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Review

A review on lignocellulose chemistry, nanostructure, and their impact on interfacial interactions for sustainable products development

Maria C. Iglesias[1], Diego Gomez-Maldonado[1], Virginia A. Davis[2], and Maria S. Peresin[1,*]

[1] *Sustainable Bio-Based Materials Laboratory, Forest Products Development Center, College of Forestry, Wildlife and Environment, Auburn University, 602 Duncan Drive, Auburn, AL 36849, USA*

[2] *Department of Chemical Engineering, Samuel Ginn College of Engineering, Auburn University, 345 West Magnolia Avenue, Auburn, AL 36849, USA*

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ABSTRACT

Over the last decade, the utilization of nanocellulose for novel applications has positioned this renewable source as a promising alternative substitution for petroleum-based materials. When attempting to utilize and incorporate lignocellulosic materials from different raw materials and varying chemical compositions into composite materials, it is crucial to understand the interfacial interactions between the different chemical components of such composites. Likewise, these interactions will dictate the behavior of the lignocellulosic suspensions, thus directly impacting the intrinsic properties of the resulting materials. As explained in this review, understanding the atomic and molecular interactions, and other phenomena occurring in the water media, opens a wide range of possible composite materials and applications that can be targeted with different renewable and sustainable materials. Consequently, the use of forest and agricultural by-products can be enhanced, increasing its potential value and providing a more environmentally friendly alternative to displace fossil-based polymers.

Introduction

The United Nations has estimated that the global population will rise to around 9.7 billion in 2050 [1], resulting in a projected production of over 25 billion metric tons of plastic waste by the same year [2, 3]. This overproduction of material shall not only impact the environment and ecosystems with the pollution linked to the manufacturing steps but most likely, significant impacts will also be related to the disposal and end-of-life management [3]. Traditional synthetic fossil-based plastics such as poly(ethylene terephthalate) (PET) and polypropylene (PP) have four

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Address correspondence to E-mail: soledad.peresin@auburn.edu

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disposal routes; (i) incineration for energy; (ii) recycling for new materials; (iii) landfill disposal for containment; or the less desirable (iv) leakage/littering [4]. Recycling is the most convenient from an environmental standpoint. However, in 2017 it was reported that less than 10% of the plastics were recycled in the USA [5]. The low number was driven by an important challenge, the common social behavior of improper disposal and disinterest [6].

Due to the elevated amount of plastic waste, the pressing need to reduce the consumption of traditional petroleum-based materials and increase the availability of more biodegradable and compostable options is imminent. Moreover, by utilizing these bio-based materials, the energy requirements and the gas emissions during production would also be decreased [3, 7, 8]. A bio-based material is defined as a product that initially and intentionally proceeded, fully or partially, form a living or once-living organism [9, 10]. Thus, all lipids, proteins, carbohydrates, and even smaller molecules such as toxins could be used to develop a bio-based material. It is worth mentioning that there is controversy on the definitions depending on the field of study, where the term "bio-based material" is used as an umbrella term, the definition could vary depending on end-use, such as biomaterials when related to biomedical applications or bioplastics when used for packaging, textiles, or automotive [11]. In this review, we utilized the term biomaterial as a general definition without differentiating among the final applications.

Understanding the main interactions between composite material elements, such as naturally occurring biomass, is essential for its use in applications. This review aims to make a comprehensive overview of the interactions forming the polysaccharides of the lignocellulosic materials at a molecular level, as well as the interactions between their different macromolecules and the seemingly bio-colloidal systems they can form. Finally, a search into different applications where these lignocellulosic materials have been applied was done, as the fundamental understanding could help elucidate improvements to the fields and a more funded application of these materials to solve day-to-day problems could be developed.

The current state of agroforest bioproducts as lignocellulosic sources

To accomplish more sustainable and green pathways for the development of the materials science field, the biorefinery concept has emerged during the last years as a viable alternative to petroleum based products, in Fig. 1, a diagram of an integrated biorefinery system with a pulp mill is presented. The inlet of new synthesis pathways, product design and innovation as well as timber management are highly related to the sustainable output of traditional pulp mills operations. Likewise, the integration of energy production and product development are crucial for a low carbon emissions and economically feasible integrated process including high-value chemical building blocks and other biomaterials. In a more encompassing term, the International Energy Agency (IEA) defined biorefinery as "the sustainable processing of biomass into a spectrum of marketable products and energy," meaning that value is added to the entire supply chain during the lifetime of that biomass [12].

The main advantage of using biomass as raw material is the possibility of obtaining it from environmental, economic, and socially responsible sources, such as well-established renewable industries like forestry, agriculture, fisheries, cattle, or sericulture. Moreover, alternative raw materials can be selected from by-products, for example stems, hulls, and leaves collected after crops harvesting or the wood residues from the timber industry.

The impact of focusing on these industries can be clearly exemplified by the forestry industry. Only in 2019, the US production of sawlogs and veneer logs was of 187 m^3, generating a result of 15.3 m^3 wood residues, also known as sawdust [14]. The large volume of such residues opens new alternatives for its recovery and utilization in the biorefinery concept aiming to generate profits in the nanotechnology areas and in new markets focused on high value-added products.

In the case of agricultural harvest, most of the crops are utilized for alimentary ends, as food security is still of public concern [15]. The most produced agricultural commodities in the USA are soybean, corn,

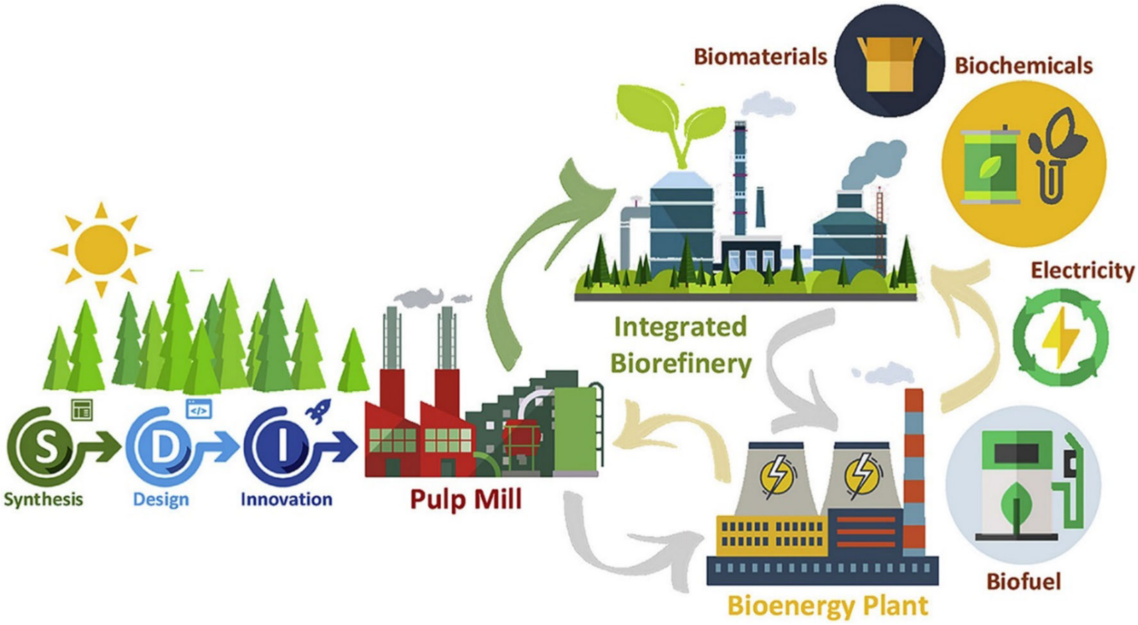

Figure 1 Diagram of integrated sustainable biorefinery system. *Adapted from* [13].

wheat, and cotton, which account for approximately 70% of the total harvested area [16]. Additionally, farmers are increasingly interested in growing hemp due to its growing market, and the versatility of the extracted oil and the fiber portion for different applications [17]. Therefore, there is enormous potential in utilizing lignocellulosic by-products acquired from agricultural sources to produce biopolymers and develop biomaterials [9, 18].

