Influence of deposition technique on functionalization of poly (l-lactic acid) films with nano layers of chitosan and nanocellulose crystals

INTERNATIONAL IBERIAN NANOTECHNOLOGY LABORATORY

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Introduction

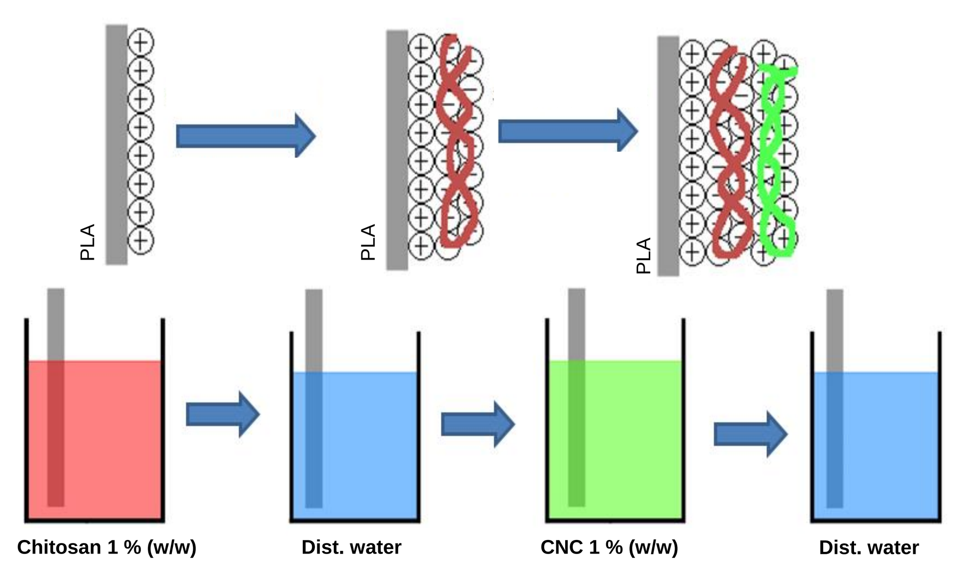
Poly (lactic acid) (PLA) is a non-toxic, compostable bio-based material derived from starch and/or sugar and has high mechanical strength and plasticity. It is accepted as GRAS (Generally Recognized as Safe) by the Food and Drug Administration (FDA) and suitable for use in food and beverage packaging. One of the strategies to incorporate active compounds in these materials is the deposition of uniform layers with active compounds (e.g. antimicrobials, vitamins). The deposition of uniform layers is a crucial step in the final properties of the product. In this work, two different coating techniques: dip-coating and ultrasonic spray coating were analysed to evaluate their effect on the barrier and functional properties of PLA films. Chitosan (Ch), a naturally occurring cationic polysaccharide, with antimicrobial properties and cellulose nanocrystals (CNC) with the ability to enhance the barrier properties were used to functionalise PLA films.

PLA films were modified by oxygen, to improve the adhesion of hydrophilic molecules to PLA. A multilayer system was developed with six active layers (Ch-CNC-Ch-CNC-Ch-CNC). For dip-coating, PLA films were immersed alternatively in each polyelectrolyte solution (1 % (w/w) chitosan and 1 % (w/w) CNC) during 15 min and dried with nitrogen air between layers. For spray-coating, it was used a ultrasonic spray and alternate layers were build on PLA films.

