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Design strategies, properties and applications of cellulose nanomaterials-enhanced products with residual, technical or nanoscale lignin – A review

Ramakrishna Trovagunta,^a Tao Zou,^b Monica Österberg,^b Stephen S Kelley^a and Nathalie Lavoine^{a*}

^aDepartment of Forest Biomaterials, College of Natural Resources, North Carolina State University, Raleigh, NC 27695-8005, U.S.A

^bAalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, Vuorimiehentie 1, 02150 Espoo, Finland

*Corresponding Author: Dr. Nathalie Lavoine, *E-mail: nmlavoin@ncsu.edu*

Abstract

With the increasing demand for greener alternatives to fossil-derived products, research on cellulose nanomaterials (CNMs) has rapidly expanded. The combination of nanoscale properties and sustainable attributes makes CNMs an asset in the quest for a sustainable society. However, challenges such as the hydrophilic nature of CNMs, their low compatibility with non-polar matrices and modest thermal stability, slow the development of end-uses. Combination of CNMs with amphiphilic lignin can improve the thermal stability, enhance the compatibility with non-polar matrices and, additionally, endow CNMs with new functionalities e.g., UV shielding or antioxidative properties.

This article comprehensively reviews the different design strategies and their influence on properties and applications of CNMs containing lignin in various forms; either as residual lignin, added technical lignin, or nanoscale particles. The review focuses especially on the synergy created between CNMs and lignin, paving the way for new production routes and use of CNM/lignin materials in high-performance applications.

Keywords: Cellulose nanomaterials, Ligno-nanocellulose, Technical lignin, Colloidal lignin particles, Residual Lignin

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Introduction

Global population increases are directly associated with increases in fossil-derived products and wastes. The rising environmental concerns linked to the manufacturing, usage and end-of-life of these products have driven the scientific and commercial interest in sustainable alternatives.

Renewable nanomaterials from (ligno)cellulosic biomass (i.e., particles with at least one dimension in the nanoscale (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011)) are being pursued as one of the most promising alternatives in response to these environmental challenges. Nanomaterials from renewable resources combine the advantages of synthetic nanotechnology and sustainable aspects such as renewability, recyclability, biodegradability, biocompatibility, and cost-efficiency (Klemm et al., 2011; Moon, Schueneman, & Simonsen, 2016). Cellulose nanomaterials (CNMs) are the most intensively studied and well-known renewable nanomaterials. They have been the subject of intense research activities over the past three decades and are now entering in an early phase of large-scale production and commercialization. In addition, other types of renewable nanomaterials have recently been reported; for instance, nanoparticles of lignin (Frangville et al., 2012; Yearla & Padmasree, 2016; Rangan, Manchiganti, Thilaividankan, Kestur, & Menon, 2017), starch (Boufi et al., 2018; Hao, Chen, Li, & Gao, 2019), chitin and chitosan (Oun & Rhim, 2018; Sivakami et al., 2013) and some early attempts with hemicelluloses (Johnson, Karaaslan, Renneckar, Mansfield, & Unda, 2018).

CNMs can be produced from diverse (ligno)cellulosic feedstocks such as wood (Isogai, 2013), agricultural waste residues (García, Gandini, Labidi, Belgacem, & Bras, 2016), tunicates (Elazzouzi-Hafraoui et al., 2008), among others, or can directly be synthesized by certain strains of bacteria (Gatenholm & Klemm, 2010). The differences in raw materials can explain some of the characteristics and properties of the resulting CNMs in terms of, e.g., particle shape, aspect ratio (i.e., length to diameter ratio), and surface chemistries (Lavoine, Durmaz, & Trovagunta, 2019). In general, CNMs can be grouped into two main categories, namely (i) cellulose nanocrystals (CNCs) and (ii) cellulose nanofibrils (CNFs) (TAPPI, 2011). The transmission electron micrographs highlighting the morphological differences between CNFs and CNCs are illustrated in **Fig.1**. CNCs are spindle-like nanoparticles of 3-50 nm in width and 5-50 in aspect ratio, commonly obtained by acid hydrolysis. In contrast, CNFs are more flexible cellulose nanoparticles of 3-100 nm in width and 10-100 in aspect ratio and can be produced by successive

high-shear mechanical treatments, after a mechanical, chemical or enzymatic pre-treatment (Nechyporchuk, Belgacem, & Bras, 2016). A high number of review articles have already discussed in detail processing, properties, and diverse applications of CNMs and CNM-based products. The readers are referred to the following articles and book chapters for further information on this topic (Dufresne, 2017; Habibi, Lucia, & Rojas, 2010; Lavoine, Desloges, Dufresne, & Bras, 2012; Moon et al., 2011; Nechyporchuk et al., 2016).

Fig. 1. Transmission electron microscopy (TEM) images of A) CNCs derived from banana rachis (Adapted and printed with permission from Zuluaga, Putaux, Restrepo, Mondragon, & Gañán (2007)); B) CNFs from softwood Kraft pulp fibers (Adapted and printed with permission from Qing et al. (2013)). (Copyright © 2007, Springer Nature and Copyright © 2013 Elsevier Ltd.)

Alternatively, this review article proposes a new perspective on CNMs and focuses more, especially on processing strategies, properties, and applications of CNMs combined with lignin, either residual lignin, technical lignin, or nanoscale particles of lignin. In the past 5-10 years, a number of sustainable solutions have been proposed to enhance the properties of CNMs, and lignin has been proposed as a promising alternative to accomplishing this goal. Specific properties of CNMs, such as low density, large surface area, high aspect ratio, versatile surface chemistry, and high mechanical strength, have fueled the development of CNM-based products for a wide spectrum of applications (Klemm et al., 2011; Moon et al., 2016). However, the use of CNMs has also been limited by their hydrophilic nature, their poor resistance to fungi decay, low compatibility with hydrophobic/non-polar matrices, and moderate thermal stability (Siró & Plackett, 2010). While surface modification approaches either via physical adsorption or chemical modification have been proposed to enhance the properties of CNMs (Rol, Belgacem, Gandini, &

Bras, 2019), these strategies remain costly, non-sustainable, or may not be adapted to the target application.

Lignin is a natural phenolic polymer obtained primarily from wood with intrinsic properties that can be complementary to the properties of CNMs, such as high stiffness, resistance to moisture and some fungi, and a different thermal behavior with charring and plasticizing effects (Boerjan, Ralph, & Baucher, 2003; Kawamoto, 2017). The combination of CNMs and lignin can thus offer a broader range of functionalities, including, improved water and gas barrier properties (Rojo et al., 2015), enhanced compatibility with hydrophobic polymer matrices (Ballner, Herzele, & Keckes, 2016), biocide activities (Xiao Wang et al., 2019), and UV-absorbing characteristic (Sadeghifar, Venditti, Jur, Gorga, & Pawlak, 2017).

Hence, this review article summarizes and elaborates on the properties of cellulose nanomaterials (as main component, >50 wt%) and lignin. The design strategies for CNM/lignin materials, processing routes, properties, and potential end-use applications will be detailed and compared to the processing routes, properties, and applications of CNMs with essentially no residual lignin. This review article will focus on three different forms of lignin and resulting nanomaterials, namely (i) residual lignin (as found in lignin-containing cellulose nanomaterials, L-CNMs), (ii) technical lignin, commonly isolated from pulp mills and added back into CNMs, and (iii) colloidal lignin particles (CLPs), also used as fillers. The influence of the different types of lignin on the properties of CNM/lignin materials will be reviewed, and the role of lignin in enhancing the properties of CNMs will be highlighted as a suggestion for new sustainable design pathways.

1. Design strategies and Processing of CNM/Lignin Materials

Two main strategies have been investigated for the design of cellulose nanomaterials (CNMs) and lignin composite materials as illustrated on **Fig. 2**. The first strategy is an *in-situ* approach (**Fig. 2A**), which involves the direct production and use of CNMs from unbleached pulps. Unbleached pulps can contain up to 20 wt% of residual lignin depending on the intensity of the pulping process. Residual lignins in unbleached pulp are still bound to the surrounding carbohydrates, partially replicating the so-called lignin-carbohydrate complexes (LCCs) (Lawoko, Henriksson, & Gellerstedt, 2003; Minor, 1986). The second strategy is a *composite* approach (**Fig. 2B**), where lignin is used as an additive to CNMs. In this case, lignin is a by-product of the

delignification process in the pulp mills and commonly referred to as technical lignin. Technical lignin can either be used as produced, meaning in a dry powder form, or be further processed and converted into colloidal lignin particles (CLPs) (Farooq, Zou, Riviere, Sipponen, & Österberg, 2019; Sadeghifar et al., 2017). Unlike residual lignins, technical lignins are more heterogeneous with a wider variety of functional groups, such as sulfonates, phenolic hydroxyls, or thiols, which result from the delignification process used to isolate lignin from the carbohydrate matrix. In this review article, we will constantly refer to three types of lignins, namely (i) residual lignin, (ii) technical lignin, and (iii) CLPs. All three types have been exploited in the design, production, and characterization of CNM/lignin materials.

Fig. 2. Production routes of CNM/lignin materials from lignocellulosic biomass. A) *In-situ* approach: Production of lignocellulose nanomaterials from lignocellulosic fibers with a residual lignin content ranging from 5 to 20 wt%; A1) L-CNFs obtained by high-shear mechanical treatment, without or with pre-treatments (Adapted and reprinted with permission from Bian et al. (2017a)); A2) L-CNCs obtained by acid hydrolysis (Adapted and reprinted with permission from Jungang Jiang et al. (2020)). B) *Composite* approach: Blending suspensions of CNMs with either B1) technical lignin, as a by-product from, e.g., pulp mills or B2) colloidal lignin particles (Adapted and reprinted with permission from Bangalore Ashok et al. (2020)). (Copyright © 2020, American Chemical Society, and Copyright © 2017 and 2020, Elsevier Ltd)

1.1. Residual-lignin containing cellulose nanomaterials (L-CNMs)

Wood is made of ~40 % cellulose, ~25 % hemicelluloses, and ~25 % lignin. Other lignocellulosic biomass such as agricultural waste residues or barks have a higher content of cellulose (~55 %) and a lower content of lignin (~15 %) than wood (Buranov & Mazza, 2008; Sjöström, 1993). The production of L-CNMs starts with the extraction of hemicelluloses and lignin from the lignocellulosic biomass by pulping. The pulping process can lower the content of lignin and hemicelluloses down to ~5 % and 15 %, respectively, depending on the chemicals and processing conditions (Sjöström & Westermarck, 1999). The resulting unbleached fibers can then be further processed into CNMs, following any typical production pathways, e.g., mechanical shearing for cellulose nanofibrils (CNFs) (Spence, Venditti, Rojas, Habibi, & Pawlak, 2011) or acid hydrolysis for cellulose nanocrystals (CNCs) (Bian, Chen, Dai, & Zhu, 2017a). Several efforts have been undertaken to prepare CNMs from various unbleached lignocellulosic sources such as wood (Herrera et al., 2018; Xuan Wang, Cui, & Zhang, 2012), agricultural waste residues (Espinosa, Sánchez, Otero, Domínguez-Robles, & Rodríguez, 2017; Tarrés et al., 2017) and bark (Huang et al., 2019). **Table 1** summarizes the processing conditions used to produce L-CNMs from lignocellulosic biomass that have been reported in the literature.

