
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Solala, Iina; Iglesias, Maria Celeste; Peresin, Maria Soledad

On the potential of lignin-containing cellulose nanofibrils (LCNFs): a review on properties and applications

Published in:
Cellulose

DOI:
[10.1007/s10570-019-02899-8](https://doi.org/10.1007/s10570-019-02899-8)

Published: 06/12/2019

Document Version
Peer reviewed version

Published under the following license:
Unspecified

Please cite the original version:
Solala, I., Iglesias, M. C., & Peresin, M. S. (2019). On the potential of lignin-containing cellulose nanofibrils (LCNFs): a review on properties and applications. *Cellulose*. <https://doi.org/10.1007/s10570-019-02899-8>

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

1 **On the potential of lignin-containing cellulose nanofibrils (LCNFs): a review on**
2 **properties and applications**

3 Iina Solala^a, Maria Celeste Iglesias^b and Maria Soledad Peresin^{*b}

4 ^aDepartment of Bioproducts and Biosystems, Aalto University School of Chemical
5 Engineering, Vuorimiehentie 1, 02150 Espoo, Finland.

6 ^bForest Products Development Center, School of Forestry and Wildlife Sciences, Auburn
7 University, 520 Devall Dr. Auburn, AL 36832, Auburn, Alabama, United States.

8 Email address: soledad.peresin@auburn.edu

9

10 **Acknowledgements**

11 This publication was supported by the Alabama Agricultural Experiment Station, and the Hatch
12 program of the National Institute of Food and Agriculture, United States Department of
13 Agriculture. Aalto University and the School of Forestry and Wildlife Sciences at Auburn
14 University financial support to complete this work is greatly appreciated.

15

16 **Abstract:**

17 This review outlines the present state and recent progress in the area of lignin-containing cellulose
18 nanofibrils (LCNFs), an emerging family of green cellulose nanomaterials. Different types of
19 LCNF raw materials are described, with main focus on wood-based raw materials, and the
20 properties of the resulting LCNFs are compared. Common problems faced in industrial utilization
21 of CNFs are discussed in the light of potential improvements from LCNFs, covering areas such as
22 chemical and energy consumption, dewatering and redispersibility. Out of the potential
23 applications, barrier films, emulsions and nanocomposites are considered.

24 Keywords: *lignin-containing nanocellulose, lignin, cellulose nanofibrils, nanofibrillated cellulose*

25 **Introduction**

26 During the last decades, the exponential growth of technology has allowed manipulating materials
27 at scales lower than 100 nm. At this scale, fundamental material properties show different
28 behaviors than those corresponding to the macroscale (Kamel 2007). Simultaneously, the
29 utilization of bio-based products, mainly cellulose, to replace petroleum-based materials has
30 generated an enormous impact, which can be directly seen on the increasing body of research on
31 cellulosic nanomaterials, or nanocellulose, over the years. As is the case with other nanomaterials,
32 also for nanocellulose, the interfacial interactions and chemical composition play a vital role in the
33 properties of the material and on their interactions with other components (Ratner et al. 2013).

34 Nanocellulose can be obtained from different raw materials utilizing diverse approaches. The two
35 most common man-made types are cellulose nanocrystals (CNCs) – produced by acid hydrolysis
36 – and cellulose nanofibrils (CNFs) – produced by mechanical disintegration of the respective
37 lignocellulosic fibers. Since the production methods are different, the properties of the fibers, as
38 well as their final application, will vary among these nanoparticles (Klemm et al. 2011; Moon et
39 al. 2011; Lavoine et al. 2012). In this review, we focus on CNFs.

40 Over time, research on CNFs has generally centered on using fully bleached cellulose nanofibrils
41 (BCNFs). Nevertheless, during the last years, efforts have been made to incorporate lignin-
42 containing cellulose nanofibrils (LCNFs) in different applications, like additives in papermaking
43 (Delgado-Aguilar et al. 2016); neat and composite LCNF films (Rojo et al. 2015; Horseman et al.

44 2017); or fillers and reinforcing agents in different matrices (Sun et al. 2014; Wang et al. 2014;
45 Ago et al. 2016; Ballner et al. 2016; Ferrer et al. 2016; Herzele et al. 2016; Visanko et al. 2017a).
46 This review aims to provide a complete overview of the current state of LCNF research; mainly
47 focused on the effect of chemical composition on their processing, properties, and applications.
48 The chemistry involved in pulping and bleaching processes is considered in an attempt to elucidate
49 their impact on the final nanocellulose properties. Additionally, the role of lignin and
50 hemicelluloses in LCNF fibers is carefully described. Finally, a summary of applications such as
51 barrier films, emulsions, and nanocomposites is presented.

52 *Structure and chemistry of wood-based biomass*

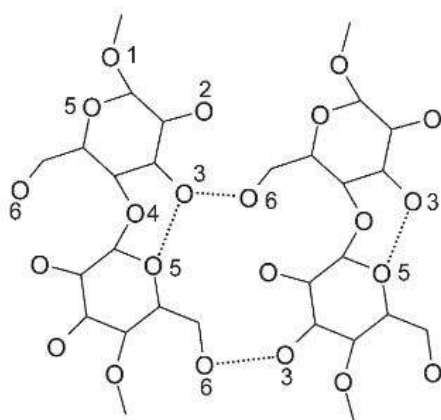
53 **In native state.** Wood forms a major part of the plant-based biomass in the world. Structurally,
54 wood can be described as a complex three-dimensional nanocomposite, composed of aligned
55 cellulose microfibrils that are embedded in a matrix of lignin and heteropolysaccharides (mainly
56 hemicelluloses). As a simplification, cellulose microfibrils act as the major load-bearing
57 component in wood, whereas the role of the surrounding matrix is to transfer mechanical stress
58 across the structure, to control the content of water in the wood tissue and to protect the tree against
59 pathogens and insects (Higuchi 1985; Hatfield and Vermerris 2001).

60 Despite ongoing controversies on the exact structure and composition of the native plant cell wall
61 (Keegstra 2010; Crestini et al. 2011; Agarwal et al. 2016), it is commonly accepted that the average
62 cellulose microfibril angle is different at different cell wall layers (primary, secondary and tertiary
63 cell wall layers) and that these microfibrils consist of alternating crystalline and less ordered
64 domains. Cellulose microfibrils are surrounded by a crosslinked lignin matrix (Fengel and
65 Wegener 1984; Kilpeläinen et al. 2007) that is covalently bound to surrounding carbohydrates
66 (Minor 1986; Tenkanen et al. 1999; Lawoko et al. 2005) in the form of the so-called lignin-
67 carbohydrate complexes (LCC). For the purpose of this review, it suffices to say that wood species
68 are generally divided into softwoods (SW) and hardwoods (HW) that have differences both in
69 structural complexity and chemical composition; the latter been summarized in Table 1.

70 **Table 1** Chemical compositions of softwood and hardwood as weight percentages of dry wood.
71 Adapted from Sjöström and Westermarck (1999) with permission of Springer Nature.

Wood type	Cellulose	Hemicelluloses	Lignin	Extractives
Softwood	37-43	20-30	25-33	2-5
Hardwood	39-45	17-35	20-25	2-4

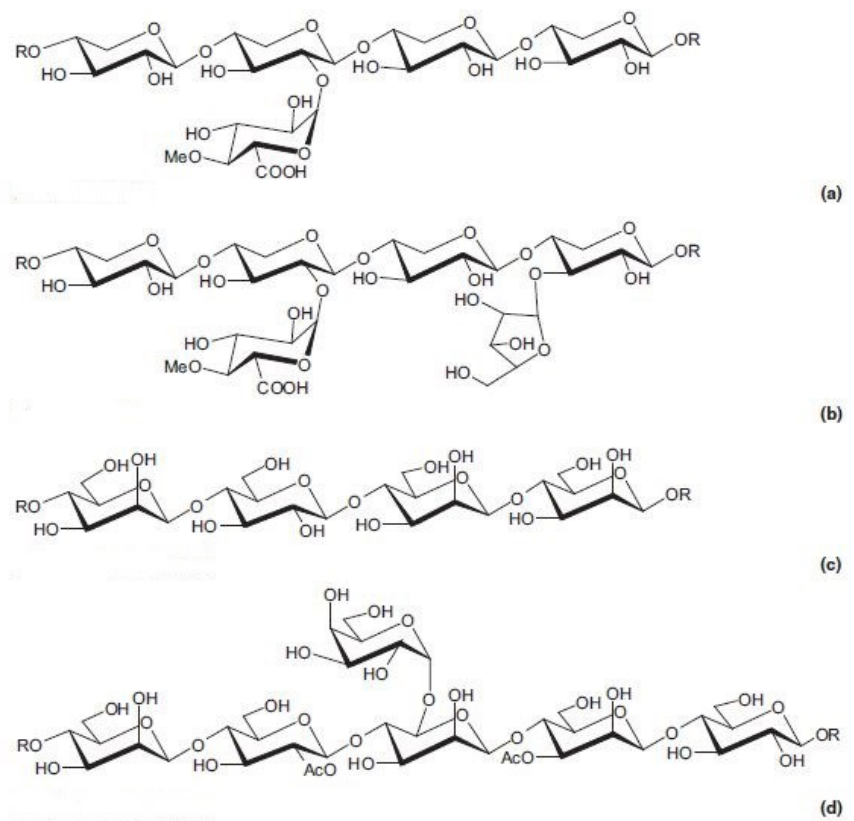
72 Cellulose is the main component in wood tissue (~40% of dry weight). It is a semicrystalline, linear
73 homopolymer that consists of thousands of anhydro-D-glucopyranosyl units linked by β -(1-4)-
74 glycosidic bonds; the degree of polymerization (DP) depending on the source and treatment history
75 of the cellulose, ranging between 15,000 in cotton cellulose and about 10,000 in native wood
76 (Sjöström 1993). A number of different crystalline structures have been identified for cellulose
77 (O’Sullivan 1997), but native celluloses are of crystallinity type I (hydrogen bond structure of
78 cellulose I shown in Fig. 1). Furthermore, for plant-based materials, the dominant crystalline form
79 is cellulose I β that consists of two conformationally different chains in a monoclinic unit cell
80 (Atalla and VanderHart 1984). In contrast, its allomorph I α has one molecular chain in a triclinic
81 unit cell, found in certain algae and bacterial cellulose (Kontturi et al. 2006). In addition to the
82 crystalline parts, cellulose contains a significant portion of less ordered or ‘amorphous’ regions
83 that are more accessible to water and chemically more reactive than the crystalline domains. As is
84 the case with the DP, also the crystallinity index (CrI) depends heavily on the raw material and its
85 chemical and mechanical processing (O’Sullivan 1997; Liitiä et al. 2003; Ago et al. 2004; Kontturi
86 et al. 2006; Karinkanta et al. 2013).



87
88 **Fig. 1** The supramolecular structure of native cellulose I. Reprinted from Kontturi et al. (2006)
89 with permission of Royal Society of Chemistry (Note: Hydrogen atoms are not indicated)

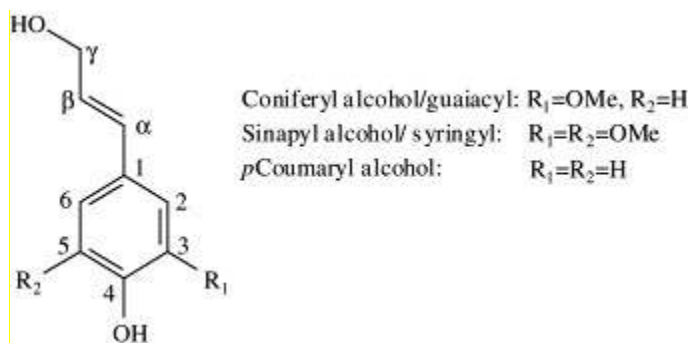
90 The next class of wood biopolymers to be discussed are hemicelluloses, amorphous
91 heteropolysaccharides that have structural resemblance to cellulose but have lower molecular

92 weight and often contain side chains (Fig. 2). Some of the hemicelluloses present in the cell wall
 93 are covalently linked to lignin (Lawoko et al. 2005; Iversen and Wännström 2009; Brunow and
 94 Lundquist 2010), and have a high affinity to cellulose (Eronen et al. 2011; Arola et al. 2013;
 95 Villares et al. 2015). These properties enable hemicelluloses to act as compatibilizers between the
 96 cellulose microfibrils and the lignin-rich matrix surrounding them. Moreover, hemicelluloses have
 97 been proposed to direct the structural development of native plant cell wall during its biosynthesis
 98 (Atalla et al. 1993; Martínez-Sanz et al. 2016). Perhaps related to the structural differences in SWs
 99 and HW fibers, also their hemicellulose compositions are different. As a generalization, the
 100 hemicelluloses in SWs typically consist of galactoglucomannans (15-20%) and
 101 arabinoglucuronoxylans (5-10%), whereas HWs are rich in glucuronoxylans (15-30%) and
 102 glucomannans (2-5%) (Sjöström and Westermarck 1999).

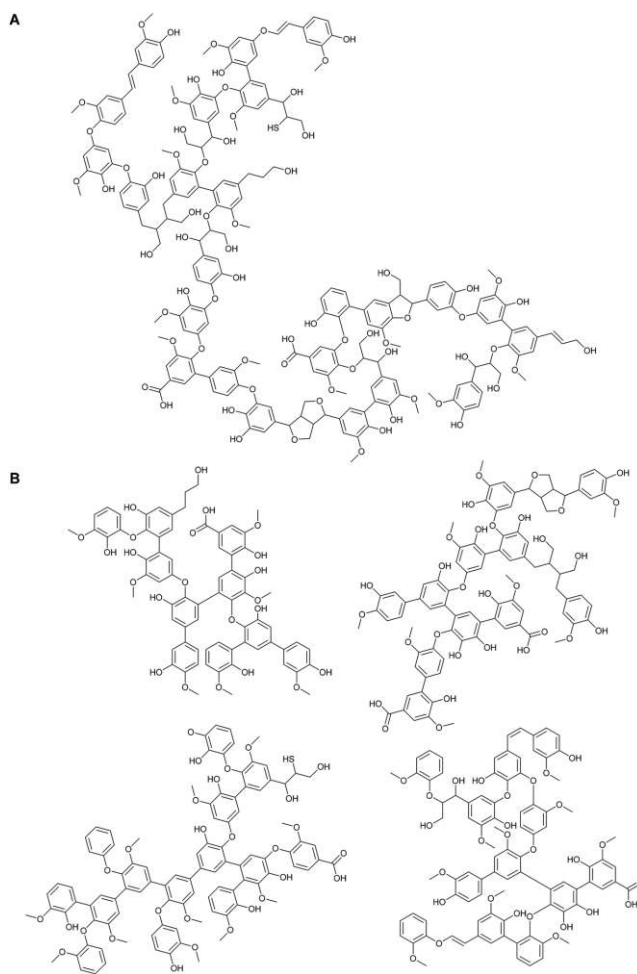


103
 104 **Fig 2.** Molecular structures of hemicelluloses on HWs and SWs; a) Harwood xylan, b) Softwood
 105 xylan, c) Hardwood glucomannan, and d) Softwood glucomannan. Adapted from Sixta (2006)
 106 With permission of John Wiley and Sons.

107 Whereas cellulose and hemicelluloses are both carbohydrates, lignin is a complex amorphous
 108 polymer that consists of phenyl propane units with one, two or three methoxy groups (Fig 3). It is
 109 often referred to in plural form to accentuate the enormous variation in its structure, depending on
 110 where and how it is isolated (proposed structure of softwood kraft lignin shown in Fig 4). Due to
 111 its complex network structure (Brunow et al. 1999; Hatfield and Vermerris 2001; Ralph et al.
 112 2004) and covalent attachment to surrounding carbohydrates (Lawoko et al. 2005; Iversen and
 113 Wännström 2009), the precise chemical structure and molecular weight of native lignin remains
 114 unknown, despite of the number of extensive studies on the chemical composition of isolated
 115 lignins (Froass et al. 1996; Ämmälähti et al. 1998; Capanema et al. 2001, 2004; Brunow 2005;
 116 Balakshin et al. 2009; Brunow and Lundquist 2010; Crestini et al. 2011, 2017; Alekhina et al.
 117 2015; Lupoi et al. 2015). In general, it can still be said that lignin is more hydrophobic than the
 118 carbohydrates that form the majority of the plant cell wall. For this reason, it has a major role in
 119 enabling water transport in living plants, as well as protecting them against microbial and fungal
 120 attacks (Ruiz-Dueñas and Martínez 2009).



