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Chapter No 4

Surface chemistry of nanocellulose and its composites

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Abstract

Cellulose is recurrently defined as the most abundant biopolymer on planet Earth, displaying an overall estimated production rate of more than 0.2 billion tons in a single day. Cellulose prompt availability allied to it its mechanical properties made it virtually indissociable from the majority of anthropogenic commodities. Nevertheless, continuous progress demands superior features form daily common materials, being most of them adequately suited by low-cost petrochemical polymers. Fortunately, the higher Environmental awareness of the global population as well as

the remarkable properties of biosynthesized polymers, has driven an extensive research on a plethora of biopolymers, including cellulose. Cellulose most notable features are associated to its crystal domains, which are impressively underscored with the development of cellulose nanotechnology. Moreover, at nanoscale the cellulose surface richness in hydroxyl groups is comprehensively more available, considerably t broadening he effectiveness and potential of their interaction per se, but also by enhancing the efficacy of surface modification and functionalization. Nanocellulose surface modification was implemented almost contemporary to its discovery and characterization, and its objectives ranged between improving yield of nanocellulose production, lower its production costs, and to provide nanocellulose a completely distinct surface properties by changing its polarity, generating different functional groups, decorating it with adsorbed or tightly bound nanoparticles, and to provide additional chemical compatibility with distinct compounds to generate advanced nanocomposites. The plethora of successfully reported modifications and functionalizations underscore notable properties of both modified nanocellulose and its composites. This Chapter intends to highlight these remarkable features, hopefully widening the scope of novel applications of these impressive bio-based polymers.

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4.1 Introduction

Cellulose was firstly described in 1838 by the French chemist Anselme Payen (Klemm et al. 2005). Cellulose is indubitably the most abundant biopolysaccharide on planet Earth, and is exclusively composed of D-glucose units (elemental chemical composition: $C_6H_{10}O_5$) covalently bounded by acetal bounds formed between the C1 atom carbon and the equatorial OH group of C4 (commonly named as β-1,4 glycosidic links) which define cellobiose (elemental chemical composition: $C_{12}H_{22}O_{11}$) (Figure 4.1.)(Saxena and Brown JR 2005). This homopolymer is only considered cellulose once the glucan chains reach at least 30 kDa, in other words, when it is composed of roughly 90 repeating units of cellobiose. Glucan chain aggregation forms an insoluble polymer due to its polymerization degree superior to 6. Cellulose encompasses amorphous domains and highly ordered regions. The ratio between amorphous and crystal domains has considerable variations, particularly between organisms, species, synthesis conditions and circumstantial damage events. However, the exact factors that determine the occurrence and abundance of the cellulose amorphous regions is still widely unknown. More importantly, the assembly process of the cellulose protofibrils into cellulose itself is yet to be unraveled (Brown Jr 2004). Cellulose displays three crystallization forms, or allomorphs: cellulose I, cellulose II and cellulose III. Cellulose I is the most common allomorph present in nature, comprising a metastable parallel cellulose polysaccharide chains, and encompasses two sub-allomorphs: I_α and I_β. The I_α structure is compose by single chain triclinic cell unit. On the other hand, I_β comprises a two-chain monoclinic cell unit, being synthesized in its pure form only by tunicates. I_β has more thermodynamic stability than I_α (Klemm et al. 2005; Saxena and Brown JR 2005). The ratio between I_α and I_β in cellulose depends on the organism species, namely I_α is dominant in algae and BNC, whereas I_β is the principal sub-allomorph in higher

plants. Cellulose II is constituted by anti-parallel polysaccharide chains, being even more stable due to the existence of one extra hydrogen bound per glucose residue (Brown Jr 2004). Cellulose II synthesis in nature is uncommon, generally only being synthesized by some algae and bacteria (Saxena and Brown JR 2005). Cellulose III allomorph, similarly to cellulose I, displays parallel chains. The addition liquid ammonia to cellulose I and cellulose II will generate cellulose III_I and III_{II}, respectively (Wada et al. 2004). Despite the differences of hydrogen bounds, crystal structure or chain orientation, all allomorphs of cellulose comprise a rich surface of hydroxyl functional groups.