183 **Table 1.** Processing of lignocellulosic biomass for the production of CNMs with residual lignin
184 (also referred to as, lignocellulose nanomaterials, or L-CNMs)
185

Processing of lignocellulosic biomass				Production of L-CNMs			
L-CNM Type	Feedstock	Pulping	Residual Lignin Content (wt%)	Pre-treatment	Mechanical / Chemical treatment	Solids content (wt%)	Ref.
L-CNFs ¹	Wood pulp	Kraft and TMP ²	0.8-31	Valley beater		0.7	(Spence et al., 2010)
	Wood pulp	Kraft and TMP	5-10	-		-	(Xuan Wang et al., 2012)
	Wood pulp fines	TMP and Kraft	-	Bauer-McNett Classifier		-	(Osong, 2013)
	Wheat/corn/oats/ barley straws	Alkali treatment	9-13	PFI refining / Enzymatic / TEMPO ³		1	(Espinosa, Sánchez, Otero, et al., 2017)
	Hardwood/ Triticale straw	Kraft/Alkali treatment	0.5-8	-		2	(Tarrés et al., 2017)
	Tagasaste and Leucaena	Alkali treatment	-	PFI refining / Enzymatic / TEMPO	Homogenizer	1	(Espinosa, Sánchez, González, et al., 2017)
	Poplar	Alkaline peroxide mechanical pulp	~0.2-23	TEMPO		1	(Wen et al., 2019)
	Bagasse pulp boards	Alkali treatment	0.7-23	Grinder		2	(N. Zhang, Tao, Lu, & Nie, 2019)
	Wheat straws	Alkali treatment	~9	PFI/TEMPO ³		1	(Espinosa, Bascón-Villegas, et al., 2019)
	Maple/Birch	CTMP ⁴ / chlorite treatment	6-22	Grinder		1	(Fu et al., 2020)
	Wheat straw	Alkali treatment	-	PFI refining / Enzymatic	Homogenizer/ Grinder/ Twin-Screw extruder (TSE)	1.5-20	(Espinosa, Rol, Bras, & Rodríguez, 2019)
	Wheat straw	Alkali treatment	2-9	PFI refining		1.5-20	(Espinosa, Rol, Bras, & Rodríguez, 2020)
	Birch	Kraft and oxygen delignified	0.5-3	PFI		1.8	(Ferrer et al., 2012)
	Spruce wood chips	SEW ⁵	2-13	-		1.5	(Morales et al., 2014)
	Spruce wood chips	SEW	0.2-14	Willey Mill		2	(Rojo et al., 2015)
	Eucalyptus / Birch and Maple	Kraft	~0.2-17	Lab disintegrator and maleic acid hydrolysis		1-2	(Bian et al., 2017a)
	Hardwood Birch and Maple mixed hardwood	Kraft	4	Lab disintegrator and maleic acid hydrolysis	Microfluidizer	1-2	(Bian et al., 2017b)
	Wood pulp	-	~0.1-17	Lab disintegrator and maleic acid hydrolysis		1-2	(Bian et al., 2018)
	Eucalyptus	Semi-chemical pulping / sulfite	~ 0.2-23	Enzymatic/ 4-AT TEMPO ⁶		2	(Herrera et al., 2018)
	Wheat straws	Alkali treatment	8-19	Disk refiner		0.5	(L. Gu, Jiang, Song, Jin, & Xiao, 2019)
	Spruce	Kraft	2-24	PFI refining		0.25	(Oliaei et al., 2020)
	Birch	Kraft cooking and oxygen delignified	0.1-2	-		2	(Solala et al., 2012)
	Softwood	Mechanical and Kraft	0.2-29	Lab disintegrator	Grinder	2	(Hoeger et al., 2013)
	Softwood/ hardwood	Kraft/TMP/ CTMP	1-26	High-shear dissolver		2	(Lahtinen, Liukkonen, Pere, Sneck, & Kangas, 2014)

	Lodgepole pine bark	Alkali/chlorite treatment	5-21	-		2	(Nair & Yan, 2015)
	Red cedar bark	Alkali treatment	23	-		2	(Nair, Kuo, Chen, & Yan, 2017)
	Spruce groundwood	Sulfate	0.2-27	-		1.5	(Visanko, Sirviö, Pilttonen, Sliz, et al., 2017)
	Hardwood wastes	Alkali treatment	~3-6	-		1	(Scatolino et al., 2017)
	Softwood and hardwood	Chlorite treatment	26-36	-		1-5	(C. Park et al., 2017)
	Softwood chips	TMP	-	-		3	(Diop et al., 2017a)
	Softwood chips	TMP	-	-		3	(Diop et al., 2017b)
	Poplar	Alkali treatment	~0.2-22	-		1	(Y. Chen et al., 2018)
	Red cedar bark	Alkali treatment	~ 25	-		2	(Nair, Chen, Peng, Huang, & Yan, 2018)
	Red cedar bark	Alkali/chlorite treatment	5-20	-		2	(Peng, Nair, Chen, Yan, & Cao, 2018)
	Paulownia wood	Pulping and Bleaching	29	-		2	(Yousefi et al., 2018)
	Wheat straw	Acid treatment (p-TsOH) ⁷		12-24		2	(Ma, Zhu, Gleisner, Yang, & Zhu, 2018)
	Willow bark and wood	Acid treatment (p-TsOH)	22 – 43	Disk refiner		-	(Dou et al., 2019)
	Wheat straw	Acid treatment (p-TsOH)	~0.2-15			1	(Bian et al., 2019)
	Red cedar bark	Alkali treatment	22	-		2	(H. Chen, Nair, Chauhan, & Yan, 2019)
	Red cedar bark	Alkali treatment	~0.2-23	-		2	(Huang et al., 2019)
	Scots Pine	Neutral Sulfite/Neutral Sulfite AQ ⁸	10-24	-		2	(Hanhikoski, Solala, Lahtinen, Niemelä, & Vuorinen, 2020)
	Reed straws	Alkali treatment	~ 2-18	Ball milling	Ultrasonication	-	(X. Liu et al., 2019)
	Wood pulp	Kraft and TMP	1.7-20	TEMPO		0.1	(Jie Jiang et al., 2020)
	Wood pulp	TMP	10-15	Hydro-pulper	Disk refiner	1-3	(Tayeb et al., 2020)
	Eucalyptus / Birch and Maple	Kraft	~0.2-17	Lab disintegrator	Maleic acid hydrolysis	-	(Bian et al., 2017a)
	hardwood Birch and Maple mixed hardwood	Kraft	3.9	Lab disintegrator		-	(Bian et al., 2017b)
L-CNCs ⁹	Luffa sponge	-	~18	-	Choline chloride and oxalic acid dihydrate / sulfuric acid and ultrasonication	-	(Hong et al., 2020)
	Softwood	TMP	~ 48	-	Choline chloride and oxalic acid dihydrate / Choline chloride and oxalic acid dihydrate with p-TsOH / sulfuric acid and blending	-	(Jungang Jiang et al., 2020)
	Aspen wood	-	10-49	Hydrothermal treatment	Sulfuric Acid	-	(Wei, Agarwal, Matuana, Sabo, & Stark, 2018)
	Poplar	Chlorite treatment	1-31			-	(Agarwal et al., 2018)

¹L-CNFs: Lignin-containing cellulose nanofibrils (or ligno-cellulose nanofibrils), ²TMP: Thermo-mechanical pulp, ³TEMPO: 2,2,6,6-tetramethylpiperidiny-1-oxyl, ⁴CTMP: Chemi-Thermo-Mechanical pulp, ⁵SEW: SO₂-ethanol-water, ⁶4-AT TEMPO: 4-Acetamido 2,2,6,6-tetramethylpiperidiny-1-oxyl, ⁷p-TsOH: p-toluene sulfonic acid, ⁸AQ: Anthraquinone, ⁹L-CNCs: Lignin-containing cellulose nanocrystals (or ligno-cellulose nanocrystals).

1.1.1. *Pulping Process*

Mechanical and chemical pulping are the most industrially used approaches to extract lignocellulosic fibers from the woody biomass. Without any additional bleaching steps, the resulting pulp still contains a certain amount of lignin. Yet, compared to the original lignin content present in the native biomass, unbleached pulps have a lower amount of lignin, since part of the lignin is removed during pulping.

Mechanical pulping such as thermomechanical pulping (TMP), subjects the biomass chips to mechanical refining under high temperature (~170 °C), and pressure (~700 kPa) to extract and separate the fibers from the chips. The TMP process typically yields unbleached pulps with a residual lignin content of ca. 20 wt% (Buzala, Przybysz, Rosicka-Kaczmarek, & Kalinowska, 2015).

Chemical pulping methods such as Kraft (using sodium hydroxide, NaOH, and sodium sulfide, Na₂S as reactive agents), sulfite (using sulfur dioxide, SO₂), or soda (using an alkali such as sodium hydroxide, NaOH) yield unbleached pulps usually with 2-8 wt% residual lignin. Among these different chemical pulping processes, the Kraft process is the most common in the pulping industries, representing nearly 90 % of the total worldwide production of chemical pulps (Hubbe, Alén, Paleologou, Kannangara, & Kihlman, 2019; Vishtal & Kraslawski, 2011). Typically, by varying the pulping temperature, pH, and time of the chemical pulping process, the removal (and degradation) of lignin and hemicelluloses can be done selectively. Additionally, pulp bleaching step using, e.g., acetic acid and sodium chlorite for 1 to 4 h, can also be performed to control the amount of residual lignin in the unbleached pulps (Nair et al., 2017; Nair & Yan, 2015; Tarrés et al., 2017). This bleaching step could be viewed as an efficient lab-scale method to remove lignin from unbleached pulps.

Over the years, several "unconventional" pulping methods have been explored on wood and agricultural waste residues to extract unbleached pulps with higher residual lignin content than Kraft pulps. For instance, GranBio Technologies (U.S.A.) uses an SO₂-ethanol-water (SEW) pulping process in their AVAP[®] (American Value-Added pulping) biorefinery (Nelson & Retsina, 2014). In this process, unbleached pulps are produced by injecting gaseous SO₂ (6-12 wt%) into a cold mixture of ethanol (55 vol.%) and water (45 vol.%) at varying temperatures (~130-160 °C) and fractionation time (~0.4-1 h) (Morales et al., 2014; Rojo et al., 2015). Unbleached pulps with different residual lignin contents, from ~1 to 14 wt%, can be extracted by varying the processing

time and temperature of the SEW process. Compared to conventional chemical pulping methods, the SEW pathway requires less harsh chemicals and can thus be considered as a "greener" pulping process.

More recently, p-toluenesulfonic acid (p-TsOH) has attracted significant attention for pulping lignocellulosic biomass with ca. 15% or more residual lignin content (Bian et al., 2019; Dou et al., 2019). The use of such catalysts allows for faster pulping (i.e., a 20-min process *versus* 2-10 h for Kraft pulping) at relatively lower temperatures (i.e., ~80 °C *versus* ~170 °C for Kraft pulping).

The specific pulping conditions (e.g., time, temperature, pH) used to extract unbleached fibers from the biomass can strongly influence the chemical composition (e.g., carbohydrate and lignin content), structure (e.g., degree of fibrillation) and properties (e.g., mechanical and barrier properties) of the subsequent CNMs. For instance, the SEW process yields sulfonated residual lignins (Morales et al., 2014; Rojo et al., 2015), which are water soluble, while the alkali treatment results in sulfur-free residual lignin, which in comparison, are more hydrophobic. The importance of pulping on the processability of L-CNMs and properties will be illustrated and discussed in the following sections of this review article.

1.1.2. Processing suspensions of L-CNMs

Lignin-containing cellulose nanofibrils (L-CNFs) are produced from unbleached pulps by either high-shear mechanical treatments using, e.g., an ultrafine-friction grinder or a homogenizer (Diop et al., 2017a; Spence et al., 2010), or combining a mechanical, chemical or enzymatic pre-treatment with the high-shear mechanical step. The pre-treatments are intended to prevent clogging of the high-shear mechanical equipment, reduce the energy consumption, and/or modify the surface chemistry of cellulose for better fibrillation and further functionalization (M. Henriksson, Henriksson, Berglund, & Lindström, 2007; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006).

The PFI mill refiner and the valley beater are the most widely used mechanical pre-treatments for the production of L-CNFs (Espinosa et al., 2020; Espinosa, Sánchez, Otero, et al., 2017; Spence et al., 2010, 2011) (**Table 1**). The mechanical pre-treatment reduces the fiber length and promotes fiber swelling to ease the deconstruction of fibers into micro- and nanofibrils (Nechyporchuk et al., 2016). In contrast, chemical pre-treatments such as the TEMPO ((2,2,6,6-tetramethylpiperidin-1-oxyl)-mediated oxidation or quaternization act on the surface of the

cellulose chains by introducing negatively or positively charged groups (Isogai, Saito, & Fukuzumi, 2011). TEMPO-mediated oxidation of unbleached pulps can also decrease the residual lignin content of the processed pulp. Herrera et al. (2018) observed a 5 % reduction in residual lignin of the as-received unbleached eucalyptus pulp (with initial residual lignin of 23 wt%) after 1 h of TEMPO-mediated oxidation using 6 mmol/g of sodium hypochlorite (NaClO). Wen et al. (2019) also observed that by varying the amount of NaClO (from 4 to 12 mmol/g), the residual lignin content was reduced by up to 6 wt%. Under TEMPO oxidation, the residual lignin can be oxidized and depolymerized into water-soluble by-products (Nutting, Rafiee, & Stahl, 2018), which ultimately lowers the overall residual lignin content in L-CNFs. As an alternative, a recent study has proposed the use of the TEMPO/laccase/O₂ (TLO) system to produce TEMPO-oxidized L-CNFs with a moderate loss of residual lignin. Applied on thermomechanical pulp with an initial residual lignin content of 20 wt%, the repetitive TLO oxidations reduced by 5 wt% only the lignin content in the pulp and resulted in a carboxylate group density of 1.82 mmol/g; against 15 wt% and 1.57 mmol/g, respectively, when using the classic TEMPO/NaBr/NaClO system (Jie Jiang et al., 2020).

