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Cellulose Based Materials: in-Depth Property Survey And Assessment

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Abstract: During the past decade, holistic efforts by academia, industries, and regulatory bodies have resulted in a paradigm shift in the area of cellulose nanomaterials for materials applications. In an effort to reduce the dependence on petroleum-based packaging materials and coatings, groups are employing advanced nano understanding to manufacture materials that can potentially replace these materials. In effect, environmental concerns and resource availability will become the main factors driving the market demand for these products. This review focuses on the properties of cellulose-based nanomaterials and the possible use of these materials in niche applications. The review covers both partially and fully biodegradable inventions covered in the past 10 years (2006-2016) in the literature. Also, where data is available, environmental footprint and cost analysis of these products are presented.

Keywords: Barrier property, cellulose nanomaterials, life cycle assessment, mechanical properties, morphological properties

I. Introduction

The emergence of the term “nano” in 21st century has transcended boundaries never noticed by any major area of research. According to Moon et al. (2011) [1], in 2009, the worldwide market for products incorporating nanotechnology was about USD 254 billion. It is postulated that this number will double each 3 years until 2020, when the value can be around USD 3 trillion. This increased demand for nanoproducts arises from the intrinsic superior properties of these materials when compared to those currently dominating the market. As can be appreciated, when the size of particles decrease to the nanoscale, important property changes are observed. One of the most important changes is the increased number of atoms of a given particle that are exposed to the surface when the size decreases. For example, a particle of size 10 nm has approximately 15 % of its atom on the surface, but a particle of size 3 nm has more than 50 % of its atom on the surface. These differences force changes in the specific surface area and the total surface energy of the particle. As a result, smaller particles have a tendency to agglomerate. As will be discussed later in this comprehensive review, this becomes a problem with cellulose nanoparticles because of the presence of abundant hydroxyl groups [2].

Cellulose is the most abundant renewable polymer resource available today. Dating back 200 years, cellulose has been used in a range of applications, inclusive of textile, composites, and polymers. In fact, the first generation of cellulosic materials relied on the hierarchical structural arrangement of the fibres. Over time with increased research attention there were developments with respect to the functionality and flexibility of using these materials. One pattern that has remained constant has been the continuous use of these materials for their mechanical properties, be it from the meso or nanoscale[3]. In the following sections, more details will be given about the chemistry and structure of cellulose, the biosynthetic pathway of cellulose, and common sources used today for materials application.

1.1Cellulose

Cellulose is the most abundant and renewable biomass material in nature [4].The annual production of this biopolymer is estimated to be between 10^{10} and 10^{11} tonne [5]. Cellulose is distributed across flora and fauna, inclusive of several fungi, bacteria, invertebrates, marine animals (e.g. tunicate), and algae. Cellulose is known as a tough, water insoluble, and fibrous-like material that plays a vital role in the everyday functional properties of these species. Specially, in trees, cellulose is essential for maintaining the integrity of plant cell walls.

1.2Structure and morphology

The basic chemical structure of cellulose consists of repetitiveβ-1,4-linked anhydro-D-glucose units. Cellulose is distinct from starch because of its unique corkscrewed 180 ° with respect to its neighbours. Hence, cellobiose units are linked and stacked to form a high molecular weight homopolymer. In addition, each cellulosic chain is characterized with directional chemical asymmetry with respect to the terminal of its molecular axis. One end is the reducing functionality or the hemiacetal unit and the other the non-reducing end or the pendant hydroxyl groups. These properties are presented in Fig 1.

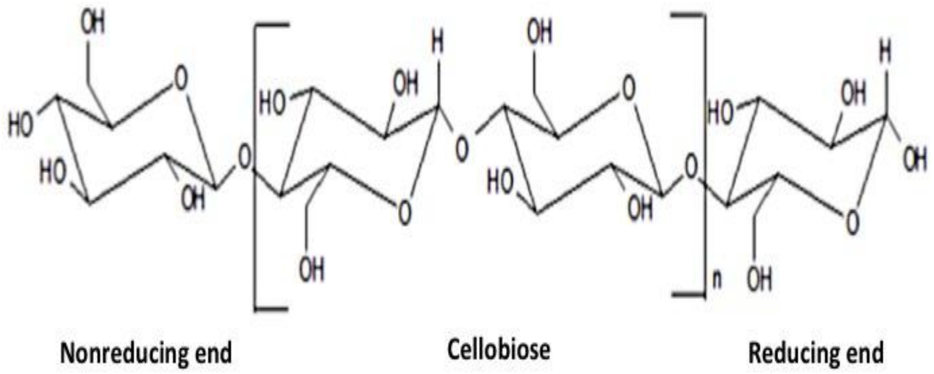

Figure 1. Basic repetitive chemical structure of cellulose

The β-D-glucopyranose rings adopt a $^4C_1$ chair conformation and all the hydroxyl groups are positioned in the equatorial plane, while hydrogen atoms are in the axial plane. The intramolecular hydrogen-bonding network stabilizes the macrostructure of this abundant resource [6]. Cellulose microfibril is the basic structural component of cellulose formed during biosynthesis. Chains of β-D-glucopyranose align to form a fibril, which is a long thread-like bundle of molecules stabilized by hydrogen bonding [5], [7]. Within these cellulose fibrils there are regions with highly organized layers (crystalline cellulose) and random disordered (amorphous cellulose) patterns. It is these crystalline regions that are isolated by many researchers to produce high strength cellulose nanomaterials. Cellulose is arranged in different small crystals referred to as polymorphs. There are four main polymorphs of crystalline cellulose (I, II, III, IV). Cellulose in its native form is referred to as cellulose I or crystalline cellulose. On the other hand, regenerated cellulose or cellulose II refers to cellulose obtained under conditions of either mercerization (alkali treatment) or regeneration by solubilisation and crystallization [8], [9]. Recent research findings have proven that cellulose I and cellulose II have chains that are aligned parallel and anti-parallel, respectively [10].Cellulose III is prepared by treatment of cellulose I with liquid ammonia or organic amines followed by removal of the chemicals. Once produced, cellulose IV$_I$ can be made from cellulose III via heat treatment in glycerol at 260 °C. On the other hand, cellulose IV$_{II}$ can be produced by thermal treatment of either cellulose II or III. A summary of the different polymorphs is given in Fig 2. It should be noted; many of the polymorphs once formed can be reversibly changed to the original state by either chemical or thermal treatments [11], [12], [13].