121
 122 **Fig 3.** Three lignin precursors. Reprinted from Chakar and Ragauskas (2004) with permission from
 123 Elsevier.



124

125 **Fig 4.** Proposed constitutional structural schemes for softwood kraft lignin. (a) Acetone insoluble
 126 fraction (AIKL); (b) acetone soluble fraction (ASKL). Reprinted from Crestini et al. (2017) with
 127 permission of the Royal Chemical Society.

128 Extractives, the remaining class of wood components, are a chemically diverse class of low-
 129 molecular weight components that typically comprise about 2-5% of wood, but their amount
 130 greatly varies, depending on the wood species and tissue in question (Fengel and Wegener 1984;
 131 Brunow et al. 1999). Their biological role is to provide microbial resistance to the wood tissue.
 132 Details of their chemistry and properties are outside the scope of this review. For the purposes of
 133 the present paper, it suffices to state that most extractives are lipophilic, and some possess
 134 antioxidant or antimicrobial properties. Examples of common wood extractives include
 135 components such as fatty and resin acids and lignans (Willför et al. 2003a, b). Despite their low
 136 content, extractives have a tendency to enrich on the fiber surfaces (Laine et al. 1994; Fardim and
 137 Holmbom 2005), potentially impacting the surface chemistry of especially unbleached pulps.

138 Chiefly, it is important to bear in mind that as wood biomass is pulped, bleached, and processed
139 into cellulose nanofibrils (CNFs), it undergoes many structural and chemical changes. These will
140 be outlined briefly in the following sections to prepare the reader for the subsequent discussion of
141 lignin-containing pulps and their potential as a raw material for cellulose nanofibrils. For a more
142 thorough overview on the subject of wood chemical composition, the reader is advised to consult
143 more extensive reviews and textbooks on the chemistry of wood and its individual components,
144 such as the ones cited here (Fengel and Wegener 1984; Salmén and Olsson 1998; Sjöström and
145 Westermark 1999; Grabber et al. 2004; Ralph et al. 2004, 2007; Klemm et al. 2005; Glasser et al.
146 2012; Lupoi et al. 2015).

147 **Mechanical pulping.** Generally speaking, mechanical pulps have approximately the same
148 chemical composition as native wood. However, the combination of mechanical shear and elevated
149 temperature (typically about 120 °C) at a high moisture content causes some changes in the
150 structure and chemistry of the material. Notably, part of the heteropolysaccharide fraction is
151 degraded, dissolved and resorbed during mechanical pulping (Thornton et al. 1994). The elevated
152 temperature and high moisture content of the mechanical pulping process cause wood to soften
153 (Salmén 1984; Blechschmidt et al. 1986), enabling the separation of individual fibers.
154 Furthermore, depolymerisation of the cell wall polymers occurs both by thermal and mechanical
155 means, resulting in the formation of reactive free radicals in the course of mechanical pulping (Hon
156 1979; Widsten et al. 2001). Widsten et al. (2001) reported that high-temperature mechanical
157 pulping causes lignin depolymerisation and formation of phenoxy radicals. However, the presence
158 of phenoxy radicals may be a consequence of their high stability and not necessarily of their role
159 as the primarily formed radicals. The significance of radical formation in CNF manufacturing will
160 be addressed in a later section (*Lignin as an antioxidant*).

161 As a process, the major advantage of mechanical pulping is its high yield, which is typically above
162 80% of the original wood material. However, the high yield comes at the expense of using
163 significant amounts of electricity and achieving only a limited degree of fiber-fiber bonding – a
164 critical property in end uses such as papermaking. For this reason, different chemical treatments
165 have been developed to ease the separation of wood fibers. These processes can be classified to
166 chemi-mechanical and chemical pulping processes, both of which will be outlined briefly in the
167 following sections.

168 **Chemi-mechanical pulping.** In addition to purely mechanical pulps, there is another class of so-
 169 called high yield pulps, namely chemi-mechanical pulps, where mechanical treatment is preceded
 170 by a sulphite treatment in alkaline or neutral conditions (Annergren and Rydholm 1959; Gellerstedt
 171 et al. 1976; Hanhikoski et al. 2016b). The lower energy consumption associated with chemi-
 172 mechanical pulping is most often attributed to sulphonation of lignin that allows a more extensive
 173 swelling of the fibers by water, accompanied by more extensive softening of the material (Beatson
 174 et al. 1984; Konn et al. 2002).

175 In alkaline conditions, a significant portion of heteropolysaccharides gets dissolved. This effect is
 176 much less pronounced in near-neutral sulphite pulping but the degree of delignification remains
 177 lower unless the reaction is catalysed with e.g. anthraquinone (Annergren et al. 1961; Gellerstedt
 178 et al. 1976; Konn et al. 2002; Hanhikoski et al. 2016b). From the point of view of nanofibrillation,
 179 it is important to note that both – a high degree of lignin sulphonation and the preservation of wood
 180 heteropolysaccharides – are expected to promote fiber swelling, thus facilitating the production of
 181 cellulose nanofibrils. Lahtinen et al. (2014) observed improved nanofibrillation of chemi-
 182 mechanical pulps in comparison to the corresponding mechanical pulps. More recently,
 183 Hanhikoski et al. (2016a) found that near-neutral sodium sulphite pulps with yields 58-64% can
 184 be efficiently fibrillated to LCNFs, which was interpreted as an indication of high hemicellulose
 185 content promoting fibrillation, provided that the remaining lignin was sufficiently degraded.

186 **Chemical pulping.** A major difference of chemical pulps to mechanical and chemi-mechanical
 187 pulps is that their yield is only about 40-50%. Unbleached chemical pulps contain 2-5% residual
 188 lignin, and fully bleached chemical pulps contain only trace amounts of it (<0.1%) (Sjöström and
 189 Westermark 1999; Chakar and Ragauskas 2004). Furthermore, the DP of their polysaccharides is
 190 lower than in native wood – typically 2,000-4,000 for cellulose and 50-100 for hemicelluloses
 191 (Sjöström and Westermark 1999). Examples of typical polysaccharide compositions in chemical
 192 pulps are given in Table 2.

193 **Table 2** Polysaccharide compositions of common bleached chemical pulps as weight percentages
 194 of dry pulp. Adapted from Sjöström and Westermark (1999) with permission of Springer Nature

Pulp type	Cellulose	Glucomannan	Xylan
Pine kraft	81.3	8	10.7

Birch kraft	67.5	1.9	30.6
Spruce sulphite	82.9	8.8	8.3

195 Kraft pulping, the most common industrially used chemical pulping method, is chosen as an
 196 example to demonstrate the chemical changes that occur in wood upon chemical treatment. During
 197 kraft pulping, wood chips are subjected to alkaline conditions (an aqueous solution of NaOH and
 198 Na₂S) at an elevated temperature (170 °C), causing lignin to break down into smaller, water-
 199 soluble molecules (Chakar and Ragauskas 2004). Towards the end of the cooking, the selectivity
 200 of the process decreases, and degradation of carbohydrates, especially hemicelluloses, takes place.

201 In comparison to the extensively fractured soluble lignin, the residual lignin that remains in the
 202 pulp has a much higher molecular weight and contains more carbohydrates, as can be expected
 203 from the presence of the aforementioned lignin-carbohydrate complexes. It has been reported for
 204 softwood kraft pulps that some of the LCCs are broken by kraft pulping, whereas some remain
 205 intact even after oxygen delignification (Tenkanen et al. 1999; Lawoko et al. 2004, 2005).
 206 Moreover, studies have shown that the lignin fraction that is attached to glucomannan undergoes
 207 condensation and is thus of higher molecular weight than the more extensively degraded lignin
 208 fraction that is attached to xylan (Lawoko et al. 2005).

209 **Bleaching.** A detailed description of pulp bleaching chemistry is outside the scope of this review,
 210 but it is worth mentioning that before commercial use, both mechanical and chemical pulps are
 211 typically bleached to reach a higher brightness. This is especially important for kraft pulps that
 212 undergo significant colour formation in the alkaline conditions of the process (Falkehag et al. 1966;
 213 Ziobro 1990). For the purpose of this review, it is sufficient to say that pulping strategies are
 214 generally based on two main principles: either removing lignin or changing the chemical structure
 215 of lignin and carbohydrates to remove their colour-causing structures, referred to as chromophores
 216 (Agarwal and Atalla 1994; Vuorinen et al. 2004; Rosenau et al. 2007; Jääskeläinen et al. 2009).

217 For understanding the chemical changes taking place during the bleaching of chemical pulps, let
 218 us consider a SW kraft pulp that is bleached by an oxidative chemical, such as ozone, oxygen, or
 219 chlorine dioxide. In this situation, the residual lignin undergoes the following changes (Lachenal
 220 et al. 1995):

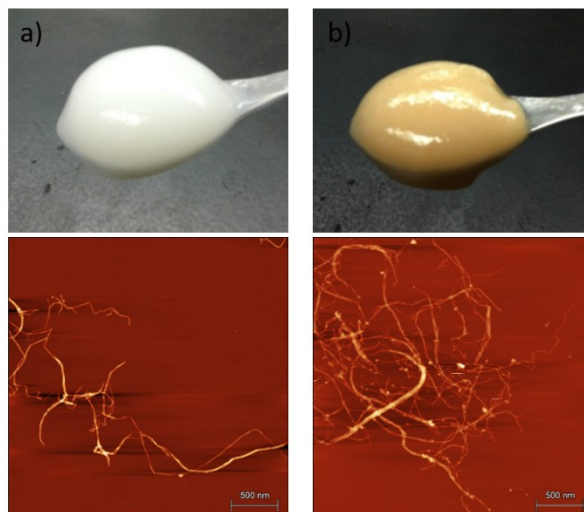
- 221 • The content of aliphatic and phenolic hydroxyls decreases slightly;
- 222 • The carboxylic acid content increases, except for ozone;
- 223 • Methoxy groups are removed;
- 224 • Some C=O is formed during oxygen and ClO₂ treatments.

225 It should be stressed that the aforementioned changes only describe the structure of the residual
226 lignin fraction, not the carbohydrates that form nearly 100% of bleached chemical pulps. Upon
227 bleaching, most of the cellulose is retained, but some hemicelluloses are lost together with the
228 residual lignin (Annergren and Rydholm 1959; Annergren et al. 1961; Hanhikoski et al. 2016b).
229 The changes that take place in hemicelluloses during bleaching include degradation and oxidation
230 (formation of carbonyl and carboxylic groups (Jääskeläinen et al. 2000)). More detailed information
231 on the chemistry of different bleaching stages is available in the articles and textbooks referenced
232 herein (Lachenal et al. 1995; Dence 1996; Dence and Reeve 1996; Vuorinen et al. 1999; Potthast
233 et al. 2009). Overall, it is important to remember that, depending on the pulping and bleaching
234 processes used, the pulps will have different chemical compositions but also different surface
235 charges and charge densities (the latter are predominantly caused by the presence of sulphonic and
236 carboxylic acid groups), both of which influence the ease of pulp fibrillation. These issues will be
237 addressed in more detail in section *The importance of hemicelluloses*.

238 ***Cellulose nanofibrils – state of the art and bottlenecks***

239 The pioneers in the production of cellulose nanofibrils (CNFs) were Turbak et al. (1982) and
240 Herrick et al. (1983) who investigated how to produce microfibrillated cellulose (MFC) by
241 homogenizing cellulose pulp suspensions under pressure during the early 80's. They discovered
242 that after intensive mechanical disintegration, cellulose pulps result in colloidal fibrous
243 suspensions at a very low solid content (typically ~2% wt.). The gel-like structure (Fig 5) and the
244 enhanced hydrogen bonding capability of CNFs confer it great potential for being incorporated in
245 formulations for thickeners and emulsifiers for food, cosmetics, and paints (Turbak et al. 1982;
246 Herrick et al. 1983; Lavoine et al. 2012). Furthermore, CNFs present high aspect ratio, low density
247 and thermal expansion, high strength modulus and stiffness (Hsieh et al. 2008; Eichhorn et al.
248 2010; Siró and Plackett 2010), as well as remarkable film-formability when dried (Spence et al.

249 2011a); properties that make them interesting in terms of producing high-strength composites and
250 barrier materials from renewable resources.



251
252 **Fig 5.** Gel-like structure and Atomic Force Microscopy image showing the morphology of a)
253 bleached CNFs, and b) unbleached CNFs.

254 Despite the versatile application potential of CNFs, the original efforts of Turbak and Herrick were
255 initially abandoned due to the inefficiency of the process; large amounts of energy were needed
256 for the refining and beating of the cellulose pulps, resulting in rather low yields of fibril
257 suspensions. To address this issue, a number of different types of mechanical treatments, including
258 homogenization (Nakagaito and Yano 2004; Spence et al. 2011b; Moser et al. 2015), grinding
259 (Taniguchi and Okamura 1998; Iwamoto et al. 2007; Spence et al. 2011a), ultrasonication (Zhao
260 et al. 2007; Cheng et al. 2009; Chen et al. 2011), and cryocrushing (Dufresne et al. 1997;
261 Chakraborty et al. 2005), have since been developed to produce CNFs. The two most common
262 methods are (1) homogenization, also referred to as microfluidization, where the cellulose
263 suspension is forced to pass through a small orifice which causes the fracture of the fibers into
264 smaller fragments (Turbak et al. 1982), and (2) micro-grinding, where the cellulose is beaten
265 between two ceramic disks, defibrillating the fibers and reducing their size (Iwamoto et al. 2005;
266 Stelte and Sanadi 2009). These methods can be used individually or in combination with one
267 another (Iwamoto et al. 2005; Stelte and Sanadi 2009) but both require several passes through the
268 system, contributing to a high energy consumption. Consequently, the main objective of CNF

269 manufacturing has been to reduce the energy consumption with different pre-treatments – these
270 can again be classified as chemical and/or enzymatic pre-treatments.

271 Of the chemical methods, carboxymethylation (Wågberg et al. 1987, 2008) and TEMPO (2,2,6,6-
272 tetramethylpiperidine-1-yl)oxyl radical) mediated oxidation (Saito et al. 2006, 2007) are the most
273 widely used. Both methods increase the fiber electrical charges, thus increasing the repulsion
274 between the individual fibrils and facilitating the fiber disintegration. Moreover, during the last
275 years, alternative chemical pre-treatments have been developed in order to obtain CNFs with
276 improved properties at reduced cost, in an effort to reduce the energy input while avoiding
277 expensive reagents. As an example of such processes, recyclable organic acids, such as oxalic and
278 maleic acid, have been used for simultaneous production of nanofibrillated and nanocrystalline
279 cellulose, while recovering hydrolysed sugars (Chen et al. 2016; Bian et al. 2017a, b, c; Wang et
280 al. 2017).

281 The enzymatic pre-treatments, on the other hand, employ different types of cellulases to weaken
282 the fiber structure, thereby decreasing the amount of mechanical energy required for efficient
283 nanofibrillation (Henriksson et al. 2007; Pääkko et al. 2007). Two main categories have been
284 identified for cellulases: cellobiohydrolases that can cleave highly crystalline cellulose, and
285 endoglucanases that tend to require a certain level of disorder in order to degrade cellulose
286 (Missoum et al. 2013). As a result, these enzyme types have synergistic effects and work best when
287 used together.

288 Despite these efforts, a few factors still limit CNF usage in an industrial scale. Such obstacles
289 include the costs of enzymes and chemical reagents (especially TEMPO), difficulties in CNF
290 dewatering and redispersibility, and the incompatibility of CNFs with commercial polymers that
291 limits the mechanical performance of CNF-reinforced composites. Presently, nearly all CNF
292 grades are produced from fully bleached chemical pulps that contain only trace amounts of residual
293 lignin. The aim of the present review, however, is to discuss the benefits and limitations of utilizing
294 cheaper, less extensively bleached lignin-containing pulp varieties in the production of
295 lignocellulosic nanofibers and assess whether they could solve some of the aforementioned
296 problems related to fully bleached CNFs.