Anthropogenic applications containing cellulose dates the most recondite of prehistorical times, nevertheless, during the last five decades, cellulose has been subjected to an interesting novel approach: nano size cellulose, or nanocellulose. Nano size materials (ranging from 1 to 100 nm in one dimension) encompass an undeniable set of advantages and enhanced properties, since their shape and volume depicts a superior importance in their properties than just their absolute size (Paul and Robeson 2008). Nanocellulose is commonly divided into five types: bacterial nanocellulose (BNC), cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), electrospuned nanocellulose (ESNC) and wet-spun nanocellulose (WSNC). In all cases, their nano size considerably enhances the surface area, thus the availability of its surface hydroxyl groups is far superior. Despite its remarkable properties and wide range of applications, nanocellulose still possesses several limitations, which can be overcome by the selective combination with other materials. A composite is generated by the combination of different materials to achieve an end product with enhanced properties. Composites are not novel, being the first known composites the papyrus paper (4000 B.C.) and mud bricks reinforced using straw (1300 B.C.). Interestingly, both composites contain cellulose in their formulation (Herakovich 2012). The first reports of

nanocellulose used as a reinforcing material of a polymeric matrix, depict the substantial improvement of the nanocomposite mechanical properties (up to two-fold). To achieve similar results with regular macroscopic size cellulose as a reinforcing agent, considerably higher quantities of cellulose had to be used, which would compromise the overall performance and viability of the composite (Favier et al. 1995). For a more straight forward comparison, Table 4.1 denotes relevant properties of BNC, CNC, CNF, fibrous cellulose (cotton and wood) and para-aramid, better known through its commercial designation: Kevlar. It is clearly observable that the properties of the different types of nanocellulose are much closer to the aramid than to macroscopic cellulose. These notable features sparked a race for nanocomposite development encompassing nanocellulose form a plethora of different origins that encompass: plant, tunicates, algae, fungi and bacteria. Each source generates nanocellulose with distinct properties and provides different levels of surface modification and functionalization (Shak, Pang, and Mah 2018).

4.2 Nanocellulose surface and nanocellulose particularities

Cellulose and nanocellulose surface is ubiquitously densely populated with hydroxyl groups, independently of its origin or allomorph type, as depicted in cellulose monomer cellobiose (Figure 4.1). Nevertheless, in nanocellulose the availability of the hydroxyl groups is extensively enhanced by the dramatic increase of the surface area in comparison to macroscopic cellulose. The availability of hydroxyl groups associated to carbon 1, 2 and 6 of each glucose monomer of cellobiose (named as O(2)H, O(3)H and (O(6)H), greatly depends on the extent of hydrogen bonding within the nanocellulose structure (Rowland and Howley 1988). Therefore, cellulose allomorph and sub-allomorph types and abundance represent an important factor to consider not

only in terms of hydroxyl group availability (were cellulose II has less hydroxyls available), but also for modification reactions complexity (cellulose I_α is the most easily modifiable) (Ling et al. 2017). Cellulose I_α possess a dislocation of cellulose sheets within the (110) lattice plane, thus in cellulose I_α displaces +c/4 crystallographic point in each succeeding hydrogen bounded cellulose sheet. Whereas I_β sub-allomorph exhibits a displacement in the (200) lattice plane with a hydrogen bounding sheets formed in alternating + c/4 and - c/4 crystallographic points (Poletto, Pistor, and Zattera 2013). Therefore, a brief description of BNC, CNC and CNF is pivotal to discern the ideal nanocellulose to be used. BNC can be considered ideal for modifications, since it does not require a delignification pretreatment and is mainly composed of sub-allomorph cellulose I_α, ranging from 70 to 60 % whether is synthesized in static or agitated culture conditions, respectively. BNC complete detailed metabolomics is not yet fully unraveled due to its plausible complexity, nevertheless several biosynthetic mechanisms were already soundly described (Valla et al. 2009; Jacek et al. 2019). Briefly, BNC producing bacteria use intracellular enzymatic machinery to produce the cellulose precursors uridine diphosphateglucose, which are subsequently assembled into cellulose in terminal enzymatic, complexes usually located at outer envelope of the bacteria. Each BNC nanofiber produced presents different thickness depending not only on the bacteria species but also on the culture environmental conditions which include: temperature, culture medium formulation, dissolved oxygen concentration, light, and if the culture is performed in static or shaking conditions (Jacek et al. 2019). Therefore, the width of BNC may vary between 10 to 100 nm and achieve a length of 50 nm to 100 μm (Nagashima, Tsuji, and Kondo 2016). The buildup of multiple fibrils eventually forms a macroscopic three dimensional nanomesh containing pores ranging between 20 to 300 nm. BNC is often regarded as a hydrogel due to its high water holding capacity (99 %) (Torres, Commeaux, and Troncoso

