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Electrospun nanocellulose/poly(vinyl alcohol) (PVA) fibers: evaluation of cellulose nanocrystals orientation on multilayer food packaging properties.

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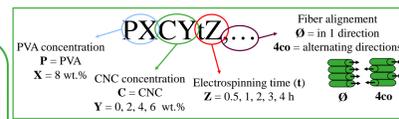
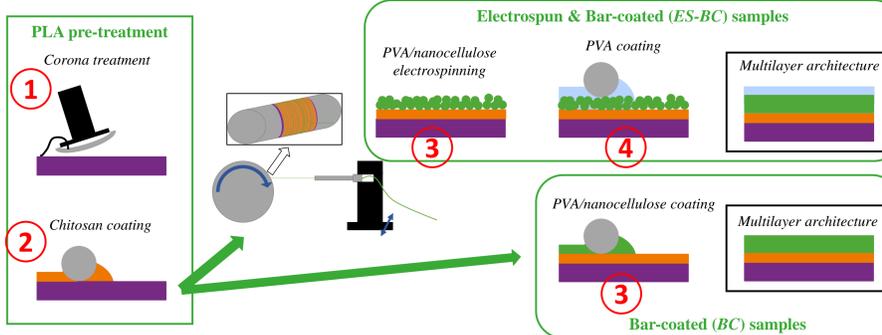
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Contexte

- The impact of plastics on our environment requires a drastic reduction of their production and uses
- New bio-based and biodegradable materials should be developed, particularly in packaging industry, which represents 36 % of the total worldwide plastic production.
- Nanocelluloses, bio-based and biodegradable polysaccharides, are biodegradable, compostable and have impressive properties, suitable for food packaging.
- Main nanocelluloses drawbacks: their sensitivity to water, not adapted to food packaging application.
- A second bio-based and biodegradable polymer should be combined with nanocelluloses = the poly(lactic acid) (PLA).
- Different architectures combining nanocelluloses and PLA have been studied and better preservation of nanocelluloses properties was observed with a multilayer structure
- To improve the barrier properties, multilayer materials should include oriented CNC.

In this work, **electrospinning**, was used to coat **aligned nanofibers of CNC/poly(vinyl alcohol) (PVA) on PLA**.
Multilayer film structure, water vapor and oxygen transport properties were investigated, to evaluate the impact of CNC alignment.

Film Preparation

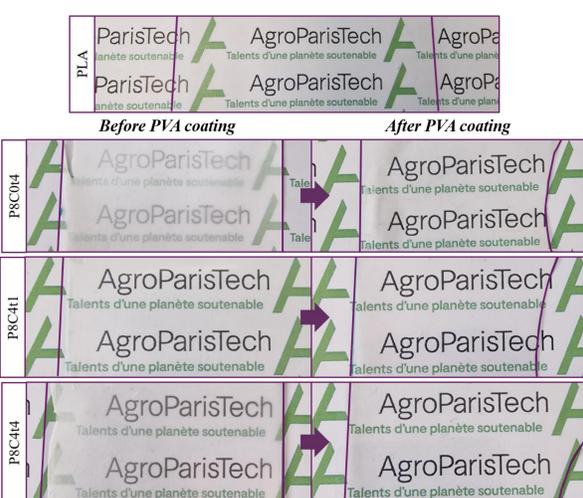


Material: Wood cellulose nanocrystals (CNC) (University of Maine), polylactic acid (PLA) (50 µm, Goodfellow), poly(vinyl alcohol) (PVA) (Gohsenol type AH-17, The Nippon Synthetic Chemical Co), chitosan (CS) (Sigma-Aldrich).

Methods: Bar coating and electrospinning (wd: 10cm, flow rate: 1-1, mL/h, rotation speed: 1700 rpm, needle speed: 0.146 m/s, voltage: 12-17 kV. Ultraviolet-visible spectroscopy, scanning electron microscopy, oxygen permeability, dynamics vapor sorption at 80% RH.