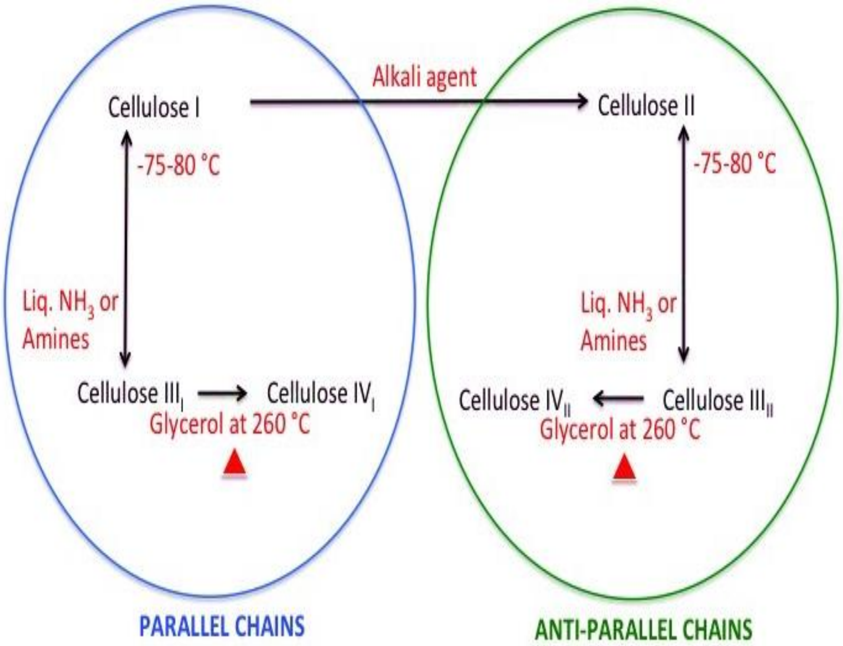

Figure 2. Polymorphs of cellulose and conditions forproduction

1.3Cellulose Micro fibril Biosynthesis

For many decades, workers in this field were tirelessly working on deciphering the intricacies behind cellulose synthesis. Eventually, they were able to identify and characterize a cellulose synthase, the enzyme responsible for the polymerization of β-1,4-glucan. With this effort, scientists were able to decipher how these chains were self-assembled to form the microfibrils that represent the characteristic form of cellulose found in nature today. The packing of cellulose networks depends on the type of organism and the biosynthetic conditions. According to Habibi et al. (2010) [5] the combined actions of biopolymerization, spinning, and crystallization occur in a rosette shaped plasma membrane terminal complex (TC) that acts as biological spinnerets (presented in Fig 3). Although, the full mechanism is not fully documented and understood, it is believed that cellulose chains must be elongated at the same rate via polymerization reactions by cellulose synthase complexes. In the end, the structure of cellulosic microfibrils implies that their synthesis and assembly involves the coordinated and holistic efforts of 36 active sites[15], [16]. The aggregation of individual chains occurs predominantly by van der Waals and hydrogen bonding (intra and inter bonds). In cases where the TCs are not protruding, they generate limitless lengths of microfibril without limited number of amorphous sections [15]. A number of researchers have proposed models for the microfibril hierarchy that predicts the supramolecular structure of cellulose, inclusive of the crystalline structure, dimensions of these crystalline regions, arrangement of the amorphous sections, and dimensions of fibrillar formation. Most of these methods differ primarily in the description of the organization and the distribution of the random less ordered regions.

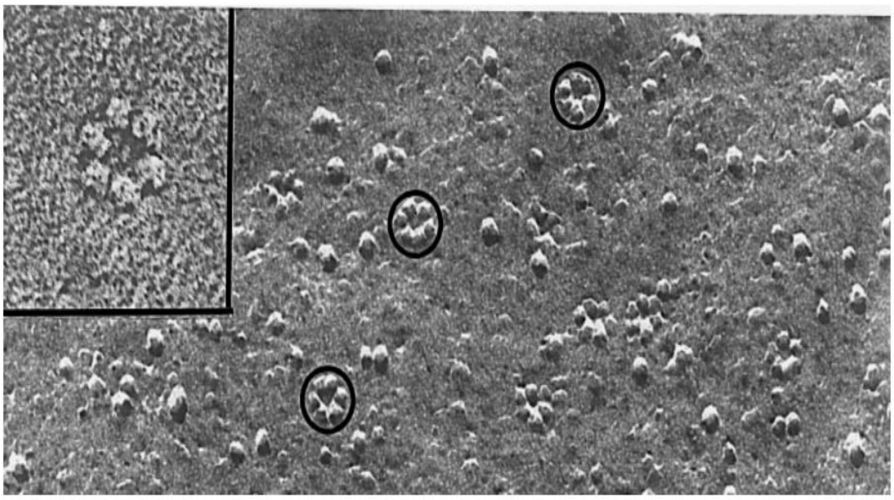

Figure 3. Freeze dried fracture replicas of rosettes associate with cellulose microfibril biogenesis. These rosettes are circled in black in the plasma membrane of differentiating tracheary element of Zinnia elegans(Main micrograph 222,000; inset 504,545). Reprinted with permission from Annual Reviews, Delmer, (1990) [16].

1.4Cellulose sources

Cellulose is native to a broad range of flora and fauna. A brief overview of some of the more studied and interesting sources of cellulose is presented below.

1.4.1Wood

Wood is abundant, renewable, and widely distributed across earth. Wood is the precursor to the pulping industry, where softwood or hardwood is obtained and exposed to varying reaction parameters to produce materials such as kraft pulp, bleached pulp, chemi-thermal mechanical pulp, or thermomechanical pulp. These products have been the cornerstone of some of the biggest industries in Canada, China, Nordic countries, and U.S.A.

There are two main types of plants that yield wood. Firstly, there are the softwood (gymnosperm) varieties, which are commonly referred to as the conifers. Softwoods account for 80 % of the world’s production of timber, with centres of production concentrated around the Nordic region, North America, and China. On the other hand, there are the hardwoods (angiosperm), usually confined to the temperate and tropical forests. Depending on the wood type, the final properties of the materials obtained will vary because of the chemical composition.

1.4.2Plant

A wide assortment of plant material has been studied for cellulose nano based products. These include, but not limited to, natural fibres (e.g. flax, hemp, ramie, sisal, cotton, bamboo etc.), agricultural waste (corn husks, barley shells, sugar-cane bagasse, sugar beat pulp, banana rachis etc.) and tubers (potato) [9]. These materials were focused on the most for the production nanomaterials because of the high cellulose content, the ease of isolation, and the low cost associated with sourcing them. But, the eventual problems with isolating the cellulose from the other components have forced a change in research direction. That is, research teams prefer to work with high cellulosic sources with minor other components, such as kraft pulp etc.

1.4.3Bacterial

In the past decade, bacterial cellulosic material has been a research area receiving a lot of attention. Shah et al. (2013) [17] reviewed the current trends and approaches for the development of bacterial cellulose (BC), prospects, classes, and possible applications. BCs are attractive because of biological method of production and can readily find applications in areas of biomaterial for artificial skin, artificial blood vessels, scaffolds, and wound dressing. According to Ul-Islam et al. (2012) [18], the properties of BCs are superior to those of plant-based cellulose and impart better properties when used in applications. BCs have been synthesized via a number of routes, broadly classified into static and agitated cultures. In static cultures, BCs are produced at the air-water interface as an assembly of reticulated crystalline ribbons that form into a pellicle and increase in thickness with increasing cultivation time [19]. On the other hand, submerged fermentation through aerated or agitated cultivation of BCs results in small pellets or granules and is seen as the best route for commercial production of BCs. One of the major challenges for the production of BCs is the sourcing of inexpensive raw material sources. Some sources that have been investigated include waste from the beer industry [19], molasses [20], and agricultural wastes [21]. In the end, BCs are seen as an integral production route for cellulosic material especially for health applications.

1.4.4Algae

Several species of algae (green, grey, red, and yellow-green) have been discovered to produce cellulose microfibrils within their cell wall. Kim et al. (1996) [22] reported the synthesis of cellulose within the cell wall of Micrasterias. In fact, they reported the formation of criss-crossed bands of cellulose rather than neatly stacked parallel bands. On the other hand, Revol (1982) [23] reported that the cellulose crystallites in Valonia ventricosa were almost square with an average side of 18 nm. That work was based on images taken using an electron microscope and was one of the earliest reports detailing the structure of algae cellulose.

Algae cellulosic materials have not taken off on a large scale at the moment because of logistics with variability in growth and poor yields. Nevertheless, if realized, they can find applications in the medical and food based (such as edible packaging films) areas.

II. ISOLATION OF CELLULOSIC MICRO AND NANO-BASED MATERIALS

In the literature, a number of methods have been used to isolate the cellulose micro/nano materials from cellulosic feedstocks. Essential to all methods is the purification and homogenization pre-treatment of the source materials. This facilitates better consistency in subsequent treatments. Pre-treatment will vary depending on the material source. For example, wood and plants involve complete removal of matrix materials (hemicellulose and lignin) and the isolation of individual complete fibres. On the other hand, bacterial cellulose pre-treatment focuses on culturing methods for growth and subsequent washing to remove the bacteria and media. An overview of the different pre-treatment methods can be found for different materials, such as tunicate [24], bacteria [35], algae [26], and wood [27].