297 ***Lignin-containing cellulose nanofibrils (LCNFs)***

298 In this review, we use the term broadly and refer to any cellulosic fibrils of <100 nm in width and
299 a lignin content of >1% as lignin-containing cellulose nanofibrils (LCNFs). Over the past decade,
300 several efforts have been made to extract LCNFs from different raw materials. Sources like empty
301 palm fruit bunches (Ago et al. 2016), wheat straw (Sánchez et al. 2016; Espinosa et al. 2017),
302 banana, jute, pineapple (Abraham et al. 2011), triticale straw (Tarrés et al. 2017), sunflower stalks
303 (Ewulonu et al. 2019), bamboo chips (Lu et al. 2018) and even bark (Chen et al. 2019) are some
304 of the recently investigated examples. Additionally, many research groups have been working on
305 the isolation, characterization, and application of LCNFs from wood sources. Wang et al. (2012)
306 produced two LCNF samples from kraft wood pulps by using an initial acid hydrolysis following
307 by homogenization at high pressure. Samples containing 5 and 10% of lignin were obtained and
308 characterized. Herrera et al. (2018) successfully isolated LCNFs with 23% lignin content from
309 Eucalyptus pulp through catalysed chemical oxidation followed by high-pressure
310 microfluidization. A method using organic acids followed by mechanical treatment was developed
311 for the integrated production of lignin containing nanocrystals (LCNCs) and LCNFs from
312 unbleached mixed hardwood pulp (mainly birch and maple). This methodology allows for the
313 recovery of the organic acids and reduces the overall energy consumption of the process (Bian et
314 al. 2017b). LCNFs with as high as 18.5% lignin content was obtained via this procedure. More
315 recently, Wen et al. (2019) isolated and characterized LCNFs containing 15.5, 18.6, and 23.15%
316 lignin from a poplar high-yield pulp via TEMPO-mediated oxidation followed by homogenization.

317 Generally, LCNFs are produced from unbleached cellulose pulps with different lignin contents.
318 However, it has been demonstrated that LCNFs can also be directly isolated from raw wood
319 microparticles. In a recent study, nanofibers were produced using alkali-treated poplar wood
320 powder followed by controlled delignification steps in order to obtain samples with 22.1, 14.1, 8.2,
321 2.0, 0.4, and 0.2% residual lignin. Subsequent mechanical grinding was utilized to produce
322 nanofibers (Chen et al. 2018). Yousefi et al. (2018), on the other hand, isolated nanofibers
323 containing 30% lignin by mechanical grinding of *Paulownia Fortunei* wood without utilizing any
324 chemical pre-treatment.

325 Regardless of the raw material, the role of lignin in the nanocellulose suspension needs to be
326 clarified in order to better understand the behaviour of the resulting suspensions in further

327 applications. More details about the properties conferred by the lignin present on LCNFs will be
328 discussed in the following sections.

329 **Lignin – a friend or a foe?**

330 Lignin can have two, seemingly contradictory effects on pulp fibrillation, based on what kind of
331 pulps are utilized as the starting material. On the one hand, it can hinder fibrillation, as has been
332 demonstrated in the case of mechanical pulps (Lahtinen et al. 2014). On the other hand, residual
333 lignin can even significantly lower the energy consumption of fibrillation in the case of chemical
334 pulps (Spence et al. 2011b), serving as an example on how lignin structure affects its function.
335 Moreover, the presence of residual lignin in chemical pulps has been reported to result in the
336 formation of finer CNFs at comparable energy consumption levels (Solala et al. 2012; Rojo et al.
337 2015).

338 Assuming a complex, network-like structure for native lignin, it seems probable that the initial
339 crosslinked structure prevents efficient fibrillation of the highest-lignin pulp grades by ‘locking’
340 the individual microfibrils together (Lahtinen et al. 2014; Hanhikoski et al. 2016a). The
341 hydrophobic character of lignin may also play an important role in preventing fiber swelling and
342 fibrillation, as will be discussed in the next section. In contrast, the residual lignin present in
343 chemical pulps is significantly degraded and present in much lower quantities, therefore less able
344 to prevent fiber swelling and fibrillation. We have previously proposed (Ferrer et al. 2012; Solala
345 et al. 2012) that the ease of fibrillation observed in lignin-containing chemical pulps is due to lignin
346 acting as an antioxidant, preventing broken covalent bonds from being formed again. This
347 hypothesis is discussed in more detail in section *Lignin as an antioxidant*.

348 ***Lignin hydrophobicity and thermoplasticity***

349 It has been extensively reported on the literature that lignin is covalently linked to cellulose and
350 hemicelluloses within the wood structure (Sjöström 1993; Tenkanen et al. 1999; Lawoko et al.
351 2003, 2005; Balakshin et al. 2009, 2011; Iversen and Wännström 2009). It is also generally
352 accepted that lignin presents more hydrophobic character than carbohydrate polymers (Abe et al.
353 2010; Laurichesse and Avérous 2014). However, different processing methods and chemical
354 compositions of raw material result in different lignin surface free energies and thereby also

355 different hydrophobicities. Understandably, processes that cleave the β -aryl ether linkages or
356 introduce electrical charges in lignin increase its hydrophilicity.

357 These effects should be kept in mind when examining literature on the hygroscopicity of LCNF
358 films or nanopapers. In literature, nanopaper water interactions are usually characterized by
359 measuring parameters such as total bound water determined with differential scanning calorimetry
360 (DSC), water retention value (WRV), film water absorption, water vapor transmission rate
361 (WVTR), and water contact angle (WCA) (Spence et al. 2010; Ferrer et al. 2012; Wang et al. 2012;
362 Horseman et al. 2017; Nair et al. 2017; Chen et al. 2018; Herrera et al. 2018; Lê et al. 2018).

363 WCAs are usually higher for LCNF nanopapers than the corresponding CNF nanopapers (Ferrer
364 et al. 2012; Rojo et al. 2015; Chen et al. 2018; Herrera et al. 2018; Lê et al. 2018), but other results
365 are less consistent, showing for example higher water absorption and WVTR for LCNF films
366 (Spence et al. 2010; Ferrer et al. 2012). Ferrer et al. reported water absorption values (g/m^2) of
367 24.6 ± 1.2 , 23.1 ± 1.2 , and 17.1 ± 1.2 for unbleached, oxygen delignified, and fully bleached CNF
368 samples, respectively. Additionally, for those samples, the WCA results were 60 ± 6 , 54 ± 6 , and
369 51 ± 4 . One might expect that the presence of lignin would automatically make the nanopapers more
370 hydrophobic, but lignin removal tends also to alter the carbohydrate chemistry, so that lignin-
371 containing CNFs often contain more hemicelluloses than the corresponding fully bleached CNFs,
372 which will contribute to their hygroscopicity (Ferrer et al. 2012; Solala et al. 2012). Moreover, the
373 method of film preparation has a significant effect on properties such as porosity, which will in
374 turn affect the WVTR and specific surface area of nanopapers prepared from these nanofibrils.
375 There is a crucial difference in film casting and hot-pressing, for example – the first tends to form
376 more porous films from lignin-containing CNFs (Spence et al. 2010), whereas pressure filtration
377 followed by hot-pressing produces denser films when lignin is present (Rojo et al. 2015). This
378 complex interdependency of film morphology, lignin content, hemicellulose content, and charge
379 density (Ferrer et al. 2012; Solala et al. 2012; Rojo et al. 2015; Herrera et al. 2018) makes direct
380 comparisons between different studies challenging, but when these factors are controlled well,
381 lignin does indeed increase the hydrophobic nature of a cellulosic pulp and the CNFs and
382 nanopapers derived from it (Rojo et al. 2015; Chen et al. 2018; Lê et al. 2018).

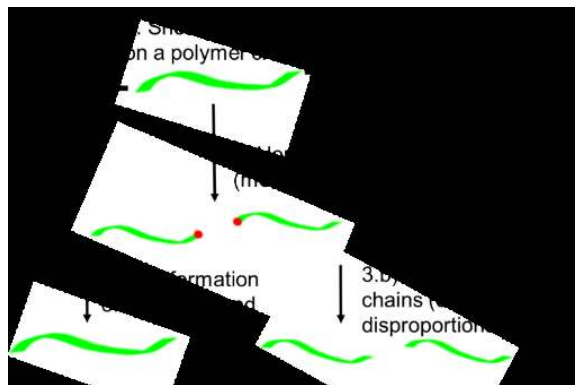
383 In addition to being hydrophobic, lignin softens at elevated temperatures, especially when
384 plasticized by water or some other component (Sakata and Senju 1975; Salmén 1984; Åkerholm
385 and Salmén 2004). It has been reported that at low water contents (<5%), lignin softening
386 temperature is approximately 135 °C, but when the water content increases to 20-40%, the
387 softening temperature decreases to 80-90 °C (Salmén 1982, 1984). Similar behavior has been
388 reported also for hemicelluloses (Olsson and Salmén 2009). This property is well-known from the
389 manufacturing of thermomechanical pulps (Johansson et al. 1998; Gustafsson et al. 2003; Solala
390 et al. 2014), but lignin softening was recently utilized to produce nanofibers from ground wood
391 pulp without applying any chemical pre-treatment (Visanko et al. 2017a). Moreover, this softening
392 behavior has sparked research efforts to develop thermoplastic lignin-based polymers based on
393 these components to replace the presently ubiquitous oil-based polymers (Nägele et al. 2002; Cui
394 et al. 2013; Hilburg et al. 2014). As packaging and barrier films are among the most promising
395 commercial applications for CNFs, the role of lignin hydrophobicity and thermoplasticity may
396 help improving CNF nanopaper moisture barrier properties, as we will discuss in section *Barrier*
397 *films*.

398 ***Lignin as an antioxidant***

399 Mechanically treated polymers typically have a limiting DP, beyond which they will not degrade
400 in the applied conditions (Glynn and van der Hoof 1973; Tomashevskii et al. 1975; Kondo et al.
401 2004). This levelling off behavior is often attributed to the chain length becoming too small to
402 absorb mechanical energy. On the other hand, the radical content in mechanically stressed polymer
403 samples typically decreases slightly after levelling off, probably due to the occurrence of
404 recombination and disproportionation reactions that quench some of the formed radicals (Kondo
405 et al. 2004).

406 Following this line of thought, the observed ease of fibrillation of lignin-containing chemical pulps
407 has been hypothesized to be a result of lignin acting as an antioxidant owing to its polyaromatic
408 resonant-stabilized structure (Dizhbite et al. 2004; Solala et al. 2012; Rojo et al. 2015). In other
409 words, as mechanical treatments – be it by grinding, microfluidization or other means – produce
410 free radicals (Sakaguchi and Sohma 1975; Hon 1979, 1983b, a; Solala et al. 2012, 2015), these
411 radicals can get stabilized by the residual lignin present in the fibers due to the resonance

412 stabilization enabled by the phenyl structures and other conjugated double bonds present in lignin.
413 This would lead to less favorable kinetics for the recombination reactions that would otherwise
414 cause a partial reformation of the ruptured covalent bonds and thereby prevent effective
415 nanofibrillation, as is illustrated schematically in Fig 6.



416
417 **Fig. 6** Schematic presentation of mechanoradical formation when a polymer chain is subjected to
418 a shear force (1). After the radicals are formed by homolytic chain scission (2), they typically react
419 fast, either forming new covalent bonds (3.a) or by undergoing other reactions, e.g.
420 disproportionation (3.b), that leave the fractured polymer chains separate. In the presence of
421 antioxidants or radical scavengers, such as lignin, the probability of type (a) reactions decreases,
422 enhancing the formation of separate polymer fragments

423 As mentioned earlier, there is enormous structural variation in different lignins, which inevitably
424 affects their ability to stabilize free radicals (Barclay et al. 1997; Dizhbite et al. 2004; Ugartondo
425 et al. 2008; Vinardell et al. 2008). These differences should be taken into account when evaluating
426 the hypothesis of lignin acting as a radical scavenger. More specifically, the following trends have
427 been found for lignin antioxidant properties (Barclay et al. 1997; Dizhbite et al. 2004; Hage et al.
428 2012; Ponomarenko et al. 2015; Sadeghifar and Argyropoulos 2015):

- 429 • Phenolic hydroxyls increase but aliphatic hydroxyls decrease antioxidant activity
- 430 • High molecular weight decreases the antioxidant activity (probably related to the relative
431 number of phenolic hydroxyls)
- 432 • Conjugated C=C bonds in the propyl side chain increase the antioxidant activity
- 433 • Carbohydrate structures may decrease the antioxidant activity
- 434 • Oxygen-containing substituents in the side chains decrease the antioxidant activity

435 Information reported on the effect of methoxy groups is contradictory; some studies have
436 associated especially ortho-positioned methoxy groups with enhanced antioxidant activity, but
437 others have found that controlled methylation of the phenolic OH groups destroyed lignin's
438 antioxidant ability (Barclay et al. 1997; Dizhbite et al. 2004; Sadeghifar and Argyropoulos 2015).

439 Given that the structure of lignin affects its radical scavenging ability significantly, it is important
440 to remember what is known about the structure of the lignin present in the pulps that are to be used
441 for CNF manufacturing. As an example, among the major structural differences between native
442 and kraft lignin is that the number of phenolic hydroxyls increases significantly both in the
443 dissolved and in the residual lignin (Froass et al. 1996; Chakar and Ragauskas 2004), which would
444 be expected to enhance the radical scavenging ability. Another change that occurs is that some
445 methoxy groups are lost during kraft pulping (Froass et al. 1996), but since various research groups
446 agree on the primary importance of phenolic hydroxyls (Barclay et al. 1997; Dizhbite et al. 2004;
447 Ponomarenko et al. 2015; Sadeghifar and Argyropoulos 2015), it seems reasonable to assume that
448 the residual lignin in chemical pulps has radical scavenging properties, despite having
449 carbohydrate structures linked to it.

450 Indirect evidence for the antioxidant activity of residual lignin was also reported by Vänskä et al.
451 (2016), showing improved thermal stability of intensely refined softwood kraft pulp in the
452 presence of residual kraft lignin, as indicated by brightness and viscosity-based DP measurements.
453 High thermal stability has also been reported for high lignin content (20%) nanofibrils derived by
454 sodium chlorite bleached pine bark (Nair and Yan 2015). On the other hand, no difference was
455 seen in the thermogravimetric analysis profile as a function of lignin content in organosolv-treated
456 pulps by Santucci et al. (2016). These inconsistencies highlight the importance of caution when
457 comparing results from different raw materials and processes. It may be speculated that
458 incorporation of a high phenolic OH lignin might be beneficial for the development of new
459 nanocellulose grades with high thermal stability, but more research is needed in this area before
460 definite conclusions can be made.

461 **The importance of hemicelluloses**

462 Depending on the chosen raw material and utilized processing method, the fibers and nanofibrils
463 prepared from them may contain not only cellulose and lignin but also hemicelluloses. Thus, a

464 complete understanding about CNF behavior and its interactions should include the properties
465 conferred not only by lignin but also by hemicelluloses.

466 Regarding CNF preparation and properties, hemicelluloses have been found to impede the
467 agglomeration of the nanofibrils. This effect is partly electrostatic in nature, as many
468 hemicelluloses possess negative charges, generating repulsion between them (Arola et al. 2013).
469 On the other hand, the side chains present in some hemicelluloses contribute to steric repulsion
470 between nanofibrils, thereby also reducing their tendency to aggregate (Hubbe and Rojas 2008;
471 Tenhunen et al. 2014). As a result of these interactions, the presence of hemicelluloses promotes
472 pulp fibrillation (Duchesne et al. 2001; Hult et al. 2001; Iwamoto et al. 2008; Tarrés et al. 2017)
473 and colloidal stability of CNF suspensions (Tenhunen et al. 2014), as will be discussed in the
474 following sections.