Results

Structure

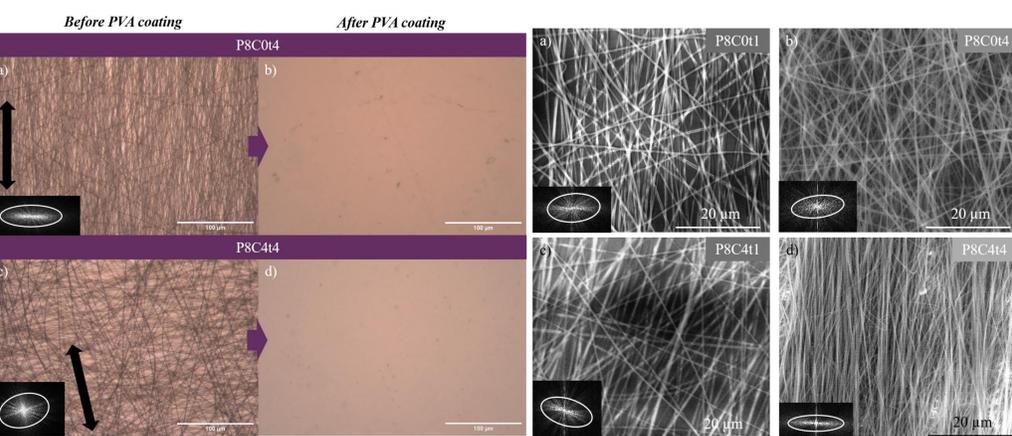


The visual observation of the samples was able to confirm the presence of PVA and PVA/CNC fibers on PLA, with the appearance of white fibers. After the addition of a bar-coated layer of PVA, the color of the fiber mat changes to become transparent. This observation was confirmed with UV-VIS measurements. Sample transmittance after the bar-coating of PVA increases drastically: by 70 to 80%.

Samples	Transmittance (%)
PLA	86.6 ± 0.7
P8C0t4 (before BC)	2.1 ± 2.5
P8C0t4 (after BC)	72 ± 2.9
P8C4t4 (before BC)	0.6 ± 0.3
P8C4t4 (after BC)	82.7 ± 1.1

*BC: bar-coating of PVA

The white color of fibers can be explained by their nanometric diameters: the high number of interface areas refracts the light¹. During PVA bar-coating, the water from PVA solution swells the nanometric fibers and fills the porosities (impregnation), creating a very homogeneous mat of PVA and PVA/CNC. The fibers disappear and the light is not refracted: PLA transparency is restored.



SEM images and their corresponding FFT images confirm the orientation of the PVA and PVA/CNC fibers. The average fiber diameter was calculated.

An average fiber diameter between **300 – 400 nm** was found, similar to literature². The fiber diameter decreases with the addition of CNC and when CNC concentration increases³.

Polarized microscopy confirms the impact of PVA bar coating on the fibers: no fiber remaining after the PVA deposition (layer of 120 nm).

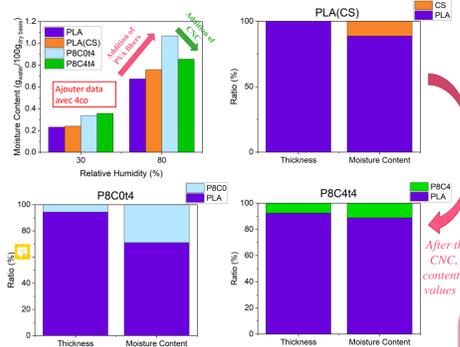
What is the objective of coating oriented-electrospun fibers if the fibers are not preserved?

- Oriented-electrospun fibers = oriented CNC inside the fibers.
- Bar-coating is applied in the fiber direction, to induce a supplementary orientation of CNC⁴.