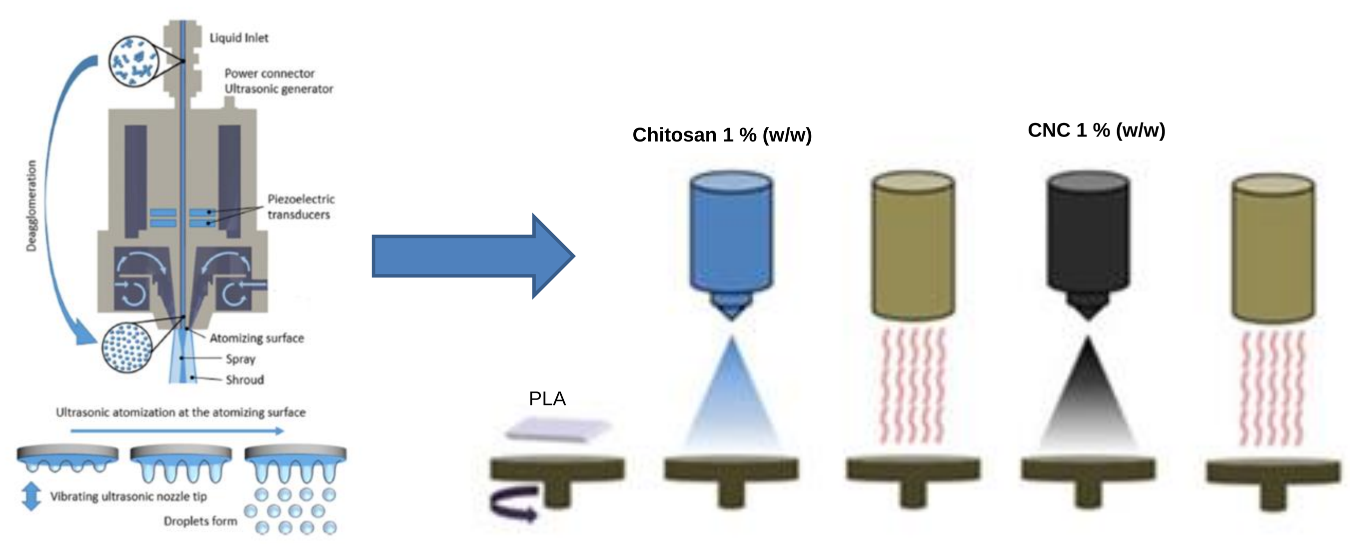
Materials and Methods

- **Functionalization of poly (l-lactic acid) films with bio-based nanolayers**

Dip-coating :



Spray-coating :



Characterization techniques :

- ✓ Transmission Electron Microscopy (TEM)
- ✓ Contact angle
- ✓ Confocal laser microscopy
- ✓ Water vapour permeability

Results and Discussion

Chitosan and cellulose nanocrystals (CNC) were used to functionalize PLA films. Figure 1 shows the morphology of CNC after aqueous dispersion.

Contact angles technique was used to confirm the formation of alternated layer deposition for dip-coating and for spray-coating (Figure 2)

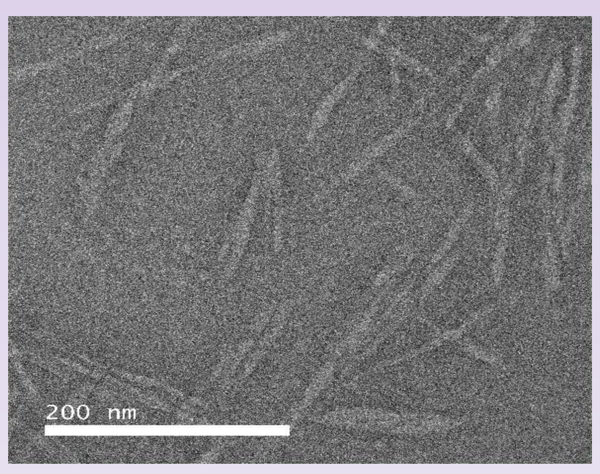


Figure 1. TEM images of CNC 1 % (w/w) in aqueous solution

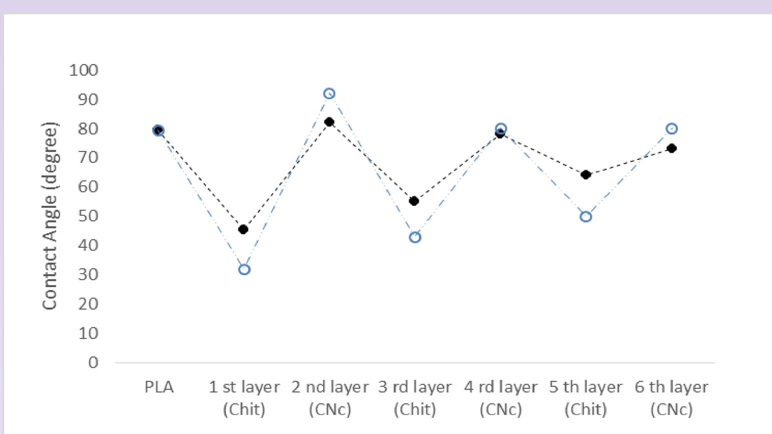


Figure 2. Contact angle of each layer during deposition of bio-polymers for **a)** dip-coating (●) and **b)** spray coating (○).

