Review on Non-conventional Fibrillation Methods of Producing Cellulose Nanofibrils and Their Applications

Lu Wang[†,‡,*], *Kai Li*[§], *Katie Copenhaver*[‖], *Susan MacKay*[‡], *Meghan E. Lamm*[‖], *Xianhui Zhao*[‖], *Brandon Dixon*[※], *Jinwu Wang*[⁁], *Yousoo Han*[†,‡], *David Neivandt*[※], *Donna A. Johnson*[⋕], *Colleen C. Walker*[⋕], *Soydan Ozcan*[‖], *Douglas J. Gardner*[†,‡,*]

[†]School of Forest Resources, University of Maine, 5755 Nutting Hall, Orono, ME 04469, USA.

[‡]Advanced Structures and Composites Center, University of Maine, 35 Flagstaff Road, Orono, ME 04469, USA.

[§]Buildings and Transportation Science Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 37830, USA

[‖]Manufacturing Science Division, Oak Ridge National Laboratory, 1 Bethel Valley Road,Oak Ridge, TN 37830, USA.

[※]Department of Chemical & Biomedical Engineering, University of Maine, 5737 Jenness Hall, Orono, ME 04469, USA.

[⅄]Forest Products Laboratory, U.S. Forest Service, 1 Gifford Pinchot Drive, Madison, WI 53726, USA.

[⁜]Process Development Center, University of Maine, 5737 Jenness Hall, Orono, ME 04469, USA.

KEYWORDS. nanocellulose, enzyme, oxidation, deep eutectic solvents (DES), extrusion, degree of fibrillation

ABSTRACT. The production of cellulose nanofibrils (CNFs) continues to receive considerable attention because of their desirable material characteristics for a variety of consumer applications. There are, however, considerable challenges that remain in transitioning CNFs from research to widespread adoption in the industrial sectors, including lowering the embodied energy and production costs, as well as the environmental footprint to produce them in an efficient manner. This review covers CNFs produced from non-conventional fibrillation methods as an alternative solution. Pretreating biomass by biological, chemical, mechanical, and/or physical means can render plant feedstocks more facile for processing and thus lower energy requirements to produce CNFs. CNFs from non-conventional fibrillation methods have been investigated for various applications, including films, composites, aerogels, and Pickering emulsifiers. Continued research is needed to develop protocols to standardize the characterization (e.g. degree of fibrillation) of the lignocellulosic fibrillation processes and resulting CNF products to make them more attractive to the industry for specific product applications.

Contents

1. INTRODUCTION

The production of nanocellulose is an extensively investigated area. Nanocellulose can be produced chemically, physically, mechanically, or biologically. Mechanical methods are commonly used for producing cellulose nanofibrils (CNFs). In a previous review, mechanical fibrillation methods were grouped into conventional and nonconventional methods.[1] Conventional fibrillation techniques, including homogenizing, grinding and refining, have proven effective in producing nanocellulose and have been scaled up to an industrial production level. There are however limitations to such methodologies, including high energy consumption, low production efficiencies (low solid content), and high cost of final products.[4] Therefore, various types of non-conventional fibrillation methods for producing nanocellulose have emerged and are becoming increasingly important. In the current work, we summarize the recent progress in developing non-conventional fibrillation methods, including extrusion, ball-milling, blending, steam explosion, aqueous counter collision, ultrasonication, cryogenic crushing (cryo-crushing), and others. Methods to characterize the degree of fibrillation, and a review of pretreatment methods employed are also presented. Finally, an overview of the current fields of application of CNFs is given. To the best of our knowledge, there has been no review article primarily focused on non-conventional methods of producing nanocellulose. This article is intended to fill that knowledge gap.

1.1 Nanocellulose

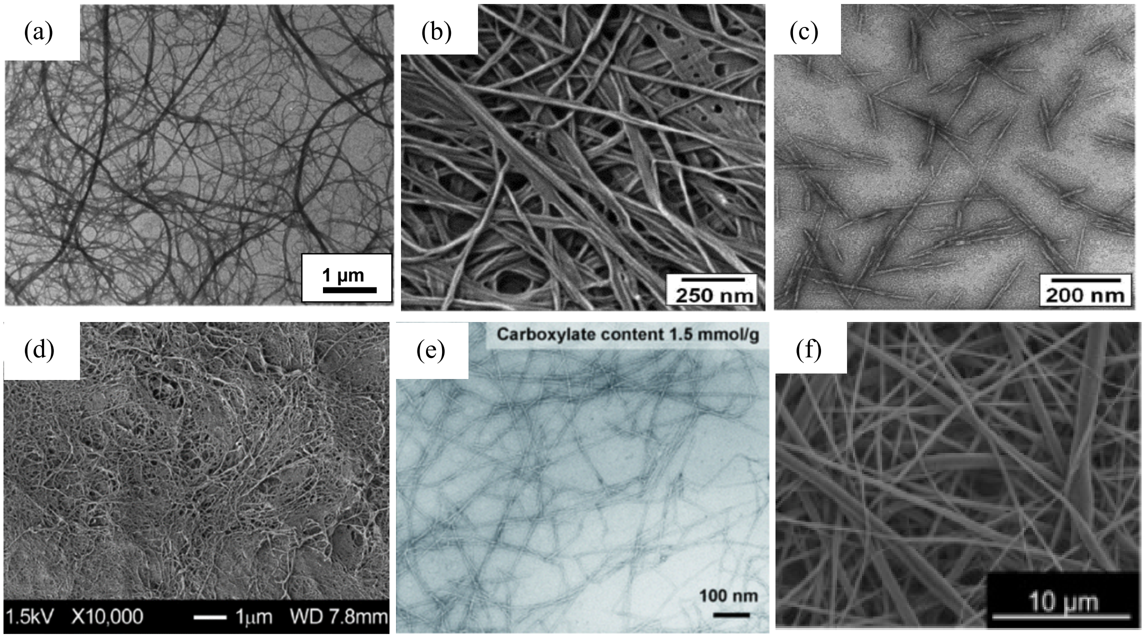

Figure 1. The various types of nanocellulose. (a) Transmission electron microscopy (TEM) graph of cellulose microfibrils (CMFs). Adapted from Ref.[4] with permission, copyright 1997 Wiley-VCH. (b) Scanning electron microscopy (SEM) graph of bacterial cellulose (BC). Adapted from Ref.[5] with permission, copyright 2007 American Chemical Society. (c) TEM graph of cellulose nanocrystals (CNCs). Adapted from Ref.[6] with permission, copyright 2011 Royal Society of Chemistry. (d) SEM graph of cellulose nanofibrils (CNFs). Adapted from Ref.[7] with permission, copyright 2009 Wiley-VCH. (e) TEM graph of TEMPO-mediated cellulose nanofibers (TOCN). Adapted from Ref.[8] with permission, copyright 2011 Royal Society of Chemistry. (f) SEM graph of electrospun cellulose nanofibers (ECNFs). Adapted from Ref.[9] with permission, copyright 2019 Elsevier.

A nanomaterial is a material with at least one dimension on the nanometer scale. By reducing the size of a common cellulose fiber (tens of microns in diameter), nanocellulose can be produced. The two common methodologies to produce nanocellulose from wood or plant cell walls follow either a chemical or mechanical route. The production of nanocellulose from plant cell walls goes back to 1950's when Rånby explored the colloidal properties of cellulose micelles from mercerized pulp.[10] In the 1980s, Turbak et al. used high pressure homogenization of cellulose pulps to produce cellulose microfibrils (CMFs) (**Figure 1a**), which comprised fibrils with diameters ranging from 25 to 100 nm.[11] Nanocellulose can also be produced in a bottom-up approach using bacteria, which is bacterial cellulose (BC) (**Figure 1b**).[12] Significant research efforts on the production and use of nanocellulose have occurred over the past three decades. Most chemically-produced nanocellulose uses acid hydrolysis to liberate the nanoscale, crystalline portions of the plant cell wall, which are referred to as cellulose nanocrystals (CNCs) (**Figure 1c**).[13] CNCs typically have uniform sizes ranging from 100 to 200 nm in length and 10 to 30 nm in diameter. Alternatively, mechanically-produced nanocellulose typically employs some form of grinding or shearing of pulp fibers in aqueous suspensions to reduce fiber dimension; equipment such as disc refiners or stone grinders (super mass colloider) are commonly utilized in such operations.[14] These mechanically derived, nanofibrillated cellulose materials, termed "cellulose nanofibrils" (CNFs), have hierarchical structures comprising interconnected fibrils ranging from sub-micron to tens of microns in length, with diameters ranging from several nanometers to several microns (**Figure 1d**). Because of this multi-scale dimensionality, mechanically-derived nanocellulose is challenging to process and characterize. Significant research efforts have combined chemical and mechanical means to produce nanocellulose, with the most researched technique being the production of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibers (TOCN) (**Figure 1e**).[8] Considering the chemical method (TEMPO), rather than the mechanical method (ultrasonication), as the primary force for fibrillating, TOCN will not be covered in this paper. Another category of nanocellulose generated from non-conventional methods is electrospun cellulose nanofibers (ECNFs) (**Figure 1f**).[15] ECNFs have attracted much attention with several review articles having been published.[15–17] Since ECNFs are not obtained through fibrillation, they will not be included in the current review. The scope of this review paper covers non-conventional fibrillation methods for producing nanocellulose fibrils (mainly CNFs and CMFs), including mechanical and physical approaches.

1.2 Limitations of conventional fibrillation methods for CNFs

CNFs are typically produced by three conventional processes: homogenization (including microfluidizing), grinding, and refining.[2] A brief explanation of the working principles of these three methods follows. During homogenization, cellulose fiber suspensions flow through extremely small gaps between an impact ring and a valve under intensive shear, which reduces the fiber into nanofibrils. Similar in principle, a microfluidizer is constructed with a chamber containing either a Z- or Y-shape channel. Such a channel enables cellulose fibers to intensively interact with the inside of the microfluidizer's chamber, resulting in significant size reduction of the fibers. To produce the high shear forces required within the microfluidizer, the channel size is very small. The limited channel size relative to large fiber dimensions can result in fiber clogging during microfluidizing.[18] A grinder consists of a stationary disk and a rotational disk, generating shear force during operation. By controlling the gap between the stationary and rotational disks, as well as rotational speed and material flow rate, high shear conditions may be applied to cellulose fibers to fibrillate them into nanofibers. Disk refining is very similar to grinding in terms of the fibrillation mechanism and differs only in that the gap size is greater in disk refining. As a result, the fibrillated fibers from the disk refining process vary largely in fiber dimensions, ranging from micron to nanoscale. As such, the product from disk refining is often referred to as CMFs. Disk refining is commonly used as a mechanical pretreatment for manufacturing more consistent CNFs.

Conventional fibrillation methods are rather energy intensive, with typical energy consumption around 20 kWh/kg for homogenizing[18], 4-15 kWh/kg for grinding[18–20], and 3 kWh/kg for microfluidizing[18]. Producing CNFs with less energy is one of the driving forces for the development of non-conventional fibrillation methods. For example, the energy consumption during twin-screw extrusion (TSE) fibrillation of biomass has been reported to be in the range of

2-6 kWh/kg, most of which involved the use of chemical/enzymatic pretreatments before fibrillation.[19–23] However, some non-conventional fibrillation methods have high energy demand, i.e. 8-12 kWh/kg for ball milling[24] and 15 kWh/kg for aqueous contour collision[25].

Another limitation of CNFs produced from conventional fibrillation methods is their low solids contents (< 5 wt.%) in aqueous suspensions.[2] These methods require processing at low solids contents to prevent the cellulose fiber suspension from becoming too viscous for feeding and fibrillation.[2] The low solids content of CNF suspensions negatively impacts their economics by increasing the transportation cost (on a mass basis) and requiring subsequent compacting and dewatering.

2. DEGREE oF FIBRILLATION

There are a range of tools for characterization of various attributes of CNFs. While the majority of these characterization methods are widely accepted, there remains unresolved challenges, particularly relating to quantification of the "degree of fibrillation". Two factors in particular should be considered with regard to characterization of fibrillation. First, the number or percentage of nanofibrils under a certain threshold diameter, as well as the average aspect ratio of the resulting fibrils, is typically reported. This quantity is commonly referred to as the "fines level" of the material.[26] Second, few authors make the distinction between internal and external fibrillation, meaning the complete isolation of individual nanofibrils versus those that are still partially affixed to larger fiber bundles. The relative amounts of each should be considered when reporting the fibrillation extent resulting from a given processing technique.[26,27] The following sections discuss how "degree of fibrillation" is commonly measured and reported.

2.1 Direct measurements

Currently the only direct method of measuring the size of CNFs is through visual observation via one of several microscopy techniques. Such methods include optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and fluorescence microscopy.[21,28–30] SEM and TEM in particular are widely used by researchers to measure the dimensions of nanofibrils on a range of scales. Measurements are relatively straightforward, as two-dimensional images are obtained, and the fibrils' lengths, diameters, and aspect ratios can be measured either manually, or via image analysis software.[31–37]

2.2 Indirect measurements

The remainder of the characterization techniques commonly employed to assess the quality of CNFs are indirect measurements. In these measurements, a property is measured which provides a qualitative estimate of fibrillation based upon a known relationship between the measured parameter and the CNF size/degree of fibrillation. The relationship itself is often determined using additional characterization techniques and it is assumed applies uniformly across samples. Indirect measurements of CNF fibrillation are often performed using cellulose suspensions in water or other solvents at a range of concentrations.

2.2.1 Viscosity

As the degree of fibrillation increases during processing, the size of the fibrils generally decreases. Creating smaller or more highly fibrillated CNFs progressively increases fibril-fibril interactions, resulting in greater suspension viscosity.[26,28,38–41] Therefore, researchers have used viscosity to qualitatively determine the degree of CNF fibrillation. Attempts have been made to fit models to viscoelastic data to gain a more quantitative correlation between the extent of CNF fibrillation and suspension viscosity.[21,42] To date, no widely accepted quantitative relationship between viscoelastic data and CNF dimensions/degree of fibrillation has been established.

2.2.2 Transmittance and turbidity

The transmittance of light through a suspension is related to the particle or fibril dimensions, surface area and inter-particle interactions at a given concentration. A higher transmittance generally correlates to a more highly fibrillated material. The turbidity of a suspension is a measurement of the light scattered at 90° to the incident light. The turbidity is a function of the number, shape, and size distribution of scatterers in a suspension, as well as the refractive indices of the scatterers and the suspension medium. Similar to transmittance, the turbidity of a suspension can be used to qualitatively assess the fibrillation of CNFs, but results are also affected by any agglomeration of fibrils in the sample.[41,43] Transmittance or absorbance, and turbidity values are most commonly measured using an ultraviolet-visible (UV-vis) spectrophotometer. Recently, more specialized and automated equipment has become available that combines transmittance measurements with optical image analyses of residual microscale fibers after fibrillation to provide an estimation of the degree of fibrillation.[27,38,41]

2.2.3 Dynamic light scattering (DLS)

DLS measures particle size in solutions or suspensions, and makes the assumption that all particles are spherical. DLS uses time-dependent fluctuations of the intensity of light scattered by particles in solution undergoing Brownian motion. These fluctuations are related to the hydrodynamic radius of the particles (assuming they are spherical) which have a constant diffusion coefficient in all directions. Due to their high-aspect ratio, many conformations, and tendency to agglomerate, CNFs are challenging to characterize via this method.[41,44]

2.2.4 Water retention value (WRV)

WRV is a widely used index in the pulp and paper industry to assess the degree of fibrillation of a sample via the amount of water retained under specific conditions.[21,37,45,46] The higher the WRV, meaning the greater the amount of water retained by fibrils, the higher the degree of fibrillation. The method was developed for use with pulp fibers with diameters on the tens of microns. Researchers have however employed centrifugation to measure the WRV of micro- or nanofibrils via the reduction of easy-to-remove bulk water, leaving water bound to fibril surfaces and in their pores.[21,47] Similarly, the Canadian Standard Freeness (CSF) measures the water drainage rate from fibers and is often correlated to a degree of fibrillation, as the CSF value is related to the surface area and swelling behavior of fibers and fibrils. Like the WRV, CSF is primarily used for larger fibers, and its efficacy with micro- and nanomaterials is problematic, as the drainage rate is reduced to near-zero as the fibril size decreases.[37,46]

2.2.5 Specific surface area

The surface area of CNFs can be used to estimate the degree of fibrillation since the surface area of fibers increases substantially when they are disaggregated into fibrils. It is noted however that a surface area measurement gives little, if any, indication of the length or aspect ratio of the fibrils or information regarding the extent of internal versus external fibrillation. Furthermore, surface area measurements of CNF are often difficult to interpret. Most surface area measurements rely upon the adsorption of a probe species onto the fibril surface (common probe species include water, gas, dyes, charged species and enzymes).[46,48] Clearly, the physical size of the probe molecule, and it propensity to adsorb, must be considered when evaluating the efficacy of a surface measurement technique as applied to cellulose fibrils.[21,26,48] UV-vis spectroscopy, coupled with a dyeing procedure and subsequent centrifugation, is commonly used to measure specific surface area of CNFs.[48] Additional adsorption-based methods for measuring the surface area of CNFs include Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses employing nitrogen gas adsorption and desorption.[26,45]

3. BIOMASS PRETREATMENTS

Mechanical fibrillation processes where high shear forces disintegrate cellulosic fibers are commonly used for CNF production. In order to obtain well-defibrillated fibers, those high shear processes consume significant amounts of energy, making the cost of the CNFs high and limiting their widespread adoption.[49] Lignocellulosic feedstocks contain various amounts of cellulose, lignin, hemicellulose, pectin, etc., with specific compositions being dependent upon the specific source.[50] Direct fibrillation of lignocellulosic feedstocks generates CNFs with various contents of these components, a fact which limits the consistency of CNF production and works against ready adoption in the marketplace. As a result, many researchers have invested significant effort in the development of pretreatments that reduce the energy consumption for CNF production and ensure consistency of the products' composition and properties.[51] Additionally, pretreatments have been shown to reduce the likelihood of clogging during the disintegration process.[47] Different strategies have been developed for the pretreatment of lignocellulosic feedstocks for CNF production. Such strategies include chemical[52–55], physical[56,57], mechanical[58,59] and enzymatic treatments [60,61], in addition to combinations thereof.[19,49] The pretreatment of lignocellulosic materials for CNF production via conventional fibrillation processes is well understood and has been reviewed in previous publications.[2,14] In this section, we will focus on pretreatments used for non-conventional fibrillation processes.

