx.doi.org/10.1016/j.mee.2016.05.023

Background and motivation for drying studies

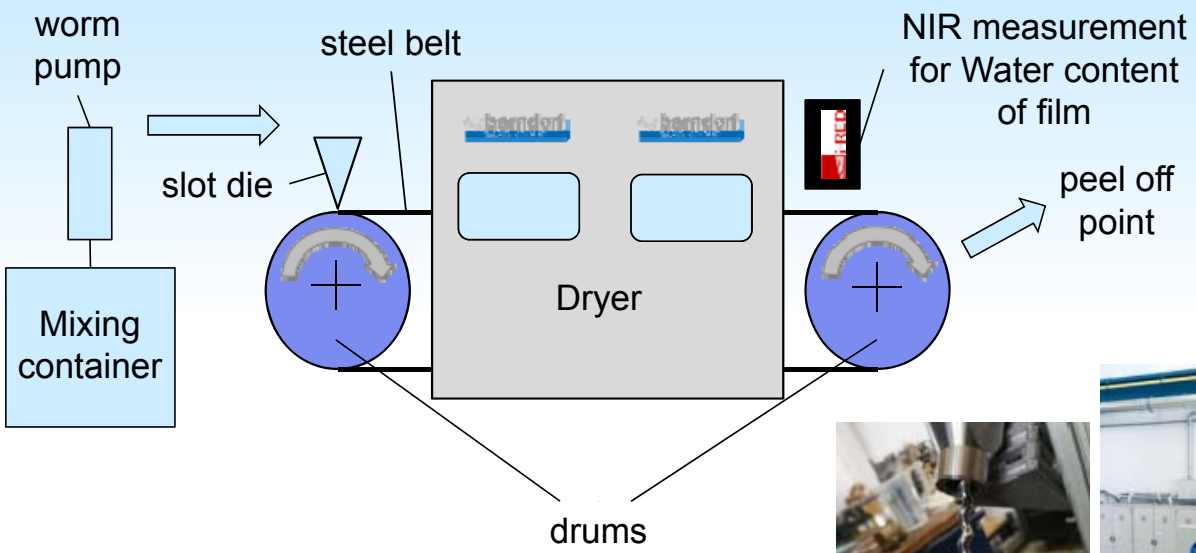
Why study drying?

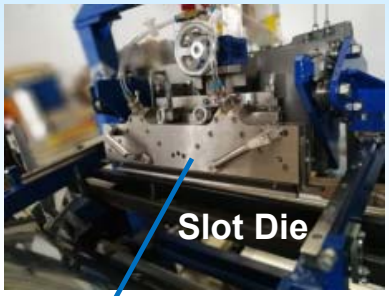
- Nanocellulose suspensions are processed into films and coatings at low solids
- Problems related to shrinkage and poor film quality
- Drying significantly affects the development of nanocellulose film and coating properties

Why cast on a steel substrate?

- Plastic substrates are not optimal for drying studies due to their sensitivity to high temperatures
- With steel substrate, heating can also be provided through the substrate itself

Casting equipment and nanocellulose materials





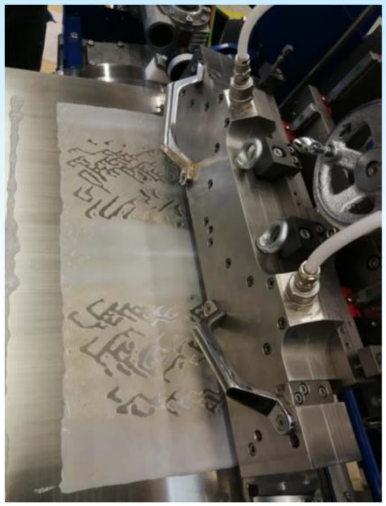
Steel Belt dimensions
9.4 m long, 0.6 m wide, 0.8 mm thick