The second step for obtaining the nanomaterials requires the separation of the purified cellulose materials into its crystalline components. The three fundamental methods for isolating these particles are acid hydrolysis [28], [29], mechanical treatment [30], [31], and enzymatic hydrolysis [32]. In the past, these methods were used separately, but of late, they are used in conjunction with each other to obtain the required morphological and particle distribution. This review will briefly outline what has been done recently with these methods and focus on other possible methods.

In this section, a few of the more popular methods and a couple recent major breakthroughs will be reported.

2.1Acid hydrolysis

The most popular method for the extraction of cellulose nanocrystals (CNCs) from cellulosic sources is based on acid hydrolysis. The main idea is to remove the disordered or randomly arranged amorphous cellulose, whereas the crystalline regions that are more resistant to the acid media, remains intact. The morphological distribution of CNCs from different sources is given in Fig 4.

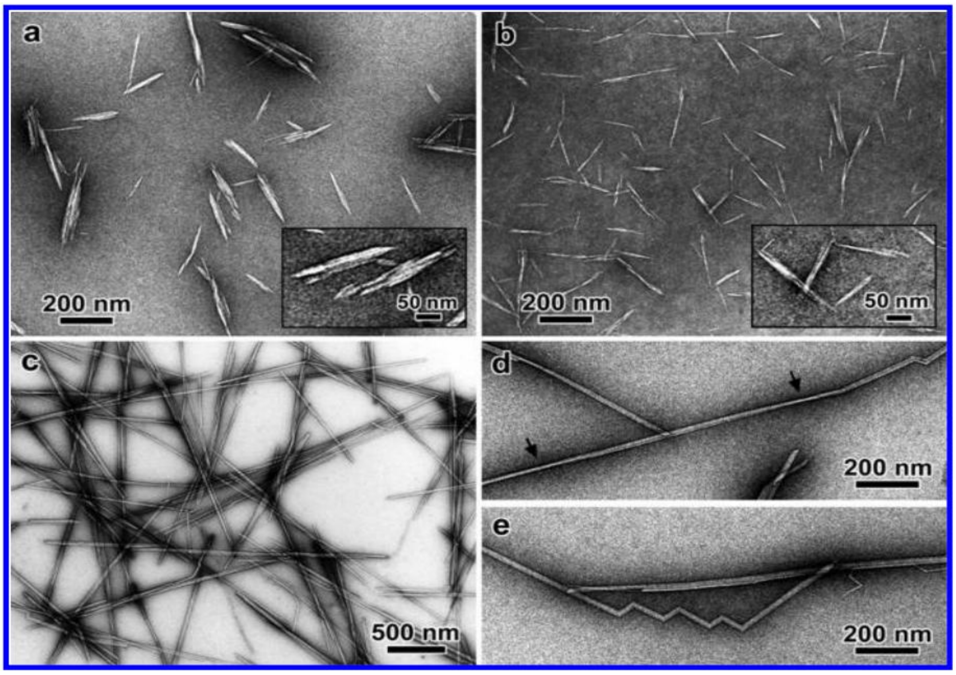

Figure 4. TEM micrographs of negatively stained cellulose whiskers obtained by sulphuric acid hydrolysis of a) cotton, b) Avicel, c-e) tunicate. Insets show enlarged views of some characteristic particles. Arrows are used to show the edgy pattern of particles. Reprinted (adapted) with permission from American Chemical Society [33].

The exact mechanism detailing the hydrolysis of the amorphous sections has been fully explored. But, it has been established, that the kinetics of acid cleavage for amorphous versus crystalline cellulose is the main determinant [34]. During the acid hydrolysis process, there is a rapid decrease in the degree of polymerization (DOP). In the end, the final DOP strongly correlates with the crystal sizes along the longitudinal direction of the cellulose chains present in the original feedstock. In fact, X-ray crystal diffraction [33], neutron diffraction [34], and electron microscopy with iodine staining [33] have been used to prove the production of homogenous crystallites after acid hydrolysis[5]. The values of final DOP or Level Off Degree of Polymerization vary for different feedstock, for example, 250 for cotton [5], 150-200 for bleached wood pulp [36], and varies as high as 6000 for crystalline Valonia cellulose [37], etc.

After decades of research interest, the conditions for the optimum production of CNCs particles from pure cellulosic material have been standardized. Conditions of reaction time, acid concentration, agitation, and temperature have been studied and standardized. The concentration of acid does not vary much from 65 % (w/w), but the temperature (room temperature to 70 °C), agitation (50 – 200 rpm), and reaction time (30 minutes to overnight, depending on the temperature employed) have been manipulated, depending on the feedstock type and properties of the CNCs desired [5], [38].

After acid hydrolysis, the resulting suspension requires extensive sample clean up to yield the CNCs. Dialysis against distilled water and successive centrifugations is used to remove any free acid molecules. Finally, filtration, ultracentrifugation, or differential centrifugation can be employed to concentrate the CNCs [5]. CNCs have been produced from acid hydrolysis of microcrystalline cellulose [39], softwood kraft pulp [40], agricultural waste [41], [42], [43],and natural fibres [44], [45].

Sulphuric acid has been the industry standard for producing CNCs because during the reaction the surface hydroxyl groups of the cellulosic feedstock reacts with the sulphate groups to yield charged surface ester groups. The formation of these esters promotes better dispersibility of CNCs in water, when compared to hydrochloric [38] and other acid systems [46]. But, the introduction of these sulphate ester groups has been shown to adversely affect the thermal stability and rheological behaviour (no time dependent behaviour) of the CNCs[5]. In summary, acid hydrolysis is the most established method used to produce CNCs, with varying properties, depending on the reaction parameters.

2.2Mechanical processing

Mechanical methods are characterized with high shear that causes the transverse cleavage along the longitudinal axis of the cellulose microfibrillar structure, yielding in the extraction of long fibrils, commonly referred to as microfribrillated cellulose (MF). In most instances, the sample is repeatedly passed through the process to enable the degree of defribrillation required. Prior to any mechanical treatment, researchers have found that pretreatment is necessary to promote the accessibility of hydroxyl groups, increase the inner surface, alter the crystallinity, and break the cellulosic bonding arrangement, hence, boosting the reactivity of the fibres [47]. According to Khalil et al. (2014) [47], there are several approaches to produce nanofibres from cellulosic feedstocks. These include refining and homogenizing [48], [49], high intensity ultrasonication [50], microfluidization [51], and grinding [52]. It should be noted that mechanical processing produces nanofibres (5-25 nm diameter and lengths up to 100 µm) instead of nanoparticles, such as rods and particles. Mechanical methods have been superseded by acid hydrolysis because of the high capital cost and energy requirement for the former. Also, the use of the acid has shown to impart properties to the CNC that are more conducive for the given application and makes it easier to work with.

2.3New research methods

In the past few years, researchers have found new and ingenious methods for producing cellulose nanoparticles. Filson and Dawson-Andoh (2008) [53] reported a sono-chemical method for the preparation of CNCs from microcrystalline cellulose, Avicel, and recycled wood pulp. They used two hydrolysis methods, namely, deionized water and maleic acid for producing the CNCs. Hydrolysis of Avicel produced cellulose nanocrystals with average diameter of 21 ± 5 nm while cellulose nanocrystals from recycled pulp were not distinctively spherical and had an average diameter of 23 ± 4 nm. Maleic acid was studied because it has been shown to degrade cellulose to yield glucose without much degradation [54]. Also, the research team hypothesized that the presence of the two carboxylic groups might aid in the eventual stabilization of the resulting cellulose nanocrystal suspension. When deiozied water was used, the yields of CNCs were very low (2-5 %). On the other hand, maleic acid hydrolysis yielded approximately 10 % of the starting mass in all cases.