3.1 Chemical pretreatment

Chemical pretreatments have been applied to lignocellulosic materials to remove lignin, hemicellulose, pectin, etc., introduce specific functional groups, and to reduce the energy requirements for fibrillation. Alkaline treatments that hydrolyze lignin are widely used for pretreatment of feedstocks for CNF production. Often, an alkaline treatment is coupled with a bleaching process, commonly employing sodium chlorite ($NaClO_2$), in order to further remove lignin residues. For instance, Chaker et al. applied a NaOH treatment (5 wt.%) at 80 ˚C for delignification and followed by bleaching with $NaClO_2$.[52] They compared the efficiency to a delignification process which only used $NaClO_2$. Their results suggested that while the cellulose content of the treated fiber increased for both methods, NaOH-treated fibers had the highest cellulose content.

Oxidative pretreatments are another important strategy for the production of high quality CNFs with reduced energy consumption.[51,62] Through the oxidation process, carboxylate and aldehyde functional groups are introduced onto native cellulose fibers. The negative charges increase the repulsion between fibers and aid in the defibrillation process. During TEMPO oxidation of CNFs, NaBr and NaClO are generally used as catalysts and primary oxidants in the pH range of 9 to 11. The cellulose content of the starting material often dictates the specifics of the TEMPO oxidation process. For example, when relatively pure cellulosic materials or bleached lignocellulosic materials are used, TEMPO oxidation can be applied directly.[63] When the starting material has a significant lignin composition however, a delignification step is typically required prior to TEMPO oxidation.[21,29,64] Baati et al. performed a TEMPO oxidation with NaBr and NaClO at pH 10 on bleached wood cellulose fiber (pretreated via $NaClO_2$/acetic acid delignification) prior to fibrillation with TSE.[21] It was found that a higher carboxyl content (900 µmol/g) resulted in a higher yield of nanofibrillated material and significantly reduced the fibers suspension gelation time during the extrusion process. Similar results with regard to the effect of the carboxyl content on the yield and viscosity of CNFs were observed by Boufi et al. during fibrillation employing a high speed blender.[64]

A range of other chemical treatment methods have been successfully applied in non-conventional fibrillation processing. Specifically, surface modifications such as carboxymethylation, phosphorylation and sulfoethylation, have been shown to introduce surface charges on cellulose fibers and to decrease energy consumption during fibrillation.[3,20,22] For example, Rol et al. applied phosphorylation to bleached eucalyptus kraft pulp using urea and ammonium phosphate dibasic solution and found that phosphorylation reduced the energy consumption required for CNF production via TSE. [20] It is noted that acid catalysts which hydrolyze lignin have also been successfully used as pretreatments of cellulosic feedstocks prior to mechanical fibrillation.[65]

3.2 Physical pretreatments

Green solvents, particularly ionic liquids (ILs) and deep eutectic solvents (DESs), have recently been utilized as pretreatment in CNF production.[56,57] ILs and DESs have unique properties, including extremely low vapor pressure, high thermal and chemical stability, low-flammability, etc.[66–68] More importantly, these solvents can dissolve biomass [69–71] and have catalytic activity [72,73], properties that make them highly attractive for biomass pretreatment. It is noted the DESs are more cost effective and easier to synthesize than ILs. The application of ILs and DESs in non-conventional fibrillation is an emerging field. For example, Ninomiya et al.[56] applied a choline acetate/dimethyl sulfoxide (ChoAc/DMSO) DES system to pretreat bagasse at 100 ˚C before fibrillation with a high speed blender. The CNFs obtained from the ChoAc-treated bagasse had five times greater surface area than CNFs that had not undergone the pretreatment. Importantly, the crystallinity of the fiber remained the same as that of the starting materials. Separately, Tahari et al.[57] employed a potassium carbonate/glycerol DES system to pretreat wood sawdust at 100 °C for 18 h before fibrillation using TSE. It was found the DES treatment improved the degree of the fibrillation and resulted in less fiber breakage. In another study, Yu et al.[55] employed a choline chloride-oxalic acid dihydrate DES to pretreat Ramie fiber, followed by ball-milling. The CNF produced had a very high cellulose content, up to 90%, and the DES pretreatment reduced the required milling time from 12 h for a standard bleached feedstock to 6 h.

An alternate physical pretreatment process of biomass for CNF production is steam explosion. The process of steam explosion entails treatment of lignocellulosic materials with high temperature and pressure steam (180-240 ˚C, 10-35 bar) followed by an explosive release to atmospheric pressure,[74] which results in the fracturing of the biomass fiber structure. The high shear forces generated during the sudden release of pressure hydrolyzes glycosidic bonds of cellulose and disrupts hydrogen bonds between glucose chains. Steam explosion has been used to separate and soften cellulose fibers to reduce energy consumption for conventional CNF production.[75] The detailed energy requirements of the steam explosion pretreatment process is in need of evaluation.

3.3 Mechanical pretreatments

Mechanical pretreatment of lignocellulosic feedstocks has been used for pre-fibrillation or size reduction in order to reduce energy expenditure during fibrillation processes. Mechanical size reduction has also been shown to reduce clogging issues during fibrillation. Various mechanical processes including disk refining and milling have been employed as pretreatments. Disk refining (DR) has been extensively used for the fibrillation of CNFs and is commonly combined with chemical or enzymatic pretreatments.[2,51] However, DR has also used as a mechanical pretreatment prior to fibrillation via other processes. For example, Rol et al.[19,20,22,76] has investigated DR pretreatment prior to the TSE fibrillation process and shown that the refining pretreatment process only consumed 0.68 kWh/kg and reduced the overall fibrillation energy. Milling is an alternate and an effective means of decreasing the size of lignocellulosic materials. Tsalagkas et al.[77] applied dry-state ball milling (BM), and separately a Valley beater (VB), to pretreat bleached softwood and hardwood fibers for fibrillation using an aqueous counter collision (ACC) system. The BM-treated feedstocks had lower yields and crystallinity index (CI) than the VB-treated feedstocks. The lower CI for the BM feedstocks was potentially caused by the rupture of crystalline regions of cellulose during processing. However, energy expenditures of the milling processes were not reported, nor was their contribution to the overall energy consumption required for fibrillation.

3.4 Biological pretreatments

Biological pretreatment, especially enzyme pretreatment, has been reported to reduce the energy required to fibrillate biomass to CNFs.[78] Appropriate enzymes act to hydrolyze cellulose and thereby facilitate mechanical fibrillation. Typically, *cellobiohydrolase* and *endoglucanase* enzymes are employed for feedstock pretreatment, which targeting the crystalline and amorphous regions of cellulose, respectively. Prior to enzymatic treatment, biomass feedstocks are often delignified and/or bleached to increase the accessibility of the enzymes to cellulose. Rol et al.[20,22,79] pretreated bleached *Eucalyptus* kraft pulp with an *endoglucanase* enzyme, followed by fibrillation with TSE. The CNFs produced from the enzyme-treated fibers had a lower degree of polymerization (DP) compared to non-treated fibers,[79] however, the energy consumption was much lower. Additionally, the turbidity of the enzyme pretreated-CNF slurry was significantly higher than that of the non-pretreated analog.

It has been shown that the efficacy of enzymatic pretreatment is heavily dependent upon the accessibility of cellulose. Indeed, the higher the surface area of the biomass feedstock, the greater the energy reduction required for defibrillation after the enzyme treatment. A combination of mechanical and chemical/enzymatic pretreatments can be more effective for reducing the energy of fibrillation. For instance, Rol et al.[19] studied the effect of different pretreatment strategies on the energy required for fibrillation employing TSE with *Eucalyptus* bleached kraft pulp. Enzymatic hydrolysis and TEMPO oxidation were performed on disk-refined pulp fibers and benchmarked with the energy requirement of fibrillation process using a grinder. With the disk-refining step, the energy required for TSE fibrillation was reduced for both enzymatic and TEMPO-oxidized pulp fibers.

4. NON-CONVENTIONAL FIBRILLATION METHODS

Table 1. Characteristics of CNFs produced by non-conventional fibrillation methods.

Fibrillation methods		Feed stocks	Pretreatment/ Post-treatment	Diameter (nm)	Degree of fibrillation	D.P.[m]	Crystal index (%)	Light transmittance (%)	Ref
Extrusion	Direct extrusion (40 min)	*Eucalyptus Grandis* wood pulp (10 wt.%)	TEMPO[c] oxidation (500 µmol/g)	3-7	81%[Y.F.,g] 724[WRV,h]	N.A.	N.A.	Suspension, 75% (λ=600 nm)	21
	Direct extrusion (20 min)	Never-dried *Eucalyptus* pulp (10 wt.%)	TEMPO oxidation (base) (1,000 µmol/g)	3-9	64% [Y.F.] 454[WRV]	N.A.	77	Suspension, 61%, (λ=600 nm)	47
	Direct extrusion (20 min)	Never-dried *Eucalyptus* pulp (10 wt.%)	Carboxy-methylation (820 µmol/g)	N.A.	58% [Y.F.] 486 [WRV]	N.A.	57	Suspension, 57% (λ=600 nm)	47
	Direct extrusion (10 passes)	Refined needle-leaf bleached kraft pulp (28 wt.%)	8-pass Refined	~50	780 s[D.T.,i]	900	76	N.A.	80
	Direct extrusion (7 passes)	Disk-beater refined *Eucalyptus*	TEMPO oxidation (820 µmol/g)	34.6	37%[Y.F.]	260	65	N.A.	19

		bleached kraft pulp (~20 wt.%)							
	Direct extrusion (7 passes)	Disk-beater refined *Eucalyptus* bleached kraft pulp (~20 wt.%)	Enzyme (300 ECU^e/g)	25.8	65%$^{Y.F.}$	200	72	N.A.	19
	Direct extrusion (7 passes)	Disk-refined Eucalyptus bleached kraft pulp (17 wt.%)	Enzyme (300 ECU/g)	52	64.3%$^{Y.F.}$	218	N.A.	289$^{T.n}$	22
	Direct extrusion (7 passes)	Disk-refined *Eucalyptus* bleached kraft pulp (17 wt.%)	Cationized (DS^d=0.31)	43	54.6%$^{Y.F.}$	731	N.A.	113$^{T.}$	22
	Direct extrusion (4 passes)	Disk-refined *Eucalyptus* bleached kraft pulp (10-20 wt.%)	Enzyme (300 ECU/g)	40	51.2%$^{F.C.,j}$ 74.2%$^{Y.F.}$	260	N.A.	384$^{T.}$	20
	Direct extrusion (4 passes)	Disk-refined *Eucalyptus* bleached kraft pulp (10-20 wt.%)	Phosphorylated (DS=0.1-0.2)	40	8.6,$^{F.C.}$ 33.8%$^{Y.F.}$	580	N.A.	214$^{T.}$	20
	Direct extrusion, modified screw (1 pass)	Disk-refined *Eucalyptus* bleached kraft pulp (20 wt.%)	Enzyme (300 ECU/g)	20.2	49.1%$^{F.C.}$ 69.4%$^{Y.F.}$	270	N.A.	397$^{T.}$	23
	Reactive extrusion NaOH (1x), H_2SO_4 (2x)	Milled soybean hull (32 wt.%)	N.A. /Ultrasonication post-treatment	80-100	50%^{w,k}	N.A.	62	N.A.	30
	Reactive extrusion H_2SO_4 (1x)	Bleached milled soybean hull (32 wt.%)	N.A. /Ultrasonication post-treatment	80-100	60%^{w}	N.A.	73	N.A.	30
	Reactive extrusion NaOH (1x), H_2SO_4 (2x)	Milled oat hull (32 wt.%)	N.A. /Ultrasonication post-treatment	100	60%^{w}	N.A.	68	N.A.	81
	Reactive extrusion H_2SO_4 (1x)	Bleached milled oat hull (32 wt.%)	N.A. /Ultrasonication post-treatment	80-100	65%^{w}	N.A.	80	N.A.	81
Ball milling	PFI mill (30,000 revolutions)	Bleached Birch kraft pulp	Periodate oxidized	10-100	N.A.	N.A.	65	Film, ~30% (λ=550 nm)	53
	Planetary mill (400 rpm, 2h)	Cellulose powder	Ionic liquids	10-25	93.1%$^{Y.F.}$	N.A.	65.8	N.A.	57
	Tumbler mill	Dry bleached softwood kraft pulp	Mechanical blending, alkaline	139-793	N.A.	N.A.	>70	N.A.	82
		Wheat straw, Kenaf fibers	Acids, peroxide, alcohol, alkaline	8-100	N.A.	N.A.	~70	N.A.	83
	Attritor mill (0.5-3h, 1000 or 3000 rpm)	Grass *(Triodia pungen)*	Bleaching and delignification	8.7 ± 4.8	N.A.	N.A.	~70	N.A.	84
	Blending (45,000 rpm, 5-60 min)	Bagasse(dewax, delignified, and alkali washed)	Acetylation	50	N.A.	N.A.	63-73	Film, ~75% (λ=500 nm)	24

	Blender (5000, 10000, or 37000 rpm, 1-60 min)	Japanese cedar pulp	Bleaching	15	N.A.	N.A.	69-71	Resin infused CNF film, 70% (λ=550 nm)	85
Steam explosion	3-stage explosion	Banana fiber	Alkaline and bleaching/stir	10 µm	N.A.	N.A.	N.A.	N.A.	31
	9-stage explosion	Banana fiber	Alkaline and bleaching/stir	<40	N.A.	N.A.	74	N.A.	86
	9-stage explosion	Pineapple leaf fibers	Alkaline and bleaching/stir	5-60	N.A.	N.A.	74	N.A.	87
	1.5 bar, 121°C, 1 h	Oil palm empty fruit bunch fibers	Alkaline/ Ultrasonication	50	N.A.	N.A.	N.A.	N.A.	88
Aqueous counter collision	180 cycles	MCC[a]	None	14	N.A.	210	50	N.A.	89
	60 cycles	BC[b]	Homogenization	34	55.9 $^{\text{SSA, FD,l}}$ /$m^2 \cdot g^{-1}$	240	70	N.A.	90
	30 cycle, 160 µm (D), 180 MPa, 170°	Rice straw	Delignification & hemicellulose removal	<200	100%$^{\text{Y.F.}}$	N.A.	79	Suspension, 20% film, ~20% (λ=500 nm)	25
	30 cycles, 140 µm (D), 200 MPa, 170°	Bleached kraft pulp	Beater refining /ultrasonication	25	80-85%$^{\text{Y.F.}}$	N.A.	~60	N.A.	77
Ultra-sonication	30 min, 20-25 KHz, 1 kW	Wood, bamboo, wheat straw, flax fibers	Delignification, hemicellulose removal	10-40	N.A.	N.A.	60-80	N.A.	91
	30 min, 20 kHz, 1.2 kW	MCC	Water soaking	~100	239$^{\text{WRV}}$	N.A.	N.A.	N.A.	92
	20 min, 20-25 kHz, 1.2 kW	bleached hard kraft pulp	Alkaline	50-150	N.A.	626	60	CNF/PVA[o] film, 70% (λ=550 nm)	93
	10 min, 20 KHz, 0.75 kW	Bagasse fibers	Delignification, refining, enzyme	~30	N.A.	N.A.	~70	N.A.	49
Cryo-crushing	N.A.	Bleached softwood pulp	Disintegrating	< 1 µm	89%$^{\text{Y.F.}}$	N.A.	N.A.	N.A.	4
	N.A.	Bast fiber, rutabaga	Alkaline, acid	40	N.A.	N.A.	54	N.A.	94
Other methods	pH-induced self-fibrillation	Bleached softwood kraft pulp	Oxidation (TEMPO, periodate)	~20	95%$^{\text{Y.F.}}$	N.A.	75	Film, 90% (λ=600 nm)	95
	Microwave hydrothermal	Pea waste	TSE[f]	5	40%$^{\text{Y.F.}}$	N.A.	~30	N.A.	45

[a]microcrystalline cellulose, [b]bacterial cellulose, [c]2,2,6,6-tetramethylpiperidine-1-oxyl, [d]degree of substitution, [e]endo cellulase units, [f]twin-screw extrusion, [g]yield of fibrillation, [h]water retention value, [i]dewatering time, [j]Fines content, [k]measured dry weight, [l] specific surface area from freeze drying, [m]degree of polymerization, [n]turbidity, [o]polyvinyl alcohol.

