MATERIALS REINFORCED WITH NANOCELLULOSE: PROMISING NANOCOMPOSITES FOR FOOD PACKAGING?

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The development of new packaging materials offering new functionalities and lower environmental impact, is now an urgent need. On one hand, the shelf life extension of packaged products can be an answer to the exponential increase of worldwide demand for food. On the other hand, the increase in the price of crude oil, together with the uncertainty related to its durability, has imposed the necessity to manufacture new structures to replace oil-derived polymers in the future. Finally, consumers' awareness towards environmental issues increasingly pushes industries to look with renewed interest to "green" solutions. Thus, in the last years' numerous polymers have been exploited to develop biodegradable food packaging materials.

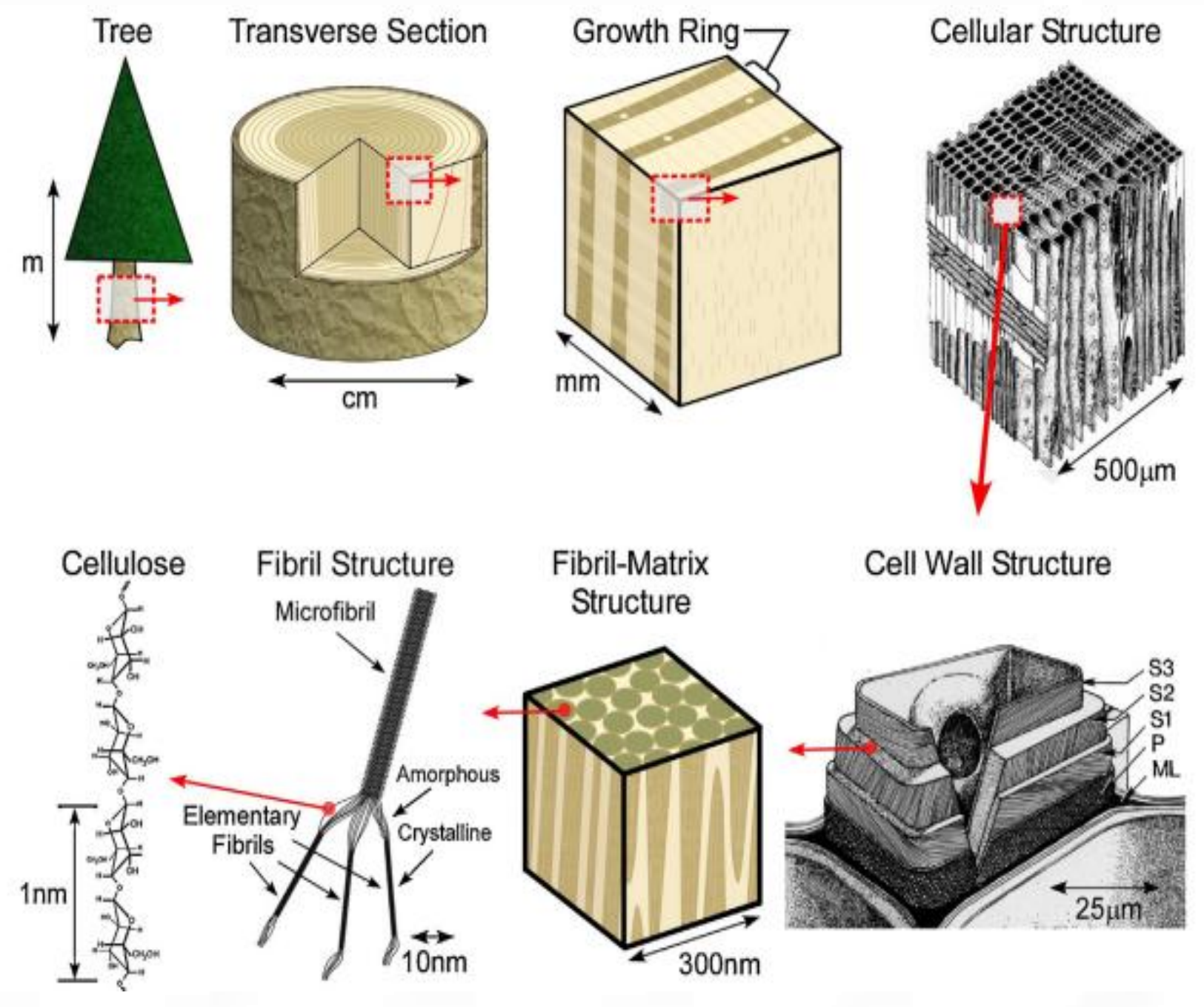

