PhD student: Ghislain Fotie

Supervisor at PackLab: Pr Luciano Piergiovanni **Supervisor at LGP2**: Pr Julien Bras

Project: **Coating and /or lamination of cellulose nanocrystals (CNCs) modified with chitosan and/or alginate to produce active packaging useful for prolonging the shelf-life of food.**

Based on the Gantt diagram proposed for the research at LGP2, the first three months contributed to the realization of the first phase of the work:

- Preparation and production of the cellulose nanocrystals from the cotton powder.
- Chemical modification of cellulose nanoparticles.
- Particles size- Z potential of modified and unmodified CNCs
- Contact angle assessment of uncoated and coated PLA with CNCs
- O_2 and WVTR permeability measurements of uncoated and CNCs coated PLA.

I started my work at LGP2 on 1st of May 2018. This report is the conclusion after the first 3 months (till the 30th of July 2018).

Materials and Methods

Preparation and production of cellulose nanocrystals (CNCs)

Two types of CNCs were used in my work: wood CNCs (OH content) were bought directly from the Canadian company called CelluForce whereas oxidized CNCs (COOH content) were produced in our lab and extracted from the cotton powder by using Ammonium Persulfate. However, only wood CNCs were actually used for the chemical modification.

The cotton powder was grinded and 10 g were weighed and put in a 1.5 mL beaker with 1L of distilled water where 228 g of ammonium persulfate were present. The solution was stirred mechanically for 16 hours at 75°C, and then centrifuged for 15 min at 10000 rpm and that for 4 times with the addition of deionized water in order to rinse the suspension. The yield of CNCs production (%) was evaluated from the weight of the freeze-dried products by comparing them with the mass of cellulosic raw materials treated. The thickness of the coating applied onto the film was assessed by a gravimetric method. Four samples (10 × 10 cm^2) were weighed (m_1, g), then the coating was removed by running hot water (~70 °C) and the resulting uncoated film was dried and weighed (m_2, g). The coating thickness (L, cm) was estimated by Equation (1): $L = \Delta m / (\rho \times 100)$,

Where $\rho = 1.58$ g cm^{-3} is assumed as the density of the CNCs and $\Delta m = m1 - m2$.

Chemical modifications of cellulose nanoparticles

- ✓ **Adsorption between CNCs and Glycerol monostearate (CNCs-GMS)**

3g of wood CNCs and 3g of GMS were added in ethanol at 3%wt and the latter solution was brought at pH 7 then stirred at room temperature for 3h. As the reaction takes place, GMS particles are adsorbed on the CNCs surface irreversibly. Afterwards, the residual part of GMS was washed out in ethanol at 30°Cx15 min and 10000rpm for 4 times and the purified GMS-CNCs were obtained.

- ✓ Sol-react with wood CNCs and citric+sorbic acid (CNCs-Cit-Sorb)

3g of wood CNCs were dispersed in 100mL of water (Sonication 2min, 50%, 5) in a 500mL round-bottom flask and the pH was adjusted to 4. After, the solution was heated and maintained at 150°C under hot oil bath then, 31g of sorbic acid and 53g of citric acid were added in the dispersed CNCs and placed in the distillation system for promoting the chemical absorption. The latter solution was stirred for 8 hours, and the water evaporated. At the end of the reaction, the product obtained was purified from unreacted acid by 5 times dispersion-centrifugation with a large excess of ethanol (10000 rpm, 30°C, 15').

CNCs Hydrodynamic diameter and Z potential-conductivity

- ✓ Hydrodynamic diameter of the dispersed CNCs was determined by dynamic light scattering (DLS) measurements (mod. Litesizer500, Anton Paar, Graz, Austria). The measurements were assessed at 25.0 ± 0.1 °C with a 35 mW laser diode light (λ = 658 nm) and collecting the scattered light at 15°and 90°. Before any measurements, the samples were diluted at 3 different concentrations with distilled water adjusted to pH 8 and maintained at 25 °C.
- ✓ Zeta potential (mV) and conductivity (mS cm^{-1}) of the CNCs in the diluted suspension at 3 different concentrations at pH 8 were performed by electrophoretic light scattering (ELS), using the PALS technology (mod. Litesizer 500, Anton Paar, Graz, Austria). Data were obtained through5 time-replication, at 25.0 ± 0.1 °C, by means of a 35 mW diode laser (λ = 658 nm) and at 15° detection angle.