2012). To remove bacterial cells, medium culture components and other debris, BNC usually undergoes a mercerization treatment with sodium hydroxide which reorganizes the packing of some BNC fibrils into allomorph cellulose type II, and reduces the endotoxin level to approximately 1 EU L^{-1}. This value is comfortably below the threshold level defined by Food and Drug Administration for materials that will contact with cerebrospinal fluid (60 EU L^{-1}) (Gonçalves et al. 2015). Therefore, BNC possess staggering differences from plant cellulose in terms of purity, crystallinity and obviously size. BNC is comprised of 100 % cellulose, without a single molecule of hemicellulose, lignin or pectin in its formulation, and its crystallinity ranges between 75 to 90 %. Due to its high crystallinity and nanometric architecture BNC displays remarkable mechanical properties. All these features quickly caught the attention of numerous Research Centers and manufacturers and several applications were developed in a wide range of different areas (Table 4.2.). The field of knowledge which encompasses the most interesting solutions is the medical field, since BNC allows an effective gas and nutrient diffusion, has no sensitization reports, and notable biocompatibility. In fact, BNC structure semblances that of collagen, which may be a strong adjuvant for its biocompatibility (Torres, Commeaux, and Troncoso 2012). Nevertheless, BNC has also been recently used as a wastewater treatment filtration membrane, exhibiting the complete removal of soybean oil from a solution when BNC was incorporated in a polyvinyl chloride filtration system (Galdino et al. 2020). On the other hand, CNC can be roughly described as the collection and purification of crystalline cellulose sections as nanocellulose needles, or whiskers (due to similar dimensional size ratio) encompassing a width of 3 nm to 25 nm and a length between 70 nm to 150 nm (George and Sabapathi 2015). CNC appear as rigid needles, usually with very little agglomeration due to its synthesis process. CNC are obtained through the chemical hydrolysis of pure or delignified

cellulose and classical CNC production uses strong acids (particularly, sulfuric acid or hydrochloric acid) to readily hydrolyze the amorphous sections of cellulose and leave solely the crystalline regions intact due to their higher resistance to acid digestion (Habibi, Lucia, and Rojas 2010). Sulfuric acid digestion for periods superior to 30 minutes impedes the clustering of CNC by providing a negative surface charge to the CNC, otherwise the abundant presence of available hydroxyl groups, due its high surface area, would lead to their prompt aggregation (Dufresne 2013). Nevertheless, the use of strong acids inevitably results in health safety and wastewater treatment issues, particularly at industrial scale. Therefore, additional CNC production processes are now well established, namely the use of enzymes, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation, ionic liquids and subcritical water (Novo et al. 2016). The reported CNC properties include a Young's modulus of approximately 130 GPa and a low degree of polymerization due to their short size. CNC is known by its high crystallinity index, however Tan and co-workers reported an impressive 96 % crystallinity index when digested microcrystalline cellulose with an ionic liquid (3-methylimidazolium hydrogen sulfate). In addition, CNC solutions display liquid crystal properties, which when assembled in a paper through vacuum filtration exhibited a transmittance of visible light up to 90 % (George and Sabapathi 2015). Finally, to date, all studies focused on assessing the cytotoxicity of CNC shown negligible values and no genotoxicity (Ventura et al. 2020). In opposition to CNC that are synthesized through a chemical treatment, CNF are obtained through using mechanical process (with or without the combination of a chemical or enzymatic process). After cellulose delignification and bleaching there is vast plethora of process to produce CNF, which include: supermasscolloider, ball milling, blending, cryocrushing, extrusion, grinding, homogenization, microfluidization, steam explosion and ultrasonication (Nagano et al. 2020). CNF produced

commonly exhibit width between 20 to 60 nm and a length of 500 to over than 1 μm. The larger length of CNF in comparison to CNC, makes CNF to appear as an entangled mesh of nanofibres. All the referred CNF producing methods consume relevant quantities of energy (more than 200 W per each gram of CNF), and some require the expenditure of considerable quantities of additional products, namely liquid nitrogen for cryocrushing (Ventura et al. 2020). An additional major limitation of CNF production is the solid content yield which leads to important limitations by reducing the feasibility of some processes, in addition to requiring larger storage areas and implying greater transportation costs. Only the twin-screw extruder is capable of producing CNF with a high of solid content (20 %), whereas the remaining processes display a problematic low CNF solid content of less than 5 %. (Rol et al. 2019; Trigui et al. 2020). Several strategies have been applied to reduce the energy requirements, that can be resumed as distinct pretreatments with a common goal, that is to improve the availability of the crystalline groups. These pretreatments include: alkaline, enzymatic and chemical pretreatments. Each has particular limitation that must be pondered. Alkaline pretreatments usually generate hazardous wastewaters, enzymatic treatments require long periods of time and the most successful chemical pretreatment is mediated by TEMPO, which implies considerable purchase costs. However, CNF exhibits higher plasticity than CNC, it also has a higher Young´s modulus of approximately 140 GPa, a tensile strength of nearly 1700 MPa, exhibits enhanced rheological performance and good optical properties (Kandhola et al. 2020). Interestingly, CNF display a highly viscous behavior, even with low solid content (between 1 and 2 %), making it a very effective edible viscosifying agent (without calories) for the food industry (Ventura et al. 2020; Heggset et al. 2020). Nevertheless, despite these impressive values per se, when used as reinforcing material in nanocomposites its performance may drop to less than 0.05 % and 4 % of its Young's modulus