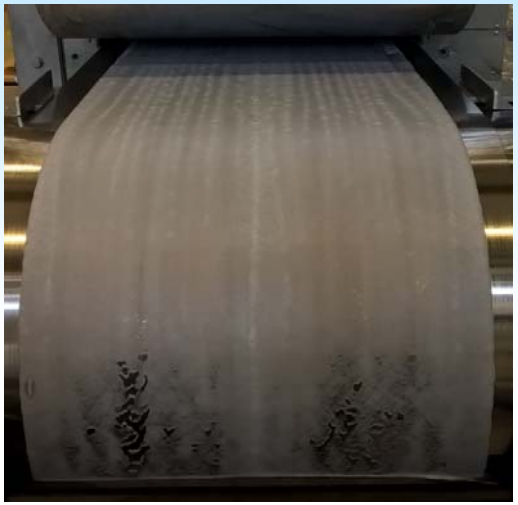
Steel Belt material
NICRO 31, CrNiTi 13 4, similar DIN 1.4313

Nanocelluloses	TEMPO-CNF (supplied by EMPA)	Industrial MFC (supplied by Borregaard, Exilva F 01-V)

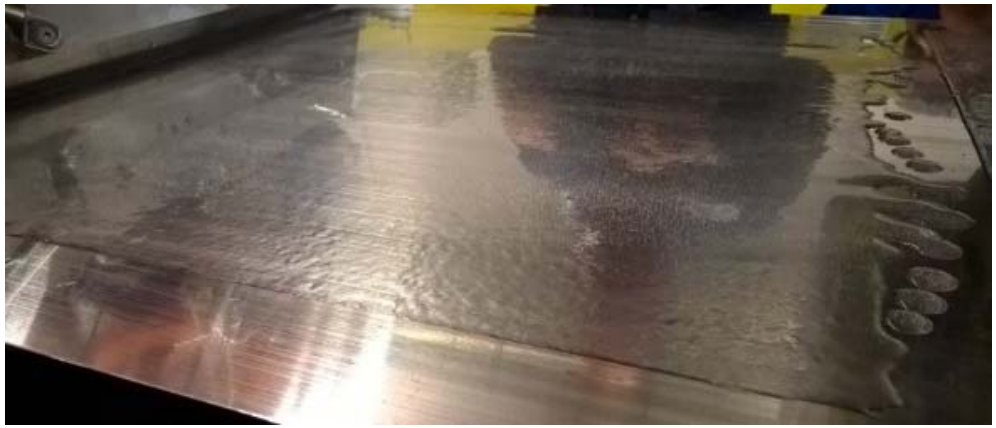
Challenges with film formation on steel belt

MFC





CNF



Goals of this work

Optimize wet film forming and releasing of dried film from the steel substrate

for

dryness and quality analysis

Produce a defect-free nanocellulose film in a continuos process

to

be characterized for strength properties

Utilize different drying strategies

to

study the impact of drying on film properties

Suspension
Rheology,
solids content,
mixing,
additives

Casting process
Slot die,
pumping,
speed

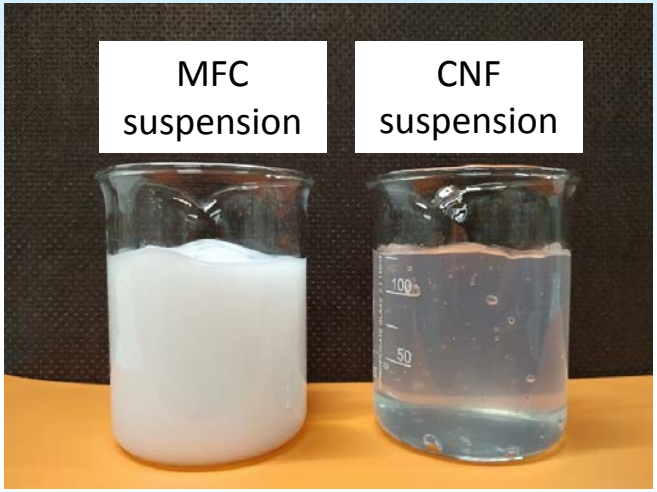
Steel belt surface
Wetting behavior,
releasing properties

Drying strategies
Hot air drying
IR drying
Room temperature drying
Combination drying