Contact angle assessment of coated PLA with CNCs

Static contact angles of the coated film were determined after the conditioning of the CNCs coated PLA films at 30°C. The sessile drop method was used by precisely dropping a droplet of 4.0 ± 0.5 µL of water onto the film. The measurements were performed at room temperature (RH about 40%) on five different positions for each sample. The instrument used was an OCA 15 Plus angle goniometer (Data Physics Instruments GmbH, Filderstadt, Germany), equipped with a high-resolution CCD camera, a high-performance digitizing adapter (Data Physics Instruments GmbH, Filderstadt, Germany) and SCA20 software (Data Physics Instruments GmbH, Filderstadt, Germany) for contact angle measurements.

O_2 and WVTR permeability measurements

Both oxygen and water vapor permeabilities were performed by an isostatic permeabilimeter (mod. Multiperm, PERMTECH S.r.l., Pieve Fosciana, Italy) according to ASTM standard methods (D-3985 and F-1249 respectively). The oxygen and water permeation of coated and uncoated PLA films were measured at 25 °C and 50 & 80%UR.

Results and discussion

The table 1 shows the main characteristics of the modified and unmodified cellulose nanocrystals dispersion, the coated and uncoated polylactic acid (PLA).

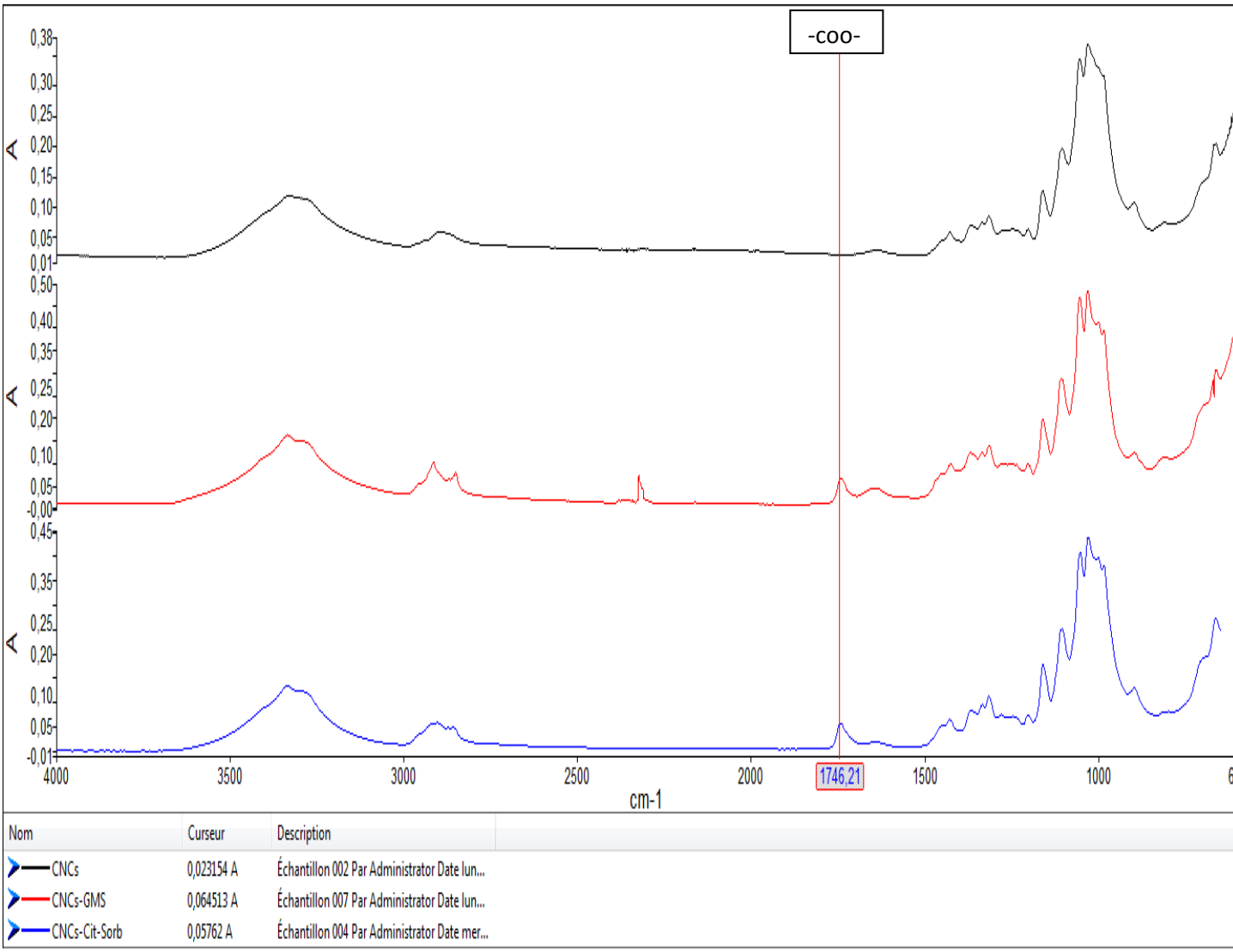
	Hydrodynamic diameter (µm)	Z-potential (mV)	Conductivity (mS cm^{-1})	PLA Thickness (µm)	Coating deposition (g/m^2)	Yield (%)	CNCs concentration solution (%)	Water contact angle (°)
Wood CNCs (unmodified)	0.28±0.01	-45±1.2	0.07±0.01					
CNCs-GMS (modified)	0.22±0.08	-38±1.1	0.24±0.03					
CNCs-Cit-Sorb (modified)	0.25±0.06	-25±1.1	0.14±0.03					
Cotton CNCs (unmodified)	0.30±0.2	-28±2	0.66±0.02			40		
PLA				25				74±2
PLA-CNCs-GMS				25	1		2.8	17±1.1
PLA-CNCs-Cit-Sorb				25	1		2.8	14±1.2
PLA-CNCS				25	1		2.8	8.8±1.1