and tensile strength, respectively (Takagi et al. 2016). Lack of nanofiber orientation may be a major parameter influencing these key mechanical properties. This is an important issue, that has been recently approached during de synthesis of ESNC (Kalantari et al. 2020). ESNC and WSNC and their composites are not covered within this chapter. Despite their promising properties, the relevant CNC and CNF production costs currently drive their manufacture solely to high end applications (Teixeira et al. 2020). In addition, the optimization of their properties is still in its infancy. As an example the Young's modulus of WSNC is only approximately 25 GPa (Kim et al. 2019). Nevertheless, the authors would like to recommend a recent review on the subject (Niinivaara and Cranston 2020).

4.2 Nanocellulose surface modification and nanocellulose composites

Independently of each type of nanocellulose, the ubiquitous chemical structure of their surface compiles a series of transversal surface modifications. These modifications may be directed to the hydroxyl groups or to break the β-D-anhydroglucopyranose (AUG) rings. Reported nanocellulose modifications include: chemical oxidation (Jorge Padrão et al. 2020), plasma treatment (Bhanthumnavin et al. 2016), acetylation (Gonçalves et al. 2016), carboxymethylation (Gonçalves et al. 2015), phosphorylation (Basta and El-Saied 2009), cationisation, ozonation, and sulfoethylation (Eyley and Thielemans 2014; Rol et al. 2019) (Figure 4.2). Acid hydrolysis may also be ascribed as nanocellulose modification, due to the generation of several impurities (namely: xylobiose, 3,4,5-trimethoxyphenol, 1,6-anhydroglucose and vanillic acid) during sulfuric acid treatment for CNC production, leading to the presence of sulfate esters which considerably hinder the reproducibility of surface modifications (Eyley and Thielemans 2014). Chemical oxidation is usually undertaken to obtain aldehyde and carboxylic groups on cellulose

surface. Periodate oxidation opens the AUG ring forming an aldehyde in C-2 and C-3. These vicinal aldehydes are prompt to generate, among others, carbinolamines through nucleophilic attack of ε-NH_2 present in lysine of proteins. Therefore, this oxidation strategy represents a straightforward production of nanocellulose functionalized with proteins (Jorge Padrão et al. 2020). After periodate oxidation, chlorite oxidation may be used to further oxidize the aldehydes formed, enhancing their stability. The introduction of sulphite groups into nanocellulose surface is possible through the reaction of aldehydes produced during periodate oxidation and metabisulfite or taurine, through sulfonation (Sirviö et al. 2014). Phosphorylation of nanocellulose surface was also successfully reported using diammonium phosphate. Sulfonation and phosphorylation, are two examples of esterification of nanocellulose and represent strategies to negatively charge the surface of nanocellulose (Rol et al. 2019; Eyley and Thielemans 2014). In particular, phosphorylation is applied to provide fire retardant properties (Basta and El-Saied 2009). In opposition, cationization provides a positive charge to nanocellulose surface, conferring it, among others, antimicrobial properties. However, cationization still requires highly toxic reactants and its process is are highly complex, thus several optimizations are still warranted. Ozonation may represent a less toxic procedure to generate aldehydes into nanocellulose and is easily scalable. Plasma treatment also generates ozone which, at least partially, is the responsible for nanoellulose oxidation. Ozone directly oxidizes nanocellulose surface or through the action of its radicals, and possesses two major limitations, it is difficult to precisely control its oxidation degree and usually results in an unsuitable loss of the degree of polymerization. TEMPO mediated oxidation introduces a carboxylic group at C6 conferring a negative charge to the nanocellulose surface, represents one of the most common nanocellulose treatment. This modification has been target of several optimizations to prevent the initial

considerable loss of polymerization degree and to use cheaper and more environmental friendly compounds. Nevertheless, the attempts to scale up this oxidation to industrial scale is still unforeseeable. On the other hand, carboxymethylation was firstly applied in the beginning of the twentieth century, although it requires several complex processes and multiple hazardous chemicals, it is a reliable method to introduce a carboxyl group into the nanocellulose surface, and it was successfully implemented at pilot scale (Rol et al. 2019).

All the referred modifications generate anions or cations throughout the nanocellulose surface promoting inter-plane repulsive forces, loosening nanocellulose hydrogen bonds and Van der Waals interactions, improving the nanocellulose swelling and further enhancing nanocellulose surface area. However, these charge generated forces are subjugated to ambient variations, namely to pH and medium ionic strength. This may limit the application or further treatments of the modified nanocellulose. Sulfoethylation of nanocellulose depicted an enhanced buffering capability to this important factors due to the low pKa values of the sulfonate group. Moreover, sulfoethylation exhibits a good scale up potential (Rol et al. 2019; Eyley and Thielemans 2014).