4.1 Extrusion

Extrusion processes are widely used in various industrial sectors for manufacturing. Heiskanen et al. first demonstrated approximately a decade ago that extrusion could also be used to produce CNFs from woody biomass.[96] A summary of the extrusion work that has been performed and the resulting properties of the CNFs are presented in **Table 1**. It is evident from Table 1 that three types of extrusion fibrillation have been studied. The first method comprises direct extrusion of never-dried cellulose fibers or fibers dispersed in solvents using TSE.[21] The second method is similar to the first with the addition of chemical reagents to a wet feedstock immediately prior to extrusion with sing-screw extrusion (SSE). The final method involves the extrusion of wet cellulose fibers together with a polymer in the solid state.[97] In all cases, the shear forces produced during extrusion have been reported to fibrillate the cellulose fibers into micron or nanoscale fibers, or a combination of both. There are several advantages in using extrusion to fibrillate cellulose fibers as compared to using conventional fibrillation methods. First, extrusion is a continuous process, so the CNF production rate is high, relative to batch processing methods. Second, CNF suspensions with very high solids contents (up to 40 wt.%) can be achieved using extrusion versus the few weight percent typically employed.[80] Third, the extruder screw configuration can be readily altered to modify the degree of fibrillation, thereby lowering the initial R&D time and cost.[19] Fourth, the energy consumption of extrusion is lower than that of conventional fibrillation methods. Fifth, extrusion generates CNFs with highly consistent fiber quality. Sixth, extrusion processes generally do not experience fiber clogging as conventional methods do.

4.1.1 Extrusion with wet pulp

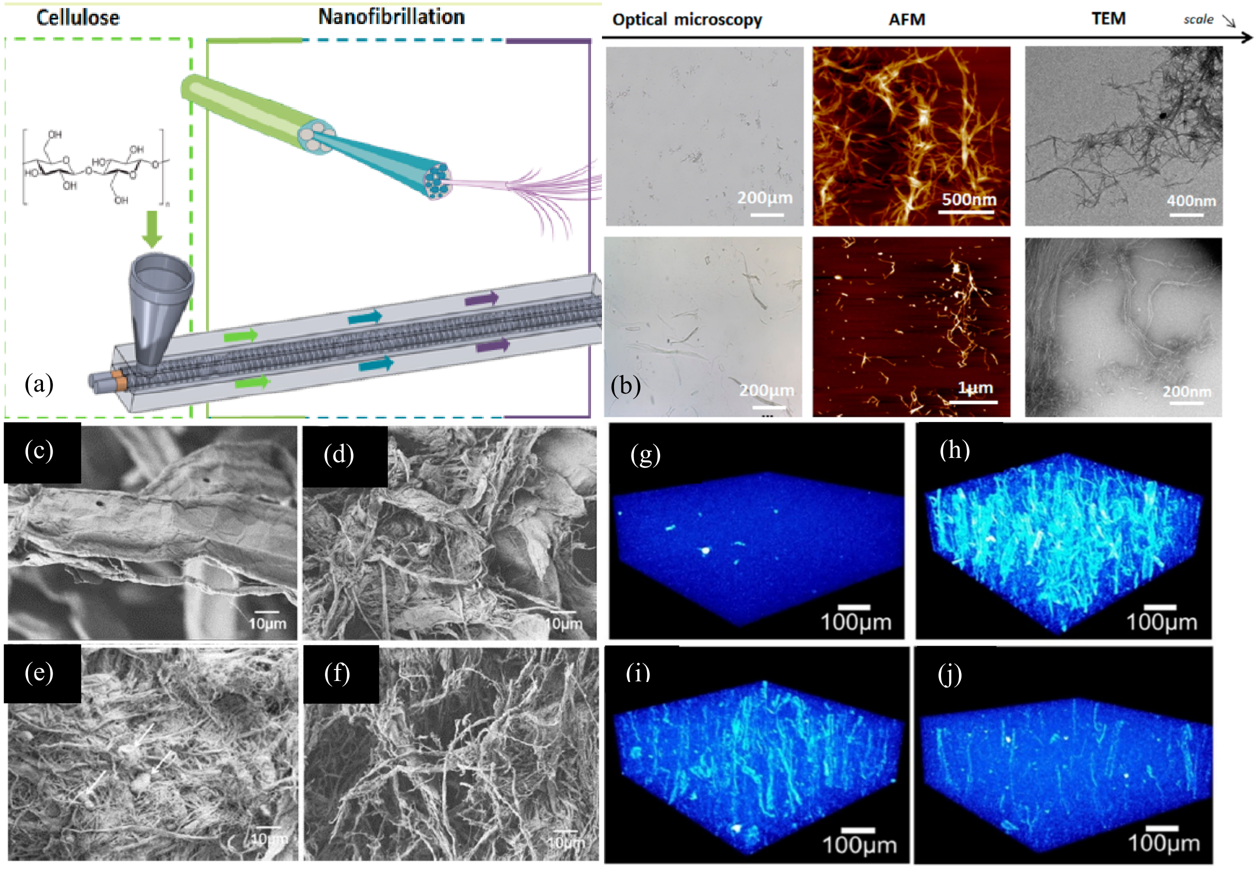

Figure 2. Schematic drawing of extrusion fibrillation of pulp fibers (a) and microscopic images of resulting CNFs (TEMPO-mediated oxidation and 7 passes of extrusion) (b). Adapted from Ref.[19] with permission, copyright 2017 American Chemical Society. SEM micrographs of materials used at different stages of extrusion fibrillating pulp fibers with polymers: never-dried kraft pulp (NDKP) (c), refiner-treated NDKP (d), a mixture of NDKP, powdered polypropylene (PP), and maleic anhydride-grafted PP (MAPP) after extrusion fibrillation (e) and CNFs after matrix removal by p-xylene washing (f). Scale bar: 10 µm. Adapted with permission from Ref.[97], copyright 2013 Springer Nature. X-ray computed tomography images of injection-molded samples of pure high-density polyethylene (HDPE) (g), HDPE (77 wt.%)/pulp fiber (10 wt.%) composite with a degree of substitution of 0 (h), 0.22 (i) and 0.43 (j) from the one-step, dry-pulp direct kneading method. Adapted with permission from Ref.[98], copyright 2018 Elsevier.

A schematic representation of cellulose fiber fibrillation employing TSE is presented in **Figure 2(a)**. Wet cellulose fibers are introduced directly into TSE. Cellulose fibers in the region between the screws of the TSE and the inner wall of the surrounding barrel experience high shear forces and are defibrillated into smaller fibers. Cellulose fibers are often passed through the extruder several times in order to achieve sufficient fibrillation when employing a conventional screw profile. It is noted however that over-processing can cause severe degradation of CNFs properties.

Factors affecting the fibrillation of cellulose include screw design (amount of shear forces), pre- and post-treatment, the feedstock employed etc.

Ho et al. published one of the earliest reports of CNF production via extrusion employing never-dried kraft pulp (NDKP) with TSE at solids contents of up to 45 wt.%.[80] Notably, during extrusion, the temperature inside the barrel rose to greater than 70 °C due to friction, resulting in a loss of water via evaporation. As such, circulating coolants were employed to maintain the process temperature at values less than 40 °C and thereby prevent water evaporation and concomitant discoloration of fibers. It was found that increasing the number of extrusion passes improved the degree of fibrillation, however, the degree of polymerization was reduced, the crystallinity was negatively impacted, the mechanical properties decreased and the thermal stability worsened. The particle size distribution of the CNFs produced was relatively broad, with a population of large particles exceeding 100 nm in diameter. Rol et al. furthered the study of TSE fibrillation of pulp fiber via examination of the effect of pretreatments employing TEMPO oxidation and enzymatic hydrolysis.[19] Micrographs of the resulting CNFs are presented in **Figure 2(b).** TEMPO-oxidized pulp fibers did not undergo extensive fibrillation, with only 37% of the sample being on the nanoscale after 7 extrusion passes. Enzyme-pretreated pulp fibers however had a much greater nanoscale fraction (~70%) after 7 passes through a TSE, with a similar morphology to CNFs created via a super mass colloider.[19] It is noted that the combination of pretreatments and TSE did not significantly impact the crystallinity of the fibers. However, the degree of polymerization was less than that of CNFs created via solely TSE. It is well known that fibrillating enzyme-pretreated pulp fibers can save considerable energy during CNF production. Employing a comparable approach, cationized- or phosphorylated-CNFs were produced from TSE.[22] The cationized- CNFs had comparable fiber properties to those produced employing enzymatic pretreatments. The phosphorylated samples consisted of large micron-scale fiber fractions with a smaller amount of nanofibers.[20] To improve the fibrillation efficiency of TSE, Rol et al. recently simulated and verified a modified screw profile to produce CNFs with a single pass TSE.[23] The optimized screw profile comprises 6 kneading zones that exert high shear on the fibers. The CNFs produced from a single pass through the optimized TSE exhibited similar properties to those made from 4 passes through a classic TSE, without an increase in the total energy consumption.

Employing a laboratory-scale mini TSE with no kneading elements other than a common conical, inter-meshing and co-rotating configuration, Baati et al. produced CNFs from TEMPO-treated pulp fibers.[21] In the absence of high-shear kneading elements, the temperature of the material was maintained at approximately 30 °C during extrusion, despite continuous processing for a period of 40 min. Employing a feedstock generated via a $NaClO_2$/acetic acid pulping process, a carboxyl content of 300 μmol/g on cellulose fibers was reported to be sufficient to facilitate nanofibrillation. The authors found that no significant fibrillation could be achieved when employing traditional NaOH-treated pulp fibers even after an oxidative pretreatment, a finding potentially attributable to the limited shearing capacity of the mini-TSE. In order to fibrillate commercially produced never-dried pulp, the authors explored more extensive TEMPO oxidation and carboxymethylation pretreatments.[47] The pH level of TEMPO oxidation was deliberately raised to 10 to achieve a carboxyl content as high as 1350 μmol/g. By fibrillating pulp fibers modified with either TEMPO oxidation or carboxymethylation at a carboxyl content of 800 μmol/g, a 50 wt.% fraction of nanoscale material was achieved. Further elevating the carboxyl content of pulp via alkline TEMPO oxidation to 1350 μmol/g yielded a nanoscale fraction as high as 92 wt.%.

4.1.2 Reactive extrusion

Various authors have investigated reactive extrusion fibrillation of soybean hulls (SH) with diluted chemical solutions.[30,81] Using SSE with moderate heating (110 °C), SH can be nanofibrillated when proper treatments and parameters were applied. For unbleached SH, 1 pass SSE in the presence of NaOH (10 wt.%), followed by 2 passes with H_2SO_4 (2 wt.%) and finally an ultrasonication post-treatment, successfully generated CNFs.[30] The NaOH and H_2SO_4 solutions were employed to partially remove hemicellulose and lignin from the SH, which facilitated fibrillation. Alternatively, bleaching SH with peracetic acid, followed by a single pass SSE in the presence of H_2SO_4 and an ultrasonication post-treatment, also resulted in the production of CNFs. It is noted that a comparable approach applied to oat hulls achieved similar fibrillation results.[81] The authors state that their reactive extrusion methods are more effective and environmentally benign than traditional fibrillation techniques as the processing time is shorter, the concentrations of the chemical reagents employed are lower, and the reagents themselves are less harmful than those employed for traditional techniques.

4.1.3 Co-extrusion with polymers

Rather than extruding a bio-based feedstock alone, or in the presence of a solution, the feedstock can be extruded in the presence of a grinding medium. Most commonly, the grinding medium employed has been powdered polymers, with the resultant product being a micro/nanofibrillated cellulose network with entrained polymer.[97,98] Such a mixture forms a structure that is highly beneficial for fiber dispersion when compounding followed by either wet or dry extrusion. Little work has been performed to characterize the CNFs generated via the co-extrusion process since to do so would require separating the CNFs and their embedded polymer particles. Indeed the only study to investigate CNFs separated from the polymer residue created by co-extrusion was that conducted by Taheri et al., in which CNFs were separated from hydroxyethyl cellulose (HEC) via vacuum filtration after extrusion fibrillation.[99]

The majority of the work centered on co-extrusion of biomass with polymers has been conducted by researchers at Kyoto University.[97,98,100–102] Initial work focused on a two-step process (in-situ fibrillation followed by wet extrusion-compounding), however recently a one-step, dry-pulp direct kneading method has been reported.[98] Representative images of the CNFs generated from the two-step process are presented in **Figure 2**. Specifically, NDKP (10-50 wt.%) was first mixed with a polyolefin and a coupling agent via an agitator. The mixture was then kneaded in an extruder at 0 °C and 400 rpm. The same extruder was subsequently employed for wet compounding of the resultant mixture at 180 °C and 200 rpm, followed by pelletizing and injection molding. Two methods were used to qualitatively characterize the resultant fiber morphology: SEM on CNFs before and after matrix removal, and direct X-ray computed-tomography (CT) scans on CNF/polymer composites. As can be seen in **Figure 2 (c-f)**, the fiber diameters ranged from a few to several tens of microns.[97] To improve the efficiency of *in-situ* fibrillation and compounding, the feedstock was changed from NDKP to acetylated pulp fibers.[98] Recently, a mixture of dried acetylated pulp fibers, polyolefin powders and coupling agent powders was fed directly into an extruder to be melt compounded before pelletizing and injection molding.[98] Based on the X-ray CT graphs presented in **Figure 2(g-j)**, the one-step approach unambiguously showed an improved fiber dispersion as compared to the two-step method. However, attention should be paid to the difference in fiber contents in the composites.[98,102]

Hietala et al. attempted to fibrillate pulp fibers in the presence of thermoplastic starch (TPS) by melt extruding a wet mixture of (treated) pulp fiber, TPS and processing aids.[103] Even with a high degree of carboxyl content (1,300 μmol/g) after TEMPO-mediated oxidation, pulp fibers were not largely fibrillated into nanofibers. One potential explanation for the lack of fibrillation is that excessive water (70 wt.%) in the mixture reduced the viscosity of the melt during extrusion, thereby lowering the shear forces experienced by the fibers. Indeed, Cobut et al. melt extruded a mixture of TEMPO-treated (980 μmol/g) pulp fiber, TPS and processing aids, at a much lower water content (17 wt.%).[104] Some nanofibrils with 30 nm in diameter were observed along with a population of microfibrils. Fourati et al. extrusion fibrillated a mixture of TEMPO-oxidized (740 μmol/g) pulp fiber, TPS, and processing aids at an intermediate water content (42 wt.%) and low extrusion temperature (25 °C), before increasing the extruder temperature to melt compound the mixture.[105] The authors reported that the pulp fibers were mostly disintegrated into micro and nanoscale fibers. Finally, Taheri et al. fibrillated never-dried softwood pulp with hydroxyethyl cellulose into CMFs using TSE with a single pass.[99] It was found that reducing the amount of polymer in the mixture (50 wt.% to 20 wt.%) shifted the peak of the particle size distribution to smaller values (13.65 μm to 12.22 μm) and decreased the aspect ratio (47 to 32) of the fibrillated fibers. The authors believed that HEC acted as a lubricant and reduced the fiber breakage during extrusion.

4.2 Ball-Milling

CNFs have been produced via ball-milling of cellulosic feedstocks for many years. Ball milling may be characterized as either direct or indirect (**Figure 3**).[106] Direct milling utilizes contact between the milling surface (e.g. rotating gears or shearing blades) and the material being processed to reduce particle size. There are three major forms of direct milling: attritor mill, pan mill, and roll mill (**Figure 3 a-c**).[107] Indirect milling utilizes an additional medium as the milling surface, often in the form of weighted balls. There are three major forms of indirect milling:

tumbler ball mill, vibratory (or shaker) mill, and planetary ball mill (**Figure 3d-f**).[107] Indirect milling transfers mechanical energy generated by the mill to the material being processed and does so in the following order: planetary > vibrational > tumbling mill.[76,108] A large portion of the energy generated (~80%) is lost as dissipated heat.[106] Heat loss can be mitigated to some extent by adjusting process conditions. For example, an increase in solids content during fibrillation can limit the amount of heat dissipated into the solvent. Processing conditions can also significantly impact the physical properties of the resultant material. For example, Liimatainen et al. determined that an increase in solids content from 7.5 to 15 wt.% resulted in an increase in tensile strength and elongation of the resulting CNF films, from 61.1 to 113.1 MPa and 6.8 to 15.9% respectively.[53] The better heat dissipation in this higher solid content sample produced a mechanically robust, interpenetrating CNF matrix.

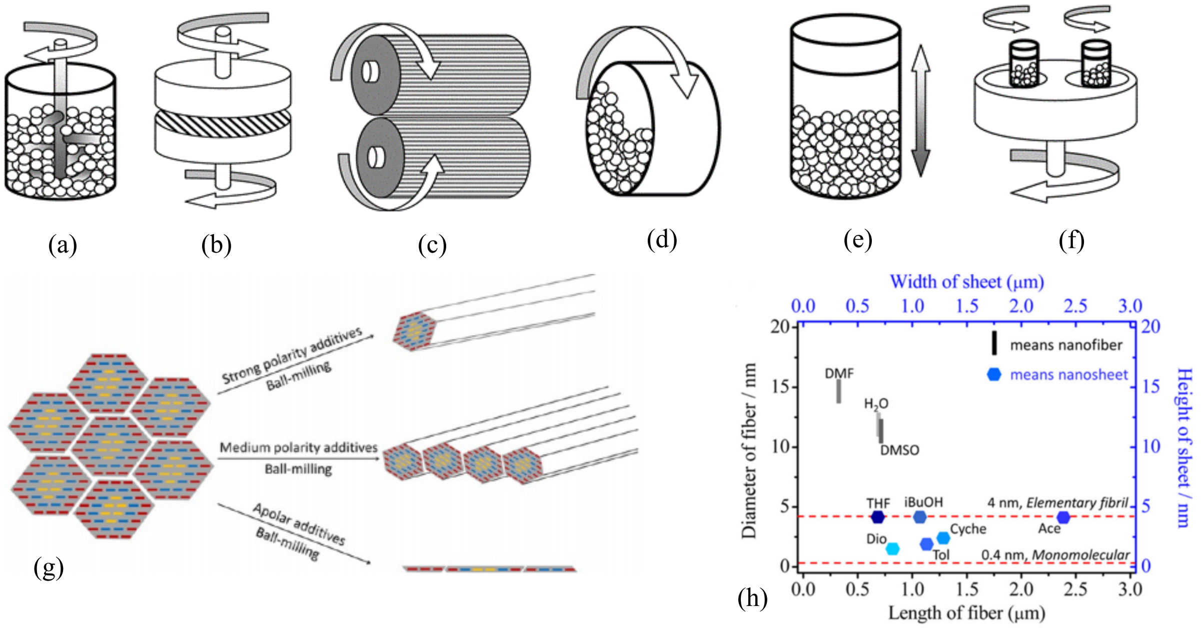

Figure 3. Schematic drawing of direct and indirect balling processes: (a) attritor mill, (b) pan mill, (c) roll mill, (d) tumbler ball mill, (e) vibratory (or shaker) mill, (f) planetary ball mill. Adapted from Ref.[106] with permission, copyright 2015 Royal Society of Chemistry. Scheme of cellulose ball-milled in the different solvents with strong polar, medium polar and apolar conditions (g).Statistical size distributions of CNFs obtained by ball-milling with varying solvent polarities (h). Adapted from Ref.[109] with permission, copyright 2020 American Chemical Society.