Although the commodity types mentioned above are different regarding their properties, uses, and chemical characteristics, they share similarities at the most fundamental level of their structure. The main component of these raw materials are polysaccharides; biomacromolecules composed of sugar monomers, most specifically cellulose, hemicellulose, and pectin. Additionally, a polyphenol also known as lignin is a highly abundant material that is present in all them [19, 20]. The chemical composition of these materials, as well as the molecular organization in which they can be found, will have a great impact on the properties that the materials derived from them will possess. As a result, analyzing the linkages within each component to further understand the interaction between them is of crucial relevance. To understand these effects, there are three levels in which to study and understand the causing phenomena: atomic, molecular, and supramolecular levels.

An insight into the lignocellulosic components of economic interest

As wood is a biosynthesized product, its chemical composition varies depending on the selected tree, genus, specie, geographical location, available soil nutrients, age, environmental condition of farming, and droughts, among others [21, 22]. As a general distinction, wood can be classified in two main groups, hardwoods (HW) and softwoods (SW) which are mainly differentiated by their variations in morphology, types of cells, and cell arrangements [23]. Nevertheless, regardless of the type of tree, the three main general components of wood are cellulose, hemicellulose, and lignin. Within these, the polysaccharides—cellulose and hemicellulose—account for 65–70% of the dry weight [24], which makes them the primary contributors of the physicochemical properties of the wood as a material. In addition to those, the remaining 2–5% correspond to the presence of

Table 1 Chemical composition of softwood, hardwood, and soybean hulls

Raw material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	Pectin (%)
Softwood [27]	37–43	20–30	25–33	2–5	–
Hardwood [27]	39–45	17–35	20–25	2–4	–
Soybean hulls [28]	29–51	10–20	1–4	–	6–15
Hemp [29, 30]	55	16	4	5.25–20	4

non-structural constituents known as extractives [25, 26]. The chemical composition of softwood and hardwood species is detailed in Table 1.

Considering the different alternatives to obtain crops by-products, soybean is the second-largest harvested crop in the USA [14], leading to a bulky amount of material that could be potentially used under the biorefinery concept. This crop is worldwide produced due to its versatility as an oil seed, proteins, and fiber source, and due to the possibility of using it as a biofuel source [31]. After the soybean seed is crushed to extract the oil, the remaining material, known as soybean hulls or coat, is rich in fiber—and therefore cellulose—content [32] and is usually utilized as fiber source for cattle [33]. Focusing on the soybean hull composition, they account on average for 35.4% cellulose, 17.2% hemicelluloses, and 2.3% lignin [34]. Additionally, some proteins, oil, and ash content are present in the soybean coat [35]. Nevertheless, the efficiency of the dehulling process will have a direct impact on the final chemical composition of the soybean hulls [36].

Another emergent crop with high fiber content is hemp, which is traditionally used for its fibers in packaging and for the extraction of the seeds oil [29, 37]. And since its reclassification by the Farm Bill, effective in 2022, [38] it is expected to be a major product in the USA. Composition-wise, the green fibers contain 55% cellulose, 16% hemicelluloses, 18% pectin, 4% lignin and extractives between 5.25 and 20% [29, 30]. The high variety of structural carbohydrates makes this crop of interest for modern biorefinery applications.

When bearing in mind wood or agricultural by-products to produce nanocellulosic suspensions, it is essential to consider that cellulose fibers do not occur independently in these raw materials. Instead, they are bonded together with hemicelluloses, lignin, extractives, and pectin, depending on the source (see Table 1 for detailed chemical composition). Nevertheless, all these materials as individual components present their own chemical functionality, thermo-mechanical, and morphological characteristics; those determine in turn the interactions and possible uses that they can have in different applications [39].

Chemistry of biopolymers composing macroscopic lignocellulosic fibers

Due to the continuous improvement of technology designed to isolate materials in the nanoscale, cellulose is of particular interest, as this biopolymer tends to bundle into nano- to microscale fibers, depending on the diameter. Analyzing in detail the characteristics of this biopolymer, cellulose is a linear homopolymer generated by repeating β (1→4) D-glucopyranose units (Fig. 2). These units are covalently linked through acetal functions between the equatorial OH group of C1 and C4 (β-1,4-glucan) [40]. Along with the cellulose structure, covalent bonds C–O and C–C are extended through the chain. Each anhydroglucose unit (AGU) has three hydroxyl groups (OH) in carbons C6, C3, and C2, being the one in C6 the one with more propensity to react. Traditionally, cellobiose has been stated to be the repeating unit for cellulose, conformed by two AGU linked together by the same β orientation [41]. However, further crystallographic and thermodynamic analysis has demonstrated that glucose is the repeating unit, as this can explain most phenomena [42]. Likewise, using glucose as monomeric unit agrees more clearly with the Joint Commission on Biochemical Nomenclature (JCBN) of the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Biochemistry and Molecular Biology (IUBMB) definitions [42]. The β(1→4) bonds among the AGU are accommodated in a thermodynamically preferred conformation with every other AGU, rotated at 180° in the plane [43].

Additionally, the presence of OH groups in carbons 2, 3, and 6 confers the possibility of forming

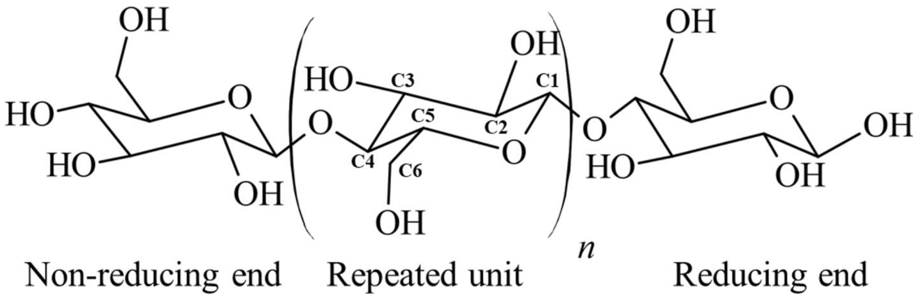

Figure 2 Cellulose chain structure.

inter- and intra-hydrogen bonds within and between OH groups from the same and different cellulose chains, giving this bio-based material the opportunity of establishing a robust supramolecular structure [44]. The presence of these OH groups also promote hydration interactions of the nanocellulose fibers in water, improving their dispersion in this media. An additional important feature of the cellulose chain is the anisotropy of their endings. While one end, called the reducing end, presents an exposed C1 hydroxyl group, the other C4 end, is the non-reducing end. The presence of the hydroxyl group in C1 and the ether group between C1 and C5 allows for the possibility of opening the AGU to from an aldehyde group, permitting targeted chemical modifications [45].

As a result of the strong supramolecular arrangement of the cellulose chains, this biopolymer can be found in different polymorphic structures. The capability of cellulose chains to share protons to form H bonds opens the possibility of multiple options for crystalline packing. For example, cellulose I, commonly known as native cellulose, can be classified as cellulose Iα and Iβ depending if the crystalline structures are packed as tricyclic or monocyclic arrangements, respectively [40]. The second most important type of polymorph is known as cellulose II. This is the most thermodynamically stable type of cellulose, and it appears as the result of the mercerization of cellulose with aqueous sodium hydroxide (NaOH) or regeneration of cellulose fibers after dissolution in selective types of media [46]. The main difference between cellulose I and II is the orientation of their chains; in the former, atoms are organized in a parallel orientation while in the latter, the cellulose chains run in an antiparallel direction [41]. Additionally, when treating cellulose, I and II with ammonia, cellulose IIIα and IIIβ can be obtained. Finally, the last and less stable polymorphs are cellulose IVα and IVβ, obtained by heating cellulose IIIα and IIIβ, respectively, with glycerol [47].