The referred nanocellulose surface modifications represent the doorway to a plethora of further modifications able to provide an impressive number of novel capabilities to nanocellulose. Surface modified nanocellulose may be functionalized through the adsorption of active molecules, polymer grafting and molecules grafting, and novel nanocomposite development. BNC, CNC and CNF display several composite applications as observable in Table 4.3, 4.4 and 4.5 respectively.

BNC composites cover a wide range of applications, nevertheless, its production costs until the beginning of the century promoted a focused development of biomedical applications, where the productions costs could be easily covered by the application justifiable higher prices.

Nevertheless, recently BNC production costs have been considerably lowered by successfully using low cost formulations comprising ethanol, corn steep liquor, molasses and ammonium sulfate and still maintain a high yield (approximately 6.5 g L^{-1}), and by using supplemented banana peel medium (Rodrigues et al. 2019; Sijabat et al. 2019, 2020). In addition, the wastewater generated during the production of BNC, the remaining culture medium after fermentation and the washing wastewaters, depicted an interesting biogas production potential, which can further mitigate production costs (da Silva et al. 2020). The BNC lower production costs provided sustainable development of textile and filtration applications, which possess less strict requirements than biomedical devices. BNC exhibited "waterproof" without hampering breathability when saturated with a common fabric hydrophobizer, and was successful used as a matrix of a nanocomposite able to mimic leather (Fernandes, Gama, et al. 2019; Fernandes, Souto, et al. 2019). To the authors knowledge BNC use as a filtration device started roughly at 20 years ago (Tiongson et al. 2002; Espiritu, Navarro, and Del Rosario 2004). Actelayated pulverized BNC was used as membrane o remove copper ions through polyelectrolyte-enhanced ultrafiltration, and BNC-graphene nanocomposite membrane was able to selectively permeate inorganic ions and (Fang et al. 2016; Espiritu, Navarro, and Del Rosario 2004) Finally, BNC has recently been used to synthesize Voronoi-nanonets when welded to electrospuned nanonets of polyacrylonitrile, displaying a rejection efficiency of nearly of 100 % titanium oxide microparticles of 0.3 μm (Tang et al. 2019). These ultrathin membranes possessed high porosity, exhibited promising antifouling properties, and reusability, all highly relevant features for effective and sustainable water filtration process. As for CNC, it is quite clear that CNC are commonly used as a reinforcing material of construction, packaging and wearable devices, displaying a clear shift from the biomedical applications to a common and wide spread

commodities application. Nevertheless, the main limitation of CNC is its brittleness, that still remains to be surpassed. CNF clearly displays an important role in food industry as a viscosifying agent or a food package reinforcement, nevertheless additional emerging applications are focused on low cost effective bioremediation.

4.6 Conclusion

Cellulose is ubiquitous and a key material of the circular economy, in a World that urgently struggles to reduce its dependence on petrochemical based commodities. Nanocellulose, independently from its origin, modification or production process will certainly play an important role in this transition. The existing main nanocellulose limitations, which can be summarized by: CNC - low yield and chemical hazardous production, CNF – high production costs and BNC – inadequate production time for its industrial demand, must be progressively mitigated. Despite CNC and CNF possess an additional advantage over BNC, which corresponds to the already established industrial infrastructures completely adapted to process their main sources, nevertheless the biotechnological potential of BNC should not be underestimated.

The estimates for the market size previous to the COVID-19 Pandemic clearly depicted the overwhelming expansion of nanocellulose: estimated to increase its production over than more than 35 million metric tons per year and reach a value of more than half a billion euros by 2023. Naturally, this value requires a revision on its estimate, however, it may not represent a downturn. General population Environmental awareness is constantly increasing, and the use of sustainable products not only for everyday commodities but also for bioremediation and pollution control, are evermore commendable. These facts allied to current overwhelming need for highly efficient filtration materials for protective personal equipment, air purification units

and wastewater treatment without further compromising the Environment, can be a strong drive to further widespread the massive application of nanocellulose per se and in composite formulation. Denoting the particularly development of nanocomposites with Voronoi-nanonets design using BNC, which exhibit a high water permeability flux and can be designed to achieve an impressive small particle rejection.