Researchers have worked to optimize ball-milling conditions for CNF production by studying the effects of various parameters on CNF properties. For example, Zhang et al.[109] and Ago et al.[100] studied the effect of solvent additives and their polarity on fibrillation efficiency (**Figures 3 g, h**). Use of polar solvents enabled the production of long, thin CNF fibers, potentially attributable to the solvents ability to penetrate the cellulose fibers. Conversely, use of solvents with reduced polarity resulted in sheet-like material, potentially attributable to the solvents inability to penetrate the cellulose fibers. Additionally, to minimize hydrogen bonding and other intermolecular interactions present in cellulose, researchers have developed additives to weaken these bonds and assist fibrillation. Some of these additives induced simultaneous fibrillation and surface functionalization during the ball-milling process.[111,112] Finally, many studies have demonstrated that longer ball-milling times result in CNFs with lower aspect ratios.[60,76,113] Increased ball-milling time results in a longer interaction between the media and milled material, which produces greater damage and separation of the cellulose, leading to poor physical properties. Indeed, Zeng et. al. determined that the degree of polymerization of CNFs decreased from approximately 350 to 200 when the ball milling processing time increased from 30 minutes to 3 hours.[60]

4.3 Blending

CNF fibrillation methods have been developed using high shear blending techniques, many of which utilize household equipment to produce CNFs.[24,29,64,85,114] It is noted however that in many cases, optimization of the operating conditions is challenging as minimal variations in process parameters would produce CNFs with significantly different qualities. Specifically, changes in blender speed, blending time, and solids content have been shown to affect the CNF morphology and other properties. For example, Sofla et al. observed that an increase in blending time from 5 to 30 minutes resulted in a decrease in CNF diameter from approximately 135 to 40 nm.[24] Uetani et al. observed similar results and demonstrated via optical imaging that ballooning of fibers and uncurling of fiber ribbons occured.[85] Not surprisingly, the longer blending times resulted in a decrease in crystallinity from 72 to 69%. Overall, this fibrillation method is promising as it produces CNFs with a range of properties and does not require the use of expensive, specialized equipment. However, work is required to optimize the blending parameters to produce predictable and tailorable CNFs.

4.4 Steam explosion

A novel method for production of CNFs is the utilization of steam explosion as a thermomechanical defibrillation method. Steam explosion was first employed as a biomass treatment method in 1927 by Mason for defibrillating wood into fibers for hardboard production.[31,75,86] The advantages of steam explosion as a biomass treatment method include a low environmental impact, relatively low energy consumption, low capital investment, and less hazardous process chemicals are used relative to traditional processing methods.[75] Fiber products from steam explosion have interesting applications. For example, Yan et al. used steam explosion to convert lignocellulosic biomass to dietary fiber.[115] Additionally, Cherian et al. steam exploded pineapple leaf fibers to produce CNFs with utility in biomedical applications including issue engineering, drug delivery, wound dressings and medical implants.[87]

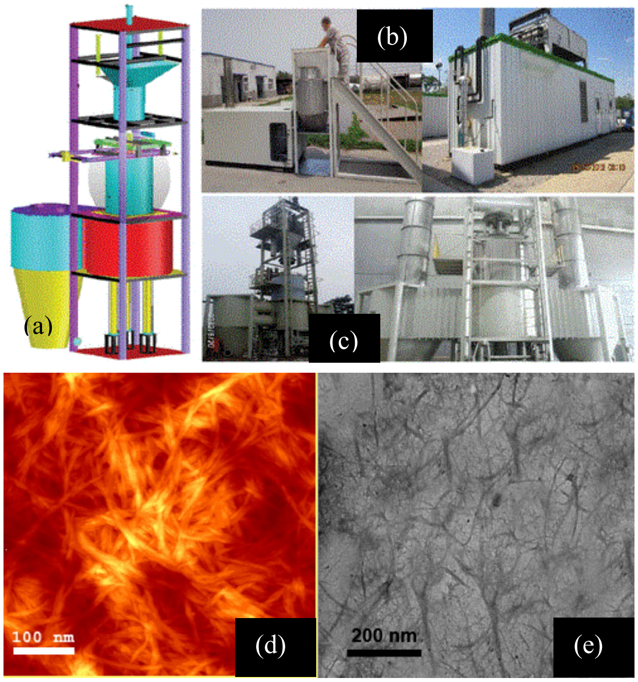

Figure 4. Diagram of a steam explosion device consisting of piston/cylinder to generate high pressures for defribillation (a) Steam explosion equipment of 100 L chamber (b) and an industrial-scale chamber of 10 m^3 (c). Adapted from Ref.[115] with permission, copyright 2018 American Chemical Society. Images of steam-explosion generated CNFs with AFM (d) and TEM (e). Adapted from Ref.[87] with permission, copyright 2010 Elsevier.

For CNF production, dry lignocellulosic biomass materials are loaded into a pressure device such as an autoclave or a custom cylinder/piston device (**Figure 4**).[115] An alkaline pretreatment may be employed to increase surface roughness of the biomass material to enhance water penetration, and to remove non-cellulosic components.[74] The pressure vessel is subsequently charged with water and pressurized to 10-35 bar at temperatures in the range of 180-240 °C (reaction conditions are selected based on desired crystallinity and degree of polymerization of the product). The pressure is subsequently abruptly dropped to ambient, resulting in a steam explosion and filbrillation of the biomass. Multiple cycles of steam explosion are typically implemented to limit the amount of exposure of the cellulose to the harsh conditions that would be required if a single cycle was performed. Higher temperatures and pressures result in greater degradation of the cellulose and lowered crystallinity and degree of polymerization. In one study, lowered steam explosion conditions of 2 bar and 120 °C were utilized to generate CMFs.[74]

The key to success of steam explosion as a novel CNF production method is its ability to separate the lignocellulosic material into its three main constituents: cellulose, hemicellulose, and lignin. With cellulose being the desirable material, it is important that hemicellulose and lignin can be removed easily during or after the process. The steam explosion process results in the hydrolysis of hemicellulose and the depolymerization of lignin.[31,74,75,86–88,115–117] Once the relevant bonds are broken, the components may be separated. The hemicellulose fraction can be dissolved in water, while the depolymerized lignin can be dissolved in an alkaline solution or an organic solvent. After steam explosion treatments, the structural, morphological, and thermal characteristics of the cellulose nanofibers are typically examined. Specific steam explosion process parameters employed in the production of CNFs, and the resultant CNFs properties are listed in **Table 1**. Though steam explosion has long been used to extract cellulose fibers from biomass, the efficacy and quality of CNFs produced remain problematic.[2] Therefore, in some studies, steam explosion has been applied as a pretreatment for subsequent fibrillation of CNFs by homogenization[74,75,115,117] and grinding[116].

4.5 Aqueous counter collision (ACC)

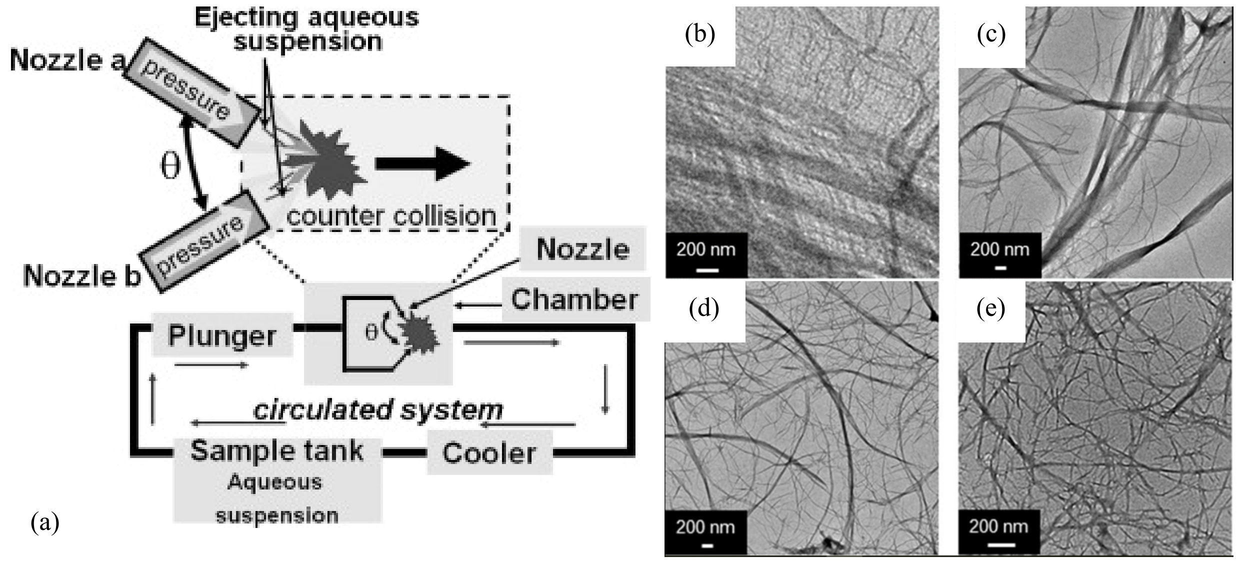

Figure 5. The Sugino Machine Star Burst aqueous counter collision system (a).Adapted from Ref.[89] with permission, copyright 2014 Elsevier. TEM images of the CNFs at different cycle numbers: 5 passes (b), 10 passes (c), 40 passes (d) and 80 passes (e). Adapted from Ref.[118] with permission, copyright 2015 Elsevier.

CNFs can be prepared by disintegrating cellulose fibers with an aqueous counter collision (ACC) system, which typically consists of an inlet reservoir, an intensifier pump unit, an interaction chamber and a connecting conduit as well as check valves, gauges, cooling coils and heat exchangers. First, cellulose fibers are dispersed in water, and the resulting suspension is stored in a reservoir. The pump aspirates a portion of the suspension, pressurizes and injects the slurry up to 245 MPa, and forces it to travel through the system at a speed up to 500 m/s.[89] An ACC system divides the pressurized suspension into two channels that form a pair of water jets which collide into each other in the interaction chamber. The streams collide at an adjustable oblique angle up to 180°, as shown in the Sugino Machine's Star Burst System (**Figure 5a**). Impact forces originate from collisions with the microchannel walls and with the fluid itself. A change in velocity or direction exposes the entrained particles to a high shear field and occasional cavitation. The sample, exiting via the heat exchanger or cooling coil outlet, is collected and recirculated or poured back into the reservoir to enable multiple passes, if desired. The advantages of ACC methods include 1) nearly 100% yield of produced CNFs, 2) higher degree of polymerize ion of CNFs, and 3) ability to produce fibrils from a wide range of polymeric materials with hierarchical structures.[89] ACC systems have also been designed with continuous processing capabilities. Ideally, they should be designed to output particles below a certain size while continuing to mill particles above that size, resulting in a narrow particle size distribution. However, separating nanoparticles from larger particles during ACC processing is difficult. Most current technologies do not have such a separation mechanism.

Because the channel size is small (microscale in diameter), the starting materials are usually microcrystalline cellulose (MCC), ground cellulose, or pretreated pulp. The concentration of the suspension is usually lower than 2 wt.%. The major work in ACC has been conducted by Kondo's research group. Kondo et al. explored the use of ACC to make CNFs from MCC[89,119], pulp fiber[120], rice straw[25] and bacterial cellulose[90]. The ACC process transformed the cellulose form from I_α to I_β, with tunable crystalline/amorphous ratios achieved by changing the processing conditions.[90] Because the ACC method produced CNFs with exposed hydrophobic surfaces, they were investigated as a potential Pickering emulsifier.[119,120]Jiang et al. also prepared CNFs with ACC from purified rice straw, with increasing weight factions yielding thinner nanofibrils.[25] The nanofibrillation yield was claimed to be 100%, more than double the yield of CNFs with other mechanical fibrillation approaches at only 1/3 of their energy consumption. More than 90% of the nanofibrils were smaller than 80 nm in diameter.

4.6 Ultrasonication

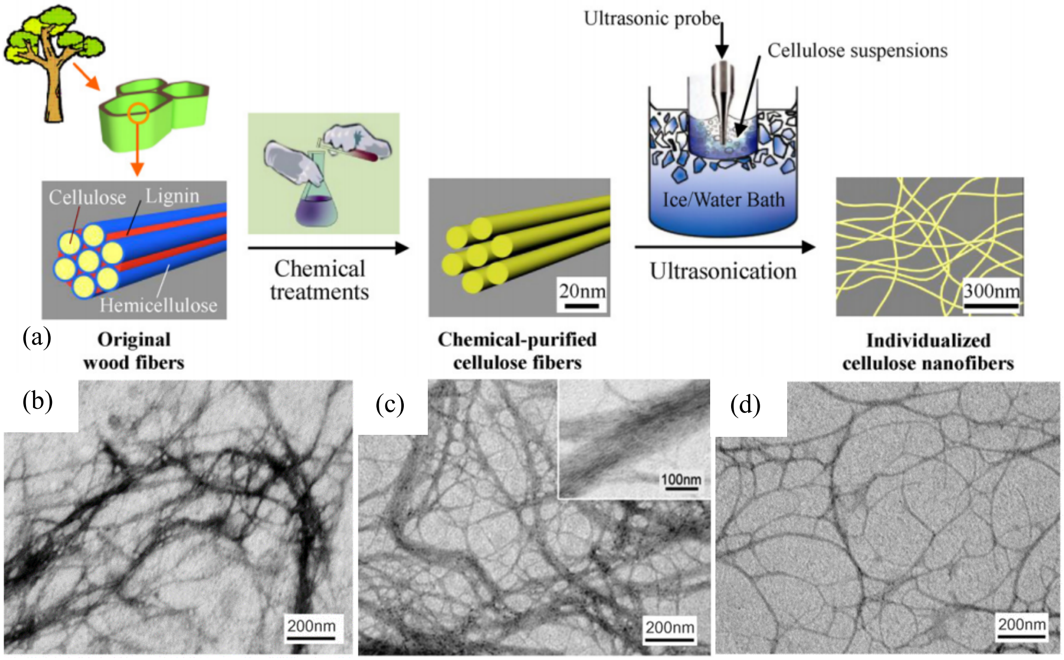

Figure 6. Schematic illustration of producing CNFs via ultrasonication with chemical pretreatments (a). TEM graphs of ultrasonication-generated CNFs with various power output: 400 W (b), 800 W (c) and 1000 W (d). Adapted from Ref.[121] with permission, copyright 2011 Elsevier.

