Short term scientific mission report – COST Action FP1405 ActinPak

Manufacturing and measurement of superhydrophobicity for paperbased active packaging

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I. Introduction

SP Technical Research Institute of Sweden are experts on material and surface science and have large range of techniques available for detailed surface characterization. They gave a special interest on hydrophobic and superhydrophobic materials and on surface energy measurement. LGP2 laboratory have expertise in nanoparticles extracted from trees and have special interest on active packaging.

The aim of collaboration between SP Technical Research Institute of Sweden and the LGP2 was to engineer superhydrophobic fiber based material replacing the commonly used styrene butadiene latex by surface modified nanocellulose. Within a short term scientific mission under Cost action FP1405 ActinPak, this was made possible.

II. Context and objectives

The workplan was defined previously as such:

- Modification of nanofibrillated cellulose (Grenoble INP - LGP2)
    - Silane aqueous modification
- Characterization of nanocellulose: FTIR and SEM-EDX (Grenoble INP – LGP2)
- Coating of nanocellulose and mineral blend (SP: STSM)
    - Elaboration with appropriate quantities
- Surface energy measurement and characterization (SP: STSM)
    - Static and dynamic contact angle measurement
    - Wetting properties with Wilhelmy plate
    - Scratching effect
- Surface mapping and adhesion
    - AFM and SEM
- Effect of superhydrophobicity on active packaging properties (Grenoble INP – LGP2)
    - Antibacterial test

Hereafter is the detail of the two weeks STSM results.

III. Materials and methods

III.1. Raw materials

Acicular Aragonite Sturcal H was provided by Specialty Minerals.

Styrene Butadiene latex DL-930 was purchased from Dow Chemical. It has a Tg of 5°C and a dry matter content of 50%.

Sodium oleate (88-92%) and sodium stearate (82%) were purchased from Riedel-de Haen and Roth respectively.

Neat nanocellulose manufactured from bleached birch pulp was purchased from CTP, France. AKD (Alkyl Ketene Dimer) hydrophobized reference MFC was purchased to InnoFib, France. Amino propyl trimethoxy silane 98% was purchased from Sigma Aldrich and used for modification of nanocellulose.

Substrate was chosen to be a paperboard of 200 g/m² from Stora Enso used for cups.

All along these experiments, MilliQ water was used.

III.2. Coating suspension preparation

Fatty acid salt was first dissolved in water at respective temperature of 75°C and 45 °C for sodium stearate and sodium oleate during 10 min. Dry pigment were added slowly and mixed for 20 min. Finally, the binder (latex or MFC) was mixed with the previous suspension for 5 min. Depending on dry matter content of the suspension, for MFC sample, an improved method was done by switching aragonite to MFC while mixing.

III.3. Coating

Coating was done with a rod coater with different wet thicknesses from 12 to 100 µm. Drying of material was achieved using an oven at 90°C for latex and neat MFC based coating suspension and 120°C for MFC-AKD and MFC-silane.

Figure 1. Coating of a suspension with the rod coater

III.4. Surface characterization

Wetting measurement

Wilhelmy method (Figure.2) for measuring wetting properties as well as advancing and receding angle of porous and hygroscopic material is ruled by the following equation:

$$F(h,t) = P\gamma cos\theta + Fw(t) - \rho Ahg$$

Where F is the detected force, P the wetted perimeter of the plate, γ the surface tension of the probe liquid, Θ the liquid-solid-air contact angle, ρ the probe liquid density, A the cross-sectional area of the plate, h the immersion depth and g the gravitational constant.

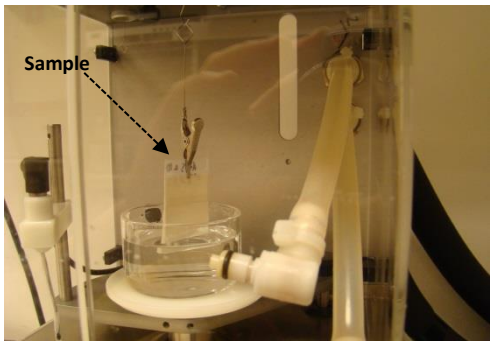

Figure 2. Wetting measurement of a sample

Samples were cut in two pieces fixed on a double side table on a glass plate. Edges were glued with a wood glue in order to avoid any water uptake from there. Wetting measurements were done by 10 consecutives immersing/withdrawal cycles of 15 mm of the sample in water.

Before any measurement, surface tension of distilled water was determined to get more precise data.