475 ***Fibrillation***

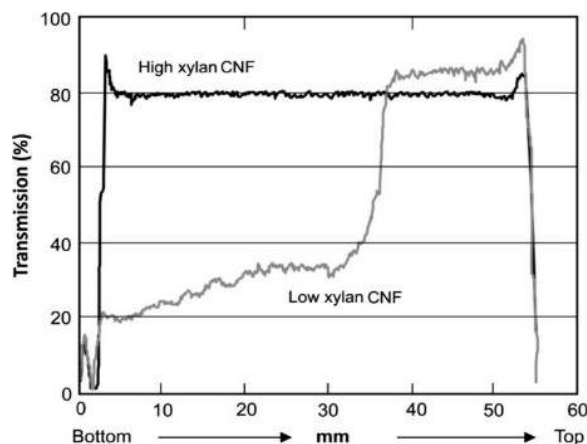
476 As mentioned before, hemicelluloses enhance pulp fibrillation. This behavior has been attributed
477 to their ability to inhibit fibril coalescence, resulting in an open, porous fiber structure (Duchesne
478 et al. 2001; Hult et al. 2001; Pönni et al. 2012). Both cellulose and hemicelluloses readily swell in
479 moist environments but, due to their lower molecular weight and often higher degree of branching,
480 hemicelluloses have higher accessibility to water than cellulose (Yang et al. 2013). It should be
481 mentioned, however, that it is not only the hemicellulose content that determines the swelling
482 behavior of a fiber material, but also the spatial distribution of cellulose and hemicelluloses within
483 the fibrils is relevant (Tenhunen et al. 2014; Kulasinski et al. 2015). The aforementioned fiber
484 swelling leads to its softening through the breakage of hydrogen bonds, contributing to efficient
485 fibrillation (Åkerholm and Salmén 2004; Kulasinski et al. 2014, 2015). Naturally, after breaking
486 the initial fiber structure into smaller fibrils and fibril bundles, reattachment of these fragments
487 needs to be prevented in order to obtain individual nanosized fibrils. This means that producing
488 high-quality CNFs requires sufficient colloidal stability, which we will address next.

489 ***Colloidal stability***

490 Colloidal stability, i.e. the ability of a particle suspension to resist agglomeration and/or
491 sedimentation by remaining in an equilibrium, plays a vital role in determining many of the

492 properties of CNF materials – from specific energy consumption (SEC) during fibrillation to
493 rheological properties and potential redispersibility after drying. As cellulose has strong affinity
494 towards itself, in practice it is necessary to prevent its characteristic tendency for fibril
495 agglomeration. One way to counteract such fibril coalescence is to introduce electrical charges in
496 the pulp material, such as in the case of TEMPO-mediated oxidation (Saito et al. 2007; Isogai et
497 al. 2011a, b) or carboxymethylation (Rácz and Borsa 1997; Wågberg et al. 2008; Siró et al. 2011),
498 in which an increase in negative charge leads to electrostatic repulsion between the fibrils at pHs
499 where the carboxyl groups are in their dissociated state. Importantly, electrostatic repulsion is
500 greatly affected by the ionic strength of the system, meaning that it can be hindered simply by
501 adding salt into the suspension (Fall et al. 2011; Junka et al. 2013). This is not the case for steric
502 stabilization, however, in which bulky molecular chains prevent particle aggregation, regardless
503 of the pH or ionic strength of the system. Nevertheless, if the bulky chains possess electrical
504 charges, such as in the case of xylan, the conformation of the polymers depends on changes in pH
505 and ionic strength (Tenhunen et al. 2014). This will in turn affect the extent of steric repulsion.

506 As mentioned, hemicelluloses can contribute to colloidal stability of CNFs by both electric and
507 steric mechanisms, depending on their structure (Hubbe and Rojas 2008). Xylans, for instance,
508 have carboxyl groups that give them a net negative charge, as well as side chains that contribute
509 to steric repulsion, and both properties influence the colloidal stability of CNFs (Tenhunen et al.
510 2014) (an example of this given in Fig.7). Similarly, galactoglucomannans can sterically stabilize
511 pitch particles in thermomechanical pulping (TMP) process waters (Hannuksela et al. 2003;
512 Tammelin et al. 2007). Recently, a number of researchers have employed the ability of
513 hemicelluloses to adsorb tightly on cellulose (Tammelin et al. 2009; Eronen et al. 2011; Littunen
514 et al. 2015) for producing core-shell structured CNFs, aiming at achieving a better control over
515 their nanostructure (Prakobna et al. 2015; Tanaka et al. 2016).



516

517 **Fig. 7** Light transmission profiles of high xylan content CNFs and low xylan content CNFs.
 518 Reprinted from Tenhunen et al. (2014) with permission of Elsevier

519 It is evident that controlling the hemicellulose type and content by careful selection of raw
 520 materials, pulping conditions, and other processing methods is vital for controlling the properties
 521 of the resulting CNFs. As an example of this, LCNFs derived from SO₂-ethanol-water (SEW)
 522 pulps (Iakovlev et al. 2010; Iakovlev and Heiningen 2012; Yamamoto et al. 2014) and neutral
 523 sulphite pulps (Hanhikoski et al. 2016b, a) with comparable lignin contents appear to have very
 524 different water retention properties. Although for methodological differences it is not possible to
 525 quantitatively compare the water retentions of these LCNFs, the SEW-LCNFs displayed effortless
 526 dewatering (Rojo et al. 2015), whereas the NS-LCNFs had markedly high water retention values
 527 (in the range of 400 g/g) even after a minimal mechanical treatment (Hanhikoski et al. 2016a).
 528 This is most probably due to the difference in their hemicellulose contents (Chakar and Ragauskas
 529 2004; Rojo et al. 2015). One of the challenges in comparing the properties of different CNFs is
 530 that there still are no established standardized tests that would allow a clear comparison between
 531 different CNF grades. However, reported results indicate that by selecting raw materials with
 532 varying (high or low) hemicellulose content for CNFs production, different performance of CNFs
 533 will be achieved. We thus recommend a complete lignin and carbohydrate analysis to be run from
 534 the fiber material processed to LCNFs to allow meaningful comparisons between LCNF grades.

535 **Practical considerations for LCNFs**

536 ***Consumption of chemicals and energy***

537 As explained before, the required energy consumption in the production of CNFs is rather high: to
538 obtain cellulose nanofibers applying only mechanical treatments, SECs of ~30,000 kWh/ton are
539 necessary (Klemm et al. 2011; Moser et al. 2016). In contrast, by utilizing the TEMPO-mediated
540 oxidation, the SEC can be lowered below 7 MJ/kg, corresponding to 1,900 kWh/ton, while
541 obtaining a uniform transparent gel with fibril width of 3-4 nm and a length of a few micrometers
542 (Isogai et al. 2011a). TEMPO-CNFs are of very high quality but due to chemical costs, still too
543 expensive for bulk industry use (Delgado-Aguilar et al. 2015). As an alternative for TEMPO-
544 mediated oxidation, Tejado et al. (2012) decreased the energy consumption for the preparation of
545 CNFs by periodate oxidation followed by a chlorite oxidation. Their results showed that cellulose
546 nanofibrils can be liberated from the original cellulose fiber structure at a constant yield with a
547 SEC of 1,250 kWh/ton when the carboxylate content is 2.5 mmol/g. They also reported that after
548 increasing the carboxylate content to 3.5 mmol/g, the energy necessary to obtain the same
549 fibrillation level decreased even further, introducing a less energy-intensive alternative for CNF
550 production. As promising as this approach is, it has, to the best of our knowledge, been thus far
551 utilized only for bleached pulps. Other affordable approaches have been sought from enzymatic
552 pre-treatments, but although enzymatically pre-treated CNFs can be prepared from bleached pulp
553 using only 350 kWh/ton (Lindström 2016), the presence of lignin hinders the efficacy of enzymatic
554 hydrolysis (Hoeger et al. 2012, 2013), limiting the use only to bleached pulp varieties. With the
555 interest of producing nanofibrils from fibers with higher yields, efforts have been made to
556 investigate the fibrillation of lignin-containing fibers.

557 A number of studies have demonstrated that unbleached pulps tend to be easier to fibrillate than
558 fully bleached pulps. Spence et al. (2011b) reported SECs in the range of 420 kWh/ton for LCNFs
559 with an estimated specific surface area (SSA) of ~80 m²/g. Generally, the achieved SSAs were
560 higher for unbleached fibrils than corresponding fully bleached fibrils at comparable specific
561 energy consumptions. Similarly, Lahtinen et al. (2014) reported that unbleached softwood kraft
562 pulp achieved a higher level of fibrillation after utilizing the same specific energy consumption
563 than fully bleached kraft pulps. Also Solala et al. (2012) reported a more thorough fibrillation of
564 unbleached of hardwood kraft pulp in comparison with its fully bleached counterpart. Since
565 unbleached pulps render higher yields of the initial lignocellulosic material and require lower
566 dosages of chemicals to be produced in the first place, LCNFs derived from them might be a viable

567 option for bulk uses where their inherent brown colour does not present problems (Solala et al.
568 2012; Delgado-Aguilar et al. 2016). In terms of particle size, Rojo et al. (2015) reported softwood
569 LCNF fibers containing 0, 2, 4, and 14% lignin with diameters of 44 ± 3 , 25 ± 1 , 20 ± 2 , and $16 \pm$
570 2 nm respectively. Also these results positively correlate with the ease of fibrillation due to
571 increases in lignin and hemicellulose contents.

572 Generally, it should be noted that the comparison of individual studies is complicated because of
573 a lack of consistent, standardized vocabulary in the field; for instance, the exact meaning of the
574 term ‘nanocellulose’ varies in the literature. Moreover, the reported values are often not
575 comparable to one another, as different analytical techniques are favored by different research
576 groups. Recently, this issue was addressed by Foster et al. (2018) on their review that discusses
577 recommended analytical protocols in this research area.

578 *Dewatering and redispersibility*

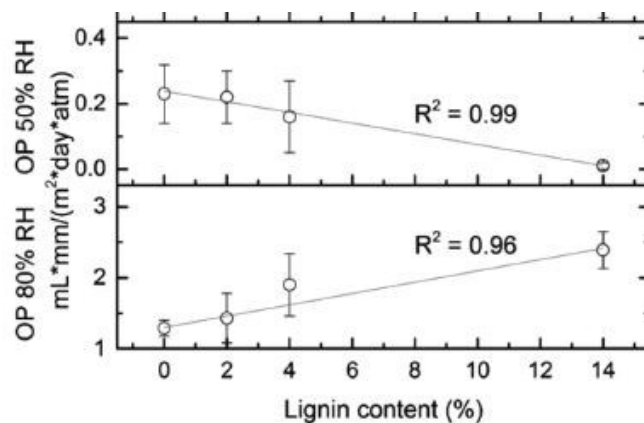
579 Typically, CNF suspensions contain 98-99% water and only 1-2% of the cellulosic nanomaterial.
580 Even when higher consistencies can be achieved, they tend to be in the range of 5%, meaning that
581 transportation costs for CNF gels are very high in relation to the transported dry mass. Water
582 removal from CNFs is energy intensive, which is not ideal on itself, but more crucially, it is
583 accompanied by irreversible fibril coalescence, often referred to as hornification by pulp and paper
584 scientists. The extent of coalescence upon drying can be limited by solvent exchanges (Henriksson
585 et al. 2008) or freeze-drying (Lovikka et al. 2016), but these methods are tedious and time-
586 consuming, rendering them impractical in an industrial scale. Alternatively, the surface chemistry
587 of the CNFs may be modified to allow redispersibility after drying by introducing electrostatic
588 repulsion, like in the case of carboxymethylated CNFs (Eyholzer et al. 2010), or by using steric
589 stabilization from pectin or other components (Hietala et al. 2017). Recently, Visanko et al. (2017)
590 reported having made redispersable LCNF nanopapers from spruce ground wood pulp (lignin
591 content 27.4%) when dried from ethanol, which can probably be attributed to the lower density
592 and interfibrillar contact in these nanopapers. Importantly, similar behavior was not seen in fully
593 bleached CNFs (Visanko et al. 2017a), suggesting that at least some lignin-containing nanofibril
594 grades have unique properties that could promote their use in an industrial scale.

595 *Barrier films*

596 One of the frequently proposed uses for CNFs has been to use it in barrier applications, for example
597 in food packaging (Lavoine et al. 2012). With a combination of moisture and pressure, CNFs can
598 be turned into dense films, or so-called nanopapers, with porosities in the range of 10-20%
599 (Sehaqui et al. 2010; Österberg et al. 2013). In dry state, the average pore size in such films is
600 typically around 1-10 nm (Henriksson et al. 2008; Lavoine et al. 2012) but the film structure
601 changes in moist conditions, causing a decline in its barrier properties for oxygen and water vapor
602 (Aulin et al. 2010). One working hypothesis has been that lignin-containing films should have
603 better barrier properties, as they are inherently less hygroscopic. However, as discussed earlier,
604 this depends heavily on the method of film formation. If films are produced at temperatures below
605 the softening temperature of lignin, efficient H-bonding between nanofibrils may be compromised,
606 leading to increased pore formation and poor barrier properties (Spence et al. 2010; Santucci et al.
607 2016). On the other hand, if hot-pressed in moist conditions, the lignin in the LCNF films will
608 soften and fill voids as schematically illustrated in Fig. 8. Rojo et al. (2015) demonstrated an
609 improvement on the barrier functionality of the films in terms of oxygen permeability as the lignin
610 content of the samples increases when measuring at 50% relative humidity. At 80% relative
611 humidity, the results showed a slight increase which was not significant when compared with the
612 improvement at 50% relative humidity (Fig 9). Moreover, lignin has been shown to decrease water
613 uptake and increase water contact angle (Wang et al. 2012; Rojo et al. 2015; Herrera et al. 2018),
614 as long as control over the hemicellulose content is maintained (Ferrer et al. 2012).



615
616 **Fig. 8** Proposed model to describe the location of the lignin within LCNF suspension after filtering
617 (left) and LCNF nanopaper after pressing (right) Reprinted and adapted from Rojo et al. (2015)
618 with permission of Royal Society of Chemistry.



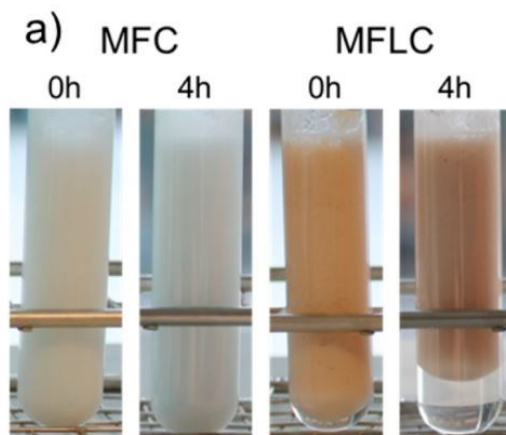
619
 620 **Fig. 9** Oxygen permeability of hot-pressed nanopapers with different lignin contents at 50 and
 621 80% relative humidity. Reprinted and adapted from Rojo et al. (2015) with permission of Royal
 622 Society of Chemistry.

623 In summary, considering just the lignin content of a potential CNF material is not sufficient; it is
 624 vital also to control the content of heteropolysaccharides and electrical charges, as both
 625 significantly affect the interactions between the material and water. In addition to the chemical
 626 composition of LCNF nanopapers, also their morphology in terms of porosity and pore size is of
 627 central importance when analysing nanopapers for their barrier properties.