Suspension Optimization

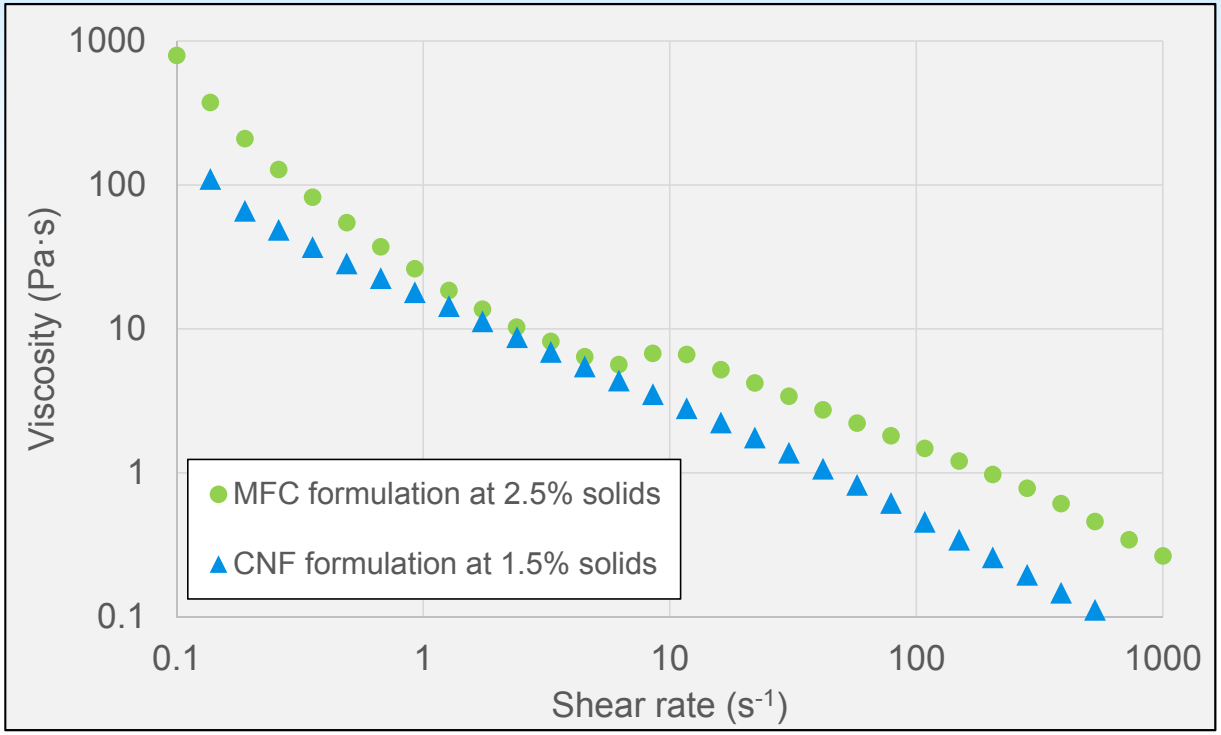
- Films from pure MFC and CNF suspensions were too brittle and were destroyed during peel off from the substrate

- Different additives such as CMC, PVOH and sorbitol were used as plasticizers to enhance film properties for improved peelability
  - CMC led to too high adhesion of the films to the steel substrate
  - PVOH and sorbitol amounts were optimized



Optimized formulations	
Components (parts per hundred)	Solids (%)
TEMPO-CNF (100), PVOH (10), Sorbitol (20)	1.5
Industrial MFC (100), PVOH (10), Sorbitol (20)	2.5