Electrospun – Bar-coated samples								
	P8C0t1	P8C0t4	P8C2t1	P8C2t4	P8C4t1	P8C4t4	P8C6t1	P8C6t4
Fiber diameter (nm)	404.2 ± 94.9	343.6 ± 60.4	349.5 ± 57	321.7 ± 48.8	348 ± 72.5	318.1 ± 48.2	337.5 ± 59.2	339.1 ± 56.2
Sample thickness (µm)	50 ± 1.9	51.4 ± 1.3	51.7 ± 3.1	50.9 ± 2.1	50.2 ± 1.7	49.4 ± 0.9	50.8 ± 2.3	51.1 ± 2
Bar-coated samples								
Sample thickness(µm)	51.8 ± 2.9	53.7 ± 4.1	54.5 ± 5.1	52.1 ± 2.6	48 ± 2	54 ± 4.7	51.3 ± 2.6	51.7 ± 2.7

Barrier Properties

Water Vapor Sorption



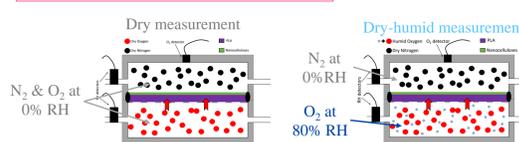
Chitosan (CS), PVA and CNC are hydrophilic polymers. Comparison between PLA and coating ratios shows the high water vapor sensitivity of coating, even with nanometric thicknesses.

The addition of CNC is able to reduce the total sample moisture content. The comparison between thickness and moisture content ratios proves the additivity between the layers (PLA, CS, PVA/CNC) when 4 wt.% of CNC is added to 8 wt.% PVA.

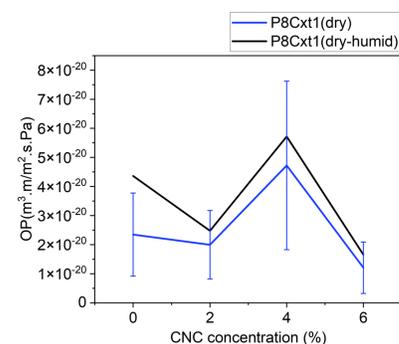
The addition of CNC is able to restore the moisture content obtained with PLA(CS) sample.

The moisture content of samples with PVA fibers is largely influenced by the PVA water sensitivity. The strong interactions between CNC and PVA reduce the number of free hydroxyl groups available for water molecules. Then, the addition of CNC drastically reduce PVA water sensibility.

Oxygen Permeability



Increasing the time deposition of electrospun fibers (from 1h to 4h), slightly increases the oxygen permeability. Optimal oxygen permeability is obtained with 2 wt.% of CNC.



The dry-humid measurements confirm the water vapor sorption results. The addition of CNC in PVA reduce PVA moisture sensitivity. Increasing the CNC concentration reduces the difference between OP in dry and dry-humid. In high relative humidity (80% RH), the water molecules hardly affect the oxygen barrier properties of PVA/CNC coated samples.

Comparison between electrospun and bar-coated samples highlights two behaviors:

- Without CNC, electrospun samples have better oxygen barrier properties.
- With CNC, bar-coated samples have improved oxygen barrier properties, compared to electrospun samples.

Conclusion

- Good PVA & PVA/CNC fiber alignment
- Absence of defect
- Micrometric layers
- CNC improved the water barrier properties of PVA fibers
- Excellent oxygen barrier properties in dry and humid environment (80% RH)
- Multilayer films with PLA, CS, PVA/CNC fibers and PVA layer are fitting food packaging requirements

The multilayer film oxygen permeabilities are outstanding, reaching highly barrier food packaging (EVOH-based food packaging (10⁻²¹ m³.m/m².s.Pa)⁵). The addition and increase in CNC concentration reduce the effect of water molecules on PVA Bar-coated samples highlight the effect of fiber orientation on oxygen barrier properties.

Perspectives

- Deeper investigation of CNC addition on PVA water sensitivity: DVS measurement with 2 & 6 wt.% of CNC
- Effect of fibers orientation on water sorption: DVS measurements of non-oriented samples
- Pursuit of the oxygen permeability investigations

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