When arranged into elementary fibrils, the cellulose chain has two differentiable packing conformations, an amorphous and a crystalline domain; the previous can be dissolved by acidic hydrolysis, which when in the nanoscale diameters leaves the crystalline domain as the nanomaterial known as cellulose nanocrystals (CNCs) [48]. On the other hand, if the cellulose fibers are subjected to mainly mechanical treatment, then both the amorphous and crystalline domains remain on the structure, giving rise to the obtention of cellulose nanofibrils (CNFs) [49]. Additionally, when producing CNFs there are different alternatives, such as bleached or unbleached cellulose nanofibrils (BCNF or LCNF, respectively), depending on the purity of the starting raw material, in terms of cellulose content [22, 50].

Hemicelluloses are also a type of polysaccharide present in lignocellulosic materials which form part of the above-mentioned fibril-matrix-like structure. Hemicelluloses are branched and less ordered polysaccharides. They are composed of several types of sugars arranged in different conformations. The most important are presented in Fig. 3 and are D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-0-methyl-D-glucuronic acid, and D-galacturonic acid. Additionally, to a lesser extent, there are also L-rhamnose, L-fucose, and various O-methylated neutral sugars [21, 51]. The type of hemicellulose will vary depending on the source of origin [52] together with the different types of linkages between the sugars units, allowing branching and shorter molecular weight structures than cellulose [53]. For example, softwood is characterized by having more mannose and galactose units than hardwood, while the latter has a larger proportion of xylose and acetyl groups [54]. Additionally, the structure of hemicelluloses will also be affected by the extraction method utilized. For example, cellulose fibers produced from kraft methods using hardwood sources contain a higher amount of carboxylic groups

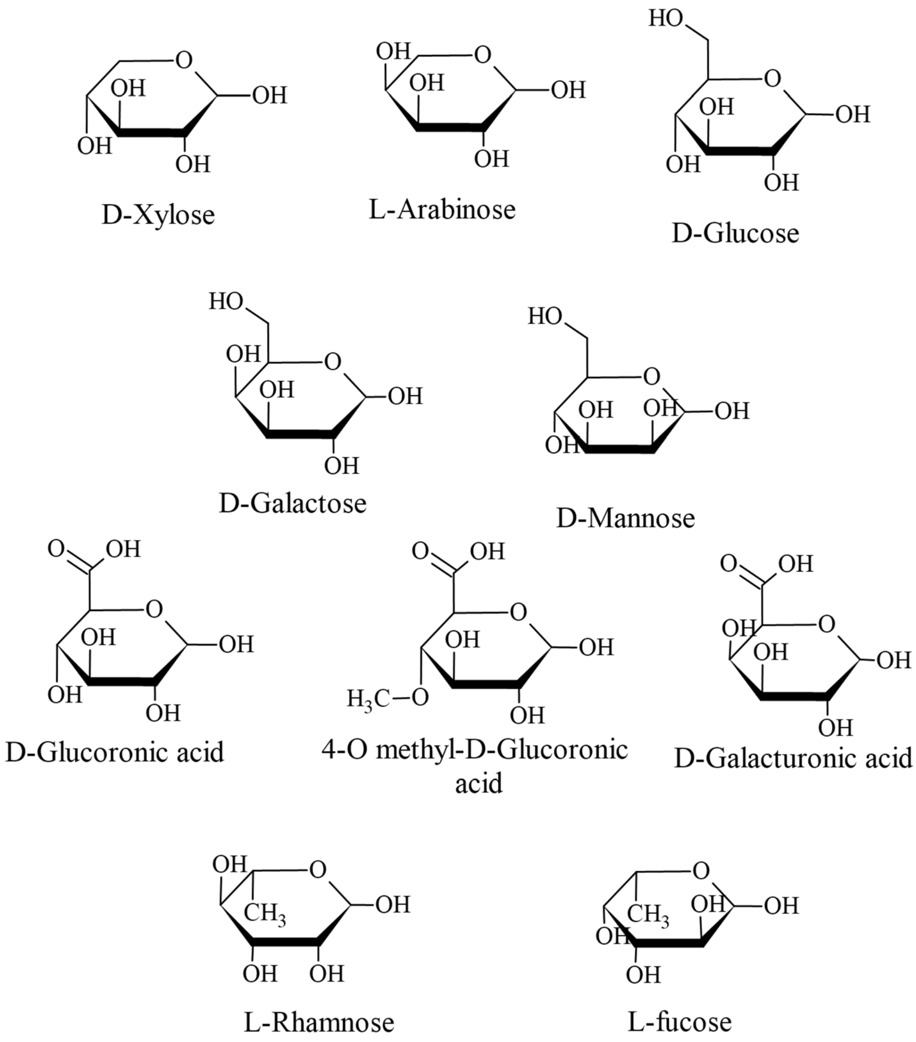

Figure 3 Most common monomers in hemicelluloses.

due to the initial hemicellulose content [55]. Structurally, similarly to cellulose, covalent C–C and C–O bonds are found among the hemicellulose structures. Due to the presence of OH groups along with its structure, hemicelluloses interact extensively with cellulose through hydrogen bonds [56]. Moreover, the connections with lignin are through covalent bonds and can also result in ester linkages in conjunction with acetyl units [51].

Specifically, the presence of hemicelluloses on CNF has been found to impede the agglomeration of the nanofibrils. This effect is partly electrostatic in nature, as many hemicelluloses possess negative charges, generating repulsion between them [57]. Conversely, the side chains present in some hemicelluloses contribute to steric repulsion between nanofibrils, thereby also reducing their tendency to aggregate [58, 59]. As a result of these interactions, the presence of hemicelluloses promotes pulp fibrillation [60–63] and colloidal stability of CNF suspensions [59].

In addition to cellulose and hemicelluloses, the second most abundant component in lignocellulosic materials is the polyphenol biopolymer: lignin (Fig. 4). It is a complex phenolic heteropolymer arising from the polymerization of three primary precursors; coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol [64]. Although the composition and content of lignin vary among the different lignocellulosic species, a general classification can be considered as (1) softwood species, 2:1 ratio of coniferyl alcohol: *p*-coumaryl alcohol; (2) hardwood species, 1:1 ratio of coniferyl alcohol: sinapyl alcohol, and (3) grass species, with a principal amount of *p*-coumaryl alcohol [65]. Furthermore, lignin structure will also be affected by the isolation method utilized, generating structural changes and cleavage of the native