628 *Emulsions*

629 About a decade ago, Andresen and Stenius (2007) reported that hydrophobized microfibrillated
 630 cellulose can be used as a stabilizer in Pickering emulsions. Since then, a number of papers have
 631 been published on the subject (Xhanari et al. 2011; Cunha et al. 2014; Gestranus et al. 2017). In
 632 order to efficiently stabilize emulsions, particles should show a certain extent of amphiphilicity
 633 (Kalashnikova et al. 2013). To achieve this, previous studies have commonly utilized synthetic
 634 hydrophobization routes (Andresen and Stenius 2007; Xhanari et al. 2011; Cunha et al. 2014), but
 635 similar effects can also be reached by utilizing LCNFs (Fig 10) (Ballner et al. 2016; Yan et al.
 636 2016) or lignin particles (Nypelö et al. 2015; Li et al. 2016). Although the exact chemical nature
 637 of residual lignin can be difficult to control, there are obvious benefits to avoiding the multistep
 638 process of first removing all lignin through sequential bleaching and then derivatizing the nearly
 639 pure cellulose with synthetic hydrophobic moieties. We therefore foresee benefits in exploration
 640 of lignin-containing nanocelluloses for emulsion stabilization, especially in applications where in-
 641 situ polymerization is feasible, as this would solve many of the problems presently associated with

642 CNFs use in composite reinforcement. In fact, Yan et al. (2016), Ballner et al. (2016) and Gindl-
643 Altmutter et al. (2015) have successfully applied this principle to produce composites of LCNFs
644 and synthetic polymers via emulsion polymerization, as discussed in the following section.



645
646 **Fig. 10** Styrene-in-water emulsions stabilized using nanofibrillated cellulose (MFC) and lignin-
647 containing nanofibrillated cellulose (MFLC), at 0 and 4 hours after after mixing. Readapted and
648 reprinted from Ballner et al. (2016) with permission of the American Chemical Society.

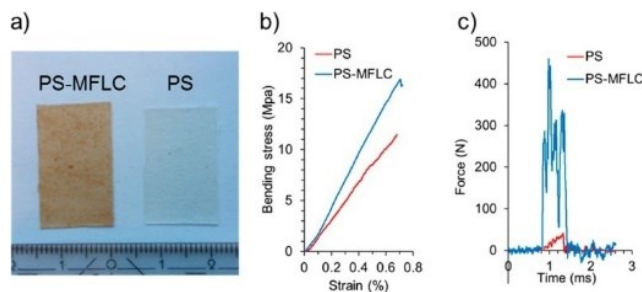
649 *Nanocomposites*

650 The utilization of cellulose nanofibrils from bleached fibers has been widely studied as a
651 reinforcing agent in composite materials, prepared by techniques such as solvent casting (Wågberg
652 et al. 1987; Leitner et al. 2007) or emulsion polymerization (Nikfarjam et al. 2015). Due to the
653 high aspect ratio and moderately low thermal stability of CNFs, melt extrusion is usually not a
654 practical method to produce such composites.

655 It is well known that the reinforcing capacity of cellulose nanoparticles combined with different
656 matrices occurs due to strong interactions between the fibrils, allowing to improve the mechanical
657 performance of the composites made thereof (Siqueira et al. 2010; Kargarzadeh et al. 2018). This
658 strong network of nanofibers can be considered the result of a percolation mechanism which
659 assumes that above certain concentration of the fibers, the mechanical properties of the composites
660 will be improved (Boufi et al. 2014) due to increased hydrogen bonding between them (Dubief et
661 al. 1999).

662 In addition to CNFs, the incorporation of LCNFs to different composite materials has become
663 more common, employing a number of matrix materials, such as polylactic acid (Sun et al. 2014;

664 Wang et al. 2014), starch (Ago et al. 2016), polypropylene (Ferrer et al. 2016), polycaprolactone
665 (Herzele et al. 2016), polystyrene (Ballner et al. 2016), and polyurethane (Visanko et al. 2017b).
666 Ballner et al. (2016) utilized in-situ polymerization of styrene in water stabilized by LCNFs,
667 followed by hot-pressing, and obtained composites with increased bending stress and Charpy
668 impact bending strength in comparison to pure PS (Fig. 11). These results are an indication of the
669 potential of LCNFs to be used in composite reinforcement.



670
671 **Fig. 11** The visual appearance of hot-pressed PS and PS-MFLC films (a) and results of mechanical
672 characterization by static three-point bending (b) and Charpy impact bending (c). Reprinted from
673 Ballner et al. (2016) with permission of Royal Society of Chemistry

674 Similarly, Nair et al. (2017) reported that the tensile strength of LCNF/epoxy composites, with
675 23% of lignin content, increased from 65 ± 6 MPa to 134 ± 10 MPa. This increment was attributed
676 to the increased compatibility between the fibrils and the epoxy matrix caused by the presence of
677 residual lignin. Following this trend, Chen et al. (2019) incorporated LCNFs as a reinforcement
678 material in polymeric diphenylmethane diisocyanate (pMDI) resins, commonly used for wood
679 composite manufacturing. Their results showed positive effects due to the increase in bond line
680 between wood and adhesive at different LCNF loadings. On the other hand, Diop et al. (2017)
681 utilized LCNFs as an adhesive in fiberboards, reporting that by adding 20% LCNFs, the modulus
682 of elasticity (MOE) was 300 MPa higher than the standard requirement of 1241 MPa. Regarding
683 the required modulus of rupture (MOR), by incorporating 20% LCNFs, they reached a MOR value
684 of 12.1 MPa which was close to the target value for commercial panels of 12.4 MPa. Moreover,
685 even if the vast majority of studies have utilized oil-based, non-biodegradable polymers, there are
686 indications that LCNFs can be successfully combined with biobased, compostable polymer
687 matrices. As an example of this, the addition of LCNFs to polylactic acid was studied by Wang et
688 al. (2014) and Sun et al. (2014) who analysed the mechanical properties of films made thereof,

689 agreeing that the addition of LCNFs improved the mechanicals properties, such as tensile strength
690 and elongation at break, when compared with pure PLA films.

691 Despite these promising findings, the reports on LCNF-reinforced composites are scattered,
692 occasionally showing moderate if any improvement in mechanical performance, often reporting
693 increases only in Young's modulus (Iwamoto et al. 2014; Ferrer et al. 2016; Horseman et al. 2017;
694 Kim et al. 2017). This highlights the complexity of the interplay between properties such as fibril
695 size and shape, their distribution in the matrix, adhesion between different components, matrix
696 crystallinity, etc. that influence the performance of composite materials.

697 Regarding the present state of the art, the use of LCNF composite materials holds great potential,
698 as the LCNFs are inherently more compatible with hydrophobic matrices than the analogous
699 bleached CNF, allowing facile mixing of the fibrils and the matrix. Combined with the potential
700 of cost and environmental impact savings through lower SEC and need of chemical processing in
701 comparison to bleached CNFs, we believe it is an area worth exploring even further to develop
702 bio-based alternatives for oil-derived synthetic polymer materials.

703 **Conclusions**

704 Pulp and paper industry has traditionally viewed lignin as something that needs to be removed in
705 order to produce high-quality paper. Although there are many similarities between pulping and
706 papermaking and the production of cellulose nanofibrils, the end uses and therefore also the desired
707 functionalities are partly different. For this reason, we promote a change of paradigm in which
708 lignin is seen as a tool that can be used to tailor the properties of CNFs rather than a problematic
709 component that is always detrimental for high-quality products.

710 For this to happen, it is of uttermost importance to consider the amount and structure of the lignin
711 in question as this will affect the ease of fibrillation, the development of interfibrillar H-bonding
712 as well as the water interactions of the material. Presently, the body of literature on LCNFs remains
713 rather scattered, including a wide range of raw materials and mechanical, chemical or enzymatic
714 processing methods. For this reason, comparisons between individual studies are not always
715 straightforward. In general it can be stated that taking into account the high yield, low chemical
716 consumption and manageable mechanical energy consumption of LCNFs, they can be viewed as

717 an economically and ecologically viable family of materials with a number of potential
718 applications.

719 In order to produce extensively fibrillated LCNFs, it is necessary to first break the network
720 structure of native lignin. In practise, this means including a moderate pre-delignification step prior
721 to fibrillation. Additionally, the presence of hemicelluloses is often linked to the presence of lignin;
722 and both can facilitate fibrillation.

723 While lignin is believed to possess antioxidant properties, stabilizing mechanically or thermally
724 formed free radicals, conclusive evidence of how this mechanism affects the fibrillation process is
725 still needed.

726 Interactions between water and LCNFs are complex and depend on a number of factors, including
727 lignin and hemicellulose contents, electrical charge density, and sample morphology. Lignin may
728 be used as a natural hydrophobizing agent in CNFs, which could be beneficial for example in
729 composite reinforcement and Pickering emulsions.

730 **Main nomenclature**

731 LCNFs: lignin-containing cellulose nanofibrils

732 BCNFs: bleached cellulose nanofibrils

733 CNFs: cellulose nanofibrils

734 CNCs: cellulose nanocrystals

735 MFC: microfibrillated cellulose

736 SW: softwood

737 HW: hardwood

738 LCCs: lignin-carbohydrate complexes

739 DP: degree of polymerization

740 CrI: crystallinity index

- 741 DSC: differential scanning calorimetry
- 742 WRV: water retention value
- 743 WVTR: water vapour transmission rate
- 744 WCA: water contact angle
- 745 MOE: modulus of elasticity
- 746 MOR: modulus of rupture

747 **References**

- 748 Abe A, Dusek K, Kobayashi S (2010) Biopolymers: lignin, proteins, bioactive nanocomposites.
749 Springer Science & Business Media, New York
- 750 Abraham E, Deepa B, Pothan LA, et al (2011) Extraction of nanocellulose fibrils from
751 lignocellulosic fibres: A novel approach. *Carbohydr Polym* 86:1468–1475. doi:
752 10.1016/j.carbpol.2011.06.034
- 753 Agarwal UP, Atalla RH (1994) Raman spectral features associated with chromophores in high-
754 yield pulps. *J Wood Chem Technol* 14:227–241. doi: 10.1080/02773819408003095
- 755 Agarwal UP, Ralph SA, Reiner RS, Baez C (2016) Probing crystallinity of never-dried wood
756 cellulose with Raman spectroscopy. *Cellulose* 23:125–144. doi: 10.1007/s10570-015-0788-
757 7
- 758 Ago M, Endo T, Hirotsu T (2004) Crystalline transformation of native cellulose from cellulose I
759 to cellulose II polymorph by a ball-milling method with a specific amount of water.
760 *Cellulose* 11:163–167. doi: 10.1023/B:CELL.0000025423.32330.fa
- 761 Ago M, Ferrer A, Rojas OJ (2016) Starch-Based Biofoams Reinforced with Lignocellulose
762 Nanofibrils from Residual Palm Empty Fruit Bunches: Water Sorption and Mechanical
763 Strength. *ACS Sustain Chem Eng* 4:5546–5552. doi: 10.1021/acssuschemeng.6b01279
- 764 Åkerholm M, Salmén L (2004) Softening of wood polymers induced by moisture studied by
765 dynamic FTIR spectroscopy. *J Appl Polym Sci* 94:2032–2040. doi: 10.1002/app.21133
- 766 Alekhina M, Ershova O, Ebert A, et al (2015) Softwood kraft lignin for value-added
767 applications: Fractionation and structural characterization. *Ind Crops Prod* 66:220–228. doi:
768 10.1016/j.indcrop.2014.12.021
- 769 Ämmälähti E, Brunow G, Bardet M, et al (1998) Identification of Side-Chain Structures in a
770 Poplar Lignin Using Three-Dimensional HMQC-HOHAHA NMR Spectroscopy. *J Agric
771 Food Chem* 46:5113–5117. doi: 10.1021/jf980249o
- 772 Andresen M, Stenius P (2007) Water-in-oil emulsions stabilized by hydrophobized
773 microfibrillated cellulose. *J Dispers Sci Technol* 28:837–844. doi:
774 10.1080/01932690701341827
- 775 Annergren G, Croon I, Enström B, Rydholm S (1961) On the stabilization of spruce
776 glucomannan in wood and holocellulose. *Sven Papperstidning* 64:386–393
- 777 Annergren G, Rydholm S (1959) On the behavior of the hemicelluloses during sulfite pulping.
778 *Sven Papperstidning* 62:737–746
- 779 Arola S, Malho JM, Laaksonen P, et al (2013) The role of hemicellulose in nanofibrillated
780 cellulose networks. *Soft Matter* 9:1319–1326. doi: 10.1039/c2sm26932e
- 781 Atalla RH, Hackney JM, Uhlin I, Thompson NS (1993) Hemicelluloses as structure regulators in
782 the aggregation of native cellulose. *Int J Biol Macromol* 15:109–112. doi: 10.1016/0141-
783 8130(93)90007-9
- 784 Atalla RH, VanderHart DL (1984) Native cellulose: A composite of two distinct crystalline
785 forms. *Science* (80-) 223:283–286. doi: 10.1126/science.223.4633.283

- 786 Aulin C, Gällstedt M, Lindström T (2010) Oxygen and oil barrier properties of microfibrillated
787 cellulose films and coatings. *Cellulose* 17:559–574. doi: 10.1007/s10570-009-9393-y
- 788 Balakshin M, Capanema E, Gracz H, et al (2011) Quantification of lignin-carbohydrate linkages
789 with high-resolution NMR spectroscopy. *Planta* 233:1097–1110. doi: 10.1007/s00425-011-
790 1359-2
- 791 Balakshin MYMY, Capanema EA, Chang HM (2009) Recent Advances in the Isolation and
792 Analysis of Lignins and Lignin-Carbohydrate Complexes. In: Hu TQ (ed) *Characterization*
793 *of Lignocellulosic Materials*. Wiley Online Library, Blackwell Publishing Ltd, pp 148–170
- 794 Ballner D, Herzele S, Keckes J, et al (2016) Lignocellulose nanofiber-reinforced polystyrene
795 produced from composite microspheres obtained in suspension polymerization shows
796 superior mechanical performance. *ACS Appl Mater interfaces* 8:13520–13525. doi:
797 10.1021/acsami.6b01992
- 798 Barclay LRC, Xi F, Norris JQ (1997) Antioxidant properties of phenolic lignin model
799 compounds. *J Wood Chem Technol* 17:73–90. doi: 10.1080/02773819708003119
- 800 Beatson R, Heitner C, Atack D (1984) Factors affecting the sulphonation of spruce. *Pulp Pap Sci*
801 10:J12–J17
- 802 Bian H, Chen L, Dai H, Zhu JY (2017a) Integrated production of lignin containing cellulose
803 nanocrystals (LCNC) and nanofibrils (LCNF) using an easily recyclable di-carboxylic acid.
804 *Carbohydr Polym* 167:167–176. doi: 10.1016/j.carbpol.2017.03.050
- 805 Bian H, Chen L, Dai H, Zhu JY (2017b) Effect of fiber drying on properties of lignin containing
806 cellulose nanocrystals and nanofibrils produced through maleic acid hydrolysis. *Cellulose*.
807 doi: 10.1007/s10570-017-1430-7
- 808 Bian H, Chen L, Gleisner R, et al (2017c) Producing wood-based nanomaterials by rapid
809 fractionation of wood at 80 °C using a recyclable acid hydrotrope. *Green Chem* 19:3370–
810 3379. doi: 10.1039/c7gc00669a
- 811 Blechschmidt J, Engert P, Stephan M (1986) The glass transition of wood from the viewpoint of
812 mechanical pulping. *Wood Sci Technol* 20:263–272. doi: 10.1007/BF00350984
- 813 Boufi S, Kaddami H, Dufresne A (2014) Mechanical performance and transparency of
814 nanocellulose reinforced polymer nanocomposites. *Macromol Mater Eng*. doi:
815 10.1002/mame.201300232
- 816 Brunow G (2005) Methods to Reveal the Structure of Lignin. In: *Biopolymers Online*
- 817 Brunow G, Lundquist K (2010) Functional Groups and Bonding Patterns in Lignin (Including
818 the Lignin-Carbohydrate Complexes). In: Heitner C, Dimmel DR, Schmidt JA (eds) *Lignin*
819 *and Lignans*, Lignin and. CRC Press, Taylor Francis Group, New York, United States, pp
820 268–291
- 821 Brunow G, Lundquist K, Gellerstedt G (1999) Analytical Methods in Wood Chemistry, Pulping,
822 and Papermaking. In: Sjöström E (ed) *Analytical methods in wood chemistry, pulping, and*
823 *papermaking*. Springer, Berlin, pp 77–124
- 824 Capanema EA, Balakshin MY, Chen CL, et al (2001) Structural analysis of residual and
825 technical lignins by 1H-13C correlation 2D NMR-spectroscopy. *Holzforschung* 55:302–