Θ_A and Θ_R (advancing and receding angle) were determined by linear regression of the immersion and withdrawal curves to zero depth (h=0). Average of three measurements was done.

Contact and roll-off angle

Contact, roll-off and advancing/receding contact angle were measured with a Data Physics OCA 40 (Figure.3). Water was dispensed with a needle of 0.25 mm diameter. Static contact angle measurements were done at least five times with a 5 µL water droplet. Whenever it was possible, roll off angle was measured by tilting the plate after dropping a 9.6 µL drop of

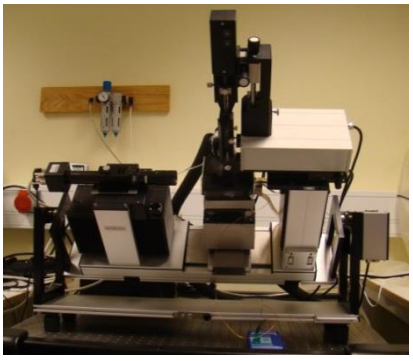

Figure 3. Contact angle measurement machine. Tilted at 45°.

water from 0° to 90°. The angle is determined as the last angle the plate was tilted before the drop rolls.

A special measurement method for sample MFC-AKD r20 0.25 was made up for roll off angle determination. As the water droplet tends to be absorbed rapidly in the material, plate was first tilted before dropping the 9.6 µL water droplet. This angle is named $\Theta^*_{roll\ off}$.
All measurements are presented as an average of at least five measurements.

IV. Results and discussion

IV.1. Coatings formulation

Formulations 1 and 2 (Table.1) were done at the LGP2. Printing paper was chosen as a foldable but thick enough to endure both liquid and viscous coating material. But coatings were not homogeneous even though different coating thickness or speeds were tried. Even reference latex coating did not show any superhydrophobic property. Suspension was phase separating during coating process.

We realized that stearate might be the problem. Indeed, steric hindrance of the long chain fatty acid causes the phase separation. Oleate was chosen as the new fatty acid to hydrophobize the aragonite as the double bond of the molecule gives a different conformation around aragonite particles and the fact that elevated temperature (75 °C or above) is not needed.

Unfortunately, sodium oleate salt was discovered to diminish the MFC-AKD hydrophobization process leading to high water absorption of the coating. This is probably due to that the oleate acts as a spreading promotor for AKD molecules in a way that AKD no longer maintains the hydrophobic character of the MFC. Thus, a study was carried out to find out to which proportion oleate could be decreased to be in the right proportion so that there is not migration out of aragonite surface. Aragonite were mixed with oleate at different proportion and then filtered. The filtrated water was analysed with an UV/VIS spectrometer to check if there was still oleate in the aqueous phase. Proportions were decreased from 2.5 pph (parts per hundred) to 0.25 pph, but even at this concentration oleate was found in the water. A 0.25 pph proportion might not be enough for designing a superhydrophobic material so this proportion was kept for MFC-AKD formulations with aragonite, expecting this would be enough for keeping MFC-AKD treatment viable.

Printing paper was then changed to paperboard as interaction between suspension and substrate were better, meaning less absorption of water and thus less buckling of paper.

Mainly formulations 3 and 4 (Table.1) were measured. Samples are referenced as (Binder) (Ratio aragonite/binder (w/w)) (fatty acid proportion toward aragonite in pph).

Ingredients	Proportion (pph)	Type	Formulation 1	Formulation 2	Formulation 3	Formulation 4
Fatty Acid	2.5	Sodium stearate	x	x		
		Sodium oleate			x	
	0.25					x
Mineral	100	Aragonite	x	x	x	x
Binding agent	25	Latex SB	x		x : “Latex r4 2.5”	“Latex r4 0.25”
		MFC	x			
		MFC-APMS	x		x: “MFC-APMS r4 2.5”	x: “MFC-APMS r4 0.25”
		MFC-AKD	x		x: “MFC-AKD r4 2.5”	
	5	MFC-APMS		x		
		MFC-AKD		x		x: “MFC-AKD r20 0.25”
	10	MFC-APMS			x: “MFC-APMS r10 2.5”	
		MFC-AKD				x: “MFC-AKD r10 0.25”
Substrate	-	Printing paper	x	x		
		Paperboard			x	x

Table. 1. Coating suspension composition

IV.2. Static and dynamic contact angle

Static contact angle with water was determined for each surface. Results marked with * showed slight absorption over time while others do not. For these samples, contact angle was measured within the first three seconds. As superhydrophobicity is defined as a water contact angle above 150°, only the latex formulation with high oleate content could be defined as such, but the "MFC-AKD r20 0.25" is on the border to superhydrophobic.
Oleate proportion regarding aragonite is important to design superhydrophobic suspension as shown by the difference between 2.5 and 0.25 pph with latex binder or MFC-APMS.
MFC-AKD r20 0.25 displays the best results with MFC as a binder water was rapidly absorbed in the coating. Probably free oleate was still problematic.
Difference between MFC-APMS r4 and r10 at same oleate level is difficult to explain as better result would be expected for r10 ratio. Perhaps, the coating was not as homogeneous as the other one because of higher dry matter content.