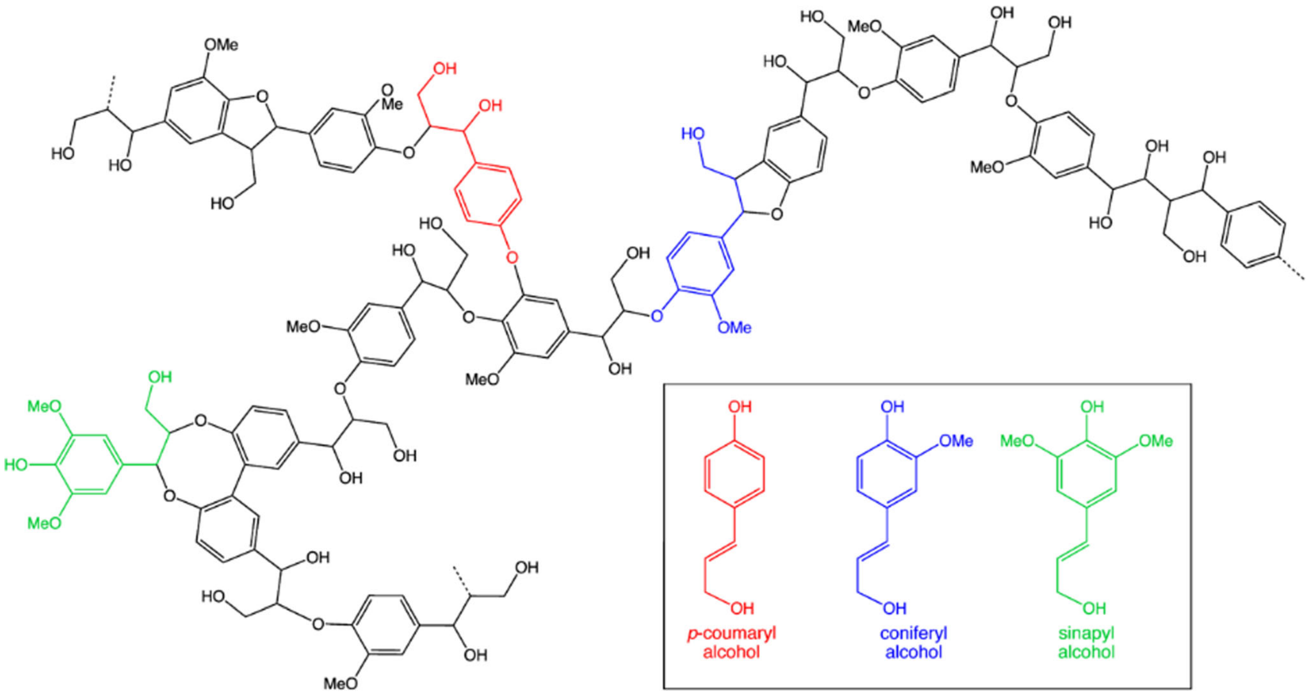

Figure 4 Proposed structure of lignin and its monomers. Image from Smokefoot, Creative Commons. Available from: http://commons.wikimedia.org/wiki/File:Lignin.png (accessed 09.06.2022).

lignin [64]. Due to the high variability of lignin, the number of functional groups will also vary; the specific functional groups on this natural polymer are methoxy, carbonyl, phenolic, and aliphatic hydroxyl groups [65].

Regarding the interactions between the above-described components present in lignocellulosic materials, the presence of OH groups allows them to interact through non-covalent links (hydrogen bonds). These interactions have been demonstrated to be essential for the structure of wood. For example, when cycles of wetting and drying were done and XRD was obtained to see the conformational changes in wood structure, it was found that this disruptions to the hydrogen bonding network resulted in the irreversible separation of the cellulose fibrils from the lignin and hemicelluloses matrix [66]. Meanwhile, it has been shown that lignin and hemicelluloses can be chemically linked through covalent bonds, forming lignin-carbohydrates complexes (LCC) [67].

In LCNFs, the dominant forces occurring on the cellulose surface containing lignin and hemicelluloses are electrostatic dipole–dipole interactions. Among them, covalent and hydrogen bonding can be considered the most important, with significant contributions from steric effects [68]. The presence of lignin, hemicelluloses, and pectin in soybean fibers, may reduce the accessibility of the three OH initially available on each AGU of the cellulose chain. However, due to the heterogeneity of the sample, other functional groups may have more predominance, such as carboxylic and phenolic hydroxyl groups from the different components.

Additionally, when considering the presence of lignin, this aromatic polymer can have two, seemingly contradictory, effects on pulp fibrillation, based on what kind of pulps are utilized as the starting material. On the one hand, it can hinder fibrillation, as has been demonstrated in the case of mechanical pulp [69]. On the other hand, residual lignin can even significantly lower the energy consumption of fibrillation in the case of chemical pulps [70] and serves as an example of how lignin structure affects its function. Moreover, the presence of residual lignin in chemical pulps has been reported to result in the formation of finer CNFs at comparable energy consumption levels [71, 72].

Assuming a complex, network-like structure for native lignin, it seems probable that the initial crosslinked structure prevents efficient fibrillation of the highest lignin pulp grades by “locking” the individual microfibrils together [73]. The hydrophobic character of lignin may also play an important role in preventing fiber swelling and fibrillation, as will be discussed in the next section. The residual lignin present in chemical pulps is significantly degrade and present in much lower quantities. Therefore it is less able to prevent fiber swelling and fibrillation. We have previously proposed [71, 74] that the ease of fibrillation observed in lignin-containing chemical pulps is due to lignin acting as an antioxidant, preventing broken covalent bonds from being formed again.

Likewise, when studying agricultural by-products as possible sources for bio-based materials, it is crucial to consider all the components those raw materials may have. For example, in the case of soybean hulls, pectin could be an additional component in the CNF fibers. Soybean contains 40% proteins, 21% oils, 34% carbohydrates, and 4% of ash [75]. Pectin is present mainly on the primary cell wall of plants, belonging to the polysaccharides family, forming branch and linear structures [76]. Pectins are composed of up to 69% D-galacturonic acid, covalently linked [77]. Among the different types of pectin, the most abundant is homogalacturonan (HG). This is a linear homopolymer, composed of (1→4)-α-linkage. The main functionalities present in HG are carboxyl, acetyl, and OH groups [78]. Overall, the presence of residual pectin in CNFs has shown to increase zeta potential, and therefore of its dispersion stability and even solubility once dried [79, 80]. This is most likely resulting from the carboxyl groups that the pectin present, as well as some steric hindrance once the deposition of them onto the CNF surface is done during the isolation process [79].

As mentioned in the previous section, hemp is another example of an agricultural by-product that besides cellulose, hemicelluloses, lignin, and pectin, contains a high percentage of extractives. In fact, extractives are present in multiple native fibers and they vary depending on the plant source. An important characteristic of these compounds is their low molecular weight [81]. Extractive compounds can be classified as fatty acids, fatty alcohols, waxes, and phenolic constituents [43]. Most of these compounds are removed after the pulping process [81]. However, in species such as southern pines with relatively high extractive content, by-products such as raw tall oil and turpentine can remain on the sample [82]. Information regarding on the effect on extractive containing CNF properties is lacking; however, CNFs have been used to carry oils and other hydrophobic compounds to enhance packaging applications and slow release [83, 84], suggesting good interactions and the capability of further hydrophobization of the fibers for targeted applications. Similarly, CNMs have been used in conjunction with oils for emulsification, mostly for the presence of the hydrophobic face on the structures [85].

Macroscopic arrangement of lignocellulosic fibers

As shown in Fig. 5, the glucose sugar monomers can be arranged in a rigid linear chain to give rise to the cellulose chain [86] which due to the presence of hydroxyl groups and van der Waals forces can interconnect in a parallel arrangement, establishing elementary fibrils (1.5–3.5 nm in diameter). Additionally, the aggregation of elementary fibrils gives rise to nanofibrils (10–30 nm in diameter), and a subsequent combination of them can form microfibrillar bands (diameters in the order of 100 nm). The combination of these polysaccharides is the main structural components of the cell walls of plants and can be further arranged in a fibril-matrix-like

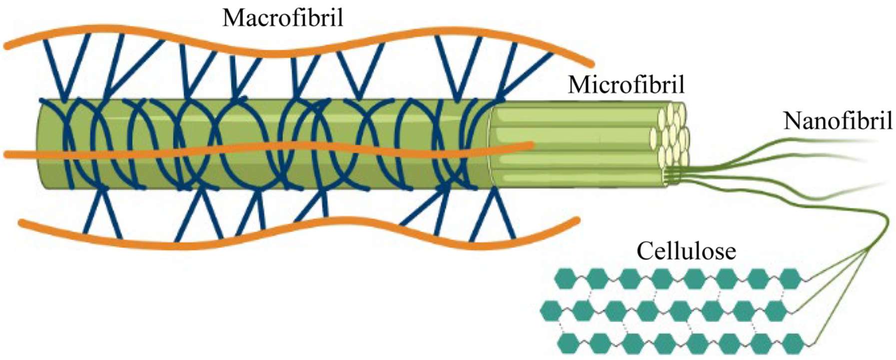

Figure 5 Scheme of the hierarchical structure of cellulose.

structure mixed with other components such as hemicelluloses, pectin, and lignin [41].