Rheology of the formulations

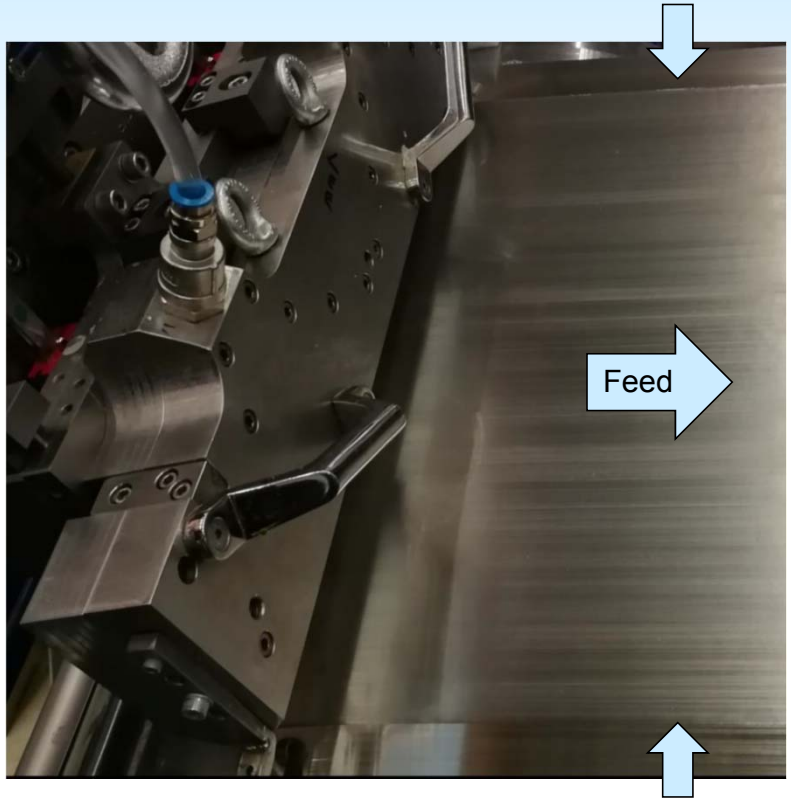


Rheology measurments were made using parallel plate geometry at a gap of 1 mm.

- Both formulations were found to be highly shear thinning allowing easy film formation with shearing.
- Viscosity of CNF formulation reaches that of MFC formulation even at lower solids due to presence of a more nanoscale material.
- Rheological prehistory was also found of importance for the casting process.
- Mixing prior to casting according to a strict protocol is crucial.

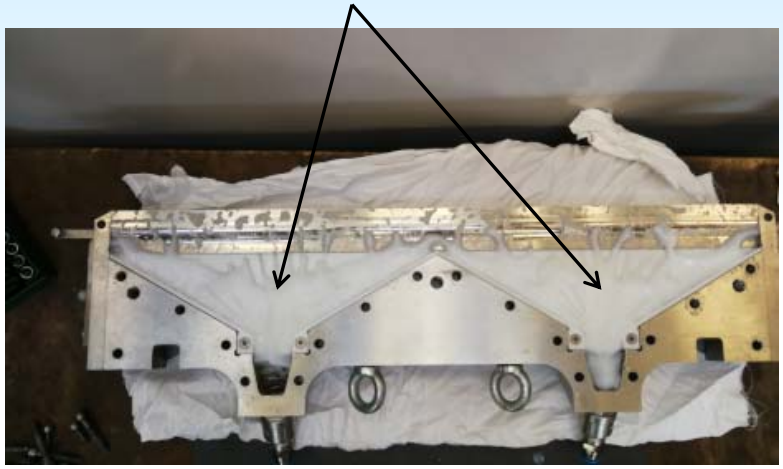
Casting process optimization

- Slot die parameters
  - Slot gap: 1000 µm was found optimal for avoiding the blockage
  - Distance between slot-die exit and substrate was optimized for a minimum wet film thickness to obtain stable films →
    - TEMPO-CNF: 1200 µm
    - Industrial MFC: 900 µm
- Pumping parameters
  - With overpressure to avoid phase separation (especially for MFC formulations) in the pumping system and lines
- Belt speed
  - Casting speed 0.1-1 m/min
  - For MFC film formation, speed of at least 1 m/min was necessary (the shear thinning effects are needed!)

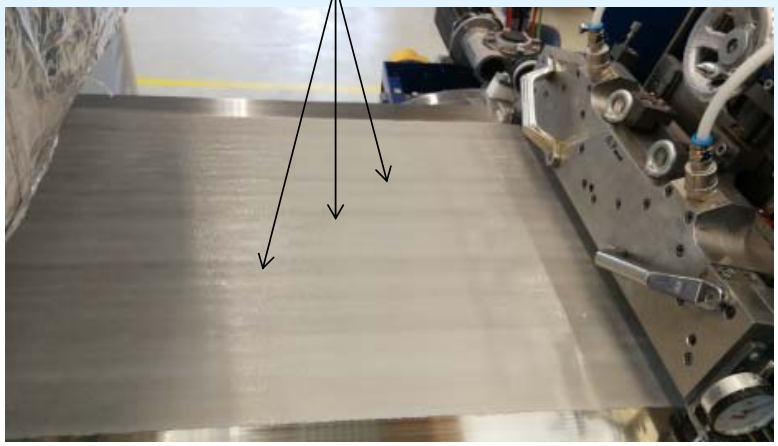


Other casting challenges

Internal Guides



Stripes



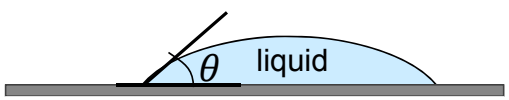
Reproduction of the slot-die internal guides in the cast film

- The different shear forces within the slot die channels are problematic. This results in different shear thinning effects.
- Due to different shear thinning extent, the casting solution does not flow evenly through the slot die. The guides in the slot-die where higher shear thinning takes place are reproduced in the film (stripes).
- Once the internal guides were removed, the wet film formation got significantly better.