- 826 308. doi: 10.1515/HF.2001.050
- 827 Capanema EA, Balakshin MY, Kadla JF (2004) A Comprehensive Approach for Quantitative
828 Lignin Characterization by NMR Spectroscopy. *J Agric Food Chem* 52:1850–1860. doi:
829 10.1021/jf035282b
- 830 Chakar FS, Ragauskas AJ (2004) Review of current and future softwood kraft lignin process
831 chemistry. *Ind Crops Prod* 20:131–141. doi: 10.1016/j.indcrop.2004.04.016
- 832 Chakraborty A, Sain M, Kortschot M (2005) Cellulose microfibrils: A novel method of
833 preparation using high shear refining and cryocrushing. *Holzforschung* 59:102–107. doi:
834 10.1515/HF.2005.016
- 835 Chen H, Nair SS, Chauhan P, Yan N (2019) Lignin containing cellulose nanofibril application in
836 pMDI wood adhesives for drastically improved gap-filling properties with robust bondline
837 interfaces. *Chem Eng J*. doi: 10.1016/j.cej.2018.11.222
- 838 Chen L, Zhu JY, Baez C, et al (2016) Highly thermal-stable and functional cellulose
839 nanocrystals and nanofibrils produced using fully recyclable organic acids. *Green Chem*
840 18:3835–3843. doi: 10.1039/c6gc00687f
- 841 Chen W, Yu H, Liu Y, et al (2011) Individualization of cellulose nanofibers from wood using
842 high-intensity ultrasonication combined with chemical pretreatments. *Carbohydr Polym*
843 83:1804–1811. doi: 10.1016/j.carbpol.2010.10.040
- 844 Chen Y, Fan D, Han Y, et al (2018) Effect of high residual lignin on the properties of cellulose
845 nanofibrils/films. *Cellulose* 25:6421–6431. doi: 10.1007/s10570-018-2006-
846 x(0123456789().,-volV()0123456789().,-volV)
- 847 Cheng Q, Wang S, Rials TG (2009) Poly(vinyl alcohol) nanocomposites reinforced with
848 cellulose fibrils isolated by high intensity ultrasonication. *Compos Part A Appl Sci Manuf*
849 40:218–224. doi: 10.1016/j.compositesa.2008.11.009
- 850 Crestini C, Lange H, Sette M, Argyropoulos DS (2017) On the structure of softwood kraft lignin.
851 *Green Chem* 19:4104. doi: 10.1039/c7gc01812f
- 852 Crestini C, Melone F, Sette M, Saladino R (2011) Milled wood lignin: A linear oligomer.
853 *Biomacromolecules* 12:3928–3935. doi: 10.1021/bm200948r
- 854 Cui C, Sadeghifar H, Sen S, Argyropoulos DS (2013) Toward thermoplastic lignin polymers;
855 Part II: Thermal & polymer characteristics of kraft lignin & derivatives. *BioResources*
856 8:864–886. doi: 10.15376/biores.8.1.864-886
- 857 Cunha AG, Mougél JB, Cathala B, et al (2014) Preparation of double pickering emulsions
858 stabilized by chemically tailored nanocelluloses. *Langmuir* 30:9327–9335. doi:
859 10.1021/la5017577
- 860 Delgado-Aguilar M, González I, Tarrés Q, et al (2016) The key role of lignin in the production
861 of low-cost lignocellulosic nanofibres for papermaking applications. *Ind Crops Prod*
862 86:295–300. doi: 10.1016/j.indcrop.2016.04.010
- 863 Delgado-Aguilar M, González I, Tarrés Q, et al (2015) Approaching a low-cost production of
864 cellulose nanofibers for papermaking applications. *BioResources* 10:5345–5355. doi:
865 10.15376/biores.10.3.5330-5344

- 866 Dence C, Reeve D (1996) *Pulp Bleaching : Principles and Practice*
- 867 Dence WC (1996) *Pulp Bleaching Principles and Practice*. TAPPI 812–815
- 868 Diop CIK, Tajvidi M, Bilodeau MA, et al (2017) Evaluation of the incorporation of
869 lignocellulose nanofibrils as sustainable adhesive replacement in medium density
870 fiberboards. *Ind Crops Prod* 24:3037–3050. doi: 10.1016/j.indcrop.2017.08.004
- 871 Dizhbite T, Telysheva G, Jurkjane V, Viesturs U (2004) Characterization of the radical
872 scavenging activity of lignins - Natural antioxidants. *Bioresour Technol* 95:309–317. doi:
873 10.1016/j.biortech.2004.02.024
- 874 Dubief D, Samain E, Dufresne A (1999) Polysaccharide microcrystals reinforced amorphous
875 poly(3-hydroxyoctanoate) nanocomposite materials. *Macromolecules*
- 876 Duchesne I, Hult E, Molin U, et al (2001) The influence of hemicellulose on fibril aggregation of
877 kraft pulp fibres as revealed by FE-SEM and CP/MAS13C-NMR. *Cellulose* 8:103–111. doi:
878 10.1023/A:1016645809958
- 879 Dufresne A, Cavaille J-Y, Vignon MR (1997) Mechanical behavior of sheets prepared from
880 sugar beet cellulose microfibrils. *J Appl Polym Sci* 64:1185–1194. doi:
881 10.1002/(SICI)1097-4628(19970509)64:6<1185::AID-APP19>3.0.CO;2-V
- 882 Eichhorn SJ, Dufresne A, Aranguren M, et al (2010) Review: Current international research into
883 cellulose nanofibres and nanocomposites. *J Mater Sci* 45:1–33. doi: 10.1007/s10853-009-
884 3874-0
- 885 Eronen P, Österberg M, Heikkinen S, et al (2011) Interactions of structurally different
886 hemicelluloses with nanofibrillar cellulose. *Carbohydr Polym* 86:1281–1290. doi:
887 10.1016/j.carbpol.2011.06.031
- 888 Espinosa E, Domínguez-Robles J, Sánchez R, et al (2017) The effect of pre-treatment on the
889 production of lignocellulosic nanofibers and their application as a reinforcing agent in
890 paper. *Cellulose* 24:2605–2618. doi: 10.1007/s10570-017-1281-2
- 891 Ewulonu CM, Liu X, Wu M, Huang Y (2019) Ultrasound-assisted mild sulphuric acid ball
892 milling preparation of lignocellulose nanofibers (LCNFs) from sunflower stalks (SFS).
893 *Cellulose* 26:4371–4389. doi: 10.1007/s10570-019-02382-4
- 894 Eyholzer C, Bordeanu N, Lopez-Suevos F, et al (2010) Preparation and characterization of
895 water-redispersible nanofibrillated cellulose in powder form. *Cellulose* 17:19–30. doi:
896 10.1007/s10570-009-9372-3
- 897 Falkehag SI, Marton J, Adler E (1966) Lignin Structure and Reactions. In: Marton J (ed) *Lignin*
898 *Structure and Reactions*. E-Publishing Inc., pp 75–89
- 899 Fall AB, Lindström SB, Sundman O, et al (2011) Colloidal stability of aqueous nanofibrillated
900 cellulose dispersions. *Langmuir* 27:11332–11338. doi: 10.1021/la201947x
- 901 Fardim P, Holmbom B (2005) ToF-SIMS imaging: A valuable chemical microscopy technique
902 for paper and paper coatings. *Appl Surf Sci* 249:393–407. doi:
903 10.1016/j.apsusc.2004.12.041
- 904 Fengel D, Wegener G (1984) *Wood: Chemistry, Ultrastructure, Reactions*. Walter de Gruyter,
905 Berlin and New York

- 906 Ferrer A, Hoeger IC, Lu X, Rojas OJ (2016) Reinforcement of polypropylene with lignocellulose
907 nanofibrils and compatibilization with biobased polymers. *J Appl Polym Sci* 133:43854.
908 doi: 10.1002/app.43854
- 909 Ferrer A, Quintana E, Filpponen I, et al (2012) Effect of residual lignin and
910 heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. *Cellulose*
911 19:2179–2193. doi: 10.1007/s10570-012-9788-z
- 912 Foster EJ, Moon RJ, Agarwal UP, et al (2018) Current characterization methods for cellulose
913 nanomaterials. *Chem. Soc. Rev.* 2609–2679
- 914 Froass PM, Ragauskas AJ, Jiang JE (1996) Chemical structure of residual lignin from kraft pulp.
915 *J Wood Chem Technol* 16:347–365. doi: 10.1080/02773819608545820
- 916 Gellerstedt G, Gierer J, Pettersson E (1976) The Reactions of Lignin during Neutral Sulfite
917 Pulping. Part VII. The Behavior of Structural Elements Containing Carbonyl Groups. *Acta*
918 *Chem Scand* 31:735–741. doi: 10.3891/acta.chem.scand.31b-0735
- 919 Gestranius M, Stenius P, Kontturi E, et al (2017) Phase behaviour and droplet size of oil-in-water
920 Pickering emulsions stabilised with plant-derived nanocellulosic materials. *Colloids*
921 *Surfaces A Physicochem Eng Asp* 519:60–70. doi: 10.1016/j.colsurfa.2016.04.025
- 922 Gindl-Altmatter W, Obersriebnig M, Veigel S, Liebner F (2015) Compatibility between
923 cellulose and hydrophobic polymer provided by microfibrillated lignocellulose.
924 *ChemSusChem* 8:87–91. doi: 10.1002/cssc.201402742
- 925 Glasser WG, Atalla RH, Blackwell J, et al (2012) About the structure of cellulose: Debating the
926 Lindman hypothesis. *Cellulose* 19:589–598. doi: 10.1007/s10570-012-9691-7
- 927 Glynn PAR, van der Hoof BME (1973) Degradation of Polystyrene in Solution by Ultrasonation
928 — A Molecular Weight Distribution Study. *J Macromol Sci Part A - Chem* 7:1695–1719.
929 doi: 10.1080/00222337308066385
- 930 Grabber JH, Ralph J, Lapierre C, Barrière Y (2004) Genetic and molecular basis of grass cell-
931 wall degradability. I. Lignin-cell wall matrix interactions. *Comptes Rendus - Biol* 327:455–
932 465. doi: 10.1016/j.crv.2004.02.009
- 933 Gustafsson J, Lehto JH, Tienvieri T, et al (2003) Surface characteristics of thermomechanical
934 pulps; the influence of defibration temperature and refining. *Colloids Surfaces A*
935 *Physicochem Eng Asp* 225:95–104. doi: 10.1016/S0927-7757(03)00320-0
- 936 Hage R El, Perrin D, Brosse N (2012) Effect of the Pre-Treatment Severity on the Antioxidant
937 Properties of Ethanol Organosolv *Miscanthus x giganteus* Lignin. *Nat Resour* 3:29–34. doi:
938 10.4236/nr.2012.32005
- 939 Hanhikoski S, Solala I, Lathinen P, et al (2016a) Lignocellulosic nanofibrils from neutral
940 sulphite pulps. 251st ACS National Meeting & Exposition, San Diego, USA
- 941 Hanhikoski S, Warsta E, Varhimo A, et al (2016b) Sodium sulphite pulping of Scots pine under
942 neutral and mildly alkaline conditions (NS pulping). *Holzforschung* 70:603–609. doi:
943 10.1515/hf-2015-0099
- 944 Hannuksela T, Fardim P, Holmbom B (2003) Sorption of spruce O-acetylated
945 galactoglucomannans onto different pulp fibres. *Cellulose* 10:317–324. doi:

946 10.1023/A:1027399920427
947 Hatfield R, Vermerris W (2001) Lignin Formation in Plants. The Dilemma of Linkage
948 Specificity. *Plant Physiol* 126:1351–1357. doi: <https://doi.org/10.1104/pp.126.4.1351>
949 Henriksson M, Berglund LA, Isaksson P, et al (2008) Cellulose nanopaper structures of high
950 toughness. *Biomacromolecules* 9:1579–1585. doi: 10.1021/bm800038n
951 Henriksson M, Henriksson G, Berglund LA, Lindström T (2007) An environmentally friendly
952 method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *Eur*
953 *Polym J* 43:3434–3441. doi: 10.1016/j.eurpolymj.2007.05.038
954 Herrera M, Thitiwutthisakul K, Yang X, et al (2018) Preparation and evaluation of high-lignin
955 content cellulose nanofibrils from eucalyptus pulp. *Cellulose* 25:3121–3133. doi:
956 10.1007/s10570-018-1764-9
957 Herrick FW, Casebier RL, Hamilton JK, et al (1983) Microfibrillated cellulose: morphology and
958 accessibility. *J Appl Polym Sci Appl Polym Symp* 37:797–813
959 Herzele S, Veigel S, Liebner F, et al (2016) Reinforcement of polycaprolactone with
960 microfibrillated lignocellulose. *Ind Crops Prod* 93:302–308. doi:
961 10.1016/j.indcrop.2015.12.051
962 Hietala M, Sain S, Oksman K (2017) Highly redispersible sugar beet nanofibers as reinforcement
963 in bionanocomposites. *Cellulose* 24:2177–2189. doi: 10.1007/s10570-017-1245-6
964 Higuchi T (1985) Biosynthesis and biodegradation of wood components. Academic Press Inc.,
965 Orlando
966 Hilburg SL, Elder AN, Chung H, et al (2014) A universal route towards thermoplastic lignin
967 composites with improved mechanical properties. *Polymer (Guildf)* 55:995–1003. doi:
968 10.1016/j.polymer.2013.12.070
969 Hoeger IC, Filpponen I, Martin-Sampedro R, et al (2012) Bicomponent lignocellulose thin films
970 to study the role of surface lignin in cellulolytic reactions. *Biomacromolecules* 13:3228–
971 3240. doi: 10.1021/bm301001q
972 Hoeger IC, Nair SS, Ragauskas AJ, et al (2013) Mechanical deconstruction of lignocellulose cell
973 walls and their enzymatic saccharification. *Cellulose* 20:807–818. doi: 10.1007/s10570-
974 013-9867-9
975 Hon DNS (1979) Formation and behavior of mechanoradicals in pulp cellulose. *J Appl Polym*
976 *Sci* 23:1487–1499. doi: 10.1002/app.1979.070230519
977 Hon DNS (1983a) Mechanochemically Initiated Copolymerization Reactions in Cotton
978 Cellulose. In: ACS Symposium Series. pp 259–279
979 Hon DNS (1983b) Mechanochemical reactions of lignocellulosic materials. In: *J. Appl. Polym.*
980 *Sci.: Appl. Polym. Symp.* United States
981 Horseman T, Tajvidi M, Diop CIK, Gardner DJ (2017) Preparation and property assessment of
982 neat lignocellulose nanofibrils (LCNF) and their composite films. *Cellulose* 24:2455–2468.
983 doi: 10.1007/s10570-017-1266-1
984 Hsieh YC, Yano H, Nogi M, Eichhorn SJ (2008) An estimation of the Young's modulus of
985 bacterial cellulose filaments. *Cellulose* 15:507–513. doi: 10.1007/s10570-008-9206-8