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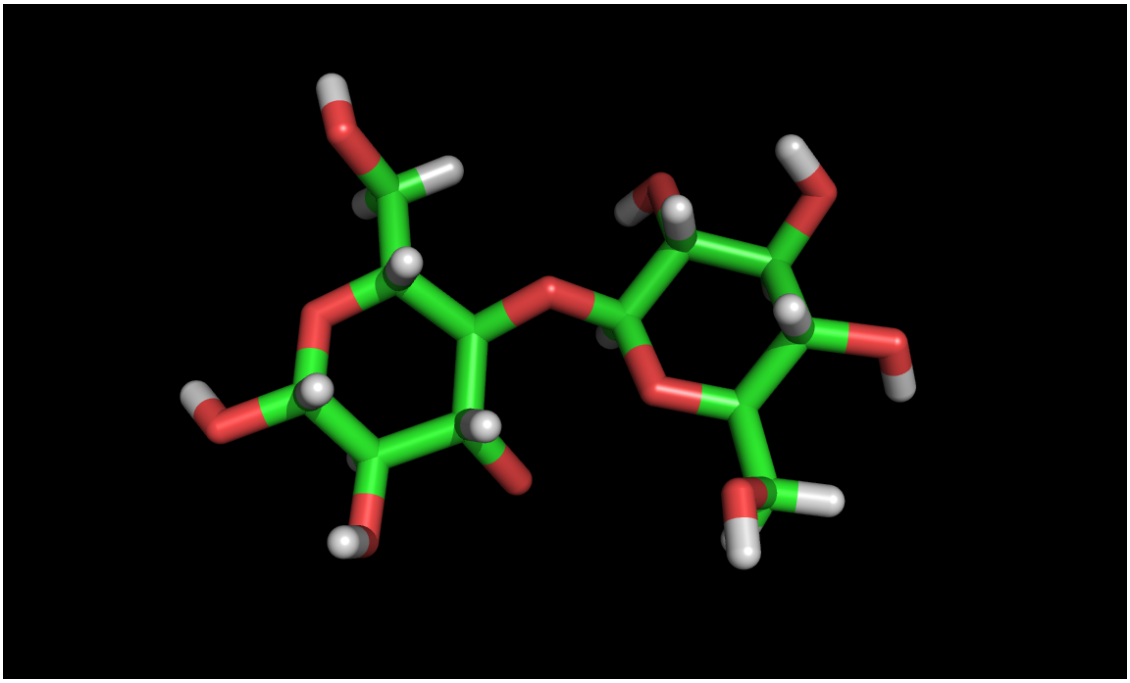

Figure 4.1. Cellobiose molecular structural formula. Atom color scheme: carbon – green, oxygen – red and hydrogen – white. Image obtained using Pymol PyMOL™ software (DeLano Scientific LLC 2006) to highlight cellobiose present in the crystallographic image of cellobiose phosphorylase from *Cellulomonas uda* (Protein Data Bank file: 3S4A).