Decoupling those fibrillar structures in solution can lead to the obtention of materials in the nanometric dimensions, known as nanocellulose suspensions, which can be utilized for high-novel applications [87]. Due to the reduction in size compared to cellulose fibers, nanocellulose suspensions are the combination of cellulose nanoparticles with enhanced surface area and, as a result, higher hydrogen bonding capability surrounded by water molecules, which confers greater stability to the suspension. Such suspensions mostly behave as what are commonly known as colloids. The importance of understanding the interfacial interaction between colloids relays in the fact that if the colloidal particles are sufficiently close, they will exert forces that will determine the capacity to form flocs or aggregates, the rate of the formation of the aggregates, and the final characteristics of the formed structures [88].

Isolation of nanocellulosic materials and its effect in CNF chemistry

During the early 1980s, Turbak et al. [89] and Herrick et al. [90] were the first to introduce the nanocelluloses commonly known at that time as microfibrillated cellulose (MFC). Utilizing cellulose pulp suspensions at a very low solid content (typically ~ 2 wt%) as starting material, and homogenizing this suspension under pressure, they discovered that after intensive mechanical disintegration they were able to obtain a colloidal-like fibrous suspension with particles in the microscale. Despite the efforts to produce MFC, the process was energy-consuming, which was why interest was lost in this material. Several years after, different types of mechanical treatments, including homogenization [70, 91, 92], grinding [70, 93, 94], ultrasonication [95–97], and cryocrushing [98, 99] together with pre-treatments such as carboxymethylation [100, 101], TEMPO (2,2,6,6-tetramethylpiperidine-1-yl)oxyl radical)-mediated oxidation [102–104], ammonium persulfate oxidation [105], and enzymatic pre-treatments [106, 107] were developed to address this problem while producing these suspensions. The new technology and pre-treatments allowed scientists to obtain what we know today as cellulose nanofibrils (CNFs), meaning that one of the fibers dimensions was in the range of the nanometers while consuming less energy for its production compared to the initial processing techniques. An example of an image of CNF obtained from softwood by atomic force microscopy (AFM) is presented in Fig. 6.

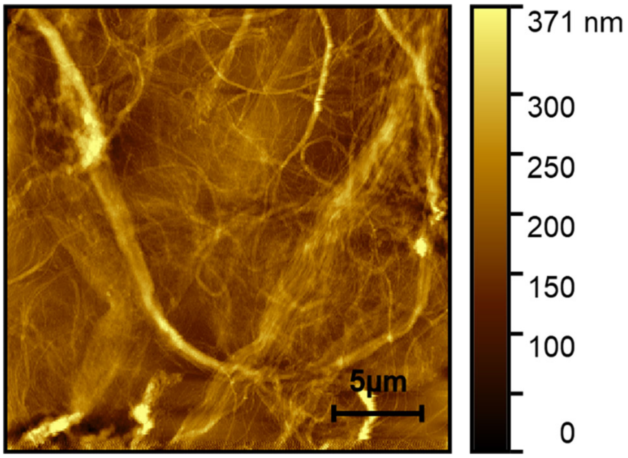

Figure 6 AFM image of softwood cellulose nanofibril.

Conversely, the pre-treatments selection will also add functional groups to the surface of the CNF by side reactions between the hydroxyl groups and the reagents used [22, 108, 109]. These new functional groups will also affect the interfacial interactions possible between the CNF and other systems. For example, both TEMPO-mediated oxidized cellulose and carboxymethyl cellulose will have more negative charge than unmodified cellulose fibrils, as carboxyl groups will be present on the surfaces. However, carboxymethyl cellulose has an intermediate ether group which increases the side chain length, and with this, steric effects will also sum in the interactions generated with fibrils containing this functional group when compared with only carboxylated cellulose. Similarly, carboxylated-modified CNF with different linkers can be obtained through pre-treatments with anhydrides such as maleic, succinic, or phthalic [110] prior to its mechanical fibrillation; or by only chemical treatments with diluted acids [111, 112].

Nanocellulose fibers as colloidal particles

Cellulose nanomaterial suspensions are a gel-like material. These lignocellulosic suspensions converge properties of fiber suspension where the microstructure determine many of the properties [113], polyelectrolyte suspensions where surface charges dictate most of the behavior [114], and colloidal suspensions where the particles are in the nanometer scale and thus prone to significant interactions and surface phenomena. As colloidal science can explain most of the phenomena and properties found in nanocellulose fiber suspensions, this work will further examine the properties and applications of CNF suspensions within this framework.

Colloidal science's history can be traced back to the mid-eighteenth century when Francesco Selmi described the mixture of solid particles—such as silver chloride, sulfur, Prussian blue, starch, and alumina—in water as "pseudo-solutions." It was later in 1861 when Thomas Graham defined these pseudo-solutions as colloids (which means glue in Greek) [115]. However, there is a lot of controversy when defining what a colloid is. As a general definition, colloids are dispersions where small solid particles (solute) are embedded in a continuous liquid media (solvent) [116]. But the question now would be: What is small enough to be considered in the group of colloids? During Graham times, he deduced that colloidal particles should have dimensions between 1 and 1 µm in diameter [115]. Nevertheless, over the years, various solutions with larger sizes such as clays, sprays, emulsions, and fiber suspensions such as nanocellulose have been studied, showing similar characteristics to the traditionally named colloids [117, 118]. The properties of colloidal suspensions are determined by the properties of the solid particles, the media, and the interface between them [118], a representation of this can be seen in Fig. 7. Thus, understanding the fundamental behavior and interactions of CNFs in water systems could help to come to a better conclusion and give an insight on how better use the suspensions for the development of different applications.

Interfacial interactions in nanofibrillated cellulosic systems

As mentioned earlier, CNF suspensions are obtained mainly by mechanical treatments of chemical isolated cellulose pulps and the extraction process of the cellulose pulp from which the nanomaterial would be obtained will also modify the available groups in the surface. When producing cellulose fibers by traditional pulping methods, such as Kraft of sulfite, fibers acquire a negative charge on the surface due to the formation of carboxylic, carbonyl, and sulfate groups, among others [22]. Consequently, CNF suspensions will have a substantially anionic surface charge [119]. Other providers of surface charge on cellulose nanomateriala are the residual hemicelluloses and lignin that also have carboxyl groups that are exposed in this interfacial volume [120]. As a result of this charge, there will be several interactions present in a CNF suspension.