Other pre-treatments such as the enzymatic hydrolysis of pulps using endoglucanases or exoglucanases have been used for the production of L-CNFs (Bian et al., 2020; Espinosa, Rol, et al., 2019; Espinosa, Sánchez, Otero, et al., 2017; Morales et al., 2014). These two families of cellulolytic enzymes allow for selective hydrolysis of the non-crystalline domains of cellulose fibers (M. Henriksson et al., 2007). However, the presence of lignin can inhibit the action of enzymes by either i) physically blocking the cellulose surface, making them inaccessible to the enzymes (Kumagai, Iwamoto, Lee, & Endo, 2014) or (ii) interacting with the enzymes via adsorption (Hoeger, Filpponen, & Martin-Sampedro, 2012; Hoeger et al., 2013).

Numerous studies have reported that the presence of residual lignin improves the fibrillation of cellulosic fibers (Rojo et al., 2015; Solala et al., 2012; Spence et al., 2011). Solala et al. (2012) studied the influence of residual lignin in Kraft birch pulp after different bleaching stages, on the pulp fibrillation using a grinder. Electron paramagnetic resonance spectroscopy (EPR) data revealed that the free radicals originating from cellulose (radicals formed by homolytic rupture of glycosidic bonds between C1 and C4) increased monotonously with increasing grinding action and reacted with the residual lignin present in unbleached pulps to form stable phenoxy radicals. In the case of bleached Kraft pulp, the authors observed relatively small changes in the

radical content with increasing mechanical action. In the absence of lignin, the radicals were rapidly quenched. The radical scavenging ability of the residual lignin (i.e., scavenging of the formed mechanoradicals of cellulose) prevented the coupling reactions between cellulose radicals, which limited subsequent fibrillation. The presence of lignin allows for more facile deconstruction of the fibrils.

However, the ease of fibrillation observed for unbleached pulps appears to be valid only for low to moderate (ca. 3 to 20 wt%) residual lignin range (Hanhikoski et al., 2020). Neutral sulfite pulps with <20 wt% residual lignin were processed into L-CNFs with high water retention capacity at a specific energy consumption (SEC) of 1400 kWh/t, while neutral sulfite pulps with ≥ 20 wt% residual lignin required a SEC as high as 12 000 kWh/t to reach comparable water retention values.

In the case of unbleached pulps with ≥ 20 wt% residual lignin (e.g., mechanical pulps), the highly branched native lignin undergoes less severe modification due to the lower intensity of the pulping process (Obst, 1990; Sixta, 2006). The LCCs present in unbleached pulps with ≥ 20 wt% are kept “more intact” than in unbleached pulps with <20 wt% residual lignin. The presence of a higher residual lignin content can make the fibers stiffer and restrict their swelling and fibrillation. In addition, certain residual lignins may have a more hydrophobic nature, for example in mechanical pulps, and can thus prevent the fibers from swelling and fibrillation. The superior hydrophobic nature of mechanical pulps has been observed from their lower swelling ability (i.e., lower water retention value and apparent viscosity) when compared to Kraft pulps (~ 200 g/g and >10 Pa.s for TMP *versus* ~ 380 g/g and ~ 60 Pa.s for Kraft pulp, respectively) (Lahtinen et al., 2014).

Unlike L-CNFs, lignin-containing cellulose nanocrystals (L-CNCs) are obtained by controlled acid hydrolysis of unbleached pulp. The role of acid hydronium ions, when using acids such as sulfuric or hydrochloric acid, is to penetrate the disordered regions of the cellulose chains for preferential hydrolytic cleavage of glycosidic linkages (Habibi et al., 2010). The resulting suspension is washed, followed by several centrifugation and dialysis steps, and is ultimately subjected to ultrasonic dispersion of the CNCs in water.

The residual lignin content in aqueous suspensions of L-CNCs has been reported to be higher than the initial residual lignin content in the starting raw material. For instance, Agarwal et al. (2018) reported sulfuric acid hydrolyzed L-CNCs produced from poplar wood with ca. 30 wt%

residual lignin *versus* 21 wt% for poplar wood. Poplar wood was directly subjected to a hydrothermal treatment (**Table 1**), which facilitated the access to the crystalline domains of the cellulose fibers (Agarwal, Ralph, Reiner, & Baez, 2016). In another study, two deep eutectic solvent (DES) systems (a mixture of choline chloride and oxalic acid) with or without *p*-toluenesulfonic acid (*p*-TsOH) resulted in L-CNCs with a residual lignin content of approximately 48 and 55 %, respectively, within 3 h of hydrolysis, compared to the 30 wt% residual lignin in the initial TMP pulp (Jungang Jiang et al., 2020). Increasing the hydrolysis time also increased the residual lignin content in the aqueous suspensions of L-CNCs to 54 and 57 %, respectively. The high lignin content in L-CNCs and its increase with increasing hydrolysis time is explained by the solubilization of a higher amount of lignin upon hydrolysis. With increasing hydrolysis time, both the cellulose and lignin content increased, suggesting that more cellulose was hydrolyzed into CNCs and more lignin was solubilized (while the hemicellulose content decreased). The use of a strong acid such as *p*-TsOH also helped solubilize more lignin, explaining the higher residual lignin content for the ternary DES system (Jungang Jiang et al., 2020). Another, yet complementary explanation, is the formation of lignin-like material termed as “pseudo-lignin” upon hydrolysis (de Carvalho & Colodette, 2017). The formation of pseudo-lignin, and thus increase in Klason lignin content, is hypothesized to be due to the re-polymerization of polysaccharides degradation products (such as furfural) and lignin under acidic conditions, with a longer hydrolysis reaction time or a greater acid concentration (de Carvalho & Colodette, 2017; Hu, Jung, & Ragauskas, 2012).

As for CNCs, the yield of L-CNCs appears to be dependent on the strength of the acid used for chemical treatment. For instance, the gravimetric yield of L-CNCs produced in the presence of *p*-TsOH was twice higher than the yield of L-CNCs produced by oxalic acid-based DES hydrolysis (Jungang Jiang et al., 2020), as a result of interaction between the lipophilic nonpolar toluene moiety in *p*-TsOH and residual lignin through π - π stacking, which reduced lignin aggregation (Song, Chandra, Zhang, Tan, & Saddler, 2019). However, when compared to CNCs from bleached pulps, a lower yield of L-CNCs has, in general, been reported. Agarwal et al. (2018) reported a 13 % gravimetric yield for L-CNCs from poplar wood compared to ca. 50 wt% yield of bleached pulp CNCs under similar acid hydrolysis conditions. Despite differences in starting materials and pulping processes (e.g., hydrothermally treated wood *versus* bleached wood pulp), the lower yield of L-CNCs can be linked to the presence of lignin. Further research is still needed on the processing

of L-CNCs for a deeper understanding of how the residual lignin content and structure can impact the yield and properties of L-CNCs.

Integrated production of both L-CNCs and L-CNFs from unbleached pulp has also been proposed and involves the combination of organic acid and high-shear mechanical treatment (Bian et al., 2017a). Two unbleached hardwood Kraft pulps with a residual lignin content of 4 and 17 wt% were subjected to hydrolysis using 60 wt% maleic acid solution at 120 °C for 2 h under ambient pressure. After the acid treatment, the resulting suspensions were washed by multiple centrifugation and dialysis steps to separate the L-CNCs from water-insoluble partially hydrolyzed lignocellulosic solid residues (LCSRs). The LCSRs were retained for the production of L-CNFs through subsequent mechanical treatment. The use of organic acids is considered as a more sustainable production pathway for L-CNMs because the solvents can be recovered and reused.

Today, four grades of L-CNFs and L-CNCs with varying amounts of residual lignin are produced at large scale by GranBio Technologies (U.S.A) from eucalyptus wood chips and sugar cane bagasse (Nelson & Retsina, 2014). The amount of residual lignin drives the end-use application of the different grades of L-CNMs. In partnership with other companies, applications ranging from plastic-like packaging to paint are being commercialized.

1.1.3. Suspension-stage properties of L-CNMs

In this sub-section, the influence of residual lignin on the suspension properties of L-CNMs will be discussed in comparison to the suspension properties of CNMs. This review is focused on the suspension properties of L-CNFs due to the limited number of publications on L-CNCs (**Table 1**).

Morphology and structure

Similar to bleached CNMs, the morphology and structure of CNMs from unbleached pulps are commonly characterized using microscopic techniques, such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Examples of AFM images of CNMs from bleached and unbleached pulps are shown in **Fig. 3**. Compared to bleached CNFs, microscopic analyses of L-CNFs have revealed the presence of small globular particles around the fibrils, which have been identified as micro- and nanoscale agglomerates of lignin (**Fig. 3 A1-A2**) (Rojo et al., 2015). The globular particles of lignin were

more prominent at higher lignin content and seemed to be dominantly located on the surface of the cellulose fibrils (Y. Chen et al., 2018).

With an increase in residual lignin content, the width of L-CNFs from unbleached chemical pulps was observed to decrease, possibly due to the radical scavenging action of lignin or the addition of repulsive charges to the system. For instance, L-CNFs with 2.7 wt% of residual lignin exhibited an AFM width of 8 nm compared to 17 nm for the fully bleached CNFs (Ferrer et al., 2012). Rojo et al. (2015) reported that mechanically obtained L-CNFs with a high residual lignin content (14 wt%) showed a 63 % reduction in their fibrils' width when compared to bleached CNFs (< 0.2 wt% residual lignin).

Fig. 3. Atomic force microscopy (AFM) topography images of A1) CNFs with <0.2 wt% residual lignin A2) L-CNFs with 4 wt% residual lignin (Rojo et al. (2015) - Published by The Royal Society of Chemistry), B1) CNCs with <0.2 wt% residual lignin and B2) L-CNCs with 4 wt% residual lignin (Adapted and reprinted with permission from Bian et al. (2017a)). The insets show the aqueous suspensions, as obtained after mechanical or chemical treatment, of the respective CNFs, L-CNFs, CNCs, and L-CNCs (Adapted and reprinted with permission from Neto et al. (2013), Solala et al. (2019) and Jungang Jiang et al. (2020). The arrows point out the globular lignin particle agglomerates. (Copyright © 2020, American Chemical Society; Copyright © 2013 and 2017, Elsevier Ltd and Copyright © 2019, Springer Nature.)

The intrinsic viscosity of L-CNFs suspension is also influenced by the amount of residual lignin and can be used to assess the degree of fibrillation of CNFs. A more effective fibrillation is expected to increase the specific surface area of the fibrils and, in turn, the viscosity of the suspension. The surface chemistry of the LCNFs will also play a role in the suspension viscosity. The intrinsic viscosity of L-CNFs was observed to increase with the residual lignin content. For instance, a viscosity value of 1320 mL g⁻¹ was recorded for unbleached Kraft L-CNFs with 3 wt% residual lignin, in comparison to 780 mL g⁻¹ for the bleached Kraft CNFs produced under similar processing conditions (Ferrer et al., 2012; Solala et al., 2012). The observed increase in viscosity may also be explained by the differences in charge density between the unbleached and bleached pulps.

The micro- and nanoscale globular lignin particles were also observed in the case of L-CNCs (**Fig. 3 B2**) (Bian et al., 2017a; Jungang Jiang et al., 2020). The AFM scans of maleic acid-hydrolyzed L-CNCs revealed crystals with heights greater (25 nm) than that of bleached CNCs (15.9 nm) (Bian et al., 2017a), probably because of the barrier role of residual lignin, which blocked the access to the crystalline domains. This observation aligns with the results from Agarwal et al. (2018), who used a hydrothermal treatment to get access to the individual cellulose crystals in wood and overcome the barrier role of residual lignin. While the effect of hydrothermal treatment of wood and lignocellulosic biomass is not fully elucidated, the hydrothermal treatment appears to give better access to the crystalline domains of biomass.

Surface Chemistry and Colloidal Stability

The surface chemistry and colloidal stability of CNMs play an important role in their assembly and properties. The colloidal stability of CNMs commonly results from the presence of surface charges, such as sulfate half-ester groups in sulfuric acid pretreated CNCs or carboxyl groups in TEMPO-oxidized CNMs (Habibi, Lucia, & Rojas, 2010; Saito et al., 2006). Classic characterization techniques to evaluate the colloidal stability and surface chemistry of CNMs include zeta-potential, turbidity measurement, and conductometric and polyelectrolyte titrations. For details on current characterization methods for cellulose nanomaterials, the readers are referred to the exhaustive review article on the topic by Foster et al. (2018).

The presence of lignin alters the charge density of L-CNMs. For example, maleic acid-hydrolyzed L-CNCs with 18 wt% residual lignin had a carboxyl group density of 0.273 mmol g⁻¹

compared to 0.368 mmol g⁻¹ for CNCs with <0.2 wt% lignin, produced under similar hydrolysis conditions (Bian et al., 2017a). Similarly, the zeta potential value of L-CNCs (-36 mV) was lower than that of the bleached references (-47mV). The low surface charge of the L-CNCs may, as discussed earlier, stem from the residual lignin acting as a barrier to the acid-catalyzed depolymerization of the cellulose.