Ultrasound occurs in the spectral range of 20 kHz to 10 MHz, and is produced by conversion of mechanical and/or electrical energy into acoustic energy. The strong oscillating power generated by the cavitation processes, produces powerful hydrodynamic forces that can facilitate the fibrillation of natural fibers into micro/nano fibers.[49,91–93,121,122] Ultrasonication can treat cellulose fibers to improve accessibility and reactivity of the cellulose during the fibrillation process as shown in **Figure 6a**.[123] Factors that have been demonstrated to affect the efficiency of fibrillation via ultrasonication include ultrasound power, time, temperature, fiber content in suspension, fiber size, and distance from the transducer, among others.[122] Chen et al. investigated the impact of ultrasonication on cellulose fibrillation of four different plant cellulose fibers.[91,121] The plant fibers were each chemically purified prior to sonication of the cellulose suspensions at 20-25 kHz to isolate the nanofibers. The ultrasonication treatment produce a modest degree of fibrillation, with fibrillation increasing progressively with the power applied.[91] The morphology of these CNFs produced via ultrasonication are shown in **Figure 6(b-d).** Besides being a major method of producing CNFs, ultrasonication has also been applied as a pretreatment for producing nanocellulose.[122,124] For example, Wang et al. reported that ultrasonication facilitated the fibrillation of cellulose fibers during homogenization and resulted in a more uniform cellulose suspension after the combined treatment.[122] Gibril et al. found that ultrasonication induced "cracking" and "erosion" on the fiber surface, making them much more accessible to subsequent acid hydrolysis. Employing an ultrasonication pretreatment has been shown to decrease the acid consumption, energy consumption, and hydrolysis time required for CNC production, all of which are considered major challenges in commercial production of CNCs.[124] Additionally, ultrasonication has been used as a post-treatment to defibrillate individual nanofibers from TEMPO-oxidize cellulose fibers.[125]

4.7 Cryo-crushing

Cryo-crushing is well known in the plastics industry, especially for the mechanical pulverizing of tough polymers such as polyolefins. Cryo-crushing for natural fiber fibrillation has only recently been investigated.[94,126] During cryo-crushing, the water in natural fibers is frozen rapidly upon immersion in liquid nitrogen. The cell wall can then be significantly fragmented by the rupture of ice crystals as the frozen fibers undergo mechanical grinding, resulting in the formation of CNFs.[4] A high yield (up to 89%) of CNF production was reported by Chakraborty et al. for cryo-crushing of pulp fibers.[126] The resulting CNFs had aspect ratios ranging from 15 to 85. With a combined acid and alkaline pretreatments, the size of CNFs produced from cryo-crushing can be reduced to 40 nm in diameter.[94] Cryo-crushed, fibrillated CNFs have exhibited a very significant reinforcing effect in PVA by more than tripling its tensile properties.[94] In addition to cryo-crushing being employed directly to create CNFs, the technique has also been used as a pretreatment for manufacturing CNFs by conventional fibrillation methods.[4,127]

4.8 Other methods

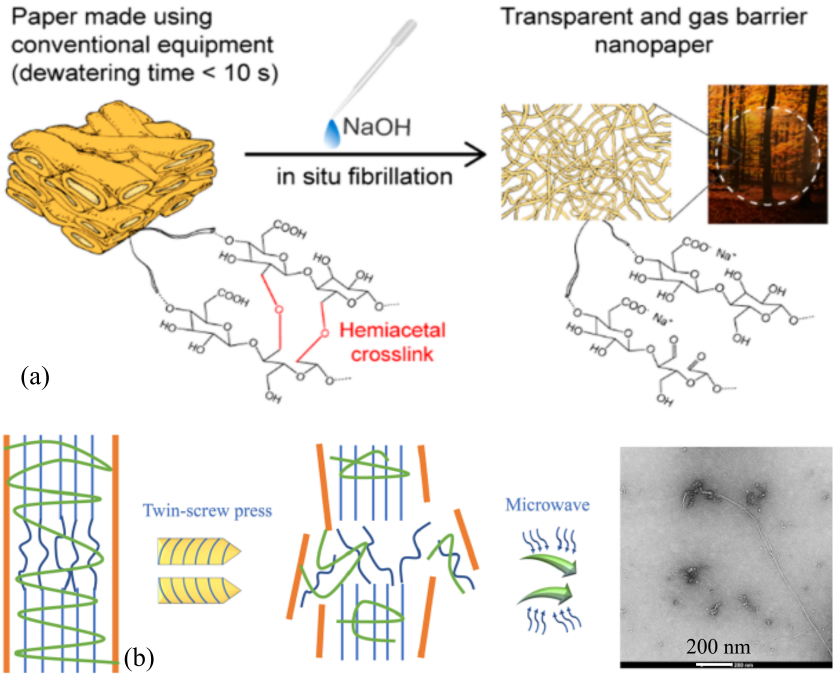

Figure 7. Schemes of producing nanocellulose by pH-induced self-fibrillation (a), adapted from Ref.[95] with permission, copyright 2020 American Chemical Society. and twin-screw extrusion and microwave hydrothermal treatment (b), adapted from Ref.[45] with permission, copyright 2019 American Chemical Society.

There are some other interesting methods for CNF fibrillation that have been less widely studied, but are worthy of attention. For example, Gorur et al. prepared nanopaper via in-situ fibrillation of paper via the process shown in **Figure 7a**.[95] Pulp fibers comprising conventional paper were pretreated by sequential TEMPO and periodate oxidation in water, which minimized the H-bonding and crosslinking among cellulose chains. Upon increasing the suspension's pH level, electrostatic repulsion among fibers was enhanced, leading to the self-fibrillation of pulp fibers into CNFs. Gao et al. made CNFs and CNCs from pea waste via a microwave hydrothermal treatment (MHT: 1.2 kW, 2.45 GHz, 120-200 °C), employing TSE pretreatment, as shown in

Figure 7b.[45] The fibers produced exhibited high crystallinity, water retention capability, and surface area. However, the fibers generated appeared to display a large variation in particle size.

5. APPLICATIONS

Commercial applications of CNFs are generally driven by their potential to improve material properties with the added value of being derived from renewable natural resources. Features of CNFs such as high aspect ratio, nanoscale dimensions and high crystallinity have the potential to provide significant improvements in material strength and flexibility, as well as oxygen resistance. A major limitation to the widespread adoption of CNFs has been the energy costs associated with their production.[14] Challenges that still need to be overcome are developing cellulose fibrillation methods that produce CNFs with the desired physical and morphological features at a high yield using less energy. Several novel fibrillation methods have been reviewed that are capable of producing CNFs with features suitable to a variety of applications. The applications, CNF feedstock, production methods and mechanical properties of the products are discussed in the following sections.

Table 2. Applications of CNFs from non-conventional production methods and their film and composite performance.

Application form	Feedstock	Pre-/post-treatment	Fibrillation methods	Product formation	Mechanical Properties			Ref.
					Tensile strength (MPa)	Tensile modulus (GPa)	Breaking Strain (%)	
Single CNF film	Refined cellulose fiber	TEMPO oxidization	Extrusion (1 pass)	Filtration, drying	41.2 (1.0)[o]	1.4 (0.1)	0.4 (0.1)	19
	Refined cellulose fiber	Enzyme (FiberCare R)	Extrusion (7 pass)	Filtration, drying	33.9 (9.5)	15.1 (0.4)	0.6 (0.2)	19
	Eucalyptus bleached kraft pulp	Refined, cationization (EPTMAC)[l]	Extrusion (7 pass)	Filtration, drying	72 (2.9)	7.3 (1.0)	N.A.	22
	Refined *eucalyptus*	Phosphorylated (DS=0.1-0.2)	Extrusion (7 passes)	Sheet forming, vacuum drying	100	14	N.A.	20

	bleached kraft pulp							
	Sugarcane bagasse fibers	Enzyme/ high intensity sonication	Planetary ball mill	Casting, evaporating	61 (3)	7.4 (1.0)	1.1 (0.2)	49
	Softwood pulp	Alkaline	Planetary ball mill	Neutralized wet sheets (dried hydrogels)	100 (4)	9.3 (0.4)	2.4 (0.2)	128
	Wood pulp	Homogenization, hexanoyl chloride	Planetary ball milling	Casting, evaporation	140 (7)	NA	21.3 (1.5)	32
	Ramie	DES[m]	Planetary ball milling	Casting	98.01 (1.8)	2.75 (0.01)	7.7 (1.1)	55
	Bleached birch kraft pulp	Oxidation, oven drying	PFI milling	Vacuum filtration	114.5	11.2	10.6	53
	Triodia pungens	Delignification, acid	Agitator ball milling	Filtration and molding	65 (2.5)	1.8 (0.3)	9 (1)	84
	Sugar Beet Pulp	Chemical treatment, homogenization	Cryo-crushing	Casting, evaporation	NA	3.2	NA	4
	Rice straw, cellulose fibers	delignification, bleaching	ACC[n]	Ultrafiltration/air drying	141	3.94	16.5	25
	Bagasse fiber	Delignification, refining, enzyme	Ultrasonication	Casting	~63	~7.5	~1	49
	Bleached kraft pulp	Oxidation	pH-induced fibrillation	Sheet forming	184	5.2	4.6	95
CNF/TPS[a] (15/85)	Kraft pulp	TEMPO oxidation	Extrusion	Compounding and molding	~7.5	~0.2	~13	105
CMF/HEC[b] (20/80)	Dissolved pulp	None	Extrusion	Hot pressing	~16	~1.4	~1.1	99
CMF/PP[c]	Wood saw dust	DES	Extrusion	Hot pressing	~17	~1.1	~2.5	129
CMF/MAPP[d]/ CPPA[e]/PP (30/4/3/63)	Unbleached kraft pulp	Refining	Extrusion	Compounding & molding	72	4.6	3.8	100
CMF/MAPP/PP (50/6.7/43.3)	Unbleached kraft pulp	Refining	Extrusion	Compounding & molding	66	5.3	3.2	97
CMF/MAPP/ $CaCO_3$/HDPE[f] (10/4/1/85)	Bleached kraft pulp	Refining and acetylation	Extrusion	Compounding & molding	56 (0.8)	3.46 (0.11)	3.2 (0.1)	98
CMF/MAPP/ CPPA/HDPE (20/6/4/70)	Bleached kraft pulp	Refining	Extrusion	Compounding & molding	45 (0.4)	3.5 (0.1)	2.5 (1.1)	101
CNF/Paper (30/70)	corn cob cellulose	Phosphorylation	Ball milling	Casting	~28	N.A.	~2.3	130
CNF/MAPP/ CPPA/PP (30/12/9/49)	Bleached kraft pulp	Refining	Bead milling	Compounding & molding	59.6 (0.6)	4.09 (0.04)	4.5 (0.1)	102
CNF/Starch (0.5/99.5)	Bleached kraft pulp	Urea	Colloid milling	Casting	~19	N.A.	~3.3	131
CNF/PCL[g] (0.5/99.5)	CMF	chloride	Ball milling	Casting	~43	~0.3	~1,100	132
CNF/PVA[h]	Kraft pulp	None	Cryo-crushing	Casting	102	7.4	N.A.	94

(10/90)	Rutabaga	Alkaline, acid	Cryo-crushing	Casting	178	10.1	N.A.	94
	Flax fiber	Alkaline, acid	Cryo-crushing	Casting	76	6.1	N.A.	94
	Hemp fiber	Alkaline, acid	Cryo-crushing	Casting	111	9.8	N.A.	94
	MCC[i]	None	Ultrasonication	Casting	~95	~5.2	N.A.	92
	PCF[j]	None	Ultrasonication	Casting	~110	~5.2	N.A.	92
	RCF[k]	None	Ultrasonication	Casting	130	6.8	N.A.	92
CNF/PVA (4/96)	Bleached kraft pulp	Alkaline	Ultrasonication	Casting	~35	~0.1	N.A.	93

[a]thermoplastic starch, [b]hydroxyethyl cellulose, [c]polypropylene, [d]maleic anhydride polypropylene, [e]cationic polymer using primary amine, [f]high-density polyethylene, [g]polycaprolactone, [h]polyvinyl alcohol,[i]microcrystal cellulose, [j]purified cellulose fiber, [k]regenerated cellulose fiber, [l]glycidyltrimethylammonium chloride, [m]deep eutectic solvent, [n]aqueous counter collision, [o]values in () are standard deviation.

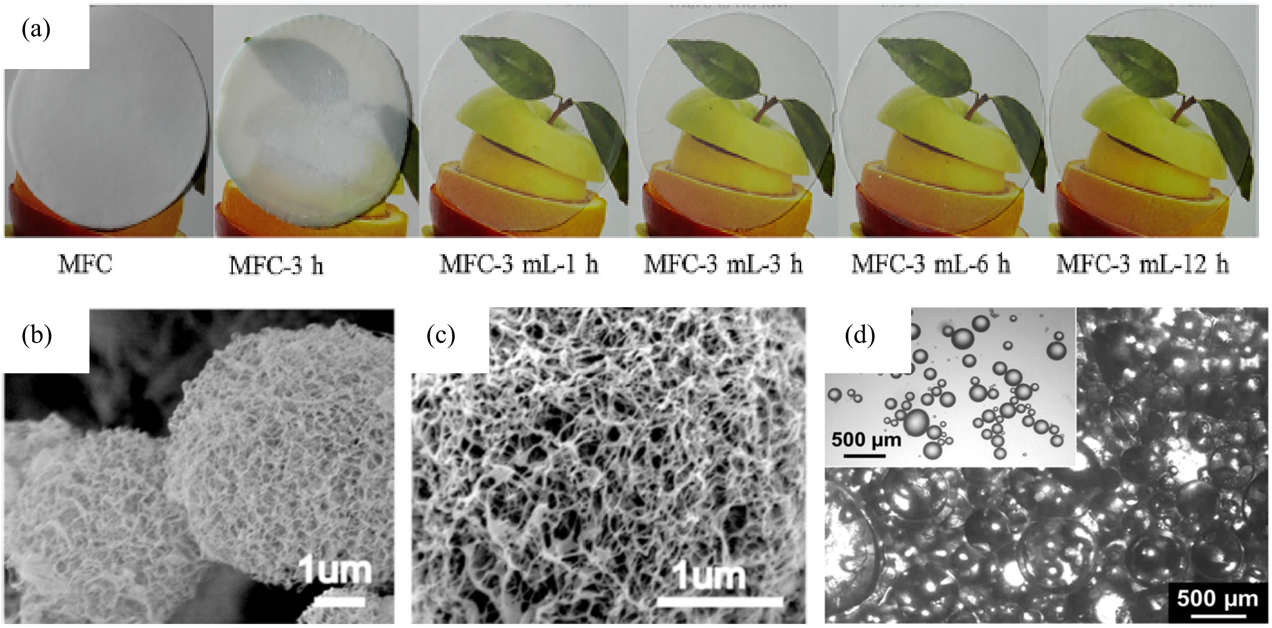

Figure 8. Effect of milling time (h) and hexanoyl chloride dose (mL) vs CMF film transparency (a).Adapted from Ref.[32] with permission, copyright 2016 Elsevier. SEM images of TEMPO-oxidized cellulose nanofiber aerogel microspheres with 6 min of ultrasonication (b) and higher magnification image reveals approximate diameter of nanofiber bundles to be dozens of nanometers (c). Adapted from Ref.[133] with permission, copyright 2017 Springer Nature. Microscopic images of Pickering emulsions in cyclohexane stabilized by ACC-CNFs observed 1 h after sonication (d). Adapted from Ref.[120] with permission, copyright 2019 Elsevier.

5.1 Films

The incorporation of CNFs has expanded the use of cellulose films beyond conventional paper applications to high performance material usage in electronics, energy storage, and water treatment.[134] The ability to manipulate the optical, mechanical, and thermal properties of CNFs has resulted in a wide range of functional nanomaterials. A summary of the properties of CNF films produced via non-conventional fibrillation methods is provided in **Table 2**. Generally, CNFs generated from non-conventional fibrillation methods are comparable to those produced from conventional methods regarding their properties.[19] Several examples of non-conventionally fibrillated, CNF-film applications are given below.

The fibrillation method employed to generate CNF can impact the strength and, in some cases, the thermal properties of the resulting films. Ball milling has been used by both Abe et al. [128] and Deng et al. [32] to modulate the strength and transparency of CNF films. Abe et al. developed a continuous process to ball mill dried pulp in a highly concentrated (8 wt.%) NaOH solution that yielded 20-50 nm diameter CNFs, largely in the cellulose I crystalline form. The minimum milling time that could be employed to produce a smooth film was found to be 90 minutes. The resultant CNF film had a Young's modulus of 9.3 GPa. Optimization of the milling conditions could potentially produce even higher strength films, as the conditions used resulted in a partial conversion from cellulose I to II crystalline form. Li et al. utilized high intensity ultrasonication to extract long (>500 μm) CNFs from bleached hardwood kraft pulp and then used them to reinforce poly (vinyl alcohol) (PVA) films.[93] The advantage of using ultrasonication was that the fibrils retained their cellulose I crystal structure which resulted in stronger films (1.86 and 1.63 times greater tensile strength and Young's modulus, respectively) when compared to neat PVA.

Several investigators have evaluated the impact of fiber pretreatments prior to non-conventional fibrillation on the physical properties of CNF films. For example, Rol et al. were able to increase the modulus of CNF films obtained using an enzymatic pretreatment followed by TSE fibrillation to 15.4 GPa while consuming 60% less energy than required to produce TEMPO-CNFs.[19] In addition to greater strength, the enzymatic pretreatment combined with TSE fibrillation produced a film with higher transparency (89%) vs. a CNF film (55%) produced merely from TSE fibrillation. The effect of chemical treatments during non-conventional fibrillation on CNF film properties have also been extensively investigated. Specifically, Deng et al. utilized ball milling in the presence of hexanoyl chloride to produce hydrophobic CMF films that were less sensitive to moisture.[32] Indeed the acylated-CMF films had a lower water vapor permeability (WVP) ($< 1 \times 10^3$ g·mm/ (m^2·day·atm)) compared to cellulose films (13×10^3 g·mm/ (m^2·day·atm). Further, acylated films had a 162% increase in tensile strength and a 1083% increase in elongation at break compared to CMF films without acylation. Finally, increases in both the extent of acylation and the milling time led to increases in optical transparency, as seen in **Figure 8a**. Other interesting CNF film functionalities that have been imparted through chemical treatments include antimicrobial characteristics via cationization[22] and fire retardancy through phosphorylation.[20,130]

CNF films derived from agricultural residues processed via non-conventional fibrillation methods have been widely investigated. Specifically, Dufresne et al. utilized cryo-crushing and a blender to fibrillate sugar beet pulp.[4] The resulting CMFs were subsequently cast into films in which the native pectin acted as a binder. It was determined that the tensile modulus of the films increased (up to 3 GPa) in proportion to the duration of the mechanical treatment of the pulp. Cryo-crushing was shown to generate individual microfibrils and to support the subsequent formation of a network of CMFs within the material. It is noted that the ability to isolate individual microfibrils is likely facilitated by the low pectin content of the feedstock. Chen et al. employed ultrasonication to isolate nanofibers from four different agricultural waste materials (wood, bamboo, wheat straw and flax) and to cast them into films.[91] The CNF properties yielded by the purification-ultrasonic pretreatments made them suitable for nanocomposites, filtration media and optically transparent films. Chemical treatment resulted in a higher α-cellulose content in the product. Specifically an increase of 30% over the starting value for the wood, bamboo and wheat straw feedstocks was observed. A similar increase in α-cellulose content was not observed for flax, which had a high initial content of 88 %. The increased crystallinity of the CNF products yielded improved thermal properties of the resultant films (thermal degradation at >330 °C compared to 210 °C for untreated fibers).