- 986 Hubbe MA, Rojas OJ (2008) Colloidal stability and aggregation of Lignocellulosic materials in
987 aqueous suspension: A review. *BioResources* 3:1419–1491
- 988 Hult EL, Larsson PT, Iversen T (2001) Cellulose fibril aggregation - An inherent property of
989 kraft pulps. *Polymer (Guildf)* 42:3309–3314. doi: 10.1016/S0032-3861(00)00774-6
- 990 Iakovlev M, Heiningen A Van (2012) Kinetics of fractionation by SO₂-ethanol-water (SEW)
991 treatment: Understanding the deconstruction of spruce wood chips. *RSC Adv* 2:3057–3068.
992 doi: 10.1039/c2ra00957a
- 993 Iakovlev M, Hiltunen E, van Heiningen A (2010) Chemical Pulping: Paper technical potential of
994 spruce SO₂-Ethanol-Water (SEW) pulp compared to kraft pulp. *Nord Pulp Pap Res J*
995 25:428–433. doi: 10.3183/npprj-2010-25-04-p428-433
- 996 Isogai A, Saito T, Fukuzumi H (2011a) TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3:71–
997 85. doi: 10.1039/c0nr00583e
- 998 Isogai T, Saito T, Isogai A (2011b) Wood cellulose nanofibrils prepared by TEMPO electro-
999 mediated oxidation. *Cellulose* 18:421–431. doi: 10.1007/s10570-010-9484-9
- 1000 Iversen T, Wännström S (2009) Lignin-Carbohydrate Bonds in a Residual Lignin Isolated from
1001 Pine Kraft Pulp. *Holzforschung* 40:19–22. doi: 10.1515/hfsg.1986.40.1.19
- 1002 Iwamoto S, Abe K, Yano H (2008) The effect of hemicelluloses on wood pulp nanofibrillation
1003 and nanofiber network characteristics. *Biomacromolecules* 9:1022–1026. doi:
1004 10.1021/bm701157n
- 1005 Iwamoto S, Nakagaito AN, Yano H (2007) Nano-fibrillation of pulp fibers for the processing of
1006 transparent nanocomposites. *Appl Phys A Mater Sci Process* 89:461–466. doi:
1007 10.1007/s00339-007-4175-6
- 1008 Iwamoto S, Nakagaito AN, Yano H, Nogi M (2005) Optically transparent composites reinforced
1009 with plant fiber-based nanofibers. *Appl Phys A Mater Sci Process* 81:1109–1112. doi:
1010 10.1007/s00339-005-3316-z
- 1011 Iwamoto S, Yamamoto S, Lee SH, Endo T (2014) Solid-state shear pulverization as effective
1012 treatment for dispersing lignocellulose nanofibers in polypropylene composites. *Cellulose*
1013 21:1573–1580. doi: 10.1007/s10570-014-0195-5
- 1014 Jääskeläinen AS, Tapanila T, Poppius-Levlin K (2000) Carbohydrate reactions in peroxyacetic
1015 acid bleaching. *J Wood Chem Technol* 20:43–59. doi: 10.1080/02773810009349623
- 1016 Jääskeläinen AS, Toikka K, Lähdetie A, et al (2009) Reactions of aromatic structures in
1017 brightness reversion of fully-bleached eucalyptus kraft pulps. *Holzforschung* 63:278–281.
1018 doi: 10.1515/HF.2009.047
- 1019 Johansson L, Peng F, Simonson R (1998) Effects of temperature and sulfonation on shear
1020 deformation of spruce wood. *Doktorsavhandlingar vid Chalmers Tek Hogsk* 31:105–117.
1021 doi: <https://doi.org/10.1007/BF00705926>
- 1022 Junka K, Filpponen I, Lindström T, Laine J (2013) Titrimetric methods for the determination of
1023 surface and total charge of functionalized nanofibrillated/microfibrillated cellulose
1024 (NFC/MFC). *Cellulose* 20:2887–2895. doi: <https://doi.org/10.1007/s10570-013-0043-z>
- 1025 Kalashnikova I, Bizot H, Bertoncini P, et al (2013) Cellulosic nanorods of various aspect ratios

- 1026 for oil in water Pickering emulsions. *Soft Matter* 9:952–959. doi: 10.1039/c2sm26472b
- 1027 Kamel S (2007) Nanotechnology and its applications in lignocellulosic composites, a mini
1028 review. *Express Polym Lett* 1:546–575. doi: 10.3144/expresspolymlett.2007.78
- 1029 Kargarzadeh H, Huang J, Lin N, et al (2018) Recent developments in nanocellulose-based
1030 biodegradable polymers, thermoplastic polymers, and porous nanocomposites. *Prog. Polym.*
1031 *Sci.*
- 1032 Karinkanta P, Illikainen M, Niinimäki J (2013) Effect of grinding conditions in oscillatory ball
1033 milling on the morphology of particles and cellulose crystallinity of Norway spruce (*Picea*
1034 *abies*). *Holzforschung* 67:277–283. doi: 10.1515/hf-2012-0098
- 1035 Keegstra K (2010) Plant cell walls. *Plant Physiol* 154:483–486. doi:
1036 <https://doi.org/10.1104/pp.110.161240>
- 1037 Kilpeläinen I, Xie H, King A, et al (2007) Dissolution of wood in ionic liquids. *J Agric Food*
1038 *Chem* 55:9142–9148. doi: 10.1021/jf071692e
- 1039 Kim B-Y, Han S-Y, Park C-W, et al (2017) Preparation and Properties of Cellulose Nanofiber
1040 Films with Various Chemical Compositions Impregnated by Ultraviolet-Curable Resin.
1041 *BioResources* 12:1767–1778. doi: 10.15376/biores.12.1.1767-1778
- 1042 Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: Fascinating biopolymer and
1043 sustainable raw material. *Angew Chemie - Int Ed* 44:3358–3393. doi:
1044 10.1002/anie.200460587
- 1045 Klemm D, Kramer F, Moritz S, et al (2011) Nanocelluloses: A new family of nature-based
1046 materials. *Angew Chemie - Int Ed* 50:5438–5466. doi: 10.1002/anie.201001273
- 1047 Kondo SI, Sasai Y, Hosaka S, et al (2004) Kinetic analysis of the mechanolysis of
1048 polymethylmethacrylate in the course of vibratory ball milling at various mechanical
1049 energy. *J Polym Sci Part A Polym Chem* 42:4161–4167. doi: 10.1002/pola.20245
- 1050 Konn J, Holmbom B, Nickull O (2002) Chemical reactions in chemimechanical pulping:
1051 material balances of wood components in a CTMP process. *Pulp Pap Sci* 28:395–399
- 1052 Kontturi E, Tammelin T, Österberg M (2006) Cellulose - Model films and the fundamental
1053 approach. *Chem Soc Rev* 35:1287–1304. doi: 10.1039/b601872f
- 1054 Kulasinski K, Guyer R, Derome D, Carmeliet J (2015) Water Adsorption in Wood Microfibril-
1055 Hemicellulose System: Role of the Crystalline-Amorphous Interface. *Biomacromolecules*
1056 16:2972–2978. doi: 10.1021/acs.biomac.5b00878
- 1057 Kulasinski K, Keten S, Churakov S V., et al (2014) Molecular mechanism of moisture-induced
1058 transition in amorphous cellulose. *ACS Macro Lett* 3:1037–1040. doi: 10.1021/mz500528m
- 1059 Lachenal D, Fernandes JC, Froment P (1995) Behaviour of residual lignin in kraft pulp during
1060 bleaching. *J pulp Pap Sci* 21:J173
- 1061 Lahtinen P, Liukkonen S, Pere J, et al (2014) A Comparative study of fibrillated fibers from
1062 different mechanical and chemical pulps. *BioResources* 9:2115–2127. doi:
1063 10.15376/biores.9.2.2115-2127
- 1064 Laine J, Stenius P, Carlsson G, Ström G (1994) Surface characterization of unbleached kraft
1065 pulps by means of ESCA. *Cellulose* 1:145–160. doi: 10.1007/BF00819664

- 1066 Laurichesse S, Avérous L (2014) Chemical modification of lignins: Towards biobased polymers.
1067 Prog Polym Sci 39:1266–1290. doi: 10.1016/j.progpolymsci.2013.11.004
- 1068 Lavoine N, Desloges I, Dufresne A, Bras J (2012) Microfibrillated cellulose - Its barrier
1069 properties and applications in cellulosic materials: A review. Carbohydr Polym 90:735–764.
1070 doi: 10.1016/j.carbpol.2012.05.026
- 1071 Lawoko M, Berggren R, Berthold F, et al (2004) Changes in the lignin-carbohydrate complex in
1072 softwood kraft pulp during kraft and oxygen delignification. Holzforschung 58:603–610.
1073 doi: 10.1515/HF.2004.114
- 1074 Lawoko M, Henriksson G, Gellerstedt G (2005) Structural differences between the lignin-
1075 carbohydrate complexes present in wood and in chemical pulps. Biomacromolecules
1076 6:3467–3473. doi: 10.1021/bm058014q
- 1077 Lawoko M, Henriksson G, Gellerstedt G (2003) New method for quantitative preparation of
1078 lignin-carbohydrate complex from unbleached softwood kraft pulp: Lignin-polysaccharide
1079 networks I. Holzforschung 57:69–74. doi: 10.1515/HF.2003.011
- 1080 Lê HQ, Dimic-Misic K, Johansson L, et al (2018) Effect of lignin on the morphology and
1081 rheological properties of nanofibrillated cellulose produced from γ -valerolactone/water
1082 fractionation process. Cellulose 25:179–194. doi: [https://doi.org/10.1007/s10570-017-1602-](https://doi.org/10.1007/s10570-017-1602-5)
1083 5
- 1084 Leitner J, Hinterstoisser B, Wastyn M, et al (2007) Sugar beet cellulose nanofibril-reinforced
1085 composites. Cellulose 14:419–425. doi: 10.1007/s10570-007-9131-2
- 1086 Li S, Willoughby JA, Rojas OJ (2016) Oil-in-Water Emulsions Stabilized by Carboxymethylated
1087 Lignins: Properties and Energy Prospects. ChemSusChem 9:2460–2469. doi:
1088 10.1002/cssc.201600704
- 1089 Liitiä T, Maunu SL, Hortling B, et al (2003) Cellulose crystallinity and ordering of
1090 hemicelluloses in pine and birch pulps as revealed by solid-state NMR spectroscopic
1091 methods. Cellulose 10:307–316. doi: 10.1023/A:1027302526861
- 1092 Lindström T (2016) Production methods of nanocellulose (CNF) - principles
- 1093 Littunen K, Kilpeläinen P, Junka K, et al (2015) Effect of Xylan Structure on Reactivity in Graft
1094 Copolymerization and Subsequent Binding to Cellulose. Biomacromolecules 16:1102–
1095 1111. doi: 10.1021/bm501732b
- 1096 Lovikka VA, Khanjani P, Väisänen S, et al (2016) Porosity of wood pulp fibers in the wet and
1097 highly open dry state. Microporous Mesoporous Mater 234:326–335. doi:
1098 10.1016/j.micromeso.2016.07.032
- 1099 Lu H, Zhang L, Liu C, et al (2018) A novel method to prepare lignocellulose nanofibrils directly
1100 from bamboo chips. Cellulose 25:7043–7051. doi: 10.1007/s10570-018-2067-x
- 1101 Lupoi JS, Singh S, Parthasarathi R, et al (2015) Recent innovations in analytical methods for the
1102 qualitative and quantitative assessment of lignin. Renew Sustain Energy Rev 49:871–906.
1103 doi: 10.1016/j.rser.2015.04.091
- 1104 Martínez-Sanz M, Gidley MJ, Gilbert EP (2016) Hierarchical architecture of bacterial cellulose
1105 and composite plant cell wall polysaccharide hydrogels using small angle neutron

1106 scattering. *Soft Matter* 12:1534–1549. doi: 10.1039/c5sm02085a

1107 Minor JL (1986) Chemical linkage of polysaccharides to residual lignin in loblolly pine kraft
1108 pulps. *J Wood Chem Technol* 6:185–201. doi: 10.1080/02773818608085223

1109 Missoum K, Belgacem MN, Bras J (2013) Nanofibrillated cellulose surface modification: A
1110 review. *Materials (Basel)* 6:1745–1766. doi: 10.3390/ma6051745

1111 Moon RJ, Martini A, Nairn J, et al (2011) Cellulose nanomaterials review: structure, properties
1112 and nanocomposites. *Chem Soc Rev Chem Soc Rev* 40:3941–3994. doi:
1113 10.1039/c0cs00108b

1114 Moser C, Henriksson G, Lindström ME (2016) Specific surface area increase during cellulose
1115 nanofiber manufacturing related to energy input. *BioResources* 11:7124–7132. doi:
1116 10.15376/biores.11.3.7124-7132

1117 Moser C, Lindström ME, Henriksson G (2015) Toward industrially feasible methods for
1118 following the process of manufacturing cellulose nanofibers. *BioResources* 10:2360–2375.
1119 doi: 10.15376/biores.10.2.2360-2375

1120 Nägele H, Pfitzer J, Nägele E, et al (2002) *Chemical Modification, Properties, and Usage of*
1121 *Lignin*. Springer

1122 Nair SS, Kuo P-YY, Chen H, Yan N (2017) Investigating the effect of lignin on the mechanical,
1123 thermal, and barrier properties of cellulose nanofibril reinforced epoxy composite. *Ind*
1124 *Crops Prod* 100:208–217. doi: 10.1016/j.indcrop.2017.02.032

1125 Nair SS, Yan N (2015) Effect of high residual lignin on the thermal stability of nanofibrils and
1126 its enhanced mechanical performance in aqueous environments. *Cellulose* 22:3137–3150.
1127 doi: 10.1007/s10570-015-0737-5

1128 Nakagaito AN, Yano H (2004) The effect of morphological changes from pulp fiber towards
1129 nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber
1130 based composites. *Appl Phys A Mater Sci Process* 78:547–552. doi: 10.1007/s00339-003-
1131 2453-5

1132 Nikfarjam N, Taheri Qazvini N, Deng Y (2015) Surfactant free Pickering emulsion
1133 polymerization of styrene in w/o/w system using cellulose nanofibrils. *Eur Polym J* 64:179–
1134 188. doi: 10.1016/j.eurpolymj.2015.01.007

1135 Nypelö TE, Carrillo CA, Rojas OJ (2015) Lignin supracolloids synthesized from (W/O)
1136 microemulsions: use in the interfacial stabilization of Pickering systems and organic carriers
1137 for silver metal. *Soft Matter* 11:2046–2054. doi: 10.1039/C4SM02851A

1138 O’Sullivan AC (1997) Cellulose: the structure slowly unravels. *Cellulose* 4:173–207. doi:
1139 *Chemistry and Materials Science*

1140 Olsson A-M, Salmén L (2009) The Softening Behavior of Hemicelluloses Related to Moisture.
1141 In: *Hemicelluloses: Science and Technology*. American Chemical Society, Swedish Pulp
1142 and Paper Research Institute, Stockholm, Sweden, pp 184–197

1143 Österberg M, Vartiainen J, Lucenius J, et al (2013) A fast method to produce strong NFC films
1144 as a platform for barrier and functional materials. *ACS Appl Mater Interfaces* 5:4640–4647.
1145 doi: 10.1021/am401046x

- 1146 Pääkko M, Ankerfors M, Kosonen H, et al (2007) Enzymatic hydrolysis combined with
1147 mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and
1148 strong gels. *Biomacromolecules* 8:1934–1941. doi: 10.1021/bm061215p
- 1149 Pönni R, Vuorinen T, Kontturi E (2012) Proposed nano-scale coalescence of cellulose in
1150 chemical pulp fibers during technical treatments. *BioResources* 7:6077–6108. doi:
1151 10.15376/biores.7.4.6077-6108
- 1152 Ponomarenko J, Dizhbite T, Lauberts M, et al (2015) Analytical pyrolysis - A tool for revealing
1153 of lignin structure-antioxidant activity relationship. *J Anal Appl Pyrolysis* 113:360–369.
1154 doi: 10.1016/j.jaap.2015.02.027
- 1155 Potthast A, Rosenau T, Kosma P (2009) *Analysis of Oxidized Functionalities in Cellulose in:*
1156 *Polysaccharides II.* Springer, Berlin
- 1157 Prakobna K, Terenzi C, Zhou Q, et al (2015) Core-shell cellulose nanofibers for biocomposites -
1158 Nanostructural effects in hydrated state. *Carbohydr Polym* 125:92–102. doi:
1159 10.1016/j.carbpol.2015.02.059
- 1160 Rácz I, Borsa J (1997) Swelling of carboxymethylated cellulose fibres. *Cellulose* 4:293–303. doi:
1161 10.1023/A:1018400226052
- 1162 Ralph J, Brunow G, Boerjan W (2007) *Lignins.* John Wiley & Sons, Ltd.
- 1163 Ralph J, Lundquist K, Brunow G, et al (2004) Lignins: Natural polymers from oxidative
1164 coupling of 4-hydroxyphenyl- propanoids. *Phytochem Rev* 3:29–60. doi:
1165 10.1023/B:PHYT.0000047809.65444.a4
- 1166 Ratner BD, Hoffman AS, Schoen FJ, Lemons JE (2013) *Biomaterials Science: An Introduction*
1167 *to Materials, Third Edit.* Academic Press
- 1168 Rojo E, Peresin MS, Sampson WW, et al (2015) Comprehensive elucidation of the effect of
1169 residual lignin on the physical, barrier, mechanical and surface properties of nanocellulose
1170 films. *Green Chem* 17:1853–1866. doi: 10.1039/c4gc02398f
- 1171 Rosenau T, Potthast A, Kosma P, et al (2007) Isolation and identification of residual
1172 chromophores from aged bleached pulp samples. *Holzforschung* 61:656–661. doi:
1173 10.1515/HF.2007.108
- 1174 Ruiz-Dueñas FJ, Martínez ÁT (2009) Microbial degradation of lignin: How a bulky recalcitrant
1175 polymer is efficiently recycled in nature and how we can take advantage of this. *Microb*
1176 *Biotechnol* 2:164–177. doi: 10.1111/j.1751-7915.2008.00078.x
- 1177 Sadeghifar H, Argyropoulos DS (2015) Correlations of the antioxidant properties of softwood
1178 kraft lignin fractions with the thermal stability of its blends with polyethylene. *ACS Sustain*
1179 *Chem Eng* 3:249–256. doi: 10.1021/sc500756n
- 1180 Saito T, Kimura S, Nishiyama Y, Isogai A (2007) Cellulose nanofibers prepared by TEMPO-
1181 mediated oxidation of native cellulose. *Biomacromolecules* 8:2485–2491. doi:
1182 10.1021/bm0703970
- 1183 Saito T, Nishiyama Y, Putaux JL, et al (2006) Homogeneous suspensions of individualized
1184 microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*
1185 7:1687–1691. doi: 10.1021/bm060154s