In the case of TEMPO-mediated oxidation, varying the amount of NaClO can also tune the amount of surface carboxyl groups of L-CNFs. An increase in carboxyl group content from 0.4 to 1.3 mmol g⁻¹ was achieved by increasing the NaClO content from 4 to 12 mmol g⁻¹, respectively (Wen et al., 2019). Compared to reported values in the literature (Saito et al., 2006), the charge densities reported for L-CNFs seem slightly lower than that of TEMPO-CNFs from bleached pulps. To date, no work has directly compared the effects of changing TEMPO concentration on the charge density of L-CNFs and CNFs made from the same pulp and produced under similar processing conditions. Additional work is thus needed to understand how such chemical pre-treatments influence the amount and structure of residual lignin in L-CNMs.

Specific Surface Area (SSA)

The determination of the SSA has been used to indirectly measure the fibrillation intensity and degree of lignocellulosic fibers for the production of L-CNMs (Bian et al., 2018; Ferrer et al., 2012; Spence et al., 2011).

The Congo red dye (CR) adsorption method is one of the most commonly reported methods to measure the SSA of CNFs and L-CNFs (Ougiya et al., 1998; Spence et al., 2010, 2011).

As the presence of residual lignin generally results in more fibrillated lignocellulosic fibers, a higher SSA value is commonly reported for L-CNFs as opposed to CNFs (e.g., 161 m² g⁻¹ for L-CNFs versus 68 m² g⁻¹ for CNFs (Spence et al., 2010)). The observed increase in SSA with the presence of residual lignin can be explained by the modification of the internal and external pore structures of the fibers during pulping, which may enhance the diffusion and thus sorption of CR molecules (Spence et al., 2010, 2011). Due to the sensitivity of the CR process to the pulping conditions, measurement of the SSA remains challenging, even with bleached CNFs, and there is a risk of overestimating the SSA of the nanomaterials.

Crystallinity

Measuring the degree of crystallinity of CNMs can provide additional information on the molecular structure and associated properties of CNMs. X-ray diffraction (XRD), Raman spectrometry, and Nuclear Magnetic Resonance (NMR) are the three common techniques used to estimate the degree of crystallinity and the quality of the crystalline regions in CNMs (S. Park, Baker, Himmel, Parilla, & Johnson, 2010).

The XRD data of CNMs can be quantitatively analyzed using either a peak intensity approach (also known as the Segal method) or a peak area approach (S. Park et al., 2010; Segal, Creely, Martin, & Conrad, 1959). L-CNMs have shown a lower crystallinity index (CrI) than CNMs, which can be attributed to the presence of residual lignin; amorphous in nature. For instance, L-CNFs with 23 wt% residual lignin was reported with a CrI of 68 % compared to CNFs with a CrI of 81 % (Wen et al., 2019). Similarly, a decrease in CrI from 57 % to 51 % was observed for L-CNCs when increasing the *p*-TsOH-based DES hydrolysis time from 3 to 6 h (Jungang Jiang et al., 2020), due to the increase in solubilized lignin content.

L-CNMs-Water Interactions

The interactions between CNMs and water can be evaluated by water retention test and water contact angle measurement. The water retention value (WRV) is a measure of the fibrils' ability to swell in the presence of water, and can, therefore, indirectly provide insight on the fibrillation degree, quality of the suspension and surface charges of fibrils. By penetrating into the nanofibril network, water breaks the interfibrillar interactions between fibrils and bonds with the fibrils via hydrogen bonding, leading to fibers' swelling (F. Gu et al., 2018; Hakalahti, Faustini, Boissière, Kontturi, & Tammelin, 2017). When extending the WRV approach to L-CNFs, the WRV has been reported to follow an opposite trend than that of CNFs, meaning that increasing the residual lignin content lowers the WRV. Unbleached hardwood L-CNFs with 13 wt% residual lignin had a WRV of 1.6 g/g, while bleached hardwood CNFs exhibited a WRV of 23 g/g (Spence et al., 2010). The hydrophobic nature of certain types of lignin, which is the case of the residual Kraft lignin in the previous study (Spence et al., 2010), can explain why a lower WRV was obtained with L-CNFs. In addition to the presence of residual lignin, residual hemicelluloses in unbleached pulps can also significantly alter the hygroscopic property of L-CNFs. The WRV usually increases with an increase in residual hemicelluloses due to the presence of readily

accessible hydroxyl groups (Pejic, Kostic, Skundric, & Praskalo, 2008). The countervailing effects of residual lignin and residual hemicelluloses on the WVR of unbleached pulps makes the comparison with bleached CNFs very challenging. The initial pulping conditions should also be considered when analyzing water interaction properties.

Thermal Stability

The thermal stability of pre-treated lignins at temperatures up to 600 °C is generally higher than that of cellulose due to the presence of aromatic and carbon-carbon double bonds, which slow the decomposition process by char formation (Brodin, Sjöholm, & Gellerstedt, 2010). Owing to the high thermal stability of lignin, L-CNMs have demonstrated improved thermal stability with char formation (up to 40-50 % at 600 °C) when compared to bleached CNMs.

For instance, alkali-treated L-CNFs with 22 wt% residual lignin from bagasse showed an onset temperature (e.g., weight loss greater than 8%) of 316 °C and a maximum decomposition temperature ($T_{\max}$) of 363 °C compared to 301 and 341 °C for the bleached bagasse CNFs, respectively (N. Zhang et al., 2019). Similarly, a higher $T_{\max}$ was reported for L-CNCs with 31 wt% residual lignin from hydrothermally treated poplar wood compared to bleached CNCs (Agarwal et al., 2018). Although the presence of residual lignin improves the thermal stability of L-CNMs, other factors such as crystallinity (Poletto, Zattera, Forte, & Santana, 2012), surface chemistry, chemical composition, and specific surface area of L-CNMs can significantly influence the thermal properties and also explain the improved thermal stability of L-CNMs. L-CNCs obtained under acidic DES hydrolysis conditions, had a $T_{\max}$ in the range 344-358 °C (depending on hydrolysis conditions) much higher than the $T_{\max}$ of the TMP pulp (325 °C) they were made from. This effect was attributed to the removal of hemicelluloses and amorphous cellulose (Jungang Jiang et al., 2020). Compared to sulfuric-acid bleached CNCs, whose degradation temperature is typically in the range 200-260 °C, L-CNCs clearly show advantages in applications where thermal stability is required.

Benchmarking

Irrespective of whether the raw material is bleached or unbleached, the direct comparison of CNMs from different studies remains challenging. The numerous steps and production pathways of CNMs can all, independently or in synergy, influence the properties of the final

product. Moreover, the absence of an established benchmarking protocol further restricts the comparison of different CNMs. Due to the effects of processing on both cellulose and lignin fractions, similar challenges can be foreseen for L-CNMs. Nevertheless, first attempts to quantify the quality or fibrillation degree of L-CNMs have been proposed by Espinosa et al. (2020). This study was inspired by the proposed multi-criteria method for benchmarking the production of CNF on an industrial and laboratory scale (Desmaisons et al., 2017). Desmaisons et al. (2017) proposed the use of a quality index (QI) for enzymatically pre-treated CNF suspensions produced by grinder at different energy consumptions by cross-referencing eight relatively easily measured criteria on the suspensions. Instead, Espinosa et al. (2020) narrowed down the QI to four key parameters (nanosized fractions, turbidity, area of microparticles, and Young's modulus of films from L-CNFs) and added three independent mechanical treatments, namely grinder, homogenizer and twin-screw extruder to assess the quality of PFI-pretreated L-CNFs. The raw materials selected for producing the nanofibrils differed in both these studies. Espinosa et al. (2020) used alkali-treated wheat straws, and Desmaisons et al. (2017) used bleached Kraft pulps of cotton, eucalyptus, and a mixture of maple and aspen.

Based on the defined QI, the presence of 9 wt% residual lignin in wheat straw CNFs improved the QI by 10 to 18 points, mostly due to an increase in the nanosized fractions in the aqueous suspensions of L-CNFs (ca. 2-fold increase compared to suspensions of bleached CNFs) and an overall improvement in Young's modulus values of the films from L-CNFs (ca. 20 % increase compared to bleached CNF films) (Espinosa et al., 2020). The use of a grinder and a homogenizer was also recommended for the production of both CNFs and L-CNFs of optimized quality, but a higher yield can be achieved for LCNFs (Besbes, Alila, & Boufi, 2011). The use of twin-screw extruder resulted in a ca. 20 % increase in fibrillation yield for L-CNFs compared to CNFs, while a grinder or homogenizer increased the fibrillation yield by 30-50%.

1.2. Suspensions of bleached CNMs and technical lignin

Unlike residual lignins, technical lignins are used as additives in the design of CNM/lignin composite materials; therefore, there exist no initial chemical bonds between CNMs and lignin, unless initiated on purpose as part of the composite design strategy.

1.2.1. Technical lignins

The delignification processes are intended to separate lignin from cellulosic fibers in lignocellulosic biomass through cleavage of ester and ether linkages in the native lignin. A combination of multiple reactions such as hydrolysis, condensation, or oxidation takes place during delignification, resulting in the break-down of lignin into smaller fragments of different chemical structures (Berlin & Balakshin, 2014). The technical lignins can be categorized into sulfur-containing and sulfur-free lignins, depending on the delignification process. **Fig. 4** illustrates the different isolation pathways of technical lignins from lignocellulosic biomass. The main features of technical lignins are summarized in **Table 2**.

Fig. 4. Isolation pathways of technical lignins from lignocellulosic biomass (Adapted and reprinted with permission from Laurichesse et al. (2014). Copyright © 2014, Elsevier Ltd.)

Lignins extracted from Kraft and sulfite pulping are sulfur-containing technical lignins, with sulfur contents varying between 0.2-3 wt% and 3-8 wt% for Kraft and lignosulfonates (LS), respectively (Aro & Fatehi, 2017; Oveissi & Fatehi, 2015). The Kraft process uses a mixture of NaOH and Na₂S under alkaline conditions (pH ~13). This process cleaves α and β -ether bonds, which results in an increase in phenolic hydroxyl groups (Laurichesse & Avérous, 2014). The extensive bond cleavage also significantly lowers the average molecular weight (M_n) of Kraft lignins, which range between 1000-3000 g mol⁻¹ after processing (Baumberger et al., 2007). The

initial ether cleavage and other condensation reactions produce isolated lignin with more carbon-carbon bonds.

In contrast, the sulfite process yields LS with higher M_n (15 000-50 000 g mol⁻¹). The sulfite process cooks the pulp in the presence of sulfur dioxide (SO₂) and a base such as calcium carbonate or magnesium hydroxide, in acidic conditions (pH 1-5) (Aro & Fatehi, 2017). Upon delignification, cleavage of the α -ether linkages usually occur, resulting in quinone methide intermediates with either phenolic or non-phenolic groups (Aro & Fatehi, 2017). The sulfite ions present in solution bind to the created intermediates at the α -position to form benzyl sulfonic acid units, which ultimately contributes to the water solubility of the LS (Matsushita, 2015).

Table 2. Characteristics of technical lignins

Features	Lignin Types			
	Kraft	Lignosulfonates	Soda	Organosolv
Raw materials	Softwood and hardwood	Softwood and hardwood	Annual plants	Softwood, hardwood and annual plants
Sulfur content (wt%)	0.2-3	3-8	Sulfur-free	Sulfur-free
Sulfonate content (mmol g ⁻¹)	~0	0.7-2.5	-	-
Water solubility (g L ⁻¹)	~0.8-1.8	10	~0.5	~1
Average molecular weight (M_n) (g mol ⁻¹)	1000-3000	15000-50000	800-3000	500-5000
Polydispersity Index of M_n	2.5-3.5	4.2-7	2.5-3.5	1.5-2.5
Anionic charge density (meq g ⁻¹)	0.01-0.67	0.9-2.25	NA	-
Purity	Moderate	Low	Moderate-low	High
Production Scale	Industrial	Industrial	Laboratory Pilot	Laboratory/Pilot
Commercialization	High	High	Low	Moderate-low
Ref.	(Kong, Wang, T. Price, Konduri, & Fatehi, 2015; Laurichesse & Avérous, 2014; Sameni, Krigstin, & Sain, 2017)	(Laurichesse & Avérous, 2014; Oveissi & Fatehi, 2015; Sameni et al., 2017)	(Laurichesse & Avérous, 2014; Sameni et al., 2017; Vishtal & Kraslawski, 2011)	(Laurichesse & Avérous, 2014; Sameni et al., 2017; Vishtal & Kraslawski, 2011)

NA: Not available

Kraft lignins are extracted from the “black liquor,” while sulfite lignins are found in the “sulfite-spent liquor.” These black/sulfite spent liquors are a liquid mixture of biomass residues,

principally lignin and hemicelluloses, along with inorganic by-products originating from the raw material or delignification processes, such as sodium sulfide or magnesium hydroxide (Hubbe et al., 2019).