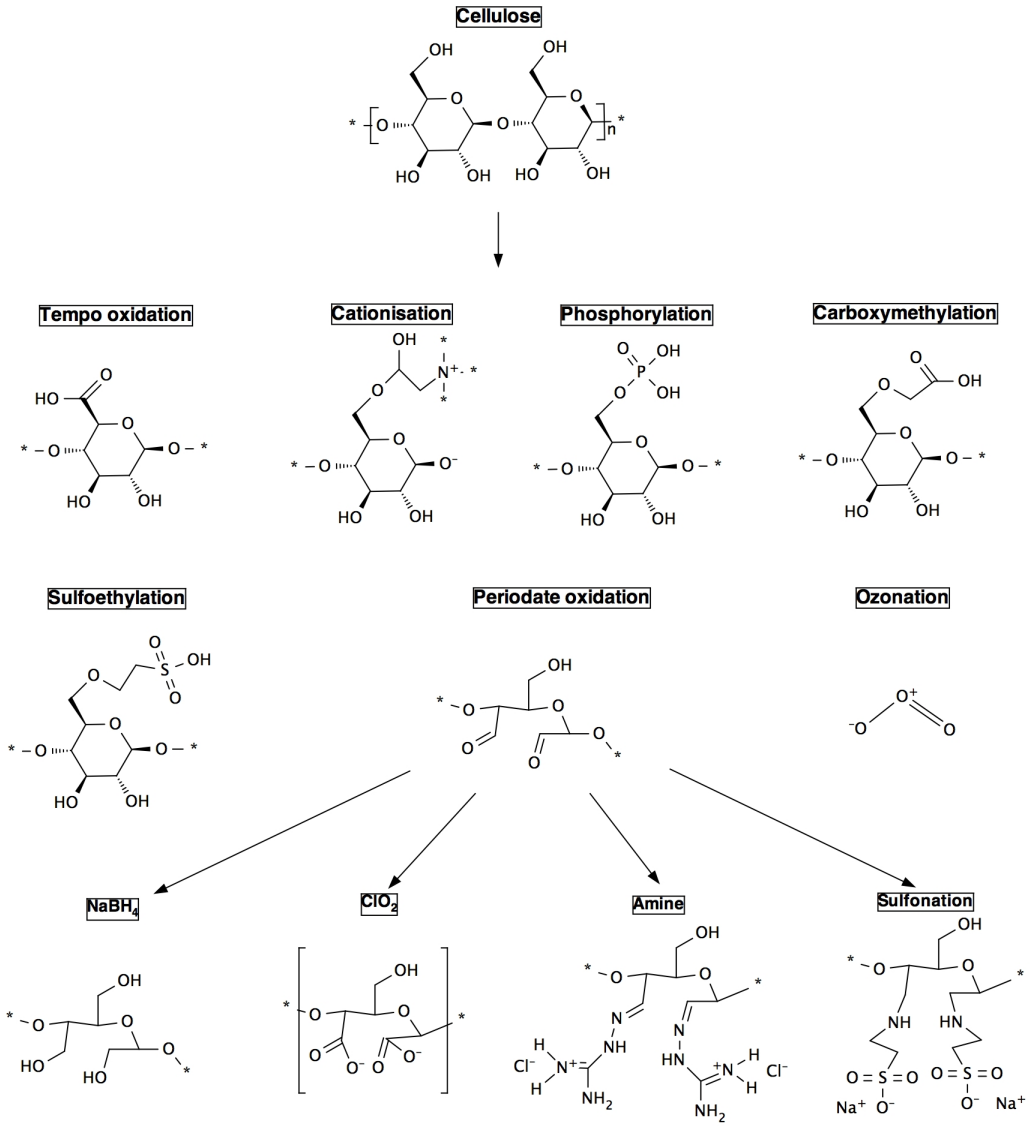

Figure 4.2. Nanocellulose surface modifications.

Table 4.1. Nanocellulose, cellulose and para-aramid properties.

	Young's modulus (GPa)	**Density (g cm^{-3})**	**Crystallinity (%)**	**Degree of polymerization**	**Reference**
BNC	114	0.86	60 - 90	2000 - 8000	(Hsieh et al. 2008)(J. Padrão et al. 2016)(Tabuchi 2007)(Klemm et al. 2005)
CNC	130	Variable	71 – 96	250 – 350	(Tan, Abd Hamid, and Lai 2015)(Xia Li et al. 2018)(Dufresne 2013)
CNF	100	Variable	77 – 86	750	(Dufresne 2013)(Correa et al. 2020)
Para-aramid (Kevlar 49)	131	1.44	75	84	(Kopeliovich 2020)(Kong, Xu, and Yu 2019)(Timm et al. 1984)(Young 1999)
Cellulose fiber (cotton)	4	1.54	73	9000 – 15000	(Kompella and

					Lambros 2002)(Barnhardt 2020)
Cellulose fiber (wood)	2	0.25	30	1190 - 1720	(Kompella and Lambros 2002)(Sweet and Winandy 1999)

Table 4.1. BNC per se applications.

Application Field	**Commodity**	**Reference**
Food	*Nata de coco*	(Yamanaka et al. 1989)
Home appliances	High fidelity acoustic diaphragm	(Uryu and Kurihara 1993)
Medical	Artificial skin, artificial blood vessel	(Schumann et al. 2009)
Wastewater treatment	Filtration membrane	(Galdino et al. 2020)

Table 4.2. Nanocellulose composites

Application	Nanocellulose	Matrix	Filler	Nanocellulose surface modification	Objective	Reference
Electronic	*Ex situ*	BNC	Multiwalled carbon nanotubes and polyaniline	None	Flexible super capacitor	(S. Li et al. 2014)
Electronic device	*Ex situ*	BNC	Nano-graphite	None	Conductive and enhanced thermal properties	(Erbas Kiziltas et al. 2016)
Electronic device	*Ex situ*	BNC	Paladium	None	Electrode	(Evans et al. 2003)
Electronic device	*Ex situ*	BNC	Multi-walled carbon nanotubes and laccase	Cyanoethylation	Electrode capable of degrading recalcitrant pollutants and generate electricity	(Xin Li et al. 2020)
Filtration membrane	*Ex situ*	BNC	Graphene	None	Selectively permeation	(Fang et al. 2016)
Filtration membrane	*Ex situ*	BNC	Polyvinyl alcohol and biochar with nanosilver	None	Potential filtration membrane with bacteriostatic properties	(L. Zhang et al. 2020)
Filtration membrane	*In situ*	BNC	Palladium decorated mesoporous	None	Dye removal	(Gholami Derami et