Steel belt optimization

- The surface properties of steel belt, its age and use is known to affect casting results
- The surface free energy of the steel belt surface has an effect on its wettability and adhesion properties
- The steel belt of the Berndorf pilot line was replaced with a new steel belt to compare the properties

Wetting behavior:



Young's equation: $\sigma_s = \sigma_{SL} + \sigma_l \cdot cos\theta$

σ_{SL}:	surface tension of the liquid
σ_l:	interface tension between liquid and solid
σ_s:	surface free energy of the steel belt surface
θ:	contact angle

Steel belt 1 (2018): NICRO 12.1	θ_{water} =	95° +/- 5°
	$\theta_{diiodomethane}$ =	69° +/- 6°
	Surface free energy (mN/m):	27.3 +/- 6.5
	Disperse part (mN/m):	25.2 +/- 4.6
	Polar part (mN/m):	2.1 +/- 1.9
Steel belt 2 (2019): NICRO 31	θ_{water} =	77° +/- 6°
	$\theta_{diiodomethane}$ =	47° +/- 4°
	Surface free energy (mN/m):	41.2 +/- 4.6
	Disperse part (mN/m):	35.8 +/- 2.1
	Polar part (mN/m):	5.4 +/- 2.5

Release properties:

- Release agent: Loctite Frekote PUR-100

- Better Wetting
- Decreased dry adhesion
- Easy peeling

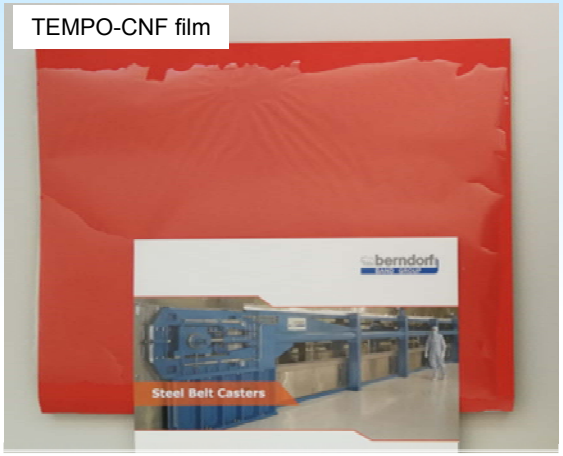
Krüss Mobile Surface Analyzer, contact angle data are averaged on 12 single measurements, the surface free energy calculation is according Owens, Wendt, Rabel and Kaelble (OWRK) method

Production of CNF and MFC Films

TEMPO-CNF film in production process

Industrial MFC film in production process

TEMPO-CNF film



Industrial MFC film

Strength properties of the films

Test parameters:

Span = 100 mm: CS dimensions = 15 mm x film thickness

Strain rate = 100 mm/min

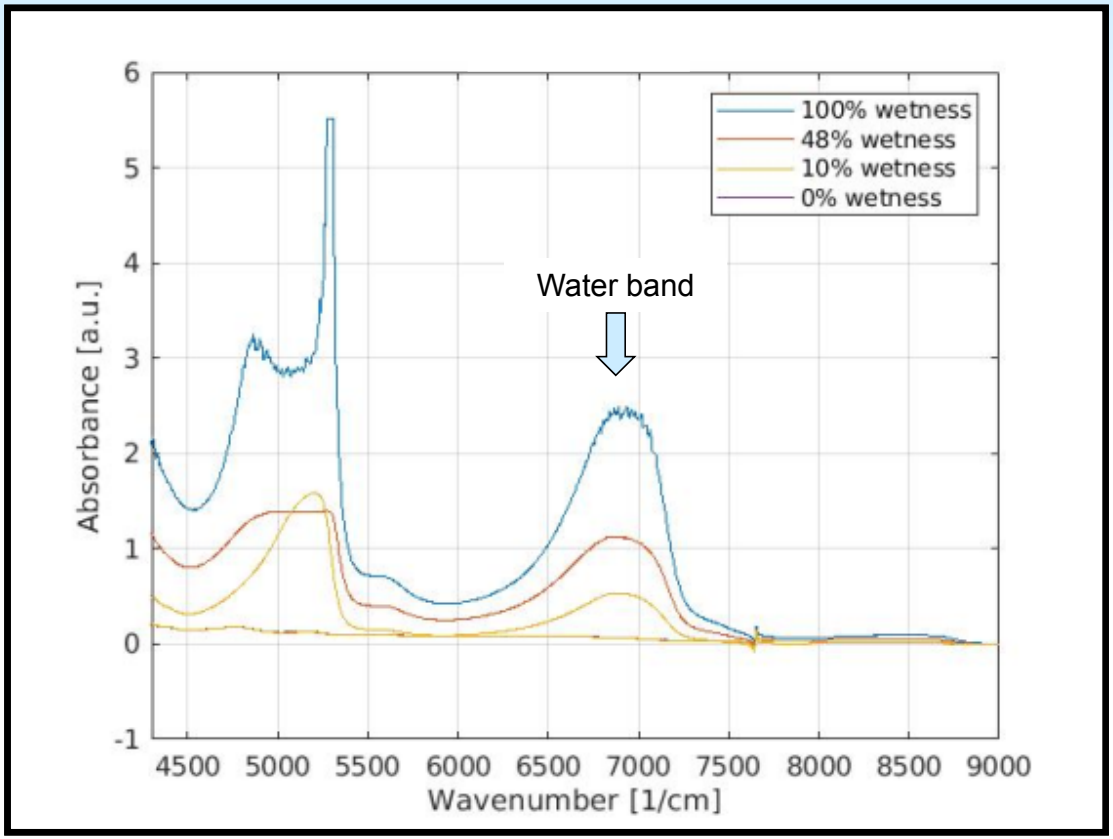
5 parallel samples chosen from or near center of the film in MD

Areas with visible holes were avoided

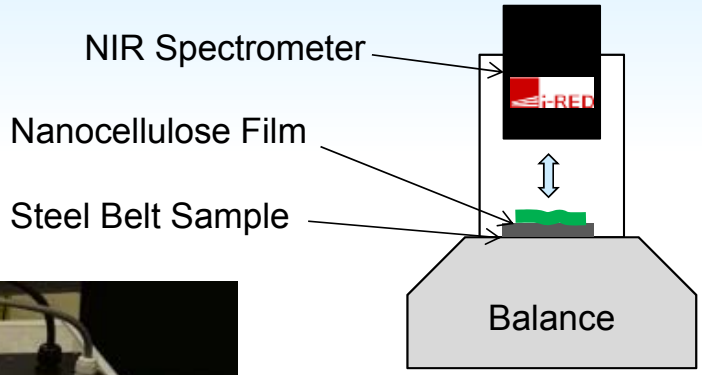
Sample	Thickness (µm)	Tensile Strength (MPa)	Strain at break (%)	Young's modulus (GPa)
TEMPO-CNF	20.7 ± 0.9	65.16 ± 2.63	2.63 ± 0.61	5.8 ± 0.8
Industrial MFC	29.5 ± 1.7	49.87 ± 4.22	3.90 ± 0.59	3.6 ± 0.3

Strength properties still need optimization through various drying strategies or changes in the recipes

Drying behavior of suspensions/films



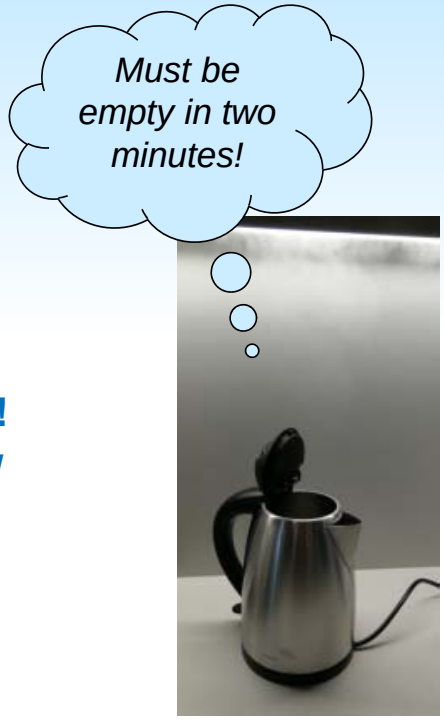
NIR Spectroscopy: water content of the film