- 1186 Sakaguchi M, Sohma J (1975) ESR evidence for main-chain scission produced by mechanical
1187 fracture of polymers at low temperature. *J Polym Sci Polym Phys Ed* 13:1233–1245. doi:
1188 10.1002/pol.1975.180130614
- 1189 Sakata I, Senju R (1975) Thermoplastic behavior of lignin with various synthetic plasticizers. *J*
1190 *Appl Polym Sci* 19:2799–2810. doi: 10.1002/app.1975.070191015
- 1191 Salmén L (1984) Viscoelastic properties of in situ lignin under water-saturated conditions. *J*
1192 *Mater Sci* 19:3093–3096. doi: 10.1007/BF01026988
- 1193 Salmén L (1982) Temperature and water induced softening behavior of wood fiber based
1194 materials. *Dep Pap Technol*
- 1195 Salmén L, Olsson A. (1998) Interaction Between Hemicelluloses, Lignin and Cellulose, Structre-
1196 Property Relationships. *J Pulp Pap Sci* 24:99–103
- 1197 Sánchez R, Espinosa E, Domínguez-Robles J, et al (2016) Isolation and characterization of
1198 lignocellulose nanofibers from different wheat straw pulps. *Int J Biol Macromol* 92:1025–
1199 1033. doi: 10.1016/j.ijbiomac.2016.08.019
- 1200 Santucci BS, Bras J, Belgacem MN, et al (2016) Evaluation of the effects of chemical
1201 composition and refining treatments on the properties of nanofibrillated cellulose films from
1202 sugarcane bagasse. *Ind Crops Prod* 91:238–248. doi: 10.1016/j.indcrop.2016.07.017
- 1203 Sehaqui H, Liu A, Zhou Q, Berglund LA (2010) Fast Preparation Procedure for Large, Flat
1204 Cellulose and Cellulose/Inorganic Nanopaper Structures. *Biomacromolecules* 11:2195–
1205 2198. doi: <https://doi.org/10.1021/bm100490s>
- 1206 Siqueira G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: A review of preparation,
1207 properties and applications. *Polymers (Basel)*. 2:728–765
- 1208 Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: A review.
1209 *Cellulose* 17:459–494. doi: 10.1007/s10570-010-9405-y
- 1210 Siró I, Plackett D, Hedenqvist M, et al (2011) Highly transparent films from carboxymethylated
1211 microfibrillated cellulose: The effect of multiple homogenization steps on key properties. *J*
1212 *Appl Polym Sci* 119:2652–2660. doi: 10.1002/app.32831
- 1213 Sixta H, Potthast A, Krotschek AW (2006) Raw material for pulp. In: Sixta H (ed) *Handbook of*
1214 *Pulp*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Lenzing Austria, pp 21–61
- 1215 Sjöström E (1993) *Wood chemistry-fundamentals and applications*, 2nd edn. Academic Press
1216 Inc., San Diego
- 1217 Sjöström E, Westermarck U (1999) *Chemical Composition of Wood and Pulps: Basic*
1218 *Constituents and Their Distribution*. Analytical Methods in Wood Chemistry, Pulping, and
1219 Papermaking. Springer, Berlin, Heidelberg
- 1220 Solala I, Antikainen T, Reza M, et al (2014) Spruce fiber properties after high-temperature
1221 thermomechanical pulping (HT-TMP). *Holzforschung* 68:195–201. doi: 10.1515/hf-2013-
1222 0083
- 1223 Solala I, Henniges U, Pirker KF, et al (2015) Mechanochemical reactions of cellulose and
1224 styrene. *Cellulose* 22:3217–3224. doi: 10.1007/s10570-015-0724-x
- 1225 Solala I, Volperts A, Andersone A, et al (2012) Mechanoradical formation and its effects on

- 1226 birch kraft pulp during the preparation of nanofibrillated cellulose with Masuko refining.
1227 *Holzforschung* 66:477–483. doi: 10.1515/HF.2011.183
- 1228 Spence KL, Venditti RA, Habibi Y, et al (2010) The effect of chemical composition on
1229 microfibrillar cellulose films from wood pulps: Mechanical processing and physical
1230 properties. *Bioresour Technol* 101:5961–5968. doi: 10.1016/j.biortech.2010.02.104
- 1231 Spence KL, Venditti RA, Rojas OJ, et al (2011a) Water vapor barrier properties of coated and
1232 filled microfibrillated cellulose composite films. *BioResources* 6:4370–4388
- 1233 Spence KL, Venditti RA, Rojas OJ, et al (2011b) A comparative study of energy consumption
1234 and physical properties of microfibrillated cellulose produced by different processing
1235 methods. *Cellulose* 18:1097–1111. doi: 10.1007/s10570-011-9533-z
- 1236 Stelte W, Sanadi AR (2009) Preparation and characterization of cellulose nanofibers from two
1237 commercial hardwood and softwood pulps. *Ind Eng Chem Res* 48:11211–11219. doi:
1238 10.1021/ie9011672
- 1239 Sun H, Wang X, Zhang L (2014) Preparation and characterization of poly(lactic acid)
1240 nanocomposites reinforced with Lignin-containing cellulose nanofibrils. *Polym* 38:464–
1241 470. doi: 10.7317/pk.2014.38.4.464
- 1242 Tammelin T, Österberg M, Johnsen IA (2007) Adsorption of colloidal extractives and dissolved
1243 hemicelluloses on thermomechanical pulp fiber components studied by QCM-D. *Nord Pulp
1244 Pap Res J* 22:93–101. doi: 10.3183/npprj-2007-22-01-p093-101
- 1245 Tammelin T, Paananen A, Österberg M (2009) Hemicelluloses at Interfaces: Some Aspects of
1246 the Interactions. In: Lucian LA, Rojas OJ (eds) *The Nanoscience and Technology of
1247 Renewable Biomaterials*. Wiley-Blackwell Publishing Ltd, Chichester, pp 149–172
- 1248 Tanaka R, Saito T, Hänninen T, et al (2016) Viscoelastic Properties of Core-Shell-Structured,
1249 Hemicellulose-Rich Nanofibrillated Cellulose in Dispersion and Wet-Film States.
1250 *Biomacromolecules* 17:2104–2111. doi: 10.1021/acs.biomac.6b00316
- 1251 Taniguchi T, Okamura K (1998) New films produced from microfibrillated natural fibres. *Polym
1252 Int* 47:291–294. doi: 10.1002/(SICI)1097-0126(199811)47:3<291::AID-PI11>3.0.CO;2-1
- 1253 Tarrés Q, Ehman NV, Vallejos ME, et al (2017) Lignocellulosic nanofibers from triticale straw:
1254 The influence of hemicelluloses and lignin in their production and properties. *Carbohydr
1255 Polym* 163:20–27. doi: 10.1016/j.carbpol.2017.01.017
- 1256 Tejado A, Alam MN, Antal M, et al (2012) Energy requirements for the disintegration of
1257 cellulose fibers into cellulose nanofibers. *Cellulose* 19:831–842. doi: 10.1007/s10570-012-
1258 9694-4
- 1259 Tenhunen TM, Peresin MS, Penttilä PA, et al (2014) Significance of xylan on the stability and
1260 water interactions of cellulosic nanofibrils. *React Funct Polym* 85:157–166. doi:
1261 10.1016/j.reactfunctpolym.2014.08.011
- 1262 Tenkanen M, Tamminen T, Hortling B (1999) Investigation of lignin-carbohydrate complexes in
1263 kraft pulps by selective enzymatic treatments. *Appl Microbiol Biotechnol* 51:241–248. doi:
1264 10.1007/s002530051388
- 1265 Thornton J, Ekman R, Holmbom B, ÖRså F (1994) Polysaccharides dissolved from norway

- 1266 spruce in thermomechanical pulping and peroxide bleaching. *J Wood Chem Technol*
1267 14:159–175. doi: 10.1080/02773819408003092
- 1268 Tomashevskii EE, Zakrevskii VA, Novak II, et al (1975) Kinetic micromechanics of polymer
1269 fracture. *Int J Fract* 11:803–815. doi: 10.1007/BF00012898
- 1270 Turbak A., Snyder F., Sandberg K (1982) Microfibrillated cellulose, a new cellulose product:
1271 Properties, uses, and commercial potential. *J Appl Polym Sci Appl Polym Symp* 37:
- 1272 Ugartondo V, Mitjans M, Vinardell MP (2008) Comparative antioxidant and cytotoxic effects of
1273 lignins from different sources. *Bioresour Technol* 99:6683–6687. doi:
1274 10.1016/j.biortech.2007.11.038
- 1275 Vänskä E, Vihelä T, Peresin MS, et al (2016) Residual lignin inhibits thermal degradation of
1276 cellulosic fiber sheets. *Cellulose* 23:199–212. doi: 10.1007/s10570-015-0791-z
- 1277 Villares A, Moreau C, Dammak A, et al (2015) Kinetic aspects of the adsorption of xyloglucan
1278 onto cellulose nanocrystals. *Soft Matter* 11:6472–6481. doi: 10.1039/c5sm01413a
- 1279 Vinardell MP, Ugartondo V, Mitjans M (2008) Potential applications of antioxidant lignins from
1280 different sources. *Ind Crops Prod* 27:220–223. doi: 10.1016/j.indcrop.2007.07.011
- 1281 Visanko M, Sirviö JA, Piltonen P, et al (2017a) Mechanical fabrication of high-strength and
1282 redispersible wood nanofibers from unbleached groundwood pulp. *Cellulose* 24:4173–4187.
1283 doi: 10.1007/s10570-017-1406-7
- 1284 Visanko M, Sirviö JA, Piltonen P, et al (2017b) Castor oil-based biopolyurethane reinforced with
1285 wood microfibers derived from mechanical pulp. *Cellulose* 24:2531–2543. doi:
1286 10.1007/s10570-017-1286-x
- 1287 Vuorinen T, Teleman A, Fagerstrom P, et al (1999) Selective hydrolysis of hexenuronic acid
1288 groups and its application in ECF and TCF bleaching of kraft pulps. *J Pulp Pap Sci* 25:155–
1289 162
- 1290 Vuorinen TJ, Buchert UJ, Teleman AB, Tenkanen TM (2004) Method of treating cellulosic pulp
1291 to remove hexenuronic acid
- 1292 Wågberg L, Decher G, Norgren M, et al (2008) The build-up of polyelectrolyte multilayers of
1293 microfibrillated cellulose and cationic polyelectrolytes. *Langmuir* 24:784–795. doi:
1294 10.1021/la702481v
- 1295 Wågberg L, Winter L, Ödberg L, Lindström T (1987) On the charge stoichiometry upon
1296 adsorption of a cationic polyelectrolyte on cellulosic materials. *Colloids and Surfaces*
1297 27:163–173. doi: 10.1016/0166-6622(87)80335-9
- 1298 Wang R, Chen L, Zhu JY, Yang R (2017) Tailored and integrated production of carboxylated
1299 cellulose nanocrystals (CNC) with nanofibrils (CNF) through maleic acid hydrolysis.
1300 *ChemNanoMat* 3:328 – 335. doi: 10.1002/cnma.201700015
- 1301 Wang X, Cui X, Zhang L (2012) Preparation and Characterization of Lignin-containing
1302 Nanofibrillar Cellulose. *Procedia Environ Sci* 16:125–130. doi:
1303 10.1016/j.proenv.2012.10.017
- 1304 Wang X, Sun H, Bai H, Zhang L (2014) Thermal, Mechanical, and Degradation Properties of
1305 Nanocomposites Prepared using Lignin-Cellulose Nanofibers and Poly(Lactic Acid).

- 1306 BioResources 9:3211–3224. doi: 10.15376/biores.9.2.3211-3224
- 1307 Wen Y, Yuan Z, Liu X, et al (2019) Preparation and Characterization of Lignin-Containing
1308 Cellulose Nanofibril from Poplar High-Yield Pulp via TEMPO-Mediated Oxidation and
1309 Homogenization. ACS Sustain Chem Eng. doi: 10.1021/acssuschemeng.8b06355
- 1310 Widsten P, Laine JE, Qvintus-Leino P, Tuominen S (2001) Effect of high-temperature
1311 fiberization on the chemical structure of softwood. J Wood Chem Technol 21:227–245. doi:
1312 10.1081/WCT-100105374
- 1313 Willför S, Hemming J, Reunanen M, et al (2003a) Lignans and lipophilic extractives in Norway
1314 spruce knots and stemwood. Holzforschung 57:27–36. doi: 10.1515/HF.2003.005
- 1315 Willför S, Hemming J, Reunanen M, Holmbom B (2003b) Phenolic and lipophilic extractives in
1316 Scots pine knots and stemwood. Holzforschung 57:359–372. doi: 10.1515/HF.2003.054
- 1317 Xhanari K, Syverud K, Stenius P (2011) Emulsions Stabilized by Microfibrillated Cellulose: The
1318 Effect of Hydrophobization, Concentration and O/W Ratio. J Dispers Sci Technol 32:447–
1319 452. doi: <https://doi.org/10.1080/01932691003658942>
- 1320 Yamamoto M, Iakovlev M, van Heiningen A (2014) Kinetics of SO₂-ethanol-water (SEW)
1321 fractionation of hardwood and softwood biomass. Bioresour Technol 155:307–313. doi:
1322 10.1016/j.biortech.2013.12.100
- 1323 Yan Y, Herzele S, Mahendran AR, et al (2016) Microfibrillated lignocellulose enables the
1324 suspension-polymerisation of unsaturated polyester resin for novel composite applications.
1325 Polymers (Basel) 8:255. doi: 10.3390/polym8070255
- 1326 Yang H, Chen Q, Wang K, Sun RC (2013) Correlation between hemicelluloses-removal-induced
1327 hydrophilicity variation and the bioconversion efficiency of lignocelluloses. Bioresour
1328 Technol 147:539–544. doi: 10.1016/j.biortech.2013.08.087
- 1329 Yousefi H, Azari V, Khazaeian A (2018) Direct mechanical production of wood nanofibers from
1330 raw wood microparticles with no chemical treatment. Ind Crops Prod 115:26–31. doi:
1331 10.1016/j.indcrop.2018.02.020
- 1332 Zhao HP, Feng XQ, Gao H (2007) Ultrasonic technique for extracting nanofibers from nature
1333 materials. Appl Phys Lett 90:073112. doi: 10.1063/1.2450666
- 1334 Ziobro GC (1990) Origin and nature of kraft colour: 1 role of aromatics. J Wood Chem Technol
1335 10:133–149. doi: 10.1080/02773819008050233
- 1336