Fig 1. Structure of wood from the tree to the CNC

The usage of biopolymers has been limited due to the poor mechanical and barrier properties. These properties can be enhanced by adding reinforcing nano-sized compounds to form nanocomposites.

Cellulose is probably the most used and well-known renewable and sustainable raw material (Fig 1). The mechanical properties, reinforcing capabilities, abundance, low density and biodegradability of the cellulose nanoparticles make them ideal candidates for the processing of polymer nanocomposites (Fig 2).

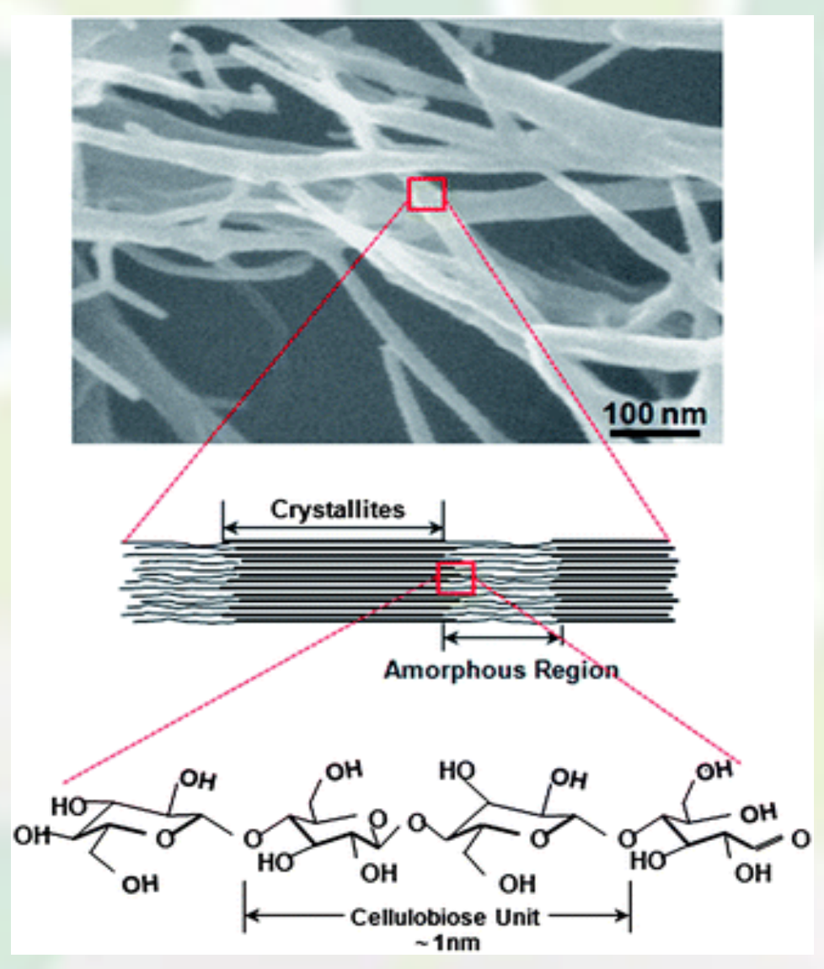

Fig 2. Structure of Nanocellulose/ Cellulose Nanocrystals (CNC

The present review focuses on the combination of nanocellulose with different polymers. Table 1 shows the methods of processing, level of incorporation and the enhanced material properties of polymers reinforced with nanocellulose.