Recently, Novo et al. (2015)[55] reported a green method for the production of CNCs using subcritical water. The authors hypothesized that the use of subcritical water (120 °C and 20.3 MPa for 60 minutes) can address the limitations associated with conventional acid hydrolysis (long washing times, low temperature resistance of CNCs produced). Their technology was carried out in a 100 mL stainless steel batch hydrolysis reactor. The reaction was done using 1 g of cellulosic material. The pressure inside the reactor was controlled by periodic release via a restrictor valve. The CNCs produced tend to agglomerate, converse to that reported for sulphuric acid digested feedstock. On the other hand, the final product was characterized with improved thermal stability, comparable crystallinity, and smaller aspect ratio when compared to sulphuric acid produced particles.

A novel one-pot hydrolysis method with mild acidic aqueous ionic liquid was used to produce near theoretical yields of CNCs [56]. Successive Taguchi experimental designs were used to identify and optimize reaction parameters using a minimum number of experiments. The two-step hydrolysis involved mild acidic ionic liquid (IL) 1-butyl-3-methylimidazolium hydrogen sulphate ([Bmim]HSO_4). The authors reported yields of 57.7 ± 3.0 %, 57.0 ± 2.0 %, and 75.6 ± 3.0 %, for soft wood pulp, hard wood pulp, and microcrystalline cellulose, respectively. Also, the particles exhibited high dispersibility, high aspect rations (36-43), and negligible sulphur content (0.02-0.21 %, hence improved thermal properties).

In summary, the superior properties of cellulose micro and nano materials are making them an attractive focus area for research. Hence, researchers are continuously searching for newer methods for isolating these particles at low cost and a green environmental footprint.

III. PROPERTIES OF CELLULOSIC NANO AND MICRO MATERIALS

In this section, a brief overview of some of the main properties of cellulose nanomaterials will be explored. This is of utmost importance because of the section to follow, which details how we can use these materials. Before we can understand the applications, we need to have a firm understandingof the property aspects.

3.1Optical properties

At first observation, one would be assuming that CNCs would have optical properties mirroring those of other cellulosic material, but this is not the case. Despite, similar chemical signatures as other cellulosic rich material (H-H, C-H, C-O-H, and O-C-O), CNCs do not exhibit absorption in the optical range. CNCs are different from other materials in three fundamental ways, namely, they are nanoscale in length, the individual structures are anisotropic, hence exhibit birefringence, and depending on the size scale, aspect ratio, and concentration, they are liquid crystalline [1].

Birefringence is the optical property of any material having a refractive index that depends on both the polarization and propagation of the direction of light. The oriented chains of cellulose are birefringent and have refractive indices of 1.618 and 1.544 in the axial and transverse directions, respectively [57], [58]. As can be appreciated, the birefringence and liquid crystallinity leads to interesting optical phenomena. As a given concentration is reached (lyotropic), the particles tend to align creating macroscopic birefringence. A depiction of this phenomenon is shown in Fig 5. The liquid crystallinity becomes apparent above a critical concentration of nanoparticle, where ordered chiral nematic liquid crystalline order forms in the aqueous suspensions ([59]. This observation has been shown to improve when placed in a magnetic field [60] because cellulose has a negative diamagnetic susceptibility, or in other words, the particles prefer to align perpendicular to the magnetic field. This behaviour phase increases with increasing concentration of particles.

In addition, CNC semi-translucent based films can be prepared by proper and careful casting of the suspension. These films are characterized with iridescence because they reflect left-handed circularly polarized light in a narrow wavelength band [61], [62].This phenomenon of reflectance can be explained on the basis of the helicoidal arrangement of the birefringent layers. Hence, the reflected wavelength becomes shorter at oblique viewing angles, giving rise to visible iridescence colours when the pitch of the helix is on the order of the wavelengths of visible light (400 - 700 nm). The phenomenon of reflectance and optics has been widely explored by Gray and his co-workers at the McGill University [61], [62].

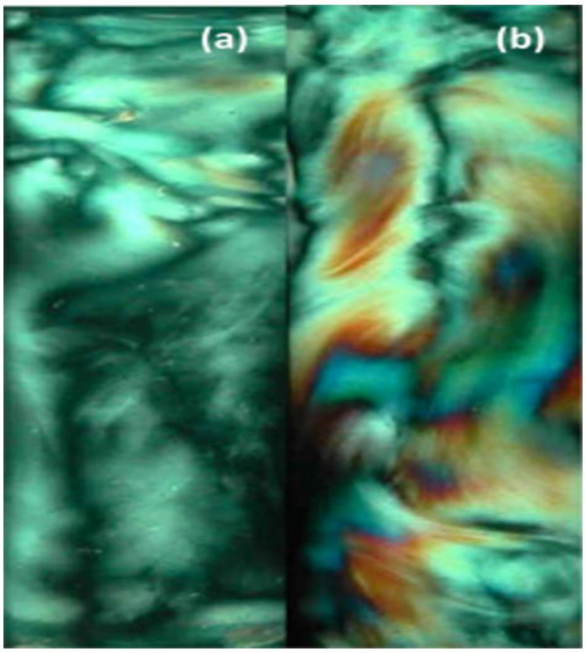

Figure 5. Images of suspensions of tunicin nanocrytals at 0.5 % wt. in a) water and b) dimethylformaide (DMF). Images were generated after observation between cross nicols, clearly showing the phenomenon of birefringent domains. Reprinted (adapted) with permission from American Chemical Society, Samir et al. 2004, [63].

3.2 Mechanical properties

There is still much to be studied and understood pertaining to the mechanical properties of CNCs. The limited metrology techniques coupled with small dimensions of CNCs render them challenging to study. In addition, several factors may influence the measured values and contribute the wide distribution published. For example, particle size distribution, crystal structure, percentage crystallinity, orientation, and aspect ratios have been shown to be determining factors. Hence, it is imperative that these factors are normalized prior to any mechanical characterization.

The limitations when measuring the mechanical properties of nanomaterials along multiple axes have made the quantitative evaluation of the tensile modulus and strength of CNC challenging [64]. Among the common methods used to estimate the elastic properties of these materials include atomic force microscopy (AFM), x-ray diffraction analysis (XRD), and Raman scattering. In fact, the theoretical tensile strength of CNC was found to be 7.5-7.7 GPa, which is significantly greater than steel, titanium, and Kevlar ([64].The mechanical properties of several particles types and the corresponding technique used are outlined in Table 1.

Table 1. Mechanical properties of different cellulose based nanomaterials and cellulose type (for comparison)

Type	**σ_f (GPa)**	**E_A (GPa)**	**E_T (GPa)**	**Technique**	**Reference**
CNC_plant	-	57-105	-	Raman	[28]
CNC_wood	-	-	18-50	AFM indentation	[3]
CNC_theoretical	7.5–7.7	-	-	Computational model	[1]
CNC_tunicate	-	15-25	-	AFM contact resonance	[65]
CNC_wood	-	10-40	-	AFM contact resonance	[65]
CNF_wood	-	8-90	-	AFM contact resonance	[65]
Cellulose Iβ	7.5-7.7	137-168	10-50	Computational model	[66], [67]
Cellulose Iα	-	128-155	5-8	Computational model	[67]

σ_f = tensile strength, E_A = elastic modulus in axial direction, E_T = elastic modulus in transverse direction, E_f = strain to failure

On the other hand, a true indication of the mechanical strengths of cellulose nanomaterials can be determined when combined with a polymer matric [68].The excellent mechanical property exhibited by these materials are due to the high stiffness of the crystalline cellulose, the nanoscale dimensions, high aspect ratios, and the high reactivity of cellulose. Numerous methods have been use to determine the reinforcing effect of the nanomatreials, the most popular being the Halpin-Kardos, which has been used to predict the elastic shear modulus of composite and semi-crystalline polymers. But, the model falls short when assessing nanomaterials. Hence, researchers have looked at the series-parallel model of Takayangi modified to include a percolation approach to better estimatethe stiffness of these systems [69]. In the end, the strong aggregation of the cellulose nanomaterials above the percolation threshold results in a 3-dimensional network continuously through out the material. The arrangement of this network forces a direct correlation in the superior mechanical and thermal properties of these materials [69].