Table 1: Main characteristics of modified and unmodified Cellulose Nanocrystals, coated and uncoated PLA.

From the table 1, we can observe that after the modification, the hydrodynamic diameter has not changed significantly but the z-potential is much more different for the grafted CNCs with sorbic and citric acids, which confirms the modification of electrical charges at the CNCs surface during the esterification.

FTIR spectra of unmodified and modified CNCs

The FTIR results are illustrated by the graph 1 and the proof of the chemical modification is easily identifiable with the presence of ester groups (-coo-) at the peak of wavelength 1746.21 cm^{-1}. FTIR spectra of CNCs clearly show the typical absorption band of ester groups for modified CNCs (CNCs-GMS and CNCs-Cit-Sorb), which is absent in the standard CNCs spectra. The peak recognizable in the inset of graph 1 is referable, according to Lam (Lam et al. 2013), to C=O stretching peaks of the ester group (1746.21 cm-1).



Graph 1: FTIR of CNCs, CNCs-GMS and CNCs-Cit-Sorb.

The table 2 below shows the oxygen and water permeabilities results performed on coated and CNCs coated PLA at 25°C in 2 different relative humidities (RH).

RH (%)	PO_2 ($cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$)				WVTR($g\ m^2\ d^{-1}$)			
	PLA	PLA-CNCs	PLA-CNCs-GMS	PLA-CNCs-Cit-Sorb	PLA	PLA-CNCs	PLA-CNCs-GMS	PLA-CNCs-Cit-Sorb
50	471.47±8.5	279.62±5.2	359.10±2.2	178.8±2.1	50.12±4.1	32.01±2	33.7±2.1	31.4±1.2
80	550±10.2	519.02±4.3	508.94±3.4	478.1±3.2	66±3	62.22±3.10	65.23±1.1	61.497±1.2

Table 2: Water and O2 permeabilities as a function of relative humidity of PLA and PLA coated with CNCs, CNCs-GMS and CNCs-Cit-Sorb.

Conclusion

The first part of my work at LGP2 was very promising and productive, because the first goal was to modify the cellulose nanocrystals surface for making them less hydrophilic. First, it was chosen to use a long hydrocarbon chain of glycerol mono stearate (GMS) and to promote its adsorption with the CNCs, and the FTIR revealed that, the adsorption took place with the presence of ester groups. Second, sorbic and citric acids were both used to be grafted onto the cellulose nanocrystals surface, promoting the esterification which is also easily observable (FTIR).
Altogether, the results obtained by evaluating the oxygen permeability confirmed that, the sensitivity of the CNCs to water can be alleviated almost twice with the grafting of sorbic and citric acids.

Future collaboration

My ongoing research will continue at LGP2 to proceed with the second phase of the project until November 2nd. I will be committed to embed the modified cellulose nanocrystals with chitosan, to make up a novel package and subsequently, I will end up with food shelf life assessment.