Table 1. Examples of polymers reinforced with cellulose nanoparticles.

Polymer	Nanomaterial origin, synthesis and modifications	Level of incorporation	Method of processing	Characterization techniques	Enhanced material properties	Reference
Wheat gluten (WG)	CNC extracted from bagasse pulp by acid hydrolysis using sulphuric acid.	CNC (2.5, 5, 7.5, 10 and 125 wt.%) based on WG content; TiO_2 nanoparticles (0.2, 0.4, 0.6, 0.8 and 1%) based on WG content.	Casting / Evaporation	SEM; DSC; Water sensitivity (contact angle); WVU; WVP	A significant enhancement of 56% and 53% in breaking length and burst index. Presented excellent antimicrobial activities.	Nahla *et al.,* 2015
Gelatin (protein matrix)	CNC were isolated from a commercial CNF using different hydrolysis conditions.	1, 3, 5 and 10 wt. % of CNF and CNC	Solvent casting	FTIR; TGA; DSC; WVP; OTR; TS; fractured surface morphologies.	Bionanocomposites showed lower tensile strength. Nanocellulose addition to gelatine matrix has not a significant impact on WVTR values. OTR values of the gelatine decrease after the addition of nanocelluloses. The addition of nanocelluloses to gelatine matrix improved the thermal stability of nanocomposites.	Mondragon *et al.*, 2015
CMC/ST	CNC were extracted at the nanometric scale from sugarcane bagasse (SCB) via sulphuric acid hydrolysis.	0.5-5.0 wt.% of CNC	Solvent casting	AFM; Rheological measurements of FFS (film-forming solution); FTIR; UV–Vis spectroscopy; TS; WVP.	Bio-nanocomposite films remain transparent. The WVP was significantly reduced and the elastic modulus and tensile strength were increased gradually, which are the main properties required for packaging applications.	Miri *et al.,* 2015
Agar	CNC was separated from paper-mulberry (*Broussonetia Kzinoki Siebold*) best pulp by sulfurc acid hydrolysis method.	1, 3, 5 and 10 wt.% of CNC based on agar weight	The agar-based nanocomposite films with nanocellulose were prepared by the solution casting method	Colour and transparency; TS; WVP; CA; MC; WS; Thermal stability; Statistical analysis.	Properties of agar film such as mechanical and water vapour barrier properties were improved significantly ($p < 0.05$) by blending with the CNC. The agar/CNC bionanocomposite film is completely biodegradable and biocompatible.	Rhim, 2014
PVA	The CNC were prepared by sulphuric acid hydrolysis at 45 ˚C for 60 min, using 15 mL of H_2SO_4 (9.17 M) for each gram of fiber CNC_{60}.	3, 6 and 9 wt. % of CNC.	PVA/CNC_{60} nanocomposite films and neat PVA film (control sample), were prepared by solution casting method at 35 ˚C for 24 h in an air-circulating oven.	UTS; WVP; Tr; UV-spectrophotometer; TGA; TS.	There was a reduction a reduction of water permeability. When compared to neat PVA film, the ultimate tensile strength of the nanocomposites improved significantly. The nanocomposites produced were quite transparent, exhibiting optical transmittance.	Silvério *et al.,* 2013
Alginate films	CNC produced from the hydrolysis of MCC using sulphuric acid.	1, 3, 5 and 10 wt.% of CNC	A bio-based nanocomposite was developed by incorporation of CNC using solution casting method.	X-ray diffraction; SEM; Film thickness; MC; WS; Surface hydrophobicity of films; WVP; TS; YM; E%; Op; Statistical analyses	Acid hydrolysis increased the crystallinity of the cellulose up to 89%. WS and WVP of the nanocomposites decreased by about 40% and 17%, respectively. The crystalline structure of the CNC increased surface hydrophobicity of the alginate film by about 98%. The tensile strength value of the composite films increased with CNC content (0 to 5%). Film transparency decreased with CNC incorporation.	Abdollahi *et al.,* 2013