In summary, the mechanical superiority of nanomaterials results from their nanodimensions, tendency to agglomerate, and the crystalline structure. Also, the modelling of nanomaterials to determine their mechanical properties has unlocked doors to better design polymer matrix systems where biomimetic, stimuli-responsive, and cellulose nanocrystals as high modulus fillers can be targeted as niche applications.

3.3Barrier properties

A key aspect when using nanofillers is to improve the barrier properties of the films produced. In the past, researchers focused on non-renewable fillers and petroleum based matrices. But, increased environmental sensitivities have resulted in a paradigm shift in research focus for the past couple decades. Nanofillers are attractive because of the increased tortuosity they enable when mixed with matrices. Specifically, the low permeability of cellulose coupled with the dense packing and high crystalline structure can be used to formulate products with applications in the medical and packaging industries.

According to Favier et al. (1995) [69], the barrier properties of cellulose nanocrystal neat films have not been as well researched as it’s counterparts, such as nanofibrillated cellulose (NFC). In fact, many researchers believe that the sulphuric acid digestion process, which introduces the sulphate ester groups, directly affects the osmotic pressure of the films and leads to separation of the crystals [70], [71]. Hence, CNC based films exhibit higher permeability to gases when compared to their NFC counterparts. The latter is superior because of the presence of traces of lignin and fatty acids [72].

The aspect of barrier effects lends to many investigations, inclusive of water vapour transfers/permeability (WVP) and oxygen permeability. These criteria are becoming increasingly demanded when researchers are publishing data with CNC based plastics. In fact, the water vapour transfer depends both on the type of nanomaterial used and the polarity of matric, whether hydrophilic or hydrophobic. For example, researchers have reported favourable reduction in WVP when using polyvinyl alcohol [73], chitosan [74], and methylcellulose [75], 76] with hydrophilic matrices. On the other hand, when used with hydrophobic matrices, these materials exhibit reduced WVP up to a critical concentration (< 5 % wt.), after which there is a critical increase in permeability. Hence, it is appreciated, depending on the matrix used; nanomaterials will be loaded based on the end applications and the properties desired.

As mentioned earlier, just as important as the WVP, is the gas permeability of nanobased materials. In fact, when these nanofilled plastics are targeted for food packaging, gas permeability becomes critical. Sanchez-Garcia and Lagaron (2010) [77] reported reduced oxygen permeability (OP) when using CNC to reinforce PLA. They concluded loading with 2-3 % wt. of CNC produced plastics with best OP. The reduced OP was as a result of the nanocrystal-indused crystallinity of the PLA matrix. Similarly, Khan et al. (2013) [78] reported decreased oxygen and carbon dioxide transmission rate when they formulated thin films made from CNC (< 5 % wt.) and polycaprolactone. In summary, the addition of small ratios of CNC can favourably improve the barrier properties of plastics, depending on the end applications.

3.4Morphological properties

The geometrical dimensions, length and width, of CNCs vary depending on the source of the cellulosic material, the hydrolysis conditions employed, and the final sample clean up process. Nevertheless, the particle size of the CNC obtained can be controlled via filtration [79], ultracentrifugation [80] or differential centrifugation [81]. Researchers have used microscopy [82] (scanning electron microscopy-SEM and tunnelling electron microscopy-TEM) or light scattering techniques [83] (dynamic light scattering and depolarized dynamic light scattering) to investigate the particle size and distribution of CNCs. Drying of CNCs results in particle aggregation and instrumental artefacts, which can significantly affect the estimation of the sizes and distribution of these particles. Elazzouzi-Hafraoui et al. (2008) [79]recently reported that these problems could be circumvented if TEM is used in the cryogenic mode (cryo-TEM).

Additionally, atomic force microscopy (AFM) has been used to study the roughness and morphological patterns of biobased materials in the past [84]. With respect to CNCs, it can be used to study the surface topography, but in most instances, samples are characterized with rounded cross-sectional profiles [85], [86]. This is primarily due to the artefacts induced by the substrate shape and the AFM tip-substrate interaction [85]. As cited earlier, AFM has emerged as a robust method for estimating the mechanical properties of CNCs particles. A summary of the different dimensional estimation from different types of CNC is summarized in Table 2.

Table 2. Dimensions of CNCs studied using different techniques and obtained from different sources

Source of CNC	**L (nm)**	**W (nm)**	**Technique**	**Ref.**
Bacterial	100-1000	10-50	TEM	[87]
Softwood	100-200	3-4	TEM	[88]
	136-222	12.4-21.4	FE-SEM	[89]
Hardwood	140-150	4-5	AFM	[90]
	130-222	11.4-18.4	FE-SEM	[89]
Tunicate	100-1000	15	TEM	[91]
Sisal	150-280	3.5-6.6	TEM	[92]
Ramie	150-250	6-8	TEM	[93, [94]
MCC	35-265	3-48	TEM	[32]
Cotton linters	216-346	29.7-36.3	FE-SEM	[89]
Red algae	345-519	14.2-23.2	FE-SEM	[89]
Mengkuang leaves	50-400	5-25	TEM	[68]

L=length, W=width

Most researchers report the width of CNCs < 50 nm, but the length can vary up to 1000 nm, depending on the source of cellulose and the processing parameters, such as acid concentration and reaction time. CNCs obtained from wood are characterized with a narrow range for both width and length. This stems from the relative homogenous distribution of the cellulosic arrangement and cellulose type. The aspect ratio of the different CNC samples can vary across a broad range. For applications requiring high mechanical properties, CNCs with lower mechanical properties are desired [95]. As previously hinted, the morphological distribution of CNCs depends on the origin of the cellulose fibres. According to Habibi et al. (2010) [5], the morphological shape of the cross-section is plausibly attributed to the action of the terminal complexes during synthesis. Additionally, depending on the biological origin of the cell wall, the different arrangement of the terminal complexes can generate cellulose crystals with varying geometries. In the end, the geometry of the CNCs is influenced by the biosynthesis, reaction parameters, and the desired end applications.

IV. NANO BASED CELLULOSIC TECHNOLOGIES

CNCs have attracted increased attention as fillers for nanocomposites because of their intrinsic properties such as nanoscale dimensions, high surface area, low density, and high mechanical strengths. Additionally, CNCs can be easily tuned based on the desired chemistries desired; it is biodegradable, hence suitable for packaging applications. Over the past decade, CNCs have been incorporated into a number of different polymers, both olefin and natural based. Some common examples include polysulfonates [96], [97], poly(caprolactone)[94], cellulose acetate butyrate[98], polyurethanes[99] polypropylene [91], polylactic acid[100]. [101], and epoxides[102]. Depending on the type of matrix, the properties of the materials developed will vary. In the following sections, a few recent and groundbreaking studies will be highlighted with key focus on the applications of CNCs.

4.1Membrane Applications

Recently, advances in nanoengineering and nanoscience suggest that many current problems involving water quality can be greatly diminished using nanomaterial. Nanomaterials are attractive because of their high surface area, good adsorption efficiency, and the presence of active sites that can interact with pollutants [106]. Utilizing increased intelligence and resources in the nanomaterial areas; researchers have been able to demonstrate that CNCs are reliable and promising nano-reinforcements/functional elements in polymers for the preparation of membranes. Several pieces of work have been recently published highlighting the attention the use of CNC and polysulfones are receiving as possible membrane system ([104], [105], [106]. Daraei and co-workers (2016) [107] used CNCs as a nonsolvent in polyethersulfone (PES) membranes. The authors reported a phase inversion method using varying concentrations of CNCs. They found that the introduction of CNCs initiated coagulation of the PES, which eventually led to a more hydrophilic, smoother surface, and increased bulk porosity. Also, because of the increased hydrophilicity, the membranes were characterized with superior antifouling abilities.