Isolation of technical Kraft lignin from the black liquor is accomplished by acidification to pH~9-10, using either carbon-dioxide and or sulfuric acid (Aro & Fatehi, 2017; Vishtal & Kraslawski, 2011). At this pH, Kraft lignins precipitate and can be recovered by filtration (Vishtal & Kraslawski, 2011) (**Fig. 4**). In industry, different acid precipitation-based technologies have been developed to maximize the Kraft lignin extraction efficiency. The LignoBoost™ technology by Innventia (Sweden) uses carbon dioxide for acidification of the black liquor. In contrast, the LignoForce™ technology by FPIinnovations, in collaboration with NORAM (Canada), oxidizes the black liquor using air before acidification with carbon dioxide and sulfuric acid (Li & Takkellapati, 2018), which allows for faster filtration rates and lower acid consumption than the LignoBoost™ technology (Kouisni et al., 2016). The LignoForce Kraft lignins also contain mineral ash (3%), which can impact the performance and purity (**Table 2**).

Due to their good water solubility, LS cannot be easily precipitated (Aro & Fatehi, 2017; Fatehi & Chen, 2016). LS are recovered from the sulfite spent liquor by membrane filtration using polysulfone or cellulose acetate size-exclusion membranes (Bhattacharya et al., 2005). These membranes are not selective to LS, and can thus collect hemicelluloses with a similar range of molecular weights as well, which significantly lowers the purity of the isolated LS (Fatehi & Chen, 2016).

The limited production of LS has led to the exploration of different approaches for producing water soluble lignins from the inherently insoluble Kraft lignins (Demuner, Colodette, Demuner, & Jardim, 2019). A widely used approach is the sulfomethylation of extracted Kraft lignin (Aro & Fatehi, 2017), which consists of introducing sulfonic groups (up to 1.48 mmol g⁻¹) on the lignin aromatic rings (instead of the aliphatic chains as for LS) to make the Kraft lignin water soluble (Konduri & Fatehi, 2015)).

Significant producers of Kraft technical lignins include today, Domtar Plymouth Mill (North Carolina, USA) and Stora Enso (Finland) with an annual production of 27 300 and 50 000 dry tons, respectively (Li & Takkellapati, 2018). Borregaard LignoTech is the largest producer of lignosulfonate lignin with ~500 000 dry tons per year. Other producers of LS include Tembec Inc.

in Canada (ca. 570 000 tons y⁻¹), Nippon Paper Industries in Japan (40 000 tons y⁻¹), and Domsjö Fabriker AB in Sweden (25 000 tons y⁻¹).

Sulfur-free technical lignins are extracted using either organic solvents at pH~4-6 (organosolv (OSL) lignins) or NaOH at pH~11-13 (soda lignins). In the OSL process, the hydrolytic cleavage of α -ether linkages breaks down the lignin into fragments that are soluble in the solvent used, e.g., ethanol, acetone, methanol or formic acid.

The soda-based pulping is similar to the Kraft process, resulting in lignins with condensed structures and high phenolic hydroxyl groups. Due to their more easily hydrolyzed lignins, soda cooking is primarily performed on non-wood biomass such as straws, flax, or bagasse (Vishtal & Kraslawski, 2011). Both the OSL and the soda-based cooking processes use acid precipitation to recover the technical lignins. Compared with Kraft and LS lignins, sulfur-free technical lignins undergo additional fractionation steps that can lower the molar mass of either the aliphatic or the aromatic groups in lignin (Laurichesse & Avérous, 2014). The purity of the soda lignin is reduced due to the presence of ash and silica from the non-wood sources, while OSLs are generally of high purity. For more detailed information on the production and properties of technical lignins, the readers are referred to the following reviews and book chapters (Berlin & Balakshin, 2014; Fatehi & Chen, 2016; G. Henriksson, Li, Zhang, & Lindström, 2010; Hubbe et al., 2019; Vishtal & Kraslawski, 2011).

1.2.2. Usage and properties of technical lignins

Presently, the main challenge with technical lignins is the lack of end-use applications that provide a financial driver for their production (Norgren & Edlund, 2014; Vishtal & Kraslawski, 2011). About 70 million tons of technical lignin is produced worldwide each year, but only 2 % of the production is being used as value-added products, for example as adhesives, sorbents, or dispersants (Cateto et al., 2014). The majority of the produced technical lignins are burned for chemical recovery and energy generation in the pulp and paper mills (Fisher & Fong 2014; Matsushita, 2015).

Technical lignins have potential as additives to endow specific functionalities to CNMs or as raw materials for the production of colloidal lignin particles, as it will be discussed in the next section (Section 1.3). For instance, the aromatic structure of lignin is known to have UV-absorbing chromophores (Barsberg, Elder, & Felby, 2003; Falkehag, Marton, & Adler, 1966), and therefore

lignin can be used when UV protection is needed. The phenolic groups of lignin are radical scavengers; hence lignin can be used as an antioxidant, for example, to enhance thermal and oxidation stabilities of blended polymers (Sánchez & Alvarez 1999). These properties will be discussed later for the elaboration of high-performance CNM/lignin composite materials.

1.2.3. Processing suspensions of CNM/lignin

A key attribute to making CNM/lignin composites with improved properties is the uniform mixing of the different phases, generally as suspensions, where CNMs are the matrix, and the technical lignin is the dispersed phase. The main challenge for processing CNM/lignin composites stems from the difference in the interaction with water of the two phases (Parit, Saha, Davis, & Jiang, 2018; Sadeghifar et al., 2017).

Table 3. Processing conditions for the production of CNM/technical lignin composites

Technical Lignins				CNM/Lignin Composites			Ref.
Raw Materials	Delignification Processing	Molecular weight (Mw) (g mol ⁻¹)	Chemical modification	Lignin ratio (wt%)	CNMs	Solvent	
Softwood	DHP ¹	2775	-	-		Dioxane/water	(Hambardzu myan et al., 2011)
Corn stalks/spruce/softwood	Organosolv/DHP	2775	-	-	CNCs	Dioxane/water or DMSO ² /water	(Hambardzu myan, Foulon, Chabbert, & Aguié-Béghin, 2012)
Maize stalks/spruce/softwood	Organosolv/DHP	2519-5662	-	9-50		Hydrogen peroxide and iron sulfate	(Hambardzu myan et al., 2015)
Softwood and alkaline lignin	Kraft	1000 for alkaline lignin	Acetylation of softwood Kraft (Phenolic OH group)	1-10		NaOH/Dioxane	(Parit et al., 2018)
Eucalyptus	MWL ³	-	-	1-33	MCCs ⁵	NaOH/urea /water	(L. Zhang, Zhang, Zhou, Wu, & Xu, 2016)
Poplar (steam pretreated)	Soda/ organosolv/ DES ⁴ / hydrotrope	-	-	5		DMAc/LiCl ⁶	(Guo et al., 2019)
Softwood	Kraft lignin	1500 [*]	Propargylation (Phenolic OH group)	0.5-2	Azide modified MCCs (C-6 OH group)	DMAc/LiCl	(Sadeghifar et al., 2017)
Softwood	Sulfite and Kraft	9000-12000	-	2-25	TEMPO ⁷ CNFs (C-6 OH group)	Water	(Y. Liu, 2018)

¹DHP: dehydrogenated polymer, ²DMSO: dimethyl sulfoxide, ³MWL: milled wood lignin, ⁴DES: deep eutectic solvent, ⁵MCCs: microcrystalline cellulose, ⁶DMAc/LiCl: dimethylacetamide /lithium chloride, ⁷TEMPO: 2,2,6,6- tetramethylpiperidiny-1-oxyl, * represent number-average molecular weight values (Mn)

Technical lignins, with the exception of lignosulfonates (LS), are generally considered to be hydrophobic because of their aromatic-aliphatic structure with fewer hydroxyl groups than CNMs. Additionally, the structural heterogeneity and the broad molecular weight distribution of technical lignins further challenge their use with CNMs.

Different strategies have been investigated to combine technical lignins and CNMs, and include (i) the use of organic or alkaline solvents to solubilize lignin prior to mixing it with CNMs, (ii) the surface chemical modification of either lignin or CNMs, and (iii) the direct grafting of lignin to CNMs. **Table 3** summarizes the processing conditions reported in the literature to produce CNM/technical lignin composites. As observed in **Table 3**, the majority of the studies on CNM/lignin composite materials have used CNCs as a matrix. Very few studies have considered CNFs (or L-CNFs) as the matrix phase.

To promote dispersion or dissolution of lignin in aqueous dispersions of CNMs and reduce particle aggregation, organic or alkaline solvents have been used to solubilize the lignin before its mixing with the suspensions of bleached CNMs. For instance, organosolv lignin was solubilized in dioxane/water or DMSO/water before blending it with a suspension of sulfuric acid-derived CNCs (Hambardzumyan et al., 2012). CNCs have good colloidal stability in these two solvent systems, and therefore their blending with the solubilized lignin resulted in a homogenous mixture without any precipitation or aggregation. Parit et al. (2018) prepared uniform dispersions of two different technical lignins (softwood Kraft and alkaline) with CNCs using an alkaline solution of NaOH. In the case of alkaline lignin, the aqueous suspension of sulfuric acid-derived CNCs was mixed with the NaOH solution first, to reduce the hydrogen bonding between the surface hydroxyl groups of CNCs, before adding the alkaline lignin solution. In the case of the softwood Kraft lignin, the phenolic hydroxyl groups of lignin were first acetylated, and then uniformly mixed with the CNCs to create homogeneous composites.

CNM/lignin composites can also be prepared by high-shear blending of aqueous LS and Kraft technical lignins with TEMPO-CNFs (Y. Liu, 2018). In the case of the water soluble LS, the LS was directly dissolved in water, while the Kraft lignin was dispersed in NaOH at pH 11 prior to its mixing with TEMPO-CNFs. The surface carboxyl groups of TEMPO-CNFs further contributed to the uniform and stable aqueous dispersions of TEMPO-CNFs and lignin (**Fig. 5**), possibly through the formation of hydrogen bonds with the aromatic groups of lignin.

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696

697 **Fig. 5.** Uniform dispersions of TEMPO-CNFs with 14 wt% of lignosulfonates (LS) (*left*) and 14
698 wt% of Kraft lignin (KL) (*right*) after sitting for 6 months at room temperature. (Reprinted with
699 permission from Y. Liu (2018). Copyright © 2018, American Chemical Society.)

700

701 The grafting of technical lignins to CNMs is another route to make CNM/lignin
702 composites. For example, propargylated softwood Kraft lignin was grafted at a weight ratio of 0.5-
703 2 wt% on azide-modified microcrystalline cellulose (MCCs) via ‘click-chemistry’ in a solution of
704 dimethylacetamide/lithium chloride (DMAc/LiCl) using copper bromide (CuBr_2) as catalyst
705 (Sadeghifar et al., 2017). The use of CuBr_2 initiated the click chemistry between the azide groups
706 of MCCs and the propargyl groups of lignin, forming covalent bonds between the two
707 functionalized groups. The covalent bonding was confirmed by infrared spectroscopy, which
708 revealed a clear decrease in the intensity of the band at 2100 cm^{-1} assigned to the asymmetric azide
709 stretching motion. Without a catalyst, no reduction in the band intensity was observed, confirming
710 the formation of covalent interactions only in the presence of a catalyst.

711 Organosolv lignin was also successfully grafted on the surface of sulfuric acid-CNCs using
712 Fenton’s reagent (hydrogen peroxide and iron(II) sulfate) as an initiator to covalently bridge
713 organosolv lignin to CNCs (Hambardzumyan et al., 2015). Fenton’s reagent involves the oxidation
714 of the surface functional groups of cellulose and lignin via free hydroxyl radicals generated in the
715 presence of iron salt, which results in the formation of aldehydes and ketones groups. The oxidized
716 functional groups can further undergo abstraction of proton or addition of free hydroxyl radicals,
717 creating organic radical species, which initiate cross-linking between lignin and CNCs.

718 Finally, another strategy that has recently attracted significant attention is the use of
719 colloidal lignin particles, and this strategy will be discussed in detail in the next section 1.3.

1.3. Suspensions of bleached CNMs and Colloidal Lignin Particles (CLPs)

The valorization of technical lignins through the preparation of CLPs, also called lignin nanoparticles (LNPs) has attracted interest. CLPs (or LNPs) are particles with a diameter in the nano- to micrometer range, which can be fabricated from unmodified technical lignins such as Kraft, alkaline or organosolv lignins (Beisl, Friedl, & Miltner, 2017; Österberg, Sipponen, Mattos, & Rojas, 2020). There are only a few studies on composites made of CLPs and CNMs due to the advent of this new type of renewable nanomaterials. This section aims to briefly summarize the main preparation methods and the resulting properties of CLPs, and the challenges encountered for the design of CNM/CLP composites.

1.3.1. Production of CLPs

As illustrated in **Figure 6**, two main routes have been reported for the preparation of CLPs, namely the (i) wet routes, which include acidification and solvent-exchange processes and (ii) dry routes, which commonly involve the use of equipment to mechanically produce the nanoparticles (Österberg et al., 2020).