CNC/CH	A sulphuric acid hydrolysis reaction was performed with eucalyptus wood pulp to obtained CNC. CNC surface was functionalized using the MAC reagent.	Two different functionalized CNC were prepared. An appropriate amount of MA-CNC (0, 1.0, 5.0, 10, 20, 30, 40, 50 or 60%, w/w) was added.	CNCs surface was functionalized using the MAC reagent, creating reactive end groups on the nanocrystals which reacted with the amino groups of the CH biopolymer, leading to a bionanocomposite with covalent linkage between the CNC and the CH.	TEM; FTIR; TGA; XRD measurements; DS; Mechanical properties;	FTIR spectroscopy showed that the CH was covalently bonded onto the surface of the functionalized CNC. The CH-c-CNCs nanocomposites demonstrated a significant improvement in mechanical performance (increase in tensile strength of up to 150%) compared to the neat chitosan. The results for water uptake measurements showed a remarkable decrease in hydrophilicity of CH, being this effect more pronounced for the CH-c-CNC nanocomposite compared to the system CH/CNCs.	Mesquita *et al.,* 2012
Starch film (derived from the potato starch)	CNC produced from the hydrolysis of MCC using sulphuric acid.	1 wt.% of CNC 1 wt.% of GA	Films were formed by solution-casting	AFM; CA; WVTR; FTIR; tensile strength and E%.	There is a significant improvement in the mechanical and barrier properties of starch-nanocellulose films prepared using GA as dispersing agent. Being completely biopolymer based, starch–nanocellulose film will revolutionize the fields of food packaging, agricultural field mulching and healthcare sectors.	Vigneshwaran *et al.,* 2011
Sodium caseinate	CNW was prepared from sol-gel method.	1, 2 and 3 wt. % of cellulose (dry weight).	Solution casting	FTIR; Opacity; WVP; CA; MC; TS; Dynamic-mechanical analysis; SEM; Porosity measurements: Statistical analysis.	Composite films are less transparent and have a more hydrophilic surface than sodium casein ones. However, the global moisture uptake is almost not affect by concentration. Addition of nanocellulose to the neat sodium caseinate films produced an initial increase in the barrier properties to water vapour. The tensile modulus and strength of composites films increased significantly with increasing cellulose concentration, while the values of elongation decreased.	Pereda *et al.,* 2011

CA – Static Contact Angle Measurements; DSC – Differential Scanning Colorimetry; E% - Percentage Elongation at Break; EB – Elongation Break; FESEM – Field Emission Scanning Electron Microscope; FTIR – Fourier Transformed Infrared Spectroscopy; MC – Moisture Content; Op – Opacity; OTR – Oxygen Transmission Rate; PF – puncture force; SEM – Scanning Electron Microscopy; TGA – Thermogravimetric Analysis; TM – Thickness Measurements; Tr – Light Transmission; TS – Thermal Stabilities; WVP - Water Vapor Permeability; WVU – Water Vapor Uptake; YM – Young´s Modulus

Apart from polylactic acid, a vast number of other polymers have been reinforced with cellulose nanoparticles, including wheat gluten, starch, gelatine, agar, polyvinyl alcohol (PVA), and chitosan. The incorporation of nanocelluloses enabled to improve mechanical (e.g. increase in tensile modulus and strength) and barrier properties (e.g. Barrier to water vapour) as well as improved the thermal stability of nanocomposites (Rhim, 2014; Mondragon *et al.*, 2015). The application of these materials to food industry has great potential. However legislation shall be revised in order to authorize the use of these materials while ensuring their safety.

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