On a more fundamental level, Bai et al. (2015) [105] investigated the effects of viscosity of the casting solutions, type, and concentration of the coagulant, and how they affected the properties of the composite CNC/polysulfone membranes. In their opinion, the viscosity of the casting solvents affects the diffusion rate between the solvent and nonsolvent. The team used different coagulation baths (water, methanol, ethanol, isopropanol) and concentrations (10, 30, 50 v/v %) and measured the resulting mechanical and morphological properties of the membranes. In the end, they concluded that the tensile properties of CNC+polysulfone membrane were greater than the polysulfone alone membrane. But, the solvents over time introduced macro-voids and short finger-like pores in the membrane, as observed using scanning electron microscopy.

Another attractive area of research has been the design of 100 % biobased membranes for water purification. In one such study, Karim et al. (2014) [108] used CNCs as the functional entities in chitosan matrix via a freeze-drying process followed by compacting. These membranes were designed for the removal of wastewater dyes. The researchers used gluteraldehyde vapour to cross-link the chitosan (10 % wt.) and CNCs. They reported scanning electron micrographs, which clearly showed individual CNC embedded in the chitosan matrix. Brunauer, Emmett, and Teller (BET) measurements showed that the membranes were nanoporous with pores in the range of 3-10 nm. In conclusion, despite low water flux, the membranes efficiently removed 98 %, 84 %, and 70 % of Victoria Blue 2B, Methyl Violet 2B, and Rhodamine 6G charged dyes, respectively, after a contact time of 24 hours. In another methodology to utilize CNCs, Morandi et al. (2009) [109] grafted CNCs on to polystyrene chains via a surface initiated atom transfer radical polymerization (SI-ATRP) to produce a material capable of adsorbing aromatic chemicals from wastewater. Firstly, the surfaces of the CNCs were activated using 2-bromoisobutyryl bromide to introduce sites for the ATRP. Further, they initiated the styrene polymerization from these modified nanocrystals using a CuBr/PMDETA (N,N,N′,N′,N″-pentamethyldiethylenetriamine) catalytic system in the presence of a sacrificial initiator. The end result was a polysaccharide nanocrystals grafted with polystyrene chains. The modified nanocrystals grafted with polystyrene chains were capable of adsorbing up to 50 % of their weight of 1,2,4-trichlorobenzene from water.

In summary, the possibilities when considering CNCs for membrane designs are limitless. The particles can either be modified or not, can be use to coat surfaces, or embedded in the macrostructure of the membrane. The membranes produced are characterized with a green index and have tunability that can be tweaked, depending on the pollutants targeted.

4.2Packaging applications

Another highly researched area has been the usage of CNCs in packaging materials for food, commodity, or medical applications. In fact, packaging (including flexible films and rigid containers) is the largest single market for plastic consumption worldwide and is one the main sources of problems for post-consumption disposal [110]. Hence, researchers have focused on making biodegradable polymers for packaging applications. For example, poly(lactic) acid (PLA) is becoming increasingly popular and competitive with olefin based polymers. PLA’s inherently high mechanical strength, biodegradability, and easy processing make it an attractive substitute for olefin-based polymers. Nevertheless, to meet standards for packaging materials, PLA needs to be filled/reinforced with an agent to give desired properties, depending on the applications.

The development of high performance nanocomposite films for packaging applications with a polymer matrix and nanofillers that are both renewable, biodegradable, and have comparable properties with accepted plastics in the market are a key point of research. CNCs with it’s superior mechanical properties, low density, and biocompatibility is a perfect fit as a filler for polymers. Fortunati et al. (2011) [101] produced nanocomposite films using CNCs, Ag nanoparticles, and PLA using a melt extrusion process. The researchers reported that surface modified CNCs were better dispersed in the polymer when compared to virgin CNCs. Also, the plastics were characterized with good antimicrobial activity against S. aureus and E. coli. The team concluded that these plastics could be used in food packaging, pending migration rate study of the Ag nanoparticles.

Li et al. (2013) [111] used an ingenious technique of coating polyethylene terephthalate (PET), polypropylene (PP), polyamide (PA), and cellophane films with a 1.5-µm layer of CNC. The coated films were characterized with reduced coefficient of friction, good transparency (maintained at 88-91 %), low haze, and significantly lowered oxygen permeability (OP). The team attributed the reduced OP of the films to the strong hydrogen bonds among CNCs and the dense packing of the coating applied. The authors were one of the first teams to introduce multi-functional CNCs coatings on olefin-based plastics. In the end, the hope was to replicate the design and the experimental to suit renewable and biodegradable plastics, using the same methodology.

Methyl ester cellulose nanocrystals (CNC-me) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) based films with a final thickness of 50-60 µm were made using a simple solution casting technique[112]. Interestingly, the CNC-me was produced using a one-pot process from commercially sourced microcrystalline cellulose (MCC). CNC-me were obtained using a novel HCOOH-HCl hydrolysis done at 90 °C for 3 hours. The cooled suspension was then neutralized with a NH_3:H_20 solution, centrifuged for 7 hours, sonicated for 10 minutes, and finally dried. After careful optimization, the CNC-me was uniformly distributed in the PHBV without the aid of surfactant or compatibilizer. As a result, the crystallization temperature and crystallinity of the resulting plastics increased with CNC-me addition. Also, the plastics were characterized with significant increases in mechanical performance, thermal stability, and reduced migration properties. In summary, the research team was able to produce transparent nanocomposites using CNC and PHBV, a renewable polymer. The effect of established sulfuric acid hydrolysis versus ammonium persulfate (APS) treatment to obtain CNCs was investigated [113]. The CNCs obtained were used to coat PET films. The properties of the different films were evaluated. Surprisingly, the APS produced CNC coated PET films were characterized with better transparency, higher crystallinity, and the casting solution had higher clarity. The team attributed this to the higher charge densities of the carboxylic groups introduced during the APS process. Nevertheless, the oxygen permeability coefficients of all plastics studied were lower than established synthetic resins commonly used in flexible packaging.

A summary of the mechanical properties of CNC based packaging materials is given in Table 3. It was observed in most of these cited works that addition of CNC above a threshold value (in most cases > 5 % wt.) resulted in mechanical property plateau, before rapid decrease. This can be attributed to the dispersion of the CNCs in the different polymer types. In fact, higher the volume of CNC added, a greater number of flaws are introduced in the macrostructure of the films, which can significantly weaken the entire structure. In the end, the casting process, dispersion of CNC in the matrix, and the type of matrix will significantly influence the mechanical behaviour of thin films.

Table 3. Mechanical properties of CNC based thin films

Source of CNC	**Matrix**	**Modulus (GPa)**	**TS[1] (MPa)**	**Reference**
MCC	PLA	2.9	-	[100]
MCC	PLA	2.9	46-50	[101]
MCC[2]	PLA	4.4	49-59	[101]
Kraft pulp	Chitosan	2.8-2.9	92-99	[75]
Kraft pulp	Xylan	-	5	[114]
Kraft pulp	PVA	0.80-1.25	12-18	[115]
Bagasse	Starch	1.6-1.7	104-111	[116]
Banana waste pulp	PLA	0.8	28.8	[117]

Tensile strength

CNC produced was modified using a surfactant-acid phosphate ester of ethoxylated nonylphenol

In general, CNC is a robust and tuneable material that can have applications in different types of packaging material. Also, as highlighted in this section, the full potential of the properties of CNC is yet to be fully understood, hence there is great room for better understanding these ubiquitous materials.