In the acidification process (not shown in Fig. 6), CLPs are formed by acidic precipitation of lignin solution using an acid such as hydrochloric acid (HCl) (Frangville et al., 2012), nitric acid (HNO₃) (Frangville et al., 2012; Richter et al., 2016), or CO₂ (Myint et al., 2016). Both Kraft and alkaline lignins have been used as raw materials for the acidification process, as they can be dissolved in NaOH aqueous solution, ethylene glycol (Frangville et al., 2012; Richter et al., 2016) or dimethylformamide (DMF) (Myint et al., 2016) solvents prior to precipitation. The formation of CLPs is attributed to the protonation of the charged groups of lignin molecules (mainly, phenolic hydroxyl groups) by the acid leading to precipitation. The particle size is controlled by the acid addition rate and final pH of the lignin solution. Rapid addition of acid (either by slow addition of concentrated acid or rapid addition of dilute acid) or addition of higher amounts of acid usually results in larger particles. For instance, the average hydrodynamic diameter (D_h) of CLPs can vary from less than 100 nanometers to few micrometers by simply varying the concentration of HCl from, e.g., 0.025 to 2.6 M with a fixed adding rate in a solution of lignin/ethylene glycol (Frangville et al., 2012). One technical challenge of the acidification method is the formation of irregular-shaped CLPs. From a general perspective, the properties of irregular-shaped particles such as

750 packing density and coloration are difficult to control compared to the properties of regular-shaped
751 particles such as spherical particles (Österberg et al., 2020).

752 While the acidification process results in irregular-shaped CLPs, the wet solvent-exchange
753 method can be used for the production of spherical CLPs (**Fig. 6B**). In this method, spherical CLPs
754 can be formed by adding an anti-solvent, such as water, to lignin dissolved in a water-miscible
755 organic solvent (**Fig. 6, A1-A2**). Similar to the acidification process, Kraft and alkaline lignins
756 have been both used as raw materials, as they can easily be dissolved in common aqueous-organic
757 solvents and carry a high density of carboxyl hydroxyl groups that can endow the particles with
758 good colloidal stability in water. Spherical particles of lignin can be formed when using aqueous
759 (diluted) organic solvents such as tetrahydrofuran (THF) (Sipponen, Smyth, Leskinen, Johansson,
760 & Österberg, 2017), ethanol (Sipponen, Lange, Ago, & Crestini, 2018) acetone (Farooq et al.,
761 2019; Yearla & Padmasree, 2016), a mixture of THF and ethanol (Lintinen et al., 2018) or non-
762 diluted pure organic solvents such as THF (Lievonon et al., 2016).

763 During the solvent-exchange process, the formation of CLPs is hypothesized to occur via
764 a nucleation-growth process. The non-solvent (e.g., water) reduces the solubility of the lignin and
765 initiates the precipitation of large lignin fragments as precursors for the critical nuclei (Sipponen
766 et al., 2018). The CLPs can directly be obtained as aqueous dispersion with a solids content of up
767 to 2.8 wt% (Lintinen et al., 2018) or as dry microclusters (**Fig. 6D**) by spray-drying (**Fig. 6, A2-**
768 **A3**). Further dilution or concentration can be performed to adjust the concentration of the CLP
769 suspension. The wet solvent-exchange route combined with spray-drying can be up-scaled using
770 a closed cycle production loop or a continuous tubular flow reactor (Bangalore Ashok et al., 2020;
771 Lintinen et al., 2018), with the potential to produce kilograms or tons of dry CLPs.

772 The particle size and distribution, and surface properties (e.g., surface charge and density)
773 of the wet CLPs can be tuned using different solvent systems or by varying the processing
774 parameters such as the concentration of the lignin solution, the pH, or the speed at which the anti-
775 solvent is added to the lignin solution (Leskinen et al., 2017; Lintinen et al., 2018; Österberg et al.,
776 2020). For instance, the use of an aqueous solution of THF/ethanol was reported to limit the typical
777 increase in D_h associated with increased lignin concentrations. Increasing the lignin concentration
778 up to 7 wt% increased the D_h from 100 to 300 nm compared to an increase from 100 to 400 nm
779 when using aqueous THF or pure THF (Lintinen et al., 2018).

Fig. 6. Production routes of spherical CLPs. Wet methods: (A1-A2) Solvent-exchange of lignin solution against anti-solvent to form wet CLPs, (A2-A3) Spray-drying of wet CLPs. Dry methods: (A1-A4) Atomization of lignin solution in an aerosol flow reactor and subsequent controlled evaporation of the solvent to produce dry CLPs. The wet and dry methods can result in B) spherical smooth, C) spherical wrinkled, or D) super-structured lignin particles. (Österberg et al. (2020) - Published by The Royal Society of Chemistry.)

Unlike the wet methods, the dry methods involve an atomization step of the dissolved lignin into droplets in an aerosol flow reactor, followed by controlled evaporation of the solvent to produce dry CLPs (**Fig. 6, A1-A4**). The raw materials can be Kraft, alkaline, and organosolv technical lignins. The solvents commonly used to dissolve the technical lignins are DMF (Ago, Huan, et al., 2016), aqueous solution of ammonia (NH_4OH) (Kämäräinen et al., 2018) and acetone (Lourencon et al., 2020). This method produces dry spherical CLPs normally with a broad range of D_h (e.g., from 30 nm to 2 μm) (Ago, Huan, et al., 2016). Similarly to the wet methods, the particle size and distribution, and surface properties of the dry CLPs are influenced by the type of solvent, concentration of lignin solution, and the properties of the unmodified technical lignin (Ago, Huan, et al., 2016; Lourencon et al., 2020). For instance, using an aqueous solution of NH_4OH as the solvent can result in CLPs with a wrinkled surface (**Fig. 6C**) (Kämäräinen et al., 2018), while acetone or DMF can produce CLPs with smooth surfaces (Ago, Huan, et al., 2016;

Lourencon et al., 2020). In addition, CLPs prepared from organosolv lignin have shown less hydrophilic surface properties, and lower surface charge density (as indicated by zeta potential values) than CLPs produced from Kraft lignin (Lourencon et al., 2020). These differences can be ascribed to the presence of fewer hydroxyl groups in organosolv lignin than in Kraft lignin (Lourencon et al., 2020). Unlike the wet solvent-exchange methods, the dry methods are still in the stage of laboratory-scale production.

1.3.2. Properties of spherical CLPs

Spherical CLPs produced from either wet or dry methods can be dispersed in water and have a negatively charged surface, as indicated by zeta potential values of usually below than -30 mV at pH 4-10 (Ago, Huan, et al., 2016; Lievonen et al., 2016; Sipponen et al., 2017). The negative surface charges of CLPs originated from the presence of carboxylic and hydroxyl groups (the technical lignin had no hemicelluloses in the cited references), which also endowed the particles with good colloidal stability in aqueous media. For further functionalization, the surface charge of CLPs can be reversed from negative to positive by, e.g., physical adsorption of cationic polymers/oligomers (Lievonen et al., 2016; Richter et al., 2016; Sipponen et al., 2017; Zou, Sipponen, & Österberg, 2019). CLPs from both wet and dry methods also exhibit amphiphilic surface properties that are reflected by their ability to stabilize Pickering emulsion with oil phases such as kerosene or toluene, without additional surfactants (Ago, Huan, et al., 2016; Sipponen et al., 2017).

CLPs have demonstrated UV-absorbing and antioxidant properties (Farooq et al., 2019; Tian et al., 2017) owing to the presence of p-quinone, quinone methide, catechol and other phenolic groups (Ajao et al., 2018). This property, in combination with CNMs, will be further discussed in section 2, on properties of CNM/lignin films and composites.

When compared with technical lignins, CLPs have the advantages of having a well-defined surface chemistry and the ability to form very stable aqueous colloids/dispersions. This facilitates their dispersion in water with polymers such as poly(vinyl alcohol) (PVA), chitosan (Yang, Fortunati, Bertoglio, et al., 2018) or CNFs (Farooq et al., 2019). In addition, their large size distribution, spherical porous morphology, and versatile surface chemistry endow them with several binding sites for improved interactions with other materials (e.g., with silver ions for antibacterial application (Richter et al., 2015)).

However, their practical utility is limited by their solubility at $\text{pH} > 10$, and in common organic solvents, (e.g., ethanol, acetone, and THF), and their aggregation and precipitation in aqueous media at low pH (<3) or in presence of high salinity (e.g., $[\text{Conc NaCl}] = 1 \text{ M}$) (Lievonon et al., 2016; Mattinen et al., 2018; Richter et al., 2016; Sipponen et al., 2018). The aggregation and precipitation of CLPs at low pH or high salinity originates from a reduction of the repulsive electric double-layer, due to protonation of the carboxylic hydroxyl groups (pK_a of 4.5) at low pH or reduction in double-layer thickness at high salinity (Österberg et al., 2020). These limitations have to be considered for the design of CNM/CLP composite materials, as it will be discussed in the next section.

1.3.3. Suspension-stage properties of CNMs/CLPs

To date, only a few studies have investigated the wet-stage properties of CNM/CLP suspensions, including a few data on rheology and colloidal behavior.

Owing to the aqueous colloidal stability of CLPs, a controllable loading amount (up to 50 wt%) and uniform distribution of CLPs can be achieved when added to suspension of CNMs (Farooq et al., 2019). CLPs from Kraft lignin can be dispersed with CNFs without aggregation, and provide improved composite properties, relative to technical Kraft lignin (Li & Takkellapati, 2018).

The low viscosity of CLPs, when dispersed in aqueous media, is also an advantage for the preparation of composites. For instance, a 25 wt% CLP loading in a suspension of CNF/alginate did not change the viscosity of the system at a shear rate above 0.2 s^{-1} (X. Zhang et al., 2020). This aspect is important to take into account for the scale-up production of CNM/CLP materials.

The tunable and versatile surface chemistry of CLPs is another significant advantage over technical lignins for making CNM-based composites with enhanced properties. However, such studies are still missing in the current literature and are expected to be investigated in the near future.

2. Properties of CNM/Lignin materials

The characterization of the properties of suspensions of CNMs containing lignin (CNM/lignin materials), either residual, technical, or as colloidal particles, that have been dried is an indirect approach to evaluate the nanoscale performance of the suspensions. Moreover, once

dry, CNM/lignin suspensions can form a film, whose properties can be studied and tuned for their applications such as packaging substrates.

Suspensions of CNMs containing either residual, technical lignin, or colloidal lignin particles can be converted into film materials, also referred to as “nanopapers” using multiple methods such as (solvent) casting and vacuum filtration. The casting method simply consists in evaporating the medium in which the lignin and CNMs are dispersed (or dissolved in the case of technical lignin). Control of the drying temperature, relative humidity, and time is necessary to produce uniform films with minimal shrinkage (M. Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008). In contrast, the vacuum filtration method aims to filter the suspension through a mesh of selected porosity and pore size using vacuum for liquid suction (Sehaqui, Liu, Zhou, & Berglund, 2010; Siró & Plackett, 2010). The longer the filtration time, the lesser the water in the CNM/lignin wet cakes. The filtration time can thus be used to control the thickness and density of the films (Nogi, Iwamoto, Nakagaito, & Yano, 2009; Österberg et al., 2013). The CNM/lignin films obtained by solvent casting or filtration can then be further processed at room or elevated temperature or hot-pressed (Österberg et al., 2013). The processing conditions and properties (namely, density, tensile strength, Young’s modulus and water contact angle) of CNM/lignin composite films, as reported in the literature, are summarized in **Table 4**.

2.1. Physical and Morphological Properties

Compared with neat films from CNFs, films from both L-CNFs (made with residual lignin) and CNM/lignin composites (made with technical lignin or CLPs) exhibit a brown color due to the presence of lignin (**Fig. 7A**). Although the color may limit the use of the films/composites where transparency and whiteness are required, the presence of lignin can have a positive effect on, e.g., UV-blocking activities, which will be discussed in section 2.3.

The bulk density of lignins is usually in the range of 500-1300 kg m⁻³ depending on the extent of delignification/pulping (Feldman, 2002a; Tomani, Axegård, Berglin, Lovell, & Nordgren, 2011), which is lower than the bulk density of cellulose (1500-1600 kg m⁻³). The density of CNM/lignin materials can be calculated by dividing the material’s basis weight (i.e. the mass per unit area of the material) by its thickness or using the weighted densities of cellulose and lignin. The density of CNM/lignin films and composites do not show a direct correlation to the lignin content (**Table 4**). This is not unexpected as the filmmaking and drying processes can both have a

strong influence on the density and porous structure of the CNM/lignin films and composites. For instance, Spence et al. (2010) reported film densities ranging from 514-972 kg m⁻³ after casting and oven-drying (at 50 °C) the aqueous dispersions of L-CNFs with a residual lignin content between 13 and 34 wt%. In contrast, the use of filtration process followed by hot-pressing at 100 °C resulted in much denser L-CNF films (1100-1240 kg m⁻³) with a residual lignin content between 2 and 14 wt% (Rojo et al., 2015). Hot-pressing can heat lignin above its glass transition temperature (*T_g*) and soften it. The lignin can flow into the voids between CNFs, bind them and, in turn, densify the films' structure (**Fig. 7B**). Lignin, in its native form, can undergo softening around 135 °C (Salmén, 1984), but when dispersed in water, the plasticizing effect of water can significantly reduce the *T_g* of lignin (Lê, Dimic-Misic, Johansson, Maloney, & Sixta, 2018; Rojo et al., 2015; Salmén, 1984). A similar reduction in *T_g* has been observed with softwood Kraft CLPs when added to CNF suspension and hot-pressed at 100 °C after filtration (Farooq et al., 2019).