5.2 Polymer composites

Inclusion of CNFs in composites can have a significant impact on the material properties (especially mechanical properties) of the resultant materials. An overview of various CNF-polymer composites and their associated properties is provided **Table 2**. In one study, Boufi and Chaker produced CNF/acrylic latex composites using a conventional high-speed blender over a range of CNF contents (1-15 wt.%).[64] It was observed that at 10 wt.% CNFs, the tensile strength and modulus of the composite were approximately 10 and 125 times higher than those of the neat latex, respectively. Fourati et al. observed increases in the tensile strength and Young's modulus when incorporating CNFs generated via an extrusion technique into TPS composites.[105] Li et al. produced CNFs using ultrasonication for use in PVA composites.[93] CNF contents of 0, 2, 4, 8, and 12 wt.% were employed. Progressively increasing mechanical performance of the composite PVA films was observed as the CNF content increased. An alternate means of incorporating CNFs into composites is to perform *in-situ* fibrillation of pulp fibers during extrusion. Specifically, Suzuki et al. produced CMF/MAPP/CPPA/PP composites with three different CMF contents (30, 40, and 50 wt.%) via *in-situ* fibrillation.[100] CPPA is a cationic polymer using a primary amine which acts as an effective coupling agent. The CMFs were produced by fibrillating pulp fibers with polymer powders during chilled extrusion. Yano et al. produced CMFs via extrusion for addition to polyolefin composites. The resultant composites displayed improved thermal properties, such as higher heat deflection temperature (up to 122 °C)[97] and lower coefficient of thermal expansion (down to 54 ppm/K)[98]. It is noted that inferior filler-matrix interactions remain a challenge in the production of CNF or CMF composites.[51] A number of research efforts have been made to incorporate surface modification into fibrillation processes to generate an improved dispersion of CNFs within hydrophobic polymer matrices. For example, Suzuki et al. fibrillated bleached kraft pulp using TSE with the addition of CPPA or MAPP coupling agents, before re-extrusion with PP to generate composites with an improved tensile strength and modulus.[100] Deng et al. functionalized and generated fibrillated CNFs in a single step by ball milling CMFs in the presence of hexanoyl chloride.[132] The resulting fibers had strong interfacial adhesion with a polycaprolactone (PCL) matrix.

5.3 Aerogels

CNFs are well suited as source materials for hydrogels and aerogels because of their inherent hydrogen bonding, electrostatic interactions and fibril structure with high aspect ratio. Fibrillation methods for preparing aerogels are largely selected based on their reduced energy or cost, as opposed to providing specific surface modification or reduction of surface charge advantages.[135] However, some researchers have investigated the direct preparation of nanocomposite CNF-based aerogels in order to mitigate the need of multi-step post processing and to efficiently add functionality throughout the aerogel network. For example, Zhang et al. prepared ultra-lightweight CNF-based aerogel microspheres via ultrasonication for use as suspension micro-reactors in tailored separation/extraction applications.[133] Softwood pulp was used to prepare TOCN suspensions, and ultrasonication was used to make a homogeneous mixture of small uniform droplets. The aerogel microspheres were isolated via freeze drying (**Figure 8 b,c**). Decreasing ultrasonication time from 6 min to 2 min yielded more compact microsphere structures (the diameter was reduced from approximately 7 μm to 2 μm), while increasing ultrasound time resulted in a more porous morphology. The use of a covalent cross-linker (polyamide-epichlorohydrin) drastically increased the aerogel stability in harsh environments and facilitated subsequent reusability without decreasing removal efficiency. The CNF-based aerogels were able to absorb 120 $g \cdot g^{-1}$ of water and to remove 93% of phenol and 82% of Cu^{2+} from solution.

5.4 Pickering emulsifiers

A Pickering emulsifier refers to a solid particle which is capable of stabilizing oil droplet in water by accumulating at the interface of the two liquids.[120] Pickering emulsion stabilization was achieved using CNFs prepared by Yokota et al. via ACC approach.[120] It is noted that ACC-CNFs are typically more hydrophobic than fibers produced by physical grinding or pulverization because of the selective cleavage of the hydrophobic *(200)* planes in native crystalline cellulose during ACC treatment.[120] Therefore, ACC-produced fibrils have pronounced amphiphilic properties and can be used as emulsifiers without the addition of a surfactant. The emulsifier capabilities of the ACC-CNFs was evaluated using a variety of solvents. It was determined that they formed stable oil/water Pickering emulsions, containing n-octane, cyclopentane, n-decane or cyclohexane (**Figure 8d**). No emulsion was observed in n-hexane, a finding which differed from the work of Tsuboi et al.[136] who observed n-hexane emulsification when employing ACC-CNFs derived from wood and bamboo kraft pulp fibers.

6. CONCLUSIONS AND FUTURE WORK

As CNF research continues to evolve in both industry and academia, the industrial-scale production of CNFs at low cost is becoming more urgent. Producing CNFs via non-conventional fibrillation methods results in materials that exhibit interesting attributes relative to those produced via conventional methods. Certainly challenges and opportunities coexist for scale-up and application of CNF materials.

Importantly, there is no single means to measure the degree of fibrillation of CNFs. In fact, the term ‘degree of fibrillation’ itself lacks a formal definition, and there is no established or direct term to encapsulate the various aspects that can be described by fibrillation such as fibril length and diameter, internal versus external fibrillation, process yield etc. Until more progress is made in CNF characterization and the characterization of mixtures of macro-, micro- and nanomaterials in general, multiple characterization methods should be employed and correlated in order to estimate the efficacy of a given fibrillation process.

Extrusion fibrillation is a promising methodology for producing CNFs from lignocellulosic feedstock. It has been shown that the size of the equipment affects the yield of fibrillation, but not the degree of fibrillation, a fortunate outcome that limits the need for large capital investment in research and development efforts. Pretreatment appears to be a prerequisite to obtain highly fibrillated CNFs from pulp fibers using TSE, although the work of Ho et al.[80] may indicate otherwise. It is recommended that future research investigate the use of more bio-based feedstocks other than wood and the use of cost-effective pretreatment methods. Co-extrusion of pulp fibers and polymers has been show to generally result in the production of a combination of CNFs and CMFs, with the latter being the major portion. However, while complete nanoscale dispersion of fibers may be a laudable goal, it may not be necessary for polymer composite applications as the mechanical properties of a host of polymer/fiber reinforced materials have been shown to significantly improve with *in-situ* fibrillated CMFs.

Employing ball-milling and blending to fabricate CNFs has not be extensively investigated to date, a surprising fact given the multitude of papers which have utilized these techniques for producing other nanomaterials. Variations in processing speed, power, and time, along with the use of additives, have produced a wide array of CNF properties via these techniques. Indeed, thermal stability, crystallinity, mechanical properties, and morphology have been observed to vary greatly. More work is needed to understand and optimize blending as a straightforward method of producing CNFs. Additionally, development of new ball-milling and blending strategies which more efficiently utilize the mechanical energy input would provide more efficient fibrillation.

Steam explosion provides an inexpensive and green solution to producing CMFs/CNFs from lignocellulosic biomass. However, caution must be taken when utilizing steam explosion as depending on the process conditions employed, it may expose cellulose to temperatures and pressures that can result in degradation. To mitigate the amount of cellulose degradation, steam explosion should be conducted at elevated temperatures and pressures in repeated cycles of shortened time periods. Lower temperature and pressure steam explosion has proven effective for pretreating cellulose for subsequent mechanical homogenization. In addition, acidic or alkaline media may be employed to promote separation of fibers during the rapid decompression process. However, solely employing water as the liquid medium where possible is preferable in order to remain environmentally friendly, maintain low cytotoxicity levels and simplify the process.

The aqueous counter collision process is an innovative and environmentally friendly method of producing CNFs which uses only water and lignocellulosic feedstocks. However, the process is energy-intensive due to the need to generate the high-pressure and high-speed water jet, which is guided to produce the various shearing, impacting and cavitating actions that fibrillate fiber. In order to reduce the energy requirements of these systems, and to make the process more economically attractive, chemical or enzymatic pretreatments are recommended. Additional work is also recommended to explore the effects of the interaction chamber configuration on the morphology and size distribution of the resulting CNFs and on the energy efficiency of the system.

CNFs produced from either ultrasonication or cryocrushing have not been as thoroughly characterized as those from other non-conventional fibrillation methods. However, it appears that the application of either technique on their own may not be sufficient to produce highly fibrillated and uniform CNFs. The majority of fibers produced by cryo-crushing are on the micron scale. Additionally, both methods are energy-intensive. Therefore, there are limited studies available in literatures using these fibrillation techniques for producing CNFs. The use of ultrasonication and cryo-crushing as pretreatments should be more thoroughly investigated and analyzed to verify their positive effects in following fibrillation.

The drive to develop materials and processes to support a circular economy is increasing. CNFs derived from non-conventional fibrillation methods have been investigated for various applications, such as films, polymer composites, aerogels, Pickering emulsifier, etc. The range of applications utilizing CNFs is attributable to the natural abundance of its feedstock, along with its sustainability. It is hoped that continued efforts will be invested in developing novel and efficient fibrillation techniques in order to further expand the use of CNFs.

AUTHOR INFORMATION

Corresponding Author

Lu Wang, Email: lu.wang@maine.edu.

Douglas J. Gardner, Phone: +1 (207) 581-2846, Email: douglasg@maine.edu

AUTHOR CONTRIBUTION

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **Lu Wang**: Conceptualization, Writing – original draft, Writing - review & editing. **Kai Li**: Writing – original draft, Writing - review & editing. **Katie Copenhaver**: Writing – original draft, Writing - review & editing. **Susan MacKay**: Writing – original draft, Writing - review & editing. **Meghan E. Lamm**: Writing – original draft, Writing - review & editing. **Xianhui Zhao**: Writing – original draft, Writing - review & editing. **Brandon Dixon**: Writing – original draft, Writing - review & editing. **Jinwu Wang**: Writing – original draft, Writing - review & editing. **Yousoo Han**: Writing – original draft, Writing - review & editing. **David Neivandt**: Writing - review & editing. **Donna A. Johnson**: Writing - review & editing. **Colleen C. Walker**: Writing - review & editing. **Soydan Ozcan**: Conceptualization, Writing - review & editing, Supervision, Funding acquisition. **Douglas J. Gardner**: Conceptualization, Writing – original draft, Writing - review & editing, Supervision, Funding acquisition.

DECLARATION OF COMPETING INTEREST

The authors report no declarations of interest.

ACKNOWLEDGMENTS

Authors from Oak Ridge National Laboratory (ORNL) are supported by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DEAC05-00OR22725 with UT-Battelle LLC. Authors from University of Maine are grateful for the funding support from UT-Battelle LLC with the U.S. Department of Energy under contract DEAC05-00OR22725 (subcontract # 4000174848). Authors are grateful to Olivia Shafer from ORNL for proof reading the manuscript before submission. This manuscript has been authored in part by UT-Battelle, LLC with the US Department of Energy. The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

REFERENCES

(1) Rajinipriya, M.; Nagalakshmaiah, M.; Robert, M.; Elkoun, S. Importance of Agricultural and Industrial Waste in the Field of Nanocellulose and Recent Industrial Developments of Wood Based Nanocellulose: A Review. *ACS Sustain. Chem. Eng.* **2018**, *6* (3), 2807–2828. https://doi.org/10.1021/acssuschemeng.7b03437.

(2) Nechyporchuk, O.; Belgacem, M. N.; Bras, J. Production of Cellulose Nanofibrils: A Review of Recent Advances. *Ind. Crops Prod.* **2016**, *93*, 2–25. https://doi.org/10.1016/j.indcrop.2016.02.016.

(3) Rol, F.; Belgacem, M. N.; Gandini, A.; Bras, J. Recent Advances in Surface-Modified Cellulose Nanofibrils. *Prog. Polym. Sci.* **2019**, *88*, 241–264. https://doi.org/10.1016/j.progpolymsci.2018.09.002.

(4) Dufresne, A.; Cavaillé, J.; Vignon, M. R. Mechanical Behavior of Sheets Prepared from Sugar Beet Cellulose Microfibrils. *J. Appl. Polym. Sci.* **1997**, *64* (6), 1185–1194.

(5) Ifuku, S.; Nogi, M.; Abe, K.; Handa, K.; Nakatsubo, F.; Yano, H. Surface Modification of Bacterial Cellulose Nanofibers for Property Enhancement of Optically Transparent Composites: Dependence on Acetyl-Group DS. *Biomacromolecules* **2007**, *8* (6), 1973–1978.

(6) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites. *Chem. Soc. Rev.* **2011**, *40* (7), 3941–3994. https://doi.org/10.1039/c0cs00108b.

(7) Nogi, M.; Iwamoto, S.; Nakagaito, A. N.; Yano, H. Optically Transparent Nanofiber Paper. *Adv. Mater.* **2009**, *21* (16), 1595–1598.

(8) Isogai, A.; Saito, T.; Fukuzumi, H. TEMPO-Oxidized Cellulose Nanofibers. *Nanoscale* **2011**, *3* (1), 71–85. https://doi.org/10.1039/c0nr00583e.

(9) Dizge, N.; Shaulsky, E.; Karanikola, V. Electrospun Cellulose Nanofibers for Superhydrophobic and Oleophobic Membranes. *J. Memb. Sci.* **2019**, *590*, 117271.

(10) Rånby, B. G. Fibrous Macromolecular Systems. Cellulose and Muscle. The Colloidal Properties of Cellulose Micelles. *Discuss. Faraday Soc.* **1951**, *11*, 158–164.

(11) Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. Microfibrillated Cellulose, a New Cellulose Product: Properties, Uses, and Commercial Potential. In *J Appl Polym Sci Appl Polym Symp*; 1983; Vol. 37, pp 815–827.

(12) Brown Jr, R. M. Bacterial Cellulose. *Cellul. Struct. Funct. Asp. Ellis Horwood, Chichester* **1989**, 145–151.

(13) Habibi, Y.; Lucia, L. A.; Rojas, O. J. Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications. *Chem. Rev.* **2010**, *110* (6), 3479–3500. https://doi.org/10.1021/cr900339w.

(14) Khalil, H. P. S. A.; Davoudpour, Y.; Islam, M. N.; Mustapha, A.; Sudesh, K.; Dungani,

R.; Jawaid, M.; Abdul Khalil, H. P. S.; Davoudpour, Y.; Islam, M. N.; et al. Production and Modification of Nanofibrillated Cellulose Using Various Mechanical Processes: A Review. *Carbohydr. Polym.* **2014**, *99*, 649–665. https://doi.org/10.1016/j.carbpol.2013.08.069.

(15) Ohkawa, K. Nanofibers of Cellulose and Its Derivatives Fabricated Using Direct Electrospinning. *Mol. 2015,* **2015**, *20*, 9139–9154. https://doi.org/10.3390/molecules20059139.

(16) Frey, M. W.; Frey, M. W. Electrospinning Cellulose and Cellulose Derivatives Electrospinning Cellulose and Cellulose Derivatives. *Polym. Rev.* **2008**, *48* (2), 378–391. https://doi.org/10.1080/15583720802022281.

(17) Schiffman, J. D.; Schauer, C. L. A Review : Electrospinning of Biopolymer Nanofibers and Their Applications. *Polym. Rev.* **2008**, *48* (2), 317–352. https://doi.org/10.1080/15583720802022182.

(18) Spence, K. L.; Venditti, R. A.; Rojas, O. J.; Habibi, Y.; Pawlak, J. J. A Comparative Study of Energy Consumption and Physical Properties of Microfibrillated Cellulose Produced by Different Processing Methods. *Cellulose* **2011**, *18* (4), 1097–1111. https://doi.org/10.1007/s10570-011-9533-z.

(19) Rol, F.; Karakashov, B.; Nechyporchuk, O.; Terrien, M.; Meyer, V.; Dufresne, A.; Belgacem, M. N.; Bras, J. Pilot-Scale Twin Screw Extrusion and Chemical Pretreatment as an Energy-Efficient Method for the Production of Nanofibrillated Cellulose at High Solid Content. *ACS Sustain. Chem. Eng.* **2017**, *5* (8), 6524–6531. https://doi.org/10.1021/acssuschemeng.7b00630.

(20) Rol, F.; Belgacem, N.; Meyer, V.; Petit-Conil, M.; Bras, J. Production of Fire-Retardant Phosphorylated Cellulose Fibrils by Twin-Screw Extrusion with Low Energy Consumption. *Cellulose* **2019**, *26* (9), 5635–5651. https://doi.org/10.1007/s10570-019-02447-4.

(21) Baati, R.; Magnin, A.; Boufi, S. High Solid Content Production of Nanofibrillar Cellulose via Continuous Extrusion. *ACS Sustain. Chem. Eng.* **2017**, *5* (3), 2350–2359. https://doi.org/10.1021/acssuschemeng.6b02673.

(22) Rol, F.; Saini, S.; Meyer, V.; Petit-Conil, M.; Bras, J. Production of Cationic Nanofibrils of Cellulose by Twin-Screw Extrusion. *Ind. Crops Prod.* **2019**, *137*, 81–88. https://doi.org/10.1016/j.indcrop.2019.04.031.

(23) Rol, F.; Vergnes, B.; El Kissi, N.; Bras, J. Nanocellulose Production by Twin-Screw Extrusion: Simulation of the Screw Profile to Increase the Productivity. *ACS Sustain. Chem. Eng.* **2020**, *8* (1), 50–59. https://doi.org/10.1021/acssuschemeng.9b01913.