The interactions experienced by materials depend on their surroundings, typically the bulk and the surface interact differently due to compensating energy values. Thus, defining the macroscopic region where two materials interact is relevant when discussing interfacial phenomena. This thin region that ranges from a few Angstroms to a few nanometers is commonly known as the interface. It can be applied

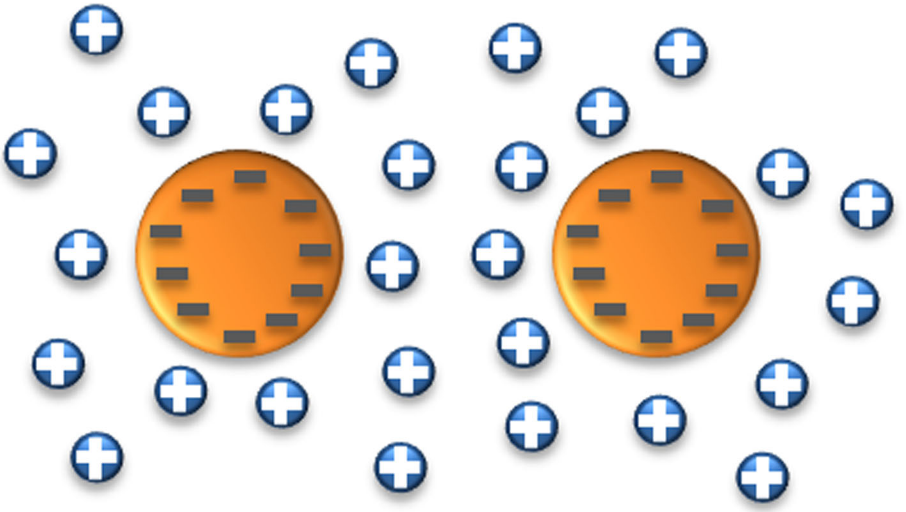

Figure 7 Representation of a charged colloidal particle interacting with the polar solvent.

to any surface boundary, such as liquid–gas, liquid–liquid, solid–liquid, gas–solid, and solid–solid [118]. Specifically, in a nanocellulosic suspension, the solid–liquid interface properties will be tightly related to the chemical composition of the raw material and the interactions between them (physicochemical properties), conferring different performances [115]. The main characteristic of this thin layer is that it is inhomogeneous compared with the bulk material [118]. Different long- and short-range interactions can occur at the interfaces when solid particles are dispersed in a liquid media. Some of them are solvation and hydration forces due to the surface swelling or the arrangement of the solvent molecules at the interface, hydrophobic forces due to the interaction between hydrophobic components in water, steric repulsion forces generated by osmotic and entropic effects, and electrostatic and double layer forces due to the ionization of surface groups, charged surfaces, and ion adsorption [121]. These interactions are usually categorized as interactions following the DLVO theory and non-DLVO interactions.

DLVO interaction forces

At a fundamental level, the most important interactions between charged particles are (i) van der Waals forces and (ii) electrostatic repulsions [122]. Van der Waals forces are dispersions forces generated by the fluctuation of the electronic clouds of the atoms. When two similar particles get close enough, attractive interactions occur between them, which will depend on the characteristics of the material and the medium [68]. Moreover, due to the presence of charge on the surface of the fibers in an aqueous solution, electrostatic repulsion interactions are also present [122]. Ions present on the solution carrying opposed charge to that of the colloids form an electrical double layer. These two different interactions in a colloidal suspension give rise to the DLVO potential between them (named after Boris Derjaguin and Lev Landau, Evert Verwey, and Theodoor Overbeek) (Fig. 8). As two particles get closer, there is an energy barrier that the particles must overcome to get in contact. If the energy of the interaction is not enough to overcome the energy barrier, the particles will not agglomerate, and they will form stable colloidal suspensions. On the contrary, if the energy is high enough to overcome the energy barrier, the particles will fall in the primary minimum dominated by van der Waals attraction and collapse, forming aggregates [68].

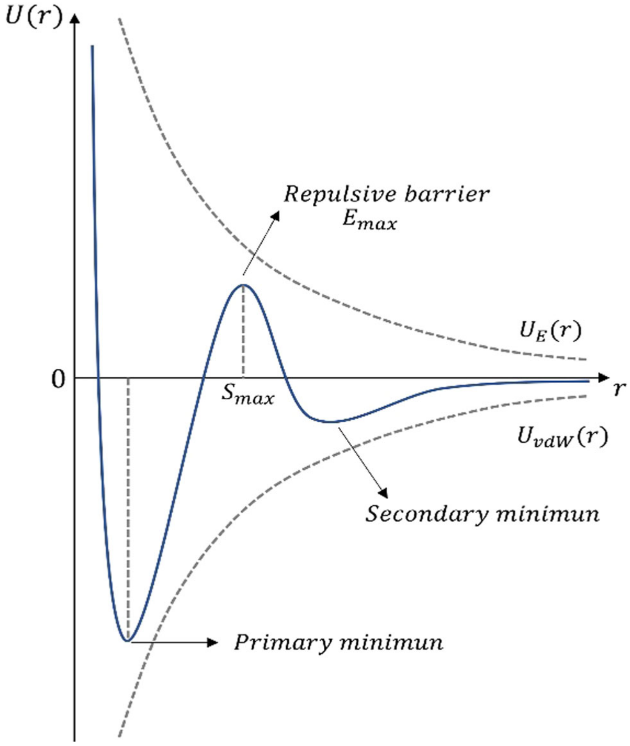

Figure 8 The presence of van der Waals attraction interactions together with electrostatic repulsive interactions leads to the DLVO potential interaction.

This electrostatically driven behavior is of particular interest as ions and other charged solutes can be present in the water media. Association constants and coordinated complexes of polarized molecules and metallic ions, as well as localized acid environments formed in the interfaces, will also impact the behavior of the suspension even as the bulk of the colloid behave more continuously [123]. The effects on the suspensions from the acid environments and pH could be either kosmotropic or chaotropic, depending on the conditions [124]. Furthermore, these localized environments, where the barrier energy is surpassed, are one of the principles for the self-assembly of gel networks with nanofibrillated cellulose [123]. Furthermore, the DLVO potential on the surface will impact the water retention, swelling, and stability of CNF suspensions. The interactions between water and ions with the CNF will generate a mixing and ion pressure on the suspension, respectively [125]. The ions present in the suspension can screen the charges on the surface of CNF—especially when higher concentrations than CNF are used, facilitating the interaction with other components of the suspension, such as water and small molecules. This impact will then depend on their kinetic constant, usually resulting in more water retained on the network [125, 126] or in the formation of hydrogen bonding between different adjacent elements, such as the molecules or other nanofibrils when water layers are depleted [127].

Non-DLVO interaction forces

In a nanocellulosic system, not only DLVO forces regarding van der Waals and repulsion forces are present (Fig. 9). There is a group of interactions linked more to the thermodynamic equilibrium of the suspension system, which is commonly known as the non-DLVO forces. When these interactions arise, they will impact how the particles present in the CNF suspensions behave between them [118].

Hydrophobic interactions are significant long-range attractive effects on nanocellulosic suspensions. They appear when hydrophobic molecules/particles approach since they are not able to bond with water molecules. The contact between water and these hydrophobic portions is entropically unfavorable [118]. As a result, the water molecules are ejected, and the hydrophobic molecules attract each other, reducing the energy of the system [119]. Lignin contained in LCNF also generates hydrophobic points in their phenolic structures. Due to the double bonds in the rings, the electronic clouds are contained in the interior of the structure, leaving the protons on the exterior tightly bound to the carbon and making difficult the formation of hydrogen bonding with water [68]. Thus, lignin tends to attract hydrophobic molecules to lower the exposed surface.