Energy considerations for drying

- **Assumptions**:
- casting width = 500 mm
- wet thickness = 1.25 mm
- water content of CNF = 98%
- belt speed = 1 m/min

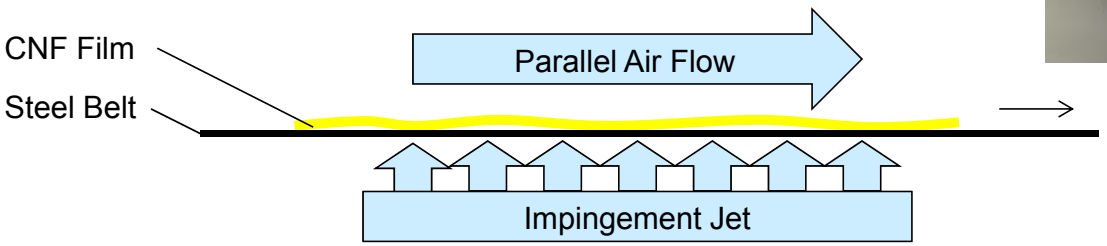
- => **1.2 kg water to evaporate in 2 minutes!**
- ΔH_{evap}(water) = 2257 kJ/kg => **P = 22.6 kW**



- Drying by hot air and hot steel belt is only possible at 0.1 m/min

- => Higher production efficiency required for economic process

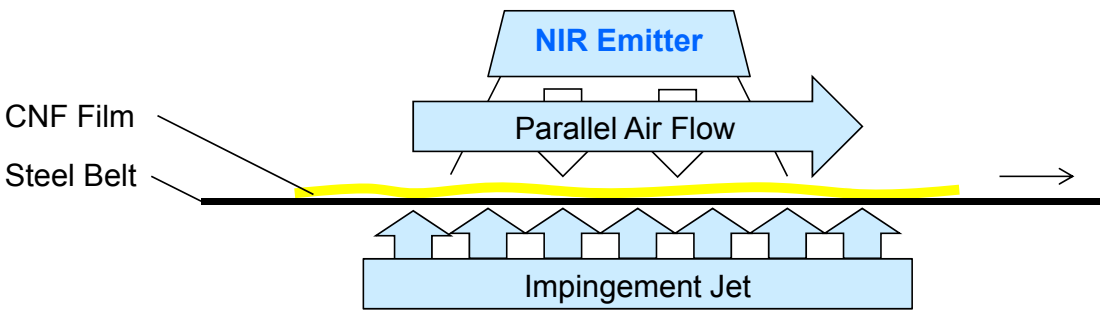
- => Additional energy input through NIR radiation may be required to achieve higher speeds



Accelerated film drying

The wet cast film is dried

- by heat from below
- by a parallel hot air flow (also to remove water vapor)
- by NIR radiation from the top



Effect of NIR Drying

- Increase of belt speed by a factor of 10
- A belt speed of 1 m/min was possible for casting and drying
- The higher belt speed also led to better properties in film casting, as shear thinning plays a significant role in CNF casting with the slot die

Summary and conclusions

Suspensions

Additives had a major influence on strength and flexibility of the films, which are necessary for non-destructive releasing.

Additives had only a minor influence on adhesion of the dried films to the steel belt.

The rheological properties affected the film forming, a minimum shear thinning effect was required to form the wet film.

The adherence of the mixing protocol is a must for reproducible results.

Casting process & steel belt surface

Casting process itself needed optimization of the slot-die and other slot-substrate gap parameters.

Pre-treatment of the steel belt by mechanical processing and/or application of release agents prior to the casting process proved to be most important for easy releasing of the films.

With the new steel belt, it was possible to cast films of 20-30 µm dry thickness using Industrial MFC and Tempo-CNF without using release agents, and the dry cast film could be peeled off by hand.

A fragile equilibrium had to be established between the releasing and adhesion of the films.

Drying strategies

A continuous casting speed of 1 m/min instead of only 0.1 m/min was possible with the infrared dryer. Different ways to dry the films will be modelled and examined in the next phase.

Thank you

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