(24) Sofla, M. R. K.; Batchelor, W.; Kosinkova, J.; Pepper, R.; Brown, R.; Rainey, T. Cellulose Nanofibres from Bagasse Using a High Speed Blender and Acetylation as a Pretreatment. *Cellulose* **2019**, *26* (8), 4799–4814. https://doi.org/10.1007/s10570-019-02441-w.

(25) Jiang, F.; Kondo, T.; Hsieh, Y.-L. Rice Straw Cellulose Nanofibrils via Aqueous Counter

Collision and Differential Centrifugation and Their Self-Assembled Structures. *ACS Sustain. Chem. Eng.* **2016**, *4* (3), 1697–1706. https://doi.org/https://doi.org/10.1021/acssuschemeng.5b01653.

(26) Kangas, H.; Lahtinen, P.; Sneck, A.; Saariaho, A.-M.; Laitinen, O.; Hellén, E. Characterization of Fibrillated Celluloses. A Short Review and Evaluation of Characteristics with a Combination of Methods. *Nord. Pulp Pap. Res. J.* **2014**, *29* (1), 129–143. https://doi.org/10.3183/npprj-2014-29-01-p129-143.

(27) Chinga-Carrasco, G. Optical Methods for the Quantification of the Fibrillation Degree of Bleached MFC Materials. *Micron* **2013**, *48*, 42–48. https://doi.org/10.1016/j.micron.2013.02.005.

(28) Abdul Khalil, H. P. S.; Bhat, A. H.; Ireana Yusra, A. F. Green Composites from Sustainable Cellulose Nanofibrils: A Review. *Carbohydr. Polym.* **2012**, *87* (2), 963–979. https://doi.org/10.1016/j.carbpol.2011.08.078.

(29) Chaker, A.; Alila, S.; Mutjé, P.; Vilar, M. R.; Boufi, S. Key Role of the Hemicellulose Content and the Cell Morphology on the Nanofibrillation Effectiveness of Cellulose Pulps. *Cellulose* **2013**, *20* (6), 2863–2875. https://doi.org/10.1007/s10570-013-0036-y.

(30) Debiagi, F.; Faria-Tischer, P. C. S.; Mali, S. Nanofibrillated Cellulose Obtained from Soybean Hull Using Simple and Eco-Friendly Processes Based on Reactive Extrusion. *Cellulose* **2020**, *27* (4), 1975–1988. https://doi.org/10.1007/s10570-019-02893-0.

(31) Deepa, B.; Abraham, E.; Cherian, B. M.; Bismarck, A.; Blaker, J. J.; Pothan, L. A.; Leao, A. L.; de Souza, S. F.; Kottaisamy, M. Structure, Morphology and Thermal Characteristics of Banana Nano Fibers Obtained by Steam Explosion. *Bioresour. Technol.* **2011**, *102* (2), 1988–1997. https://doi.org/10.1016/j.biortech.2010.09.030.

(32) Deng, S.; Huang, R.; Zhou, M.; Chen, F.; Fu, Q. Hydrophobic Cellulose Films with Excellent Strength and Toughness via Ball Milling Activated Acylation of Microfibrillated Cellulose. *Carbohydr. Polym.* **2016**, *154*, 129–138. https://doi.org/10.1016/j.carbpol.2016.07.101.

(33) Ferrer, A.; Filpponen, I.; Rodríguez, A.; Laine, J.; Rojas, O. J. Valorization of Residual Empty Palm Fruit Bunch Fibers (EPFBF) by Microfluidization: Production of Nanofibrillated Cellulose and EPFBF Nanopaper. *Bioresour. Technol.* **2012**, *125*, 249–255. https://doi.org/10.1016/j.biortech.2012.08.108.

(34) Jiang, Y.; Liu, X.; Yang, Q.; Song, X.; Qin, C.; Wang, S.; Li, K. Effects of Residual Lignin on Mechanical Defibrillation Process of Cellulosic Fiber for Producing Lignocellulose Nanofibrils. *Cellulose* **2018**, *25* (11), 6479–6494. https://doi.org/10.1007/s10570-018-2042-6.

(35) Lee, J. A.; Yoon, M. J.; Lee, E. S.; Lim, D. Y.; Kim, K. Y. Preparation and Characterization of Cellulose Nanofibers (CNFs) from Microcrystalline Cellulose (MCC) and CNF/Polyamide 6 Composites. *Macromol. Res.* **2014**, *22* (7), 738–745. https://doi.org/10.1007/s13233-014-2121-y.

(36) Lee, S. H.; Teramoto, Y.; Endo, T. Enzymatic Saccharification of Woody Biomass

Micro/Nanofibrillated by Continuous Extrusion Process I - Effect of Additives with Cellulose Affinity. *Bioresour. Technol.* **2009**, *100* (1), 275–279. https://doi.org/10.1016/j.biortech.2008.05.051.

(37) Nair, S. S.; Zhu, J. Y.; Deng, Y.; Ragauskas, A. J. Characterization of Cellulose Nanofibrillation by Micro Grinding. *J. Nanoparticle Res.* **2014**, *16* (4). https://doi.org/10.1007/s11051-014-2349-7.

(38) Karande, V. S.; Bharimalla, A. K.; Hadge, G. B.; Mhaske, S. T.; Vigneshwaran, N. Nanofibrillation of Cotton Fibers by Disc Refiner and Its Characterization. *Fibers Polym.* **2011**, *12* (3), 399–404. https://doi.org/10.1007/s12221-011-0399-3.

(39) Ang, S.; Haritos, V.; Batchelor, W. Effect of Refining and Homogenization on Nanocellulose Fiber Development, Sheet Strength and Energy Consumption. *Cellulose* **2019**, *26* (8), 4767–4786. https://doi.org/10.1007/s10570-019-02400-5.

(40) Buffiere, J.; Balogh-Michels, Z.; Borrega, M.; Geiger, T.; Zimmermann, T.; Sixta, H. The Chemical-Free Production of Nanocelluloses from Microcrystalline Cellulose and Their Use as Pickering Emulsion Stabilizer. *Carbohydr. Polym.* **2017**, *178*, 48–56. https://doi.org/10.1016/j.carbpol.2017.09.028.

(41) Foster, E. J.; Moon, R. J.; Agarwal, U. P.; Bortner, M. J.; Bras, J.; Camarero-Espinosa, S.; Chan, K. J.; Clift, M. J. D.; Cranston, E. D.; Eichhorn, S. J.; et al. Current Characterization Methods for Cellulose Nanomaterials. *Chem. Soc. Rev.* **2018**, *47* (8), 2609–2679. https://doi.org/10.1039/c6cs00895j.

(42) Tatsumi, D.; Ishioka, S.; Matsumoto, T. Effect of Fiber Concentration and Axial Ratio on the Rheological Properties of Cellulose Fiber Suspensions. *Nihon Reoroji Gakkaishi* **2002**, *30* (1), 27–32. https://doi.org/10.1678/rheology.30.27.

(43) Desmaisons, J.; Boutonnet, E.; Rueff, M.; Dufresne, A.; Bras, J. A New Quality Index for Benchmarking of Different Cellulose Nanofibrils. *Carbohydr. Polym.* **2017**, *174*, 318–329. https://doi.org/10.1016/j.carbpol.2017.06.032.

(44) Julie Chandra, C. S.; George, N.; Narayanankutty, S. K. Isolation and Characterization of Cellulose Nanofibrils from Arecanut Husk Fibre. *Carbohydr. Polym.* **2016**, *142*, 158–166. https://doi.org/10.1016/j.carbpol.2016.01.015.

(45) Gao, Y.; Xia, H.; Sulaeman, A. P.; De Melo, E. M.; Dugmore, T. I. J.; Matharu, A. S. Defibrillated Celluloses via Dual Twin-Screw Extrusion and Microwave Hydrothermal Treatment of Spent Pea Biomass. *ACS Sustain. Chem. Eng.* **2019**, *7* (13), 11861–11871. https://doi.org/10.1021/acssuschemeng.9b02440.

(46) Gu, F.; Wang, W.; Cai, Z.; Xue, F.; Jin, Y.; Zhu, J. Y. Water Retention Value for Characterizing Fibrillation Degree of Cellulosic Fibers at Micro and Nanometer Scales. *Cellulose* **2018**, *25* (5), 2861–2871. https://doi.org/10.1007/s10570-018-1765-8.

(47) Trigui, K.; De Loubens, C.; Magnin, A.; Putaux, J. L.; Boufi, S. Cellulose Nanofibrils Prepared by Twin-Screw Extrusion: Effect of the Fiber Pretreatment on the Fibrillation Efficiency. *Carbohydr. Polym.* **2020**, *240*, 116342. https://doi.org/10.1016/j.carbpol.2020.116342.

(48) Liu, W.; Wang, B.; Hou, Q.; Chen, W.; Wu, M. Effects of Fibrillation on the Wood Fibers' Enzymatic Hydrolysis Enhanced by Mechanical Refining. *Bioresour. Technol.* **2016**, *206*, 99–103. https://doi.org/10.1016/j.biortech.2016.01.074.

(49) Santucci, B. S.; Bras, J.; Belgacem, M. N.; Curvelo, A. A. D.; Pimenta, M. T. B. Evaluation of the Effects of Chemical Composition and Refining Treatments on the Properties of Nanofibrillated Cellulose Films from Sugarcane Bagasse. *Ind. Crops Prod.* **2016**, *91*, 238–248. https://doi.org/10.1016/j.indcrop.2016.07.017.

(50) Yan, J.; Oyedeji, O.; Leal, J. H.; Donohoe, B. S.; Semelsberger, T. A.; Li, C.; Hoover, A. N.; Webb, E.; Bose, E. A.; Zeng, Y.; et al. Characterizing Variability in Lignocellulosic Biomass: A Review. *ACS Sustain. Chem. Eng.* **2020**, *8* (22), 8059–8085. https://doi.org/10.1021/acssuschemeng.9b06263.

(51) Siró, I.; Plackett, D. Microfibrillated Cellulose and New Nanocomposite Materials: A Review. *Cellulose*. 2010, pp 459–494. https://doi.org/10.1007/s10570-010-9405-y.

(52) Chaker, A.; Mutje, P.; Vilar, M. R.; Boufi, S. Agriculture Crop Residues as a Source for the Production of Nanofibrillated Cellulose with Low Energy Demand. *Cellulose* **2014**, *21* (6), 4247–4259. https://doi.org/10.1007/s10570-014-0454-5.

(53) Liimatainen, H.; Sirvio, J. A.; Kekalainen, K.; Hormi, O. High-Consistency Milling of Oxidized Cellulose for Preparing Microfibrillated Cellulose Films. *Cellulose* **2015**, *22* (5), 3151–3160. https://doi.org/10.1007/s10570-015-0700-5.

(54) Suopajärvi, T.; Sirviö, J. A.; Liimatainen, H. Nanofibrillation of Deep Eutectic Solvent-Treated Paper and Board Cellulose Pulps. *Carbohydr. Polym.* **2017**, *169*, 167–175. https://doi.org/10.1016/j.carbpol.2017.04.009.

(55) Wang, Y.; Wang, C.; Yi, Y.; Wang, H.; Yang, Y.; Zeng, L.; Tan, Z. Direct Pretreatment of Raw Ramie Fibers Using an Acidic Deep Eutectic Solvent to Produce Cellulose Nanofibrils in High Purity. *Cellulose* **2021**, *28* (1), 175–188. https://doi.org/10.1007/s10570-020-03538-3.

(56) Ninomiya, K.; Abe, M.; Tsukegi, T.; Kuroda, K.; Tsuge, Y.; Ogino, C.; Taki, K.; Taima, T.; Saito, J.; Kimizu, M.; et al. Lignocellulose Nanofibers Prepared by Ionic Liquid Pretreatment and Subsequent Mechanical Nanofibrillation of Bagasse Powder: Application to Esterified Bagasse/Polypropylene Composites. *Carbohydr Polym* **2018**, *182*, 8–14. https://doi.org/10.1016/j.carbpol.2017.11.003.

(57) Phanthong, P.; Karnjanakom, S.; Reubroycharoen, P.; Hao, X. G.; Abudula, A.; Guan, G. Q. A Facile One-Step Way for Extraction of Nanocellulose with High Yield by Ball Milling with Ionic Liquid. *Cellulose* **2017**, *24* (5), 2083–2093. https://doi.org/10.1007/s10570-017-1238-5.

(58) Cheng, Q.; Tong, Z.; Dempere, L.; Ingram, L.; Wang, L.; Zhu, J. Y. Disk Refining and Ultrasonication Treated Sugarcane Bagasse Residues for Poly(Vinyl Alcohol) Bio-Composites. *J. Polym. Environ.* **2012**, *21* (3), 648–657. https://doi.org/10.1007/s10924-012-0562-y.

(59) Lee, H.; Mani, S. Mechanical Pretreatment of Cellulose Pulp to Produce Cellulose

Nanofibrils Using a Dry Grinding Method. *Ind. Crops Prod.* **2017**, *104*, 179–187. https://doi.org/10.1016/j.indcrop.2017.04.044.

(60) Zeng, J. S.; Liu, L.; Li, J. P.; Dong, J. R.; Cheng, Z. Properties of Cellulose Nanofibril Produced from Wet Ball Milling after Enzymatic Treatment vs. Mechanical Grinding of Bleached Softwood Kraft Fibers. *BioResources* **2020**, *15* (2), 3809–3820. https://doi.org/10.15376/biores.15.2.3809-3820.

(61) Pelletier, A. L.; Zhao, Y.; Lei, X.; Li, K. Improved Fiber Separation and Energy Reduction in Thermomechanical Pulp Refining Using Enzyme-Pretreated Wood. *BioResources* **2013**, *8* (3).

(62) Saito, T.; Isogai, A. Ion-Exchange Behavior of Carboxylate Groups in Fibrous Cellulose Oxidized by the TEMPO-Mediated System. *Carbohydr. Polym.* **2005**, *61* (2), 183–190. https://doi.org/https://doi.org/10.1016/j.carbpol.2005.04.009.

(63) Kekäläinen, K.; Liimatainen, H.; Biale, F.; Niinimäki, J. Nanofibrillation of TEMPO-Oxidized Bleached Hardwood Kraft Cellulose at High Solids Content. *Holzforschung* **2015**, *69* (9), 1077–1088.

(64) Boufi, S.; Chaker, A. Easy Production of Cellulose Nanofibrils from Corn Stalk by a Conventional High Speed Blender. *Ind. Crops Prod.* **2016**, *93*, 39–47. https://doi.org/10.1016/j.indcrop.2016.05.030.

(65) Bian, H.; Gao, Y.; Luo, J.; Jiao, L.; Wu, W.; Fang, G.; Dai, H. Lignocellulosic Nanofibrils Produced Using Wheat Straw and Their Pulping Solid Residue: From Agricultural Waste to Cellulose Nanomaterials. *Waste Manag.* **2019**, *91*, 1–8. https://doi.org/10.1016/j.wasman.2019.04.052.

(66) Li, K.; Noguchi, S.; Kobayashi, T. Ultrasound-Responsive Behavior of Gelatinous Ionic Liquid/Poly(Vinyl Alcohol) Composites. *Ind. Eng. Chem. Res.* **2016**, *55* (37), 9915–9924. https://doi.org/10.1021/acs.iecr.6b02264.

(67) Li, K.; Kobayashi, T. Ultrasound Response of Aqueous Poly(Ionic Liquid) Solution. *Ultrason. Sonochem.* **2016**, *30*, 52–60. https://doi.org/http://dx.doi.org/10.1016/j.ultsonch.2015.10.021.

(68) Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W.; et al. Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chem. Rev.* **2021**, *121* (3), 1232–1285. https://doi.org/10.1021/acs.chemrev.0c00385.

(69) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of Cellulose with Ionic Liquids. *J. Am. Chem. Soc.* **2002**, *124* (18), 4974–4975. https://doi.org/10.1021/ja025790m.

(70) Lynam, J. G.; Kumar, N.; Wong, M. J. Deep Eutectic Solvents' Ability to Solubilize Lignin, Cellulose, and Hemicellulose; Thermal Stability; and Density. *Bioresour. Technol.* **2017**, *238*, 684–689. https://doi.org/10.1016/j.biortech.2017.04.079.

(71) Li, K.; Berton, P.; Kelley, S. P.; Rogers, R. D. Singlet Oxygen Production and Tunable Optical Properties of Deacetylated Chitin-Porphyrin Crosslinked Films.

Biomacromolecules **2018**, *19* (8), 3291–3300. https://doi.org/10.1021/acs.biomac.8b00605.

(72) Li, K.; Choudhary, H.; Rogers, R. D. Ionic Liquids for Sustainable Processes: Liquid Metal Catalysis. *Curr. Opin. Green Sustain. Chem.* **2018**, *11*, 15–21. https://doi.org/DOI: 10.1016/j.cogsc.2018.02.011.

(73) Xu, P.; Zheng, G. W.; Zong, M. H.; Li, N.; Lou, W. Y. Recent Progress on Deep Eutectic Solvents in Biocatalysis. *Bioresour. Bioprocess.* **2017**, *4* (1), 34. https://doi.org/10.1186/s40643-017-0165-5.

(74) Reis, R. S.; Tienne, L. G. P.; Souza, D. de H. S.; Marques, M. de F. V.; Monteiro, S. N. Characterization of Coffee Parchment and Innovative Steam Explosion Treatment to Obtain Microfibrillated Cellulose as Potential Composite Reinforcement. *J. Mater. Res. Technol.* **2020**, *9* (4), 9412–9421. https://doi.org/10.1016/j.jmrt.2020.05.099.