Fig. 7. Visual appearance of films made from A) L-CNFs with 27 wt% residual lignin (*left*) and CNFs with <0.2 wt% residual lignin (*right*) (Adapted and reprinted with permission from Visanko, Sirviö, Piltonen, Liimatainen, & Illikainen (2017)). Schematic of the structure of B1) CNF films and residual lignin-containing CNF (L-CNFs) films B2) before and B3) after drying using hot-press. (Adapted and reprinted with permission from B. Jiang et al. (2020)) (Copyright © 2020, John Wiley & Sons and Copyright © 2017, Springer Nature.)

915 **Table 4.** Processing and properties of CNM/lignin films and composites

Composition			Processing			Properties			
Lignin type and Source	CNMs	Lignin (wt%)	Preparation route	Drying process	Density (kg m ⁻³)	Tensile strength (MPa)	Elastic modulus (GPa)	Water contact angle (°)	Ref.
Residual	CNFs ¹	13-31	Casting	OD, 50 °C	514-972	-	-	20-92	(Spence et al., 2010)
		2-9		RT ⁵	1060-1240	59-92	13.5-19	-	(Espinosa et al., 2020)
		0.5-3			710-990	-	9-11	-	(Ferrer et al., 2012)
		22.5-42		HP ⁶ , 100 °C	1170-1230	29-55	6-6.5	65-104	(Dou et al., 2019)
		~0.2-14			1100-1240	116-164	10.5-14	35-78	(Rojo et al., 2015)
		0.2-27		HP, 100-150 °C	1210-1440	79-166	5-8	70-89	(Visanko, Sirviö, Piltanen, Sliz, et al., 2017)
		26-36		HP, 105 °C	330-1630	7-187	~1-5	-	(C. Park et al., 2017)
		15-25		HP, 85 °C	870-1180	113-224	8-14	62	(Imani et al., 2019)
		6-22	Filtration	HP, 60 °C	700-1490	23-145	0.5-4	57-87	(Fu et al., 2020)
		10-24		HP, 80 °C	900-940	71-125	3-5	41-58	(Hanhikoski et al., 2020)
		~18		HP, 93 °C	1739-1307	105-134	4-8	-	(Hong et al., 2020)
		~2-18		OD ⁷ , 60 °C	-	~60-100	~4-5	45-76	(X. Liu et al., 2019)
		10-15		OD, 70 °C	~757-800	36-45	-	59-82	(Tayeb et al., 2020)
		2-24		OD, 50 °C	1170-1410	116-237	8-14	39-88	(Oliaei et al., 2020)
		5-21		OD, 50 °C	-	7-75	~2-17	-	(Nair & Yan, 2015)
		0.2-22		RT	-	-	-	9-45	(Y. Chen et al., 2018)
		0.1-17		RT	1420-1520	89-115	9-15	65-88	(Bian et al., 2018)
		0.2-23		RT	1260-1420	90-131	7-8	-	(Huang et al., 2019)
	Cationized CNFs	~28		RT	527-774	61-71	~4	-	(Sirviö et al., 2020)
	Technical (Softwood LS ² and commercial Kraft)	TEMPO ³ -CNFs	Casting	Dried at 30 °C and 50% RH ⁸	1180-1290	120-245	3-7	-	(Y. Liu, 2018)
	Technical (Propagrylated Softwood Kraft)	Azide modified MCCs ⁴		RT	-	81-90	-	-	(Sadeghifar et al., 2017)
	Colloidal (Softwood Kraft)	CNFs	Filtration	HP, 100 °C or Dried at 23 °C and 50% RH	859-1157	38-160	3-9	-	(Farooq et al., 2019)

¹CNFs: Cellulose nanofibrils, ²LS: lignosulfonates, ³TEMPO: 2,2,6,6-tetramethylpiperidiny-1-oxyl, ⁴MCCs: microcrystalline cellulose, ⁵RT: room temperature, ⁶HP: hot-pressed, ⁷OD: oven-dried, ⁸RH: relative humidity

2.2. Mechanical Properties

Unlike CNCs, CNFs can form self-standing films through interfibrillar hydrogen bonding owing to their high aspect ratio, flexibility, and ability to entangle (Lavoine et al., 2012). Neat CNC (or MCC) films are usually brittle if no plasticizers or flexible polymeric matrix is added to the system. The direct measurement of the mechanical properties of CNC (or MCC) film thus remains a challenge. As seen in **Table 4**, only one research paper has discussed the mechanical properties of CNC/lignin composites. The measurement of the composite's tensile strength was made possible through the grafting of propargylated softwood Kraft lignin on the surface of azide-modified MCCs (Sadeghifar et al., 2017). The grafting approach considerably reduced the brittleness of the MCC films, and by varying the lignin content from 0.5 to 2 wt% in the composites, the tensile strength could slightly be tuned from 81 to 90 MPa.

More studies have reported the mechanical performance of CNF/lignin films and composites. The Young's modulus of CNF/lignin films and composites have been reported to range from 1-2 to 19 GPa, depending on the film processing conditions (**Table 4**).

The presence of lignin has a seemingly contradictory effect on the mechanical properties of films and composites. CNF/lignin films from unbleached pulps have demonstrated lower mechanical performance than neat CNF films. For instance, Rojo et al. (2015) reported a 14% decrease in the Young's modulus of films made using L-CNFs with 14 wt% residual lignin compared to the CNF reference film. In another study, a 23 % reduction in specific tensile strength was observed for L-CNF films with 23 wt% residual lignin from alkali-treated wood pulps compared to the films from bleached CNFs (Huang et al., 2019). The loss in the mechanical performance of CNF films in the presence of residual lignin may be due to various reasons, for example, (i) differences in pulping process inducing physicochemical modifications of the structure of residual lignin and affecting, in turn, its bonding with cellulose (Herrera et al., 2018; Rojo et al., 2015); (ii) high-shear action of the mechanical treatment used to produce L-CNFs, which may have disrupted the LCC network and created defects in the film structure; or (iii) the amorphous nature of lignin, which may result in an overall decrease of the films' strength (Rojo et al., 2015).

In contrast, when adding lignin as fillers, either as CLPs or technical lignin, to CNFs, the resulted composites showed about a 2-fold increase in mechanical performance compared with neat CNF films (Farooq et al., 2019; Y. Liu, 2018). Lignin, when used as an additive in CNMs,

can disrupt the interfibrillar hydrogen bonding between the cellulose nanofibrils and form hydrogen bonds with the fibrils (Farooq et al., 2019; Y. Liu, 2018), which may explain the observed improvement in the mechanical performance of the composite films. In addition, the use of hot-press as a drying or post-processing step can further enhance the mechanical properties of the composite films, benefiting from the thermoplasticity of lignin, which can act as a binder or stress-transfer agent (**Fig. 7B**) (Rojo et al., 2015).

2.3. Optical Properties

The optical properties of CNM/lignin film materials are typically measured by UV-visible spectrometry in the range of 200-1000 nm. Irrespective of the lignin type (residual, technical, or CLPs), the addition of lignin results in a decrease in light transmittance across the UV region (200-400 nm). The reduction in light transmittance is due to the presence of lignin (Barsberg et al., 2003; Falkehag et al., 1966), which can absorb UV light through the presence of chromophores in its structure. Representative structures of chromophores present in residual or technical lignins are shown in **Fig. 8A**. The typical UV absorption spectrum of lignin is illustrated in **Fig. 8B**.

Recent studies have focused on the influence of adding technical lignin or CLPs to a CNM matrix on the UV absorption property of CNM/lignin composite films (Guo et al., 2019; Hambardzumyan et al., 2012; Sadeghifar et al., 2017; Xiao Wang et al., 2019). Propargylated lignin-grafted azide-modified MCC composites showed a 15-30 % absorption in UV-B light (280-320 nm) with just 0.5 wt% lignin (Sadeghifar et al., 2017). Increasing the lignin content to 2 wt% with respect to the MCC content resulted in a 100 % absorption of the UV-B light. The UV absorption property of CNM/lignin film materials depends on the type of technical lignin (Parit et al., 2018). For instance, CNC films with 1 wt% softwood Kraft lignin were able to completely block the UV-C light (200-280 nm), while the use of 1 wt% alkaline lignin resulted instead, in partial absorption of the UV-C light. The differences in the molecular structure of the technical lignins can explain the disparities in the optical transmittance (Sadeghifar & Ragauskas, 2020). The morphology of lignin, as present in the composite films, is also suggested to alter the UV absorption property of the films. With a similar lignin content of 10 wt%, CNF/CLP films had a higher transmittance (18 %) than CNF/Kraft technical lignin films (0.5 %) at the visible region 750 nm, while it still blocked light in UV region (Farooq et al., 2019), which is attributed to the

larger and more aggregated particle state of technical lignin. Aggregated particles of lignin are more susceptible to light scattering than CLPs.

Fig. 8. A) Chromophores in the structure of residual and technical lignins with their approximate absorption wavelength; B) Typical UV light absorption spectrum of lignin. (Adapted from Sadeghifar & Ragauskas (2020) – Published by MDPI).

2.4. Barrier properties

Dense CNF networks can be effective barriers against gases and liquids (Aulin et al., 2009; Lavoine et al., 2012). The presence of lignin with CNFs can further enhance the barrier performance of the composite films by increasing the density, altering the porous structure, or changing the hydrophilic/hydrophobic balance.

Water contact angle (WCA) values are useful in rapidly determining the hydrophilic-hydrophobic interactions of lignin-containing CNF films. As expected, the WCA of films from L-CNFs has been reported to be higher than that of the corresponding CNF films (Espinosa et al., 2020; Lê et al., 2018; Rojo et al., 2015). For instance, Rojo et al. (2015) observed a 59 % increase in WCA of L-CNF films with 14 wt% residual lignin, compared to the bleached CNF films. In another study, the WCA of L-CNF films with 27 wt% residual lignin was found 25 % higher than that of films from CNFs (Visanko, Sirviö, Piltonen, Sliz, et al., 2017). The presence of residual

lignin is believed to prevent the accessible hydroxyl groups of cellulose from forming hydrogen bonding with water molecules, thus making the films more water resistant (Nair & Yan, 2015).

The water resistance of CNM films containing technical lignin or CLPs also depends on the amount of added lignin, the lignin type (e.g., sulfonate lignins are soluble in water) and the chemical interactions between lignin and CNMs. For instance, the use of Fenton's reagent was reported to promote the water resistance of composite films through covalent bonding between organosolv lignin and CNCs (Hambardzumyan et al., 2015), while the use of an alkaline solvent like NaOH helped impregnate lignin into CNMs, enhancing the water absorption of the films (Parit et al., 2018). The film density and porous structure (incl. porosity) are other parameters that can alter the film-water (and gases) interactions. Yet, very few studies have studied the relationships between the structure, processing, and film-water (or gases) interaction of CNM/lignin films and composites. Spence et al. (2010), for instance, initiated a few tests on the water vapor transmission rate (WVTR) of films made from L-CNFs. Films from softwood L-CNFs with ca. 14 wt% residual lignin and a density of 792 kg m^{-3} had a WVTR of $460 \text{ g m}^{-2} \text{ day}^{-1}$, while the bleached references with a slightly higher density of 860 kg m^{-3} had a much lower WVTR of $240 \text{ g m}^{-2} \text{ day}^{-1}$. The difference in WVTR may possibly be explained by differences in the porous structure of the films.

The oxygen barrier performance of L-CNF films is also dependent on the films' structure and density, which in turn can be partially controlled with the film making and drying processes. As discussed earlier, above its T_g , lignin will undergo viscose flow, which can reduce the presence of pores that allow for gas permeation. For instance, the oxygen transmission rate (OTR) of hot-pressed films from L-CNFs was found much lower than that of the films from CNFs prepared under similar processing conditions ($0.01 \text{ mL mm m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ versus $0.23 \text{ mL mm m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ at 50 % RH, respectively) (Rojo et al., 2015). The slower oxygen diffusion and thus, the higher barrier against oxygen permeation of the films made using L-CNFs was attributed to the denser structure of the films, which was the result of the softening of lignin at 100°C (**Fig. 7B**). The OTR of films from L-CNFs and CNFs is impacted differently by relative humidity of the atmosphere used for the test. The OTR for films of L-CNFs prepared by casting and oven-drying at 70°C increased by about 1.5-fold at 50 % RH and 2-fold at 100 % RH compared to neat CNF films prepared under similar conditions (Tayeb et al., 2020). Compared to the previously discussed hot-pressed films of L-CNFs, the high OTR values of the L-CNF films dried at 70°C may come from a more porous structure of the films. The authors also considered the non-uniformity of their

L-CNFs as a possible explanation for these high OTR values (Tayeb et al., 2020). The presence of lignin may also have altered the CNF network and bonding, thus affecting the porous structure and porosity of the films.

