





# Superhydrophobic surfaces manufacturing with nanocellulose

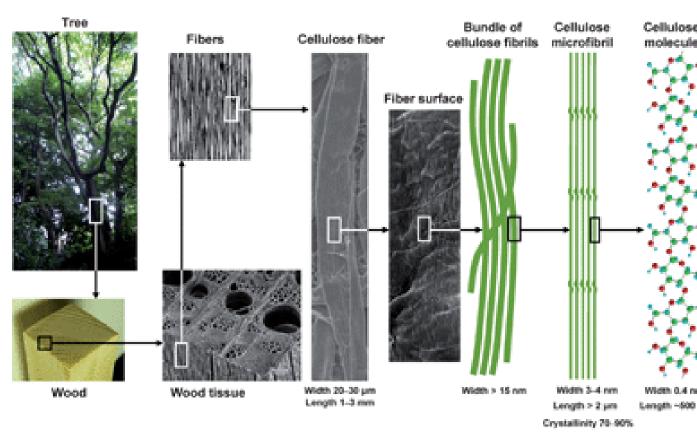
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### **Abstract**

Researchers in natural fibers see opportunities in superhydrophobicity for fabrics or paper. The first challenge with natural fiber is their high hydrophilicity when the second is the perpetual search for water born coating in papermaking. These challenges were overcome by a one pot formulation comprising a latex binder, precipitated calcium carbonate and fatty acids to give their hydrophobicity to pigments 1. In this study, we want to go further by replacing the petro-sourced latex with a new kind of fibers that are cellulose nanofibers (CNF).

Inspired by the Lotus leaf, superhydrophobic surfaces have been a center of interest in the last decade because of their high potential in industry for a variety of applications. It is seen as the next generation of surface for anti-fouling and corrosive retardant in navy industry but also in general anti corrosive materials industry. Now widely studied, mechanisms for manufacturing superhydrophobicity are well understood. Born from the alliance of low surface energy chemistry and physical structuration of surface, superhydrophobic materials give a water contact angle above 150° and a slidding angle below 10°.



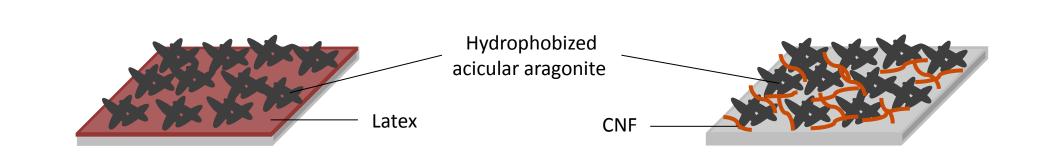
## Current collaboration work

#### Introduction

Cellulose nanofibrils (CNFs) is a biobased and biodegradable nanoscale and fibrillar shape material extracted from trees. CNF tend to naturally form an entangled network that could possibly homogeneously disperse particles in coating applications for example.

In this study, cellulose nanofiber (CNF) is expected to act as a binder and dispersive agent for roughening particles that are essential for superhydrophobic surfaces.

This collaboration project between SP and LGP2 groups was done under COST Action ActinPack FP1405. Hereafter is presented the results of dynamic and static contact angle as well as SEM on coated surface.



#### Materials & Methods

#### **Materials**

Acicular Aragonite (PCC) Sturcal H was provided by Specialty Minerals. **Sodium oleate** (88-92%) was purchased from Riedel-de Haen. Styrene Butadiene latex DL-930 was purchased from Dow Chemical. It has

a Tg of 5°C and a dry matter content of 50%. Neat nanocellulose manufactured from bleached birch pulp was

purchased from CTP, France. AKD (Alkyl Ketene Dimer) hydrophobized reference CNF was purchased to InnoFib, France. Amino propyl trimethoxy silane (APMS) 98% was purchased from Sigma

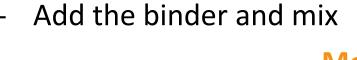
Aldrich and used for modification of nanocellulose. Substrate was chosen to be a paperboard of 230 g/m<sup>2</sup> from Stora Enso

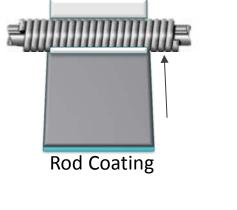
used for cups.

### **Coatings preparation**

Coatings preparation include the following steps: Dissolve Sodium oleate at 45°C for 10min

- Add Aragonite and mix for at least 20min



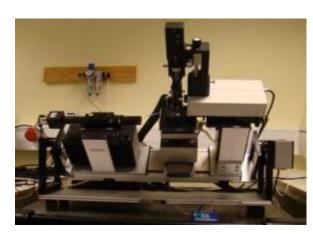


#### **Measurements methods Wetting measurements**

#### Wilhelmy method for measuring wetting properties as well as advancing and receding angle of porous and hygroscopic material is ruled by the

following equation:  $F(h,t)=P\gamma\cos\theta+Fw(t)-\rho Ahg$ Samples were glued at the edge to avoid water penetration.