4.3Emerging applications

Apart from established packaging and membrane technology platforms, CNC has found utilization in some other areas of research. This is possible because of the many desirable properties of CNC and the ease of modification. For example, CNC has been used in bionanocomposite hydrogels for tissue engineering applications [118] and as a possible drilling mechanism in the mining industry [119]. The mechanical properties of CNC make them ideal for these applications. Injectable hyaluronic acid (HA)/CNC hydrogels were prepared for potential tissue engineering (TE) and regenerative medicine [118]. Hyaluronic acid was targeted because it is a linear polysaccharide that is ubiquitously found in tissues and body fluids of vertebrates and some bacteria and it is naturally degraded in the body by hyaluronidases (HAses). HAs are mechanical labile and needs to be either cross-linked or reinforced with a suitable active agent to improve the strength of the scaffolds. Hydrogels were made via a hydrazine covalent cross-linking reaction between adipic acid dihydrazide-modified HA and aldehyde HAs. Varying concentrations of aldehyde-modified CNC were added to the system. The key findings revealed that the incorporation of CNC in the hydrogels resulted in a more organized and compact network structure. As a result, the mechanical properties of the hydrogels increased significantly. The biological performance of the hydrogels was assessed against human adipose derived stem cells (hASCs). HA-CNCs nanocomposite hydrogels were characterized with preferential cell supportive properties in in vitro culture conditions because ofthe higher structural integrity and plausible interaction of the micro-environmental cues with CNC’s sulfate groups. Also, hASCs encapsulated in HA-CNCs hydrogels demonstrated the ability to spread within the volume of gels and exhibited pronounced proliferative activity. This research clearly signalled the potential range of application of HA-CNC in the biomedical field.

CNCs have been used as reinforcing nanofillers in electrospun scaffolds based on natural/synthethic polymer blend matrix. In one such case, Domingues et al. (2016) [120] studied the effect of incorporation of small quantities of CNC in poly-ε-caprolactone/chitosan (PCL/CHT) tendon mimetic nanofibre bundles. The addition of CNC was found to significantly toughen the material and raised the mechanical properties of the tendon/ligament to accepted ranges. In fact, the authors stated that the PCL/CHT/CNC fibrous scaffolds satisfied not only the mechanical criteria for tendon applications, but also provided tendon mimetic extracellular matrix (ECM) cues, a very important parameter for maintaining the tendon cell's morphology and physical integrity. The team concluded that this scheme could be applied to any natural/synthetic polymer system for the creation of mimetic fibrous structures.

A list of some of the advances where CNC has been used is presented in Table 4. The end application, the targeted properties, and polymer used are highlighted.

Table 4. Variety of medical applications where CNC played different roles depending on the targeted property

Polymer/motif	Targeted property	Application	References
POEGMA[1]	-Improved mechanical strength -Increased stability -Decreased swelling ratios	Hydrogels	[121]
UPy[2]	-Wide range of mechanical elasticity	Self assembled cholesteric nanocomposite	[122]
Chitosan+PEO[3]	-Reduced porosity -Increased mechanical strength	Randomly oriented wound dressing mats	[123]
Curcumin-cyclodextrin	-Increased solubility in water -Increased antiproliferative effect of curcumin	Anti-cancer drug carrier	[124]

[1] Poly(oligoethylene glycol methacrylate)
[2] 4-fold hydrogen bonded ureidopyrimidinone motifs
[3] Polyethylene oxide

Table 4 clearly illustrates the diversity of medical applications using CNCs. The addition of CNC to motifs allow for tuneable control of their mechanical elasticity, making them ideal for self-assembled cholesteric nanocomposites [122]. In another application, Naseri et al. (2015) [123] demonstrated that CNC could be added to polymer mats to produce materials suitable for wound dressing. Finally, to highlight the versatility of CNC, researchers have used it as a binding agent and carrier for anticancer drugs. Many of these drugs are hydrophobic and are insoluble; hence their transport is inhibited. CNC circumvents this problem by careful encapsulation and release when the drug reaches the target cells. The release of the drug is possible because CNC can be retrofitted with sensors which respond to a given stimuli [124].

Another debated and controversial area of research using CNC deals with drilling fluids. The controversy stems from whether the end application will be able to recover the cost of CNC, which at the moment, is not readily available and cheap. Nevertheless, some teams have looked at using CNC in conjunction with other agents to develop drilling fluids. Li et al. (2015) [119] reported a low cost, sustainable, environmental friendly, and high performance water-based drilling fluid developed using bentonite (BT), polyanionic cellulose (PAC), and CNCs. They studied the rheological and filtration properties of varying PAC/CNC/BT blends. After considering eight models, they concluded that CNCs significantly improved the rheological properties of the fluids. In fact, when used together, PAC and CNC yielded cakes with better rheological and filtration properties.

The same team previously investigated the use of CNCs and BT as water-based drilling fluids [125]. The authors reported a core-shell structure was created when CNC/BT were mixed. This macrostructure resulted from the strong surface interactions among BT layers, CNCs, and the immobilized water molecules. The performance of the CNC+BT system outperformed microfibrillated cellulose (MFC) +BT systems. This plausibly resulted from the superior interaction between the nanoparticles and BT. CNC+BT cakes were characterized with superior rheological properties, higher temperature stability, and thinner filter cakes. In summary, the true potential of using CNC in different application has not been fully realized. This goal will be achieved when these nanomaterials are fully understood and how their interactions with other materials influence the end properties. Nevertheless, CNC will remain an attractive research topic because of its many desired properties; it's tunability, and renewable index.

V. ASSESSMENT OF CELLULOSIC NANO/MICRO MATERIALS

This section will detail the possible human, environmental, and resource usage of producing cellulosic nanomaterials and their microfibrillated counterparts. Also, the production of specific products from these materials will be presented.

5.1Environmental and human impact of CNC and its products

Before global acceptance of CNCs in commercial applications, there is a need to address their environmental and safety aspects because of their nanoscale features, which can impart chemical property changes. Shatkin and Kim (2015) [126] employed a NANO life cycle risk assessment (LCRA) framework to screen pre-commercial applications of CNCs. They identified and assessed the potential risks of CNC from a consumer, environmental, and occupational exposures through out the product life cycle. Their analysis revealed that occupational inhalation exposure during the handling of CNC, as a dry product was the highest knowledge gap, followed by the toxicity of CNC presence in consumer products, such as food packaging. Most published data sets and assessment of CNC on human exposure have been done at the production setting and not on the consumer exposure. Vartiainen et al. (2011) [127] evaluated worker exposure to unmodified CNC during a two stage post-production process using friction grinding and spray drying. Real time measurements of aerosolized nanoparticles were monitored. The researchers observed no significant increase in CNC in either step. In a similar study, O'Connor et al. (2014) [128] monitored the dustiness index as a simulation of occupational exposure to spray-dried CNC. They estimated the fraction of inhalable, thoracic, and respirable particles to be within moderate ranges.

At the moment, there is lack of studies in the literature reporting the in vitro and in vivohealth effects inclusive of carcinogenicity, reproductive effects, and neurotoxicity. One of the first studies employed an in vivo nematic modelwith a primitive nervous system, C. elegans, to study the neurotic and behavioural endpoints. In the end, the researchers concluded that CNC did not have any adverse neurologic effects [129]. The environmental effects of CNC has been more researched and published of late. Kovacs et al. (2010) [130] assessed a set of organisms from different trophic levels and studied the sub-lethal and lethal endpoints, including cell viability, oxidative stress, genotoxicity, reproductive and development effects using monitoring test, in depth whole organisms test, and fish cell tests. The researchers found that a pilot plant producing 1000 tons per day CNC with corresponding losses would not be hazardous to aquatic species. In that research, aquatic species were studied because they are most susceptible to the effects of CNC loss from manufacturing facilities.

In a more fundamental life cycle assessment, Li et al. (2013) [131] studied four comparable lab scale nanocellulose fabrication routes via a cradle-to-gate using Eco-Indicator 99 method. Their findings revealed that the subsequent chemical modification of CNC imparted a greater effect on the environment. Also, the chemical and mechanical processing of the pulp into CNC had the highest environmental footprint. In fact, the extraction of CNC from the pulp had a greater effect than the raw material extraction process (kraft pulping) on the key indicators. Nevertheless, the team was optimistic because their work illustrated than there are environmental advantages over competing technologies platforms, such as carbon nanotubes fabrication.