2.5. Antioxidant and antimicrobial properties

Owing to the presence of free radical scavenger structures, lignin exhibits excellent antioxidant properties. The aromatic ring structure of lignin contains methoxy and hydroxyl functional groups that enable the termination of oxidation reactions through hydrogen donation (Dizhbite et al., 2004), thus acting as radical scavengers.

The antioxidant properties (AOP) of technical and residual lignins can be analyzed by measuring the radical scavenging capacity of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in polar solvents, such as ethanol or methanol (Domenek et al., 2013; Zadeh et al., 2018). Lignin, especially its low molecular weight fragments, can be solubilized in both ethanol and methanol and, thus, interact with the free radicals generated by DPPH (used here as a radical generator). The AOP of lignin is highly dependent on its molecular structure. The use of soda or organosolv technical lignin in CNM/lignin composite films demonstrated higher antioxidant activities than sodium salicylate hydrotrope or DES solvent-derived technical lignins, as a result of their higher syringyl phenolic hydroxyl content (Guo et al., 2019). A limitation of the DPPH assay is the need for a solvent that may not dissolve all of a particular lignin.

Alternatively, an aqueous assay, namely ABTS (2–20 azino-di-3-ethylbenzthiazoline sulfonate), has been proposed as an indirect method for measuring the AOP of CNM/lignin films (Espinosa et al., 2020; Farooq et al., 2019). In these cases, the CNM/lignin materials were immersed in an aqueous ABTS solution, and changes in solution's radical concentration were measured. Espinosa et al. (2020) observed a 2-fold increase of the AOP of wheat straw L-CNFs films with 9 wt% residual lignin compared to CNF films. Farooq et al. (2019) observed that an increase of the CLP loadings in CNF films from 2 to 10 wt% increased the AOP of the CNF/CLP composite films by about 50 %. To date, the number of studies investigating the antioxidant properties of CNM/lignin composites are still limited, and no comparison can easily be conducted between the two assays proposed for AOP measurements. The end-use application considered for the designed composites should dictate the selection of the measurement method.

Another interesting property of lignin is its resistance to fungi and bacteria (Dizhbite et al., 2004; Dong et al., 2011). The antimicrobial properties of CNM/lignin films may stem from the phenolics of lignin (Baurhoo, Ruiz-Feria, & Zhao, 2008; Qin et al., 2016), especially from the presence of double bonds in α and β positions of the side chain and methyl groups, which can damage the cell wall of microorganisms through lysis (Yang, Fortunati, Gao, et al., 2018). The CLPs may endow the composites with a stronger antimicrobial activity over residual or technical lignin due to their higher surface area and higher accessibility to the surface phenolic groups (Qian et al., 2015; Yearla & Padmasree, 2016). Further studies are still needed to evaluate the antimicrobial potential and mechanisms of CNM/lignin materials, but the observed synergy resulting from the combination of CNMs and lignin significantly broadens the spectrum of applications of cellulose nanomaterials, as lignin can counterbalance some undesired aspects of cellulose, such as hydrophilicity and poor resistance against some fungi and bacteria.

CNM/lignin films and composites exhibit different properties from their non-lignin containing counterparts and, therefore, may be useful for new applications relative to CNM films. The next section of this review article will give an overview of the end-use applications which have so far been considered with CNMs containing residual lignin, technical lignins, or CLPs.

3. Applications of CNM/Lignin materials

This section reviews recent studies on CNM/lignin suspensions used as either mechanical reinforcement of composite materials or packaging substrates. Other interesting novel applications for CNM/lignin include sunscreen (Sadeghifar et al., 2017), flexible integrated circuit boards (B. Jiang et al., 2020), and emulsion stabilizers (Ballner et al., 2016; Gindl-Altmutter, Obersriebnig, Veigel, & Liebner, 2015). However, these applications are still in their infancy, and therefore, they will not be discussed in the following section. Additional applications of technical lignin and CLPs, such as the use of CLPs as emulsions stabilizers (Ago, Huan, et al., 2016), for corrosion inhibition (Dastpak et al., 2018), drug release (Larrañeta et al., 2018) have been proposed, but the focus of this section is on applications where both CNMs and lignin are combined in an attempt to create a synergy between the two biopolymers, resulting in high-performance materials.

3.1. Mechanical reinforcement

Similar to neat CNMs, residual lignin-containing CNMs have been used as mechanical reinforcement of different materials such as polyvinyl alcohol (Horseman, Tajvidi, Diop, & Gardner, 2017), polylactic acid (Xuan Wang, Jia, Liu, & Miao, 2018), starch (Ago, Ferrer, & Rojas, 2016), polypropylene (Peng et al., 2018), polycaprolactone (Herzele et al., 2016), polystyrene (Ballner et al., 2016) and polyurethane (Visanko, Sirviö, Piltonen, Liimatainen, et al., 2017). The benefit of using unbleached CNMs instead of bleached CNMs as mechanical reinforcement can be linked to lignin's ability to act as a compatibilizer between the polar reinforcing phase (i.e., the fibers) and the non-polar matrix. Ballner et al. (2016) exploited the amphiphilic feature of residual lignin and hemicelluloses present in L-CNFs for the stabilization of an aqueous emulsion of styrene. The emulsion polymerization of styrene in water resulted in polystyrene (PS) microspheres coated on the surface of L-CNFs. The PS microsphere-coated L-CNFs were converted to a film by hot-press and showed a 50 % increase in bending stiffness of PS films reinforced with L-CNFs (**Fig. 9A**).

The use of L-CNFs as a replacement for adhesives in medium-density fiberboards (MDFs) was also considered to reduce the environmental impact of formaldehyde-based adhesive (Diop et al., 2017a). The addition of 20 wt% of L-CNFs from TMP pulp followed by hot-pressing at 180 °C increased the modulus of elasticity (MOE) of the MDF by ca. 300 MPa or 24 %, which is higher than the American National Standard Institute (ANSI) requirement for MDFs (recommended value of 1241 MPa) (**Fig. 9B**). The authors suggested that the thermoplastic effect of the residual lignin present in the L-CNFs can explain the significant increase in mechanical performance of the fiberboards upon hot-pressing.

Fig. 9. Applications of CNM/lignin materials. A) L-CNF-reinforced polystyrene (PS) films: A1) Pictures of PS and L-CNF-reinforced PS films, A2) Bending stress of the films as a function of the strain (Adapted and reprinted with permission from Ballner et al. (2016)). B) L-CNF-based wood adhesives as replacement of formaldehyde-based adhesive in the manufacturing of medium-density fiberboards: Images of the resin-free fiberboards from L-CNFs, B1) before and B2) after hot-press, B3) Modulus of elasticity of the board as a function of the L-CNF content and drying temperature (Adapted and reprinted with permission from Diop et al. (2017a, 2017b)). C) UV shielding property of CNCs and CLPs fillers in a PLA matrix: C1) Transmittance of the different composite films with either 1 or 3 wt% of CNCs and CLPs (interchangeably), C2) Proposed mechanisms of UV light reflectance and absorption by CNCs and CLPs (Adapted and reprinted with permission from Yang et al. (2016a)). (Copyright © 2016, American Chemical Society, Copyright © 2016 and 2017, Elsevier Ltd. and Copyright © 2017, Spring Nature.)

3.2. Packaging applications

Strong UV radiation from sunlight can reduce the performance of materials through weathering and yellowing of plastics or loss in mechanical strength through depolymerization and

cracking (Feldman 2002b). The UV-absorbing properties of L-CNMs can thus be exploited in the design of materials intended for outdoor exposure or for packaging where the product is light-sensitive. With the addition of only 3 wt% CNCs and 1 wt% CLPs (produced from *Arundo Donax* biomass through an acidification process), the UV light transmittance of the CNC/CLP/PLA composite films at 320 nm was reduced to 52 % from the original 91 % of the neat PLA film (Yang et al., 2016a). The authors suggested a synergistic effect between the CNCs and CLPs. While the CLPs adsorbed the UV light, the CNCs acted as ‘mirrors,’ scattering and reflecting parts of the UV light (**Fig. 9C**). Composite films composed of poly(vinyl alcohol) (PVA) and 7 wt% of L-CNFs produced with and without TEMPO-mediated oxidation pre-treatment, were able to block 47 % and 54 % of the UV light, respectively, compared to 10 % for neat PVA films (Espinosa, Bascón-Villegas, et al., 2019). While the presence of lignin clearly explains the higher absorption of UV light of the composite films, the amount of lignin influences the percentage of UV absorbed. The above-mentioned study does not report the residual amount of lignin in both the mechanically pre-treated and TEMPO-oxidized L-CNFs (Espinosa, Bascón-Villegas, et al., 2019), but we can hypothesize that the TEMPO-oxidized CNFs had less residual lignin, resulting in a lower amount of UV light absorbed.

Recent work has also shown that CNM/lignin materials can offer biocide properties when blended with plastics such as PLA. The PLA blend containing 1 wt% CNCs and 3 wt% CLPs showed antibacterial activity against *Pseudomonas syringae* pv. *tomato* (Pst) (Yang et al., 2016a), which is known to severely damage the growth of tomatoes (Quattrucci et al., 2013). The antibacterial activity of the composites increased by ca. 73 % in the first 3 h of Pst inoculation compared to neat PLA. The ternary polymeric blend of PLA, CLPs, and CNCs was also tested against other bacterial plant pathogens, e.g., *X. arboricola* pv. *pruni* (Xap) and *X. axonopodis* pv. *vesicatoria* (Xav) (Yang et al., 2016b). After 48 h, the antibacterial activity of PLA/3 wt% CLP/1 wt% CNC increased by ca. 84 % against the Xav inoculation and 30 % against the Xap inoculation.

Conclusion and Perspectives

Combining cellulose nanomaterials with lignin (residual, technical, or colloidal lignin particles) is an attractive strategy for the development of high-performance CNM-based products with improved properties, and more especially with respect to water and moisture resistance, compatibility with non-polar matrices and enhanced thermal stability. Moreover, the use of lignin can further broaden the end-uses of CNMs with the addition of novel functions, such as UV-protection and antimicrobial activity.

Several design strategies have been considered for the production of CNM/lignin materials. The *in-situ* approach offers a pathway to directly produce CNMs from unbleached pulps, with the properties of the resulting L-CNMs having a strong dependence on the pulping process. In contrast, the *composite* approach exploits technical lignin or colloidal lignin particles as an additive to CNMs, with the properties of the subsequent CNM/lignin composites relying on the interactions, uniformity and colloidal stability of the CNM/lignin suspensions. This latter strategy can exploit different types of technical lignins, e.g., Kraft or organosolv lignin, as received from the pulp mill and biorefinery, or further processed into CLPs. The variety in lignin types and the possibility to control and tune the lignin content and its properties (e.g., shape, surface chemistry, solubility) can ease the mixing of lignin with aqueous suspensions of CNMs and in turn, facilitate the development of high-performance tailored CNM/lignin materials.

From a commercialization and sustainability standpoint, the use of unbleached pulps for CNM production can significantly reduce the use of harsh pulping/bleaching chemicals and, subsequently, the cost associated with such treatments. In many applications, the use of L-CNMs instead of CNMs can be of interest to reduce the overall production costs, without affecting the properties of the final product. In the *composite* approach, both the technical lignins and CLPs can be easily scaled. The water-dispersible character of CLPs facilitates the production of homogeneous mixtures with CNMs.

Research on the *in-situ* approach for the production of L-CNMs has just started. Several works have been published on the production of L-CNFs, investigating various and diverse raw materials and production routes, however systematic studies on the production of L-CNCs are still scarce. There is yet a clear lack of information on the role of residual lignin and its interaction with cellulosic fibers upon processing, and while several hypotheses have already been proposed, additional research is needed. Additionally, the influence of residual lignin on the properties of

films of L-CNMs and other products is still inconsistent, and further work is needed before pursuing the commercialization of L-CNM products.

Despite the limited number of publications, the *composite* approach has already shown great potential to overcome some of the challenges highlighted with L-CNMs. The use of CLPs, in particular, seems to be an excellent pathway for the development of advanced functional CNM/lignin materials. While this review article has focused on CNM-based materials containing lignin, the *composite* approach can also be considered the other way around, specifically for the development of lignin-based materials containing CNMs as the dispersed phase. The flexibility and versatility of this approach could allow for targeting a broader range of applications.

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