### **Contact and roll-off angle**

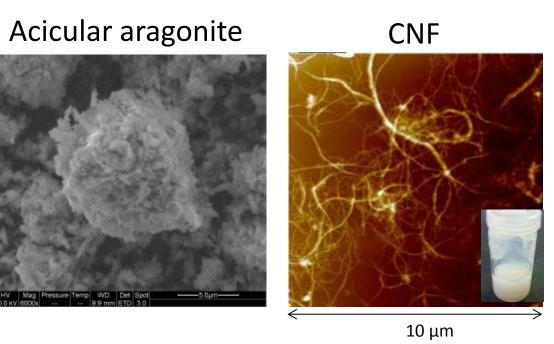


Static contact angle measurements were done with a 5 μL water droplet.

Water shedding angle (WSA)<sup>2</sup> was measured by tilting the plate before dropping a 10 µL water drop to be able to compared with CNF based coating (water adhesion).

## Results & discussion

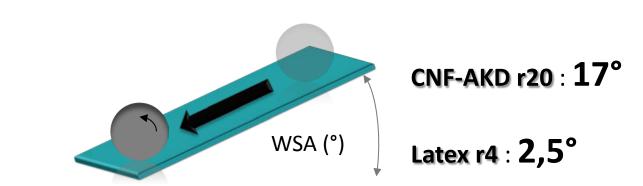
#### Raw materials coating formulation



	Composition of dry matter (wt%)			Dry Matter
	Pigments	Fatty acid	Binder	content (%)
Latex	78,4	2,0	19,6	33,0
CNF-APMS r10	88,9	2,2	8,9	15,0
CNF-APMS r4	78,4	2,0	20,4	9,0
CNF-AKD r10	91,0	0,3	8,7	15,0
CNF-AKD r20	95,2	0,3	4,6	18,0

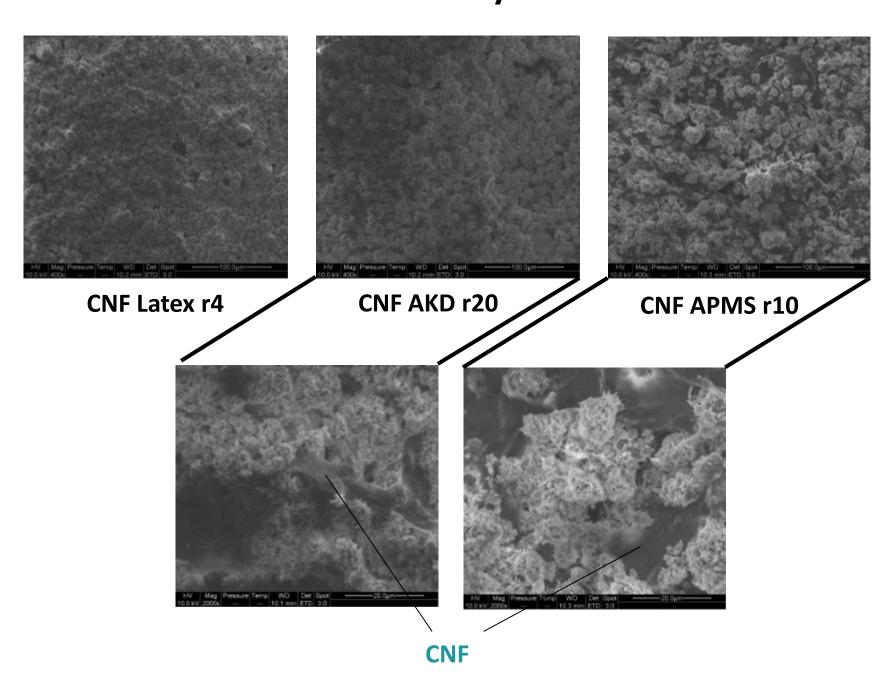
Different formulations had to be developed for replacing latex as the fatty acid was chemically altering the modified CNF. The high hydrophilicity of CNF as well as the higher water content was not favoring superhydrophobic state. Proportion of PCC had thus to be increased. Unfortunately, PCC seemed to leech off the surface with CNF when it is not the case in the presence of latex.