			polydopamine			al. 2020)
Food film	*Ex situ*	BNC	Lactoferrin	None	Antibacterial activity	(J. Padrão et al. 2016)
Medical device	*In situ* /*ex situ*	BNC	Silver nanoparticles	None	Wound dressing with antibacterial activity	(Eardley, Watts, and Clasper 2012)
Medical device	*Ex situ*	BNC	Catalase	None	Wound dressing Antibacterial activity	(Sampaio et al. 2016)
Medical device	*Ex situ*	BNC	Benzalkoniumchloride	None	Antibacterial activity	(Wei, Yang, and Hong 2011)
Medical device	*Ex situ*	BNC	Chitosan and carboxymethyl cellulose	Carboxymethylation	Corneal regeneration	(Gonçalves et al. 2015)
Medical device	*Ex situ*	BNC	Urinary bladder matrix	Acetylation	Corenal regenaration	(Gonçalves et al. 2016)
Medical device	*Ex situ*	BNC	Hydroxyapatite	None	Bone regenetration	(Tazi et al. 2012)
Pharmaceutical	*Ex situ*	BNC	Ibuprofen	None	Controlled drug release	(Jiji, Thenmozhi, and Kadirvelu 2018)

Paper	*Ex situ*	Cotton line pulp	BNC pulp	None	High quality paper	(Yamanaka et al. 1989)
Paper	*Ex situ*	BNC	Europium	None	Resilient florescent paper	(M. Zhang et al. 2019)
Paper	*In situ*	BNC	Phosphate	None	Fire retardant	(Basta and El-Saied 2009)
Textile	*Ex situ*	BNC	Acrylated epoxidized soybean oil	None	Leather replacement	(Fernandes, Souto, et al. 2019)
Textile	*Ex situ*	BNC	Polydimethylsiloxane and perfluorocarbon	None	Hydrophobization	(Fernandes, Gama, et al. 2019)

Table 4.3. Recent CNC nanocomposites

Application	Matrix	Filler	Nanocellulose surface modification	Objective	Reference
Biodegradable polymer	Poly(vinyl alcohol)	CNC	None	Petrochemical-based plastic replacement	(Sonker et al. 2016)
Packaging and construction	Poly (butylene succinate)	CNC	Acetylation	Enhanced thermal insulation	(Yin et al. 2020)
Packing material	CNC	Nanochitin and Heptadecafluoro-1,1,2,2-tetrahydrodecyl dimethylchlorosilane modified nano SiO2	TEMPO oxidation	Superhydrophobic and transparent	(Xu et al. 2020)
Packaging Material	Poly(vinyl alcohol)	CNC	Citric acid	Food active film	(W. Yang et al. 2020)
Bioremediation	CNC	Polyvinylamine	Periodate oxidation	Pesticide adsoption	(J. Yang et al. 2020)
Agronomy	Starch, poly(acrylic acid (AA)-co-acrylamide and polyvinyl alcohol	CNC	None	Superabsorbent hydrogel for agronomical applications	(Olad, Doustdar, and Gharekhani 2020)
Pharmaceutical	CNC	Glycerol and	None	Drug capsule	(Y. Zhang

		polyethylene glycol			et al. 2017)
Electronic device	Pig skin	CNC and carbon nanotubes	TEMPO oxidation	Flexible sensor and supercapacitor electrode	(Y. Wu et al. 2020)
Pharmaceutical	Alginate	CNC	None	Drug carrier	(J. Zhao et al. 2020)
Textile and electronic devices	Poly(vinyl alcohol)	CNC	None	Wearable devices	(X. Wu et al. 2020)

Table 4.4. Recent CNC nanocomposites

Application	Matrix	Filler	CNF production equipment	Nanocellulose surface modification	Objective	Reference
Food	Beeswax-in-water	CNF and carboxymethyl chitosan	High pressure homogenizer	None	Edible food coating	(Xie et al. 2020)
Food	Mayonnaise	CNF	Microfluidizer	None	Viscosifying agent	(Heggset et al. 2020)
Packaging	Poly(vinyl alcohol)	CNF and graphene oxide	High-pressure homogenizer	TEMPO oxidation	Ultra violet shield	(Jia et al. 2020)
Bioremediation	CNF	L-methionine	Steam explosion	Methionine grafting	Mercury adsorption	(Bisla et al. 2020)
Active packaging	CNF	Nisin	Disk refiner nano-grinder	None	Antibacterial and low oxygen and vapor premaeability	(Y. Yang et al. 2020)
Security paper	CNF	Cadium/selenium/sulfur quantum dots	Ultrasonicator	None	1D ink application and 2D film preparation	(Y. Zhao and Li 2020)
Smart packaging	CNF	Chitosan	High-pressure homogenizer	None	Enhanced barrier and antibacterial properties	(M. Wu et al. 2020)

Medical device	CNF	Carbon spheres containing silver nanoparticles	Not available (commercially purchased)	None	Antibacterial paper	(Jiang et al. 2020)