Similarly, Arvidsson et al. (2015) [30] modelled the cradle-to-gate life cycle assessment for producing cellulose nanowhiskers (CNF) from wood pulp using three production routes. The routes investigated involved pretreatment before acid hydrolysis. These routes included an enzymatic route, a carboxymethylation route, and a route that involved no pretreatment. The team considered a functional unit of 1 kg nanomaterial that allowed for comparisons across the treatments. They stated the limitations with modelling nanomaterial, inclusive of data gaps, scale-up effects, choosing a relevant functional unit, and the comparability to other products. They gathered most of their data from other researchers working in the space (previous publications and collaboration) and the Ecoinvent database (version 2.2). In their study, four impact categories were selected: energy use, climate change, acidification, and water use. These categories were chosen because of environmental concerns and the possible impact on resource abundance. Their results showed that CNF produced via the carboxymethylation route has highest environmental impacts because of the large quantity of solvents used. The other two methods have similar impacts. The authors compared their results to those of others and concluded that the enzymatic and no pretreatment routes have comparatively low environmental impacts. Nevertheless, these comparisons are not recommended because of the difference in technology and functional units, the data used (inventory versus published data), and most importantly, differences in methodology.

Recently, Hervy et al. (2015) [131] carried out a comprehensive study assessing the life cycle impact of reinforcing epoxy composites with bacterial cellulose (BC) and nanofibrillated cellulose (NFC). The systems were compared to neat PLA and 30 wt. % of randomly oriented glass-fibre reinforced polypropylene (GF-PP). Although, not using smaller CNCs, the study can give an insight into the cradle-to-gate assessment of the different systems, because the processing to get from NFC to CNC just requires longer reaction time and the presence of acid. The BC and NFC epoxy based composites were characterized with higher global warming potential (GWP) and abiotic depletion of potential fossil fuels (ADf). Despite this, encouragingly, the tensile properties of the BC and NFC composites were superior to the other systems. Another key finding that the team reported was that if the end of life was considered and if at least 60 % (vol.) of nanocellulose was used, the footprint of the BC and NFC would be lower than the PLA system. The authors concluded that nanocellulose-reinforced polymers could be competitive if high loadings of nanocellulose and proper disposal of product are employed at end of life.

Researchers are continuously searching for sustainable feedstocks for CNC production. But, if the feedstock can be a waste stream from another process, that would give the process an avenue for capital generation and reduce the environmental footprint for the entire process. One such case was reported by Piccinno et al. (2015) [132] when they optimized the production of cellulose nanofibres from carrot waste. The used an enzymatic process to isolate the CNF, before applying a functionalized coat and then proceeded to orient the CNF via different spinning techniques. After this, they performed a laboratory scale life cycle assessment to assess the various routes of the entire process from an environmental perspective. From preliminary modelling, the researchers concluded that electrospinning of the fibres had a higher impact when compared to the alternative wet spinning process.

The studies highlighted in this section clearly illustrates that much work needs to be done on investigating the human and environmental impacts of cellulose nanomaterial production and their corresponding products. Also, more comprehensive databases need to be developed for these specific materials, to allow less data compromise during the modelling stage. Nevertheless, these studies have shown what questions need to be tackled in coming years and to some extent, have shown that nanomaterials are not harmful to humans and the environment at a given exposure limits

5.2Cost and energy analysis

An exhaustive search for techno-economic and cost analysis pertaining to cellulose nanomaterials was carried out. The results yielded were surprisingly disappointing. For an area of research that has drawn the attention of some of the best researchers and agencies worldwide, not one paper could be found detailing these important parameters. Nevertheless, the few studies found will be carefully studied and reported below to provide any idea of the technical and economic factors. Durna et al. (2011) [133] presented a mini review of cellulose nanocrystals and its potential integration as co-product in bioethanol production. In their publication, they stated that a consortium led by North Dakota State University (NDSU) studied the use of cellulose nanowhiskers derived from straw to make products to substitute for fibreglass and plastics in many industrial applications. The team used an Aspen Plus-based process model to evaluate the cost of producing bioethanol and CNC, in conjunction. They found that the production cost of ethanol including by-product credit was $ 0.41 per liter. When the production of cellulose nanowhiskers was added to the base case model, the manufacturing cost of producing these nanoparticles from wheat straw was estimated to be $ 1.25 per kg. These data suggested that production of cellulose nanowhiskers would be an enhancement to the economical feasibility of a wheat straw to ethanol production.In a chapter, Rojas et al. (2015) [134] detailed the current trends for the production of cellulose nanoparticles and nanocomposites and highlighted that mechanical production of these materials using methods such as microfluidization and high-intensity ultrasonic treatment are characterized with high production cost (tools and materials) and they are less efficient and typical require significantly more energy than chemical methods. Hence, it is not surprising; most pilot scale facilities employ chemical method for the production of nanoparticles.

Spence et al. (2011) [135] reported a comparative study of energy consumption and physical properties of microfibrillated cellulose (MFC) produced by different processing methods. They cited that MFC are produced by four main methods, namely, microfluidization, micro-grinding, homogenization, and cyrocrushing. Their main aim was to determine the influence of the different production methods on the physical properties of the MFC produced and to determine the energy requirement for each process. The team concluded that homogenization (assuming an energy cost of $60 per megawatt-hour) was the least cost effective method for producing MFC, with an energy cost of $650/ton. On the other hand, microfluidization and micro-grinding of bleached hard wood pulp required $140/ton and $95/ton, respectively. But, in the end, homogenization yielded MFC with higher specific surface area and films with lower water vapour transmission rate (when compounded with low density polyethylene). Hence, when selecting which method is best suited for large-scale production of MFC, a compromise will be needed between energy consumption and required properties of the MFC.

In summary, after careful investigation, it can be concluded that one of the major gaps with respect to cellulose nano and micro materials is the lack of studies detailing energy and cost requirements for the process. In order for this technology platform to be successful there needs to be a general research effort in addressing these shortcomings. Nevertheless, we have found that the production of these materials require high-energy inputs and are associated with high feedstock cost. To circumvent these problems in the future a better direction would be to employ waste cellulosic material and technologies that are less intensive.

VI. RECOMMENDATIONS AND FUTURE DIRECTIONS

After several months of careful study of the literature pertaining to cellulose nanobased materials, a few key recommendations were extracted. These study paths are crucial for the full realization of the utilization of nanobased materials. A list of these criteria is given below.

- Investigate why the superior nanoproperties of cellulosic material are not transferred when used in nanocomposites
- Study what factors are most energy intensive during the production phase
- Comprehensive funding for long term ecotoxicity studies
- Need for life cycle analysis where cradle-to-grave studies are considered instead of cradle-to-gate. This will enable better understanding of the potential integration of these materials back to nature and give a real indication of the environmental impact
- Develop ingenious methods to extract nanomaterials from cellulosic waste. Focus on methods requiring less chemicals and energy
- Re-ignite the enzymatic interest in the production of nanomaterials. The cost of production of enzymes are getting lower and their environmental benign nature make them ideal candidates

There are several key areas in the literature where gaps are obvious; those listed above are just somewhere our team feels best interest should be warranted. Strategies which employ outside the box thinking and exploring new applications/production methods may provide faster realization of the potential of cellulose based nanomaterials.

VII. CONCLUSIONS

Cellulose based materials are potentially the answer to many of today’s problems pertaining to environmental and economic concerns. This is confirmed by the research interest and investments being made in this area of study. Hence, the present review seeks to outline a holistic summary on the synthesis, source, properties, and applications of cellulose nanobased materials. In special cases, where data gaps were obvious, cellulose microbased materials were reported. Also, an effort was made to report ingenious methods used to isolate these materials. The research undertaking explicitly reports the main applications of CNC over the past decade. Based on a comprehensive survey of the literature, alarming data gaps were found for the techno economic, cost analysis, and energy analysis for the production of CNC or its subsequent use in a given application. Nevertheless, an effort was made to highlight the few studies found and pave a path forward for more research in this area. In the end, the main focus areas that should be studied are recommended based on our team’s personal assessment.

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