Confocal microscopy was used to analyse the dispersion of each biopolymer during the layer deposition for both techniques. Chitosan was stained with Rhodamine B and CNC was stained with Calcofluor (Figure 3).

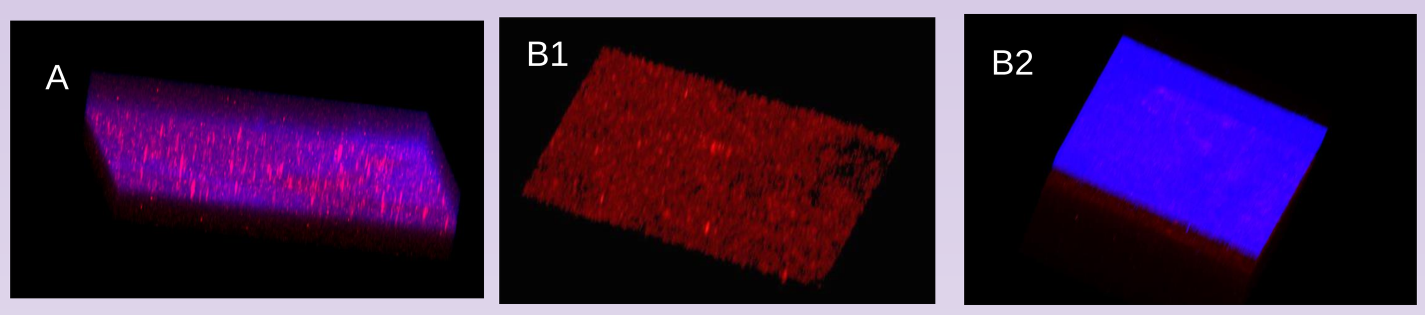


Figure 3. Confocal images of A) Chit and CNC deposition by dip-coating; B) Chit deposition by spray coating and C) Chit and CNC deposition by spray coating.

Table 1. Water vapour permeability of functionalized PLA by different techniques

	Dip-coating	Spray-coating
	WVP (g/Pa.s.m2)	WVP (g/Pa.s.m2)
PLA	$1.26 \times 10^{-11} \pm 8.23 \times 10^{-13}$	
1 st Layer (Chit)	$1.09 \times 10^{-11} \pm 1.32 \times 10^{-13}$	$7.13 \times 10^{-12} \pm 3.54 \times 10^{-14}$
2 nd Layer (CNC)	$1.97 \times 10^{-12} \pm 1.01 \times 10^{-14}$	$9.51 \times 10^{-13} \pm 3.54 \times 10^{-14}$
3 rd Layer (Chit)	$1.90 \times 10^{-12} \pm 0.95 \times 10^{-14}$	$6.70 \times 10^{-13} \pm 1.12 \times 10^{-14}$
4 th Layer (CNC)	$1.22 \times 10^{-12} \pm 1.58 \times 10^{-15}$	$4.20 \times 10^{-13} \pm 1.07 \times 10^{-15}$
5 th Layer (Chit)	$1.02 \times 10^{-12} \pm 1.36 \times 10^{-14}$	$3.95 \times 10^{-14} \pm 0.98 \times 10^{-15}$
6 th Layer (CNC)	$1.85 \times 10^{-13} \pm 5.68 \times 10^{-15}$	$3.05 \times 10^{-14} \pm 1.27 \times 10^{-15}$

Conclusion

Spray coating is a promising route toward a reliable, flexible, and cost efficient fabrication method to create uniform multilayer systems. PLA functionalized by spray coating demonstrated a lower water vapour permeability compared to functionalized PLA by dip-coating.

Acknowledgments

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