#### Water shedding angle

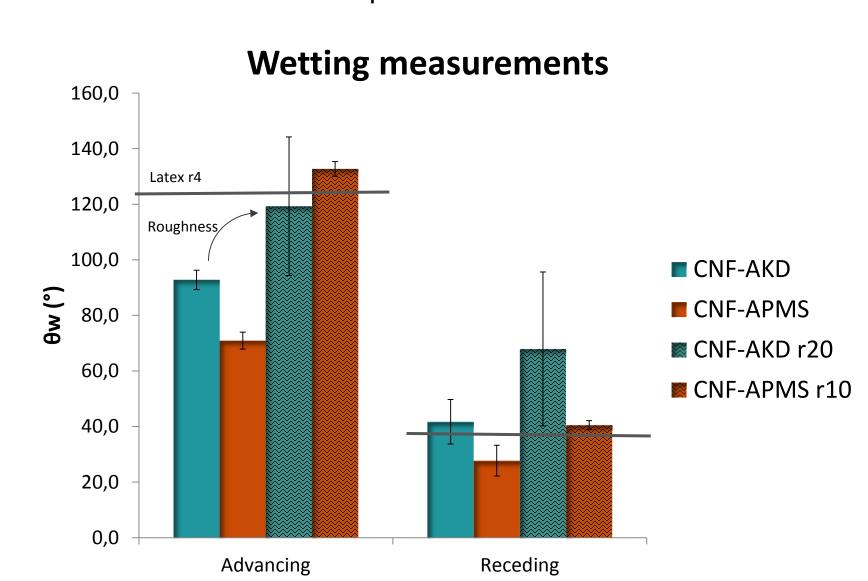


Water shedding angle was achieved with high loading PCC and CNF-AKD formulation. Roll-off angle was not measurable because of water adhesion on CNF-AKD r20 surface.

### **SEM** analysis

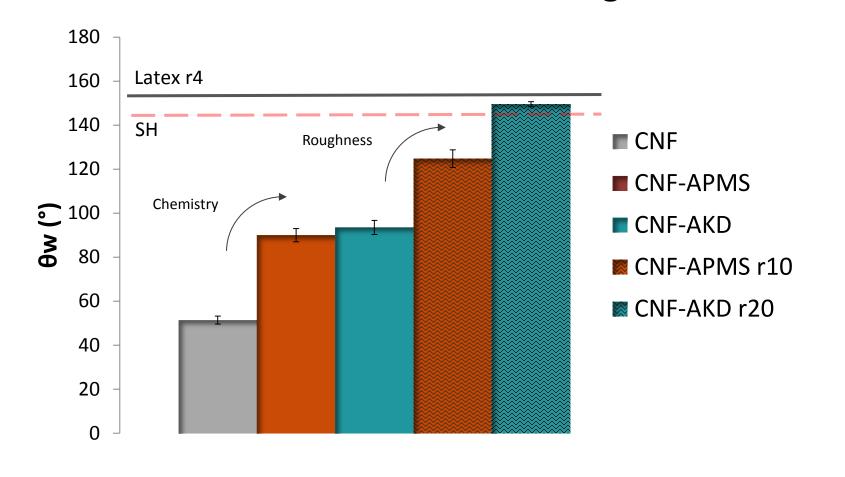


SEM images revealed surface topography of coated paperboard. When related to static water contact angle, closer packing of aragonites gives better hydrophobicity. CNF and high loading of PCC coating (CNF AKD r20) shows few CNF at the surface while low loading show more. This could explain water adhesion on the surface due to enlargement of pitch<sup>3</sup> and/or to strong attraction between water and cellulose eventhough CNF are previously hydrophobized.



Wetting measurements were made only with one cycle as the sample became wet after withdrawal probably because of inhomogeneity in the coating and also absorption of water of CNF. Roll-off angle with an already tilted plate was achieved with high loading PCC and CNF-AKD formulation.

## Static water contact angle



Latex coating is showing evidence of superhydrophobic state as expected. High loading PCC formulation with CNF-AKD achieved superhydrophobic 150° water contact angle. With CNF-APMS, contact angle above 125° wasn't obtained. Lower amount of PCC has for consequence the drop of contact angle.

# **Conclusions & Perspectives**

- o A water repellent surface was successfully achieved with a combination of commercial AKD modified CNF and acicular aragonite.
- A water contact angle higher than 150° was obtained and a water shedding angle also.
- Wetting measurement were difficult because of water interaction with nanocellulose and paperboard and also because of porosity.
- o Obtaining a superhydrophobic coating is related to close packing of aragonites regarding SEM images obtained. This close packing can be achieved with modified CNF but leeching of PCC is observed.
- o Also, CNF appears at the surface, what is assumed to create the water adhesion. This water adhesion creates more a rose petal effect<sup>3</sup> surface than a Lotus effect meaning high static water contact angle with high adhesion of water.

### **PERSPECTIVES**

**Achieve lower** coating weight

Different hydrophobization of CNF

Hydrophobized PCC with a more stable fatty acid

Use of different PCC and effects

Have a look on antibacterial activity