Another type of non-DLVO force is steric force, which originated mostly when large polymer structures are present in the suspension. When polymers tails from different surfaces get in contact, two effects arise in the system; (i) when mingling of the fibers, there is an increase in the osmotic pressure of the system due to the difference in concentration solute/solvent, and (ii) there is a loss on the freedom of the polymers chains to move, this reduction on movement decreases the entropy and as a result

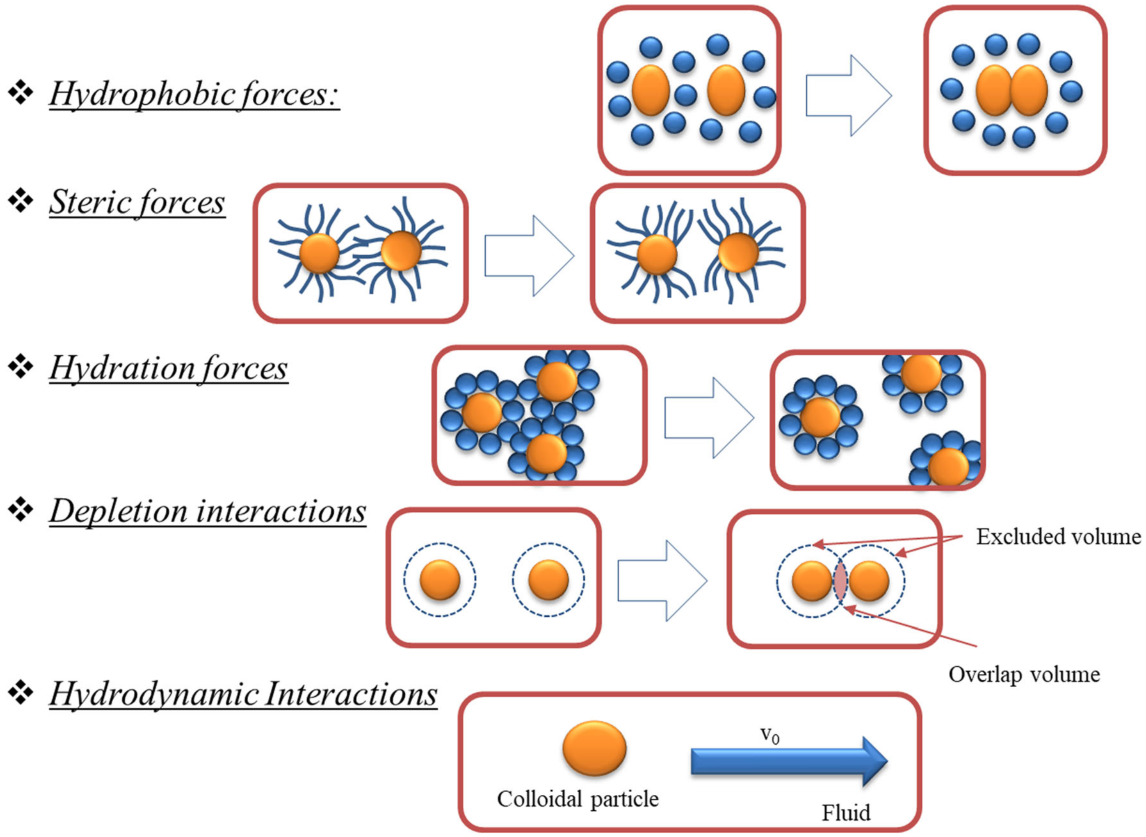

Figure 9 Schematic of the most relevant non-DLVO interactions in colloidal systems.

increases the free energy of the system, which is thermodynamically less stable. As a result, a repulsion force is generated on the system to reduce the free energy and return to the most stable position [116, 122].

Hydration forces also contribute to the non-DLVO forces. They are considered short-range structural repulsive forces. They appear due to the movement of the particles getting closer to one another. As a result, the structure and orientation of the water molecules are affected [128], generating a repulsion between the particles. Nevertheless, it has been reported that in cellulosic systems, these forces are not observable since the steric repulsion between the fibers overcomes this effect [119].

An additional type of interaction is the so-called depletion interaction. In the case of nanocellulosic systems, they can appear when the surfaces of the fibers are fully saturated with water. When two particles with depletion layers come closer enough, the polymer is excluded generating osmotic pressure, as a result leading to flocculation of the particles [118]. Finally, hydrodynamic forces are also present in cellulosic systems due to the flow of the water molecules surrounding the fibers, affecting the dynamics of the solution [116].

Relevant suspension properties

Other essential properties to describe in nanocellulosic suspensions are charge density, zeta potential, and surface free energy. Surface charge density is related to surface charge coming from functional groups on the surface of the fibers from lignin, hemicelluloses, or in the case of soybean CNF from residual pectins. The most common groups that contribute to the surface charge density are carboxyl and carboxymethyl [104, 106]. Zeta potential is related to the surface potential and surface charge of the sample and is a valuable measurement to indicate the colloidal stability of the sample [129]. The zeta potential is a result of the screening of the surface charge with a tightly bound layer of ions or water that in turn will interact with and structure water layers, contributing to the hydration and depletion forces present in the suspension and determining then the colloidal stability.

Finally, the surface free energy of a material is an important parameter that can provide information about its compatibility with other species. This can be estimated as the sum of the dispersive intermolecular forces, the polar interactions, and the hydrophobic attractions [68], as well as the wettability of the surface [130]. Knowing the surface free energy on a solid surface can help to predict (i) its behavior when interacting with liquids, including water, and (ii) the energy required to propitiate the intermolecular and interatomic interactions with other surfaces, phenomena also known as adhesion [131]. It has been reported in the literature that LCNF films possess a lower surface free energy than their bleached counterpart [72]. This can be related to the presence of lignin which has a more hydrophobic behavior, reducing, as a result, the interactions with water.

Viscoelastic properties

When characterizing colloidal suspensions made from bleached and unbleached cellulose nanofibrils, it is essential to consider all the information detailed above about the chemistry of the different natural components. Additionally, if the system is not in equilibrium, which is usually the case, and external forces are applied, hydrodynamic interactions will need to be considered. Hydrodynamic forces start playing a role when the solvent where the solid particles are embedded flows. Then, considering these external forces, the intrinsic dynamics of the particles will change. For distant particles, the expression to calculate the force of the particle proposed by George Stokes is relatively simple [68]. However, for more concentrated samples, the interactions between particles cannot be neglected. This being said, if the objective is to study the rheological behavior of the cellulose nanofibrils suspensions, with entangled structures and with varying chemical composition, then the rheological analysis becomes more complicated due to the shape, flexibility, size polydispersity, transient physical entanglements, and physicochemical interactions.

It has been extensively reported in the literature that nanocellulosic suspensions at different concentrations present shear-thinning behavior [107, 132]. Additionally, rheological studies of lignin-containing cellulose nanofibrils with varying chemical compositions show the same trend [50]. Due to the anisotropy of the particles in nanocellulosic suspensions, this behavior in which the viscosity of the sample decreases as the velocity of the deformation increases is expected [118]. During this process, the velocity gradients break down the flocks between the fibrils, allowing their alignment and movement [118]. However, when lignin is present on the surface of the particles in suspension, covalent linkages between lignin and hemicelluloses [133], and hydrogen bond interactions with the cellulose chain could be the reason why the viscosity of the LCNF samples is always higher than their bleached counterpart at low shear rates. Furthermore, the same rheological behavior was found for bleached and unbleached samples from soybean fibers [134]. Moreover, the unbleached CNF from soybeans has a yield stress, which can be due to the gel formation or flocculation. Thus, the presence of pectins from soybean could be responsible for this behavior due to the gelling properties of pectins [76]. In summary, as detailed in the previous sections, there are several different interactions present in nanocellulosic particles and systems, which will result in the properties of the suspensions. The surface groups will contribute to the surface free energy, but other factors such as position, surface structure, atomic neighbors, and even shape would also be important to determine it. Thus, understanding all the properties of the nanocellulosic system will contribute to gaining a better insight into the interactions with other materials when utilizing nanocellulosic suspensions for different applications.