	Θ_{CA}		Θ_A		Θ_R		$\Theta_{roll\ off}$		$\Theta^*_{roll\ off}$
MFC-AKD (reference) *	94	3	—		—		—		—
MFC - APMS (reference) *	90	3	—		—		—		—
Latex r4 2,5	157	5	146	11	115	12	21	12	2.5
Latex r4 0,25	139	1	—		—		—		—
MFC-APMS r10 2,5	103	2	—		—		—		—
MFC-APMS r10 0,25 *	32	9	—		—		—		—
MFC-APMS r4 2,5	125	4	—		—		—		—
MFC-AKD r10 0,25 *	142	4	—		—		—		—
MFC-AKD r20 0,25 *	150	1	—		—		—		17

Table. 2. Static and dynamic contact angles with standard deviations.

As the latex formulation was giving superhydropobic surface, advancing and receding contact angle was measured as well as roll off angle (Table.2). Θ_A and Θ_R are high showing low adhesion of the water on the surface. The roll off angle is very low but inhomogeneity of the coating gave rise to a large spread in values. The roll off angle measured with a pre-tilted plate is also very low for latex formulation but for MFC-AKD r20 0.25 it is very good also, showing a superhydrophobic effect.

IV.3. Wilhelmy plate

Advancing and receding angle were measured from the first cycle of hysteresis. For all samples, after the first cycle, the surface became wet and so advancing and receding angle could not be measured for the next cycles. This could be explained by some inhomogeneity in the coating but also in the case of the presence of MFC, by an absorbing phenomenon of the surface. Also, edge sealing with wood glue was absorbing some water after a while and water may have migrated into the sample.
Also, surface tension of water after was measured after each measurement. For all samples, surface tension was decreased pointing out that there is a release of chemicals or aragonite.

Almost all samples showed high standard deviation (Table.3). This could be explained by a lack of homogeneity of samples coating.

All formulations containing aragonite display a relatively high advancing contact angle (Θ_A) compared to nanocellulose reference coatings. On the opposite, Θ_R is very low giving rise to high contact angle hysteresis (Θ_A - Θ_R). This hysteresis is reflecting liquid adhesion on samples.

	Θ			
	Advancing		Receding	
MFC-AKD (reference)	93	–	42	–
MFC APMS (reference)	71	3	28	6
Latex r4 2,5 pph	140	13	39	10
MFC-APMS r10 2,5pph	133	3	41	2
MFC-APMS r4 2,5pph	112	17	35	4
MFC-AKD R20 0,25pph	119	25	68	28
MFC-AKD R10 0,25pph	144	11	40	1

Table. 3. Advancing and receding average angle at first cycle

V. Conclusion

During the STSM, several coating formulations were tested in order to optimize conditions and to achieve superhydrophobic properties using a green and sustainable MFC instead of a styrene-butadiene latex as binder in the coating. Sodium stearate as fatty acid for aragonite hydrophobization was not compatible with coating formulation because of resulting phase separation requiring too high temperatures for mixing and coating. Oleate was thus chosen as a preferred fatty acid. Unfortunately, it was not compatible with MFC-AKD hydrophobic reference MFC so different proportion were tested in order to find out up to which level it could be decreased to avoid release in the aqueous phase.

A superhydrophobic material with latex as reference was obtained and all measurement that could be possibly made on such surface were carried out. Problem of absorption of water with formulation with MFC were still a problem even though there were previously hydrophobized. One sample containing hydrophobized MFC as binder proved superhydrophobic with a static water contact angle of 150 degrees but still a fairly high roll-off angle compared to the latex binder. Scratching properties were not explored due to a lack of time.

Formulations with MFC are in a good way but a new method of hydrophobization should be found. Also, find a more stable fatty acid over time than oleate would be a great trial as it degrades by oxidation within 2-3 months. The next steps could be the characterization of the surface via AFM and SEM and antibacterial measurement of MFC-APMS coating after hydrophobization with aragonite.

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