Examples of applications and the influence of interfacial interactions

As explained throughout this text, nanocellulose suspensions over a wide concentration range possess a gel-like structure and are the combination of cellulose nanoparticles with enhanced hydrogen bonding capability surrounded by and entrapping water molecules which confer stability to the colloidal suspension. Due to this property, CNFs have been demonstrated to have an excellent potential for being incorporated in formulations for thickeners and emulsifiers for food, cosmetics, and paints [90, 135, 136]. Furthermore, CNFs possess a high aspect ratio, low density and thermal expansion, high-strength modulus and stiffness [137–139], as well as remarkable film-formability when dried [140]. These properties that make them attractive in terms of producing high-strength composites and barrier materials from renewable resources. Hence, the following sections aim to relate the interactions present on these suspensions and their use in some applications.

Interfacial interactions between CNF systems and wood adhesives

Over the years, urea–formaldehyde (UF) has been positioned as one of the most utilized wood binders in the wood panel industry [141]. Based on the literature trends, during the last decade, we observed an increased interest in research replacing wood-based adhesives to a certain extent for more renewable alternatives, such as nanocellulose [142, 143]. The idea of replacing petroleum-based adhesives and improving the mechanical and dimensional stability of the wood panels with a natural filler has been the driver for such growing interest.

UF is a thermosetting amino resin characterized for being water-soluble, with good adhesion properties, highly curing rates, and relatively low cost [144]. It is synthesized from two components: urea and formaldehyde. The structure of this resin is highly changeable due to the variety of reactions that can occur during the obtention process. UF is formed by a mixture of linear and branch macromolecules [145] containing different functional groups, most predominantly carboxyl and amine groups [144]. Additionally, as UF is produced in an aqueous formaldehyde solution, these resins are soluble in water. Among the interactions at a molecular level, they are mainly covalent bonds and van der Waals interactions.

When utilizing bleached and unbleached CNF as a replacement of UF in particle boards, interfacial interactions occur between them. Compared with the fully bleached CNF samples, it is expected an additional surface charge on the fibers due to the presence of lignin, hemicelluloses, and even pectin (in the case of soybean CNF), improving the interactions of these materials with the UF [146]. These components will interact through non-covalent links (hydrogen bonds). Additionally, steric repulsion can occur, increasing the osmotic pressure of the system.

The incorporation of LCNF to the UF resins can decrease its surface free energy due to the hydrophobic behavior of this natural polymer. Due to the chemistry on the surface of both components, lignin could adhere to the surface of the adhesive, repelling the adhesion of water molecules, thus, reducing the wettability of the surface [68, 146]. To measure these characteristics, contact angle, in particular the sessile drop method, can be used. A contact angle lower than 90°, indicates the surface has hydrophilic properties. If oppositely, the contact angle is>90°, then the surface is hydrophobic [118].

As mentioned before, UF has been widely used in the wood adhesive industry due to the advantages it presents for industrial applications [147]. Nevertheless, the release of aldehydes and formaldehyde from products such as particle board, medium density fiberboard (MDF), and oriented strand board (OSB) panels during the pressing of the products, and over time, is what increased the necessity of its modification and/or replacement with more environmentally friendly alternatives [148, 149]. Based on these issues, isocyanate wood binders were introduced to the German market in the early 1970s [150]. More specific, the use of MDI (4,4′-methylenediphenyl isocyanate) with a variety of functionalities, reactivity, and different structures [151] made this polymer a suitable alternative for the forest products market.

PMDI is an aromatic polymer containing two isocyanate groups per monomer. The reactivity of this polymer is highly variable due to the diversity of the isocyanate groups. These functional groups reactivity will vary depending on their substitution [151]. The aromatic structure on this adhesive confers rigidity as well as more hydrophobic characteristics. Isocyanates groups are highly reactive in contact with hydroxyl groups, forming polyurethanes and releasing CO_2 as consequence [151]. Due to the available OH groups in the structure, LCNF could be a better option to interact with PMDI than bleached CNF [152].

Solubilization and regeneration of cellulosic systems

Another example of the impact of the interactions of the media with the material can have on the properties is the solubilization of cellulose in sodium-urea solutions. Cellulose is insoluble in water due to the high crystallinity of the formed fibers, which contain a high density of hydrogen bonding generating stronger interaction between the molecule chains than the interactions that could be formed with water [153]. However, if these bonds are broken, solubilization of cellulose could be possible. To achieve this, one can make use of ions such as sodium, which has a high enough electro-attractive force (ion–dipole) that the surface hydroxyl groups release the bound proton and interact with it, breaking some of the H-bonds formed [154]. However, solvation (the complete surrounding of water to the molecule to become a solvate) is still not possible as other type of interactions are still present, such as hydrophobic interactions on the surface. To eliminate this, urea is able to attach to this plane on the crystals while also interacting with the water, allowing the dissolution [155–158]. The high concentration of the sodium and urea also come with an alkaline pH, so when the solution is dropped into an acid bath, the solubility of the cellulose drops, regenerating its crystalline structure and forming 3-D compacted bead hydrogels [159]. However, the resulting new structure will be cellulose II, as hydrogen bonding arrangement will be most beneficial here [160]. Here, the interactions not only affect the solubility, but the surface and crystalline structure is modified. An important factor to address is concerning the interactions between cellulose in solution and atmospheric CO_2, which has demonstrated chemisorption to C6 on the cellulose surface resulting in carbonate ions, decreasing pH and forming microenvironments that could induce gelation [161]. Moreover, urea in solution has also shown carbon capturing properties, with the associated carbonate reversible formation [162]. Both phenomena have been linked to the formation of highly porous structures upon regeneration in acid media [163], making them ideal for high surface hydrogels that can be used for pollutant capturing [164, 165] or immobilization of other active macromolecules [166–168].

Likewise, composite materials have been generated from dissolved cellulose without the formation of covalent bonds. As mentioned before, the hydroxyl groups of cellulose are exposed in the equatorial axis [169], which makes the surface rich in hydroxyl groups. These groups can be used to form strong and seemly irreversible hydrogen bonding with other β-lineal polysaccharides such as chitosan or alginate [166, 170], which would add functionality to the surface, and therefore surface energy, as the available groups of these new polymers would be exposed in the new generated surface without further processing [164]. Here the surface energy is decreased by the intermediate state where salts form an intermediate species where they displace the present hydrogen before being displaced by the new polymer, enhancing the density of hydrogen bond interactions, and irreversibly adsorbing onto the surface.

Conclusions

As a summary, when utilizing different raw materials to produce and apply nanocellulose suspensions into products, two main characteristics need to be considered to understand the interfacial interactions; (1) all the different chemical components of the selected raw material and (2) the utilized treatments to obtain the colloidal suspension (chemical, mechanical, and/or enzymatical), which will confer different properties to the fibers. Understanding of the atomic and molecular interactions will help to take full advantage of the wood, soybean, and hemp derivates, particularly the cellulose nanomaterials.

Despite origin and processing, CNF suspensions will display an active surface predominantly guided by DLVO forces like van der Waals and electrostatic interactions, as well as non-DLVO forces such as hydrophobic and hydration effects. The ions present in the solvent will also strongly interact with the CNF, forming microenvironments with pH effects that can result in CO_2 capturing, kosmo- and chaotropic changes, or gelation. Thus, understanding the solvent composition is important factor to consider in the processing. Likewise, macroscopic properties like concentration, particle size, shape, and entanglement, among others, will also impact the viscoelastic and colloidal properties. The sum of these properties and a holistic understanding are necessary for the design of new and sustainable products for multiple applications. Overall, enhancing the use of the forest, and increasing its potential value for the USA and other countries with abundant forestry and agricultural industries, will provide a more environmentally friendly alternative to displace many fossil-based polymer applications.

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Declarations

Conflict of interest The authors declare no conflicts of interest.

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