(75) Kaushik, A.; Singh, M. Isolation and Characterization of Cellulose Nanofibrils from Wheat Straw Using Steam Explosion Coupled with High Shear Homogenization. *Carbohydr. Res.* **2011**, *346* (1), 76–85. https://doi.org/10.1016/j.carres.2010.10.020.

(76) Avolio, R.; Bonadies, I.; Capitani, D.; Errico, M. E.; Gentile, G.; Avella, M. A Multitechnique Approach to Assess the Effect of Ball Milling on Cellulose. *Carbohydr. Polym.* **2012**, *87* (1), 265–273. https://doi.org/https://doi.org/10.1016/j.carbpol.2011.07.047.

(77) Tsalagkas, D.; Zhai, L. D.; Kafy, A.; Kim, J. W.; Kim, H. C.; Kim, J. Production of Micro- and Nanofibrillated Cellulose through an Aqueous Counter Collision System Followed by Ultrasound: Effect of Mechanical Pretreatments. *J. Nat. Fibers* **2020**, *17* (8), 1099–1110. https://doi.org/10.1080/15440478.2018.1558144.

(78) Michelin, M.; Gomes, D. G.; Romaní, A.; Polizeli, M. de L.; Teixeira, J. A. Nanocellulose Production: Exploring the Enzymatic Route and Residues of Pulp and Paper Industry. *Molecules* **2020**, *25* (15), 3411.

(79) Rol, F.; Banvillet, G.; Meyer, V.; Petit-Conil, M.; Bras, J. Combination of Twin-Screw Extruder and Homogenizer to Produce High-Quality Nanofibrillated Cellulose with Low Energy Consumption. *J. Mater. Sci.* **2018**, *53* (17), 12604–12615. https://doi.org/10.1007/s10853-018-2414-1.

(80) Ho, T. T. T.; Abe, K.; Zimmermann, T.; Yano, H. Nanofibrillation of Pulp Fibers by Twin-Screw Extrusion. *Cellulose* **2015**, *22* (1), 421–433. https://doi.org/10.1007/s10570-014-0518-6.

(81) Debiagi, F.; Faria-Tischer, P. C. S.; Mali, S. A Green Approach Based on Reactive Extrusion to Produce Nanofibrillated Cellulose from Oat Hull. *Waste and Biomass Valorization* **2021**, *12*, 1051–1060. https://doi.org/10.1007/s12649-020-01025-1.

(82) Zhang, L. Y.; Tsuzuki, T.; Wang, X. G. Preparation of Cellulose Nanofiber from Softwood Pulp by Ball Milling. *Cellulose* **2015**, *22* (3), 1729–1741. https://doi.org/10.1007/s10570-015-0582-6.

(83) Nuruddin, M.; Hosur, M.; Uddin, M. J.; Baah, D.; Jeelani, S. A Novel Approach for

Extracting Cellulose Nanofibers from Lignocellulosic Biomass by Ball Milling Combined with Chemical Treatment. *J. Appl. Polym. Sci.* **2016**, *133* (9). https://doi.org/ARTN 42990 10.1002/app.42990.

(84) Amiralian, N.; Annamalai, P. K.; Memmott, P.; Martin, D. J. Isolation of Cellulose Nanofibrils from Triodia Pungens via Different Mechanical Methods. *Cellulose* **2015**, *22* (4), 2483–2498. https://doi.org/10.1007/s10570-015-0688-x.

(85) Uetani, K.; Yano, H. Nanofibrillation of Wood Pulp Using a High-Speed Blender. *Biomacromolecules* **2011**, *12* (2), 348–353. https://doi.org/10.1021/bm101103p.

(86) Cherian, B. M.; Pothan, L. A.; Nguyen-Chung, T.; Mennig, G.; Kottaisamy, M.; Thomas, S. A Novel Method for the Synthesis of Cellulose Nanofibril Whiskers from Banana Fibers and Characterization. *J. Agric. Food Chem.* **2008**, *56* (14), 5617–5627. https://doi.org/10.1021/jf8003674.

(87) Cherian, B. M.; Leão, A. L.; de Souza, S. F.; Thomas, S.; Pothan, L. A.; Kottaisamy, M. Isolation of Nanocellulose from Pineapple Leaf Fibres by Steam Explosion. *Carbohydr. Polym.* **2010**, *81* (3), 720–725. https://doi.org/10.1016/j.carbpol.2010.03.046.

(88) Solikhin, A.; Hermawan, B.; Octaviani, E. A.; Prabuningrum, D. S.; Nurmadina; Gazali, I.; Mangurai, S. U. N. M.; Murayama, K.; Saad, S. Morphological, Chemical, and Thermal Characteristics of Chitosan Nanocomposite Films Reinforced with Steam-Exploded Microfibrillated Cellulose. *J. Indian Acad. Wood Sci.* **2018**, *15* (1), 68–79. https://doi.org/10.1007/s13196-018-0210-9.

(89) Kondo, T.; Kose, R.; Naito, H.; Kasai, W. Aqueous Counter Collision Using Paired Water Jets as a Novel Means of Preparing Bio-Nanofibers. *Carbohydr. Polym.* **2014**, *112*, 284–290.

(90) Kose, R.; Mitani, I.; Kasai, W.; Kondo, T. "Nanocellulose" as a Single Nanofiber Prepared from Pellicle Secreted by Gluconacetobacter Xylinus Using Aqueous Counter Collision. *Biomacromolecules* **2011**, *12* (3), 716–720.

(91) Chen, W.; Yu, H.; Liu, Y.; Hai, Y.; Zhang, M.; Chen, P. Isolation and Characterization of Cellulose Nanofibers from Four Plant Cellulose Fibers Using a Chemical-Ultrasonic Process. *Cellulose* **2011**, *18* (2), 433–442. https://doi.org/10.1007/s10570-011-9497-z.

(92) Cheng, Q.; Wang, S.; Rials, T. G. Poly(Vinyl Alcohol) Nanocomposites Reinforced with Cellulose Fibrils Isolated by High Intensity Ultrasonication. *Compos. Part A Appl. Sci. Manuf.* **2009**, *40* (2), 218–224. https://doi.org/10.1016/j.compositesa.2008.11.009.

(93) Li, W.; Zhao, X.; Huang, Z.; Liu, S. Nanocellulose Fibrils Isolated from BHKP Using Ultrasonication and Their Reinforcing Properties in Transparent Poly (Vinyl Alcohol) Films. *J. Polym. Res.* **2013**, *20* (8). https://doi.org/10.1007/s10965-013-0210-9.

(94) Bhatnagar, A.; Sain, M. Processing of Cellulose Nanofiber-Reinforced Composites. *J. Reinf. Plast. Compos.* **2005**, *24* (12), 1259–1268. https://doi.org/10.1177/0731684405049864.

(95) Gorur, Y. C.; Larsson, P. A.; Wågberg, L. Self-Fibrillating Cellulose Fibers: Rapid in Situ Nanofibrillation to Prepare Strong, Transparent, and Gas Barrier Nanopapers.

Biomacromolecules **2020**, *21* (4), 1480–1488. https://doi.org/10.1021/acs.biomac.0c00040.

(96) Heiskanen, I.; Harlin, A.; Backfolk, K.; Laitinen, R. Process for the Production of Microfibrillated Cellulose in an Extruder and Microfibrillated Cellulose Produced According to the Process, June 10, 2014.

(97) Suzuki, K.; Okumura, H.; Kitagawa, K.; Sato, S.; Antonio, N. N.; Yano, H. Development of Continuous Process Enabling Nanofibrillation of Pulp and Melt Compounding. *Cellulose* **2013**, *20*, 201–210. https://doi.org/10.1007/s10570-012-9843-9.

(98) Igarashi, Y.; Sato, A.; Okumura, H.; Nakatsubo, F.; Yano, H. Manufacturing Process Centered on Dry-Pulp Direct Kneading Method Opens a Door for Commercialization of Cellulose Nanofiber Reinforced Composites. *Chem. Eng. J.* **2018**, *354*, 563–568. https://doi.org/10.1016/j.cej.2018.08.020.

(99) Taheri, H.; Hietala, M.; Oksman, K. One-Step Twin-Screw Extrusion Process of Cellulose Fibers and Hydroxyethyl Cellulose to Produce Fibrillated Cellulose Biocomposite. *Cellulose* **2020**, *27* (14), 8105–8119. https://doi.org/10.1007/s10570-020-03287-3.

(100) Suzuki, K.; Sato, A.; Okumura, H.; Hashimoto, T.; Antonio, N. N.; Yano, H. Novel High-Strength, Micro Fibrillated Cellulose-Reinforced Polypropylene Composites Using a Cationic Polymer as Compatibilizer. *Cellulose* **2014**, *21* (1), 507–518. https://doi.org/10.1007/s10570-013-0143-9.

(101) Suzuki, K.; Homma, Y.; Igarashi, Y.; Okumura, H.; Semba, T.; Nakatsubo, F.; Yano, H. Investigation of the Mechanism and Effectiveness of Cationic Polymer as a Compatibilizer in Microfibrillated Cellulose-Reinforced Polyolefins. *Cellulose* **2016**, *23* (1), 623–635. https://doi.org/10.1007/s10570-015-0845-2.

(102) Suzuki, K.; Homma, Y.; Igarashi, Y.; Okumura, H.; Yano, H. Effect of Preparation Process of Microfibrillated Cellulose-Reinforced Polypropylene upon Dispersion and Mechanical Properties. *Cellulose* **2017**, *24* (9), 3789–3801. https://doi.org/10.1007/s10570-017-1355-1.

(103) Hietala, M.; Rollo, P.; Kekäläinen, K.; Oksman, K. Extrusion Processing of Green Biocomposites: Compounding, Fibrillation Efficiency, and Fiber Dispersion. *J. Appl. Polym. Sci.* **2014**, *131* (6), 4393–4404. https://doi.org/10.1002/app.39981.

(104) Cobut, A.; Sehaqui, H.; Berglund, L. A. Cellulose Nanocomposites by Melt Compounding of TEMPO-Treated Wood Fibers in Thermoplastic Starch Matrix. *BioResources* **2014**, *9* (2), 3276–3289. https://doi.org/10.15376/biores.9.2.3276-3289.

(105) Fourati, Y.; Magnin, A.; Putaux, J. L.; Boufi, S. One-Step Processing of Plasticized Starch/Cellulose Nanofibrils Nanocomposites via Twin-Screw Extrusion of Starch and Cellulose Fibers. *Carbohydr. Polym.* **2020**, *229*. https://doi.org/10.1016/j.carbpol.2019.115554.

(106) Gorrasi, G.; Sorrentino, A. Mechanical Milling as a Technology to Produce Structural and Functional Bio-Nanocomposites. *Green Chem.* **2015**, *17* (5), 2610–2625. https://doi.org/10.1039/c5gc00029g.

(107) Piras, C. C.; Fernández-Prieto, S.; De Borggraeve, W. M. Ball Milling: A Green Technology for the Preparation and Functionalisation of Nanocellulose Derivatives. *Nanoscale Adv.* **2019**, *1* (3), 937–947.

(108) Varin, R. A.; Czujko, T.; Wronski, Z. S. Nanomaterials for Solid State Hydrogen Storage. In *Fuel Cells and Hydrogen Energy*; Springer: Boston, MA, 2009. https://doi.org/https://doi.org/10.1007/978-0-387-77712-2.

(109) Zhang, Y. X.; Zhang, T. L.; Kuga, S.; Wu, M.; Huang, Y. Polarities-Induced Weakening of Molecular Interaction and Formation of Nanocellulose with Different Dimensions. *Acs Sustain. Chem. Eng.* **2020**, *8* (25), 9277–9290. https://doi.org/10.1021/acssuschemeng.0c00464.

(110) Ago, M.; Endo, T.; Okajima, K. Effect of Solvent on Morphological and Structural Change of Cellulose under Ball-Milling. *Polym. J.* **2007**, *39* (5), 435–441. https://doi.org/DOI 10.1295/polymj.PJ2006096.

(111) Huang, P.; Wu, M.; Kuga, S.; Huang, Y. Aqueous Pretreatment for Reactive Ball Milling of Cellulose. *Cellulose* **2013**, *20* (4), 2175–2178. https://doi.org/10.1007/s10570-013-9940-4.

(112) Huang, P.; Zhao, Y.; Kuga, S.; Wu, M.; Huang, Y. A Versatile Method for Producing Functionalized Cellulose Nanofibers and Their Application. *Nanoscale* **2016**, *8* (6), 3753–3759. https://doi.org/10.1039/c5nr08179c.

(113) Mattonai, M.; Pawcenis, D.; Seppia, S. d.; Łojewska, J.; Ribechini, E. Effect of Ball-Milling on Crystallinity Index, Degree of Polymerization and Thermal Stability of Cellulose. *Bioresour. Technol.* **2018**, *270*, 270–277. https://doi.org/https://doi.org/10.1016/j.biortech.2018.09.029.

(114) Nakagaito, A. N.; Ikenaga, K.; Takagi, H. Cellulose Nanofiber Extraction from Grass by a Modified Kitchen Blender. *Mod. Phys. Lett. B* **2015**, *29* (6–7), 1540039. https://doi.org/Artn 1540039 10.1142/S0217984915400394.

(115) Yan, J.; Hu, J.; Yang, R.; Zhang, Z.; Zhao, W. Innovative Nanofibrillated Cellulose from Rice Straw as Dietary Fiber for Enhanced Health Benefits Prepared by a Green and Scale Production Method. *ACS Sustain. Chem. Eng.* **2018**, *6* (3), 3481–3492. https://doi.org/10.1021/acssuschemeng.7b03765.

(116) Tuzzin, G.; Godinho, M.; Dettmer, A.; Zattera, A. J. Nanofibrillated Cellulose from Tobacco Industry Wastes. *Carbohydr. Polym.* **2016**, *148*, 69–77. https://doi.org/10.1016/j.carbpol.2016.04.045.

(117) Solikhin, A.; Hadi, Y. S.; Massijaya, M. Y.; Nikmatin, S. Production of Microfibrillated Cellulose by Novel Continuous Steam Explosion Assisted Chemo-Mechanical Methods and Its Characterizations. *Waste and Biomass Valorization* **2019**, *10* (2), 275–286. https://doi.org/10.1007/s12649-017-0066-z.

(118) Oishi, Y.; Nakaya, M.; Matsui, E.; Hotta, A. Structural and Mechanical Properties of Cellulose Composites Made of Isolated Cellulose Nanofibers and Poly (Vinyl Alcohol). *Compos. Part A Appl. Sci. Manuf.* **2015**, *73*, 72–79.

(119) Huan, S.; Yokota, S.; Bai, L.; Ago, M.; Borghei, M.; Kondo, T.; Rojas, O. J. Formulation and Composition Effects in Phase Transitions of Emulsions Costabilized by Cellulose Nanofibrils and an Ionic Surfactant. *Biomacromolecules* **2017**, *18* (12), 4393–4404. https://doi.org/https://doi.org/10.1021/acs.biomac.7b01452.

(120) Yokota, S.; Kamada, K.; Sugiyama, A.; Kondo, T. Pickering Emulsion Stabilization by Using Amphiphilic Cellulose Nanofibrils Prepared by Aqueous Counter Collision. *Carbohydr. Polym.* **2019**, *226*, 115293.

(121) Chen, W.; Yu, H.; Liu, Y.; Chen, P.; Zhang, M.; Hai, Y. Individualization of Cellulose Nanofibers from Wood Using High-Intensity Ultrasonication Combined with Chemical Pretreatments. *Carbohydr. Polym.* **2011**, *83* (4), 1804–1811.

(122) Wang, S.; Cheng, Q. A Novel Process to Isolate Fibrils from Cellulose Fibers by High-Intensity Ultrasonication, Part 1: Process Optimization. *J. Appl. Polym. Sci.* **2009**, *113* (2), 1270–1275. https://doi.org/10.1002/app.30072.

(123) Aimin, T.; Hongwei, Z.; Gang, C.; Guohui, X.; Wenzhi, L. Influence of Ultrasound Treatment on Accessibility and Regioselective Oxidation Reactivity of Cellulose. *Ultrason. Sonochem.* **2005**, *12* (6), 467–472. https://doi.org/10.1016/j.ultsonch.2004.07.003.

(124) Gibril, M.; Tesfaye, T.; Sithole, B.; Lekha, P.; Ramjugernath, D. Optimisation and Enhancement of Crystalline Nanocellulose Production by Ultrasonic Pretreatment of Dissolving Wood Pulp Fibres. *Cellul. Chem. Technol.* **2018**, *52*, 9–10.

(125) Saito, T.; Hirota, M.; Tamura, N.; Kimura, S.; Fukuzumi, H.; Heux, L.; Isogai, A. Individualization of Nano-Sized Plant Cellulose Fibrils by Direct Surface Carboxylation Using TEMPO Catalyst under Neutral Conditions. *Biomacromolecules* **2009**, *10* (7), 1992–1996.

(126) Chakraborty, A.; Sain, M.; Kortschot, M. Cellulose Microfibrils: A Novel Method of Preparation Using High Shear Refining and Cryocrushing. *Holzforschung* **2005**, *59* (1), 102–107. https://doi.org/10.1515/HF.2005.016.

(127) Wang, B.; Sain, M.; Oksman, K. Study of Structural Morphology of Hemp Fiber from the Micro to the Nanoscale. *Appl. Compos. Mater.* **2007**, *14* (2), 89–103. https://doi.org/10.1007/s10443-006-9032-9.

(128) Abe, K. Novel Fabrication of High-Modulus Cellulose-Based Films by Nanofibrillation under Alkaline Conditions. *Carbohydr. Polym.* **2019**, *205*, 488–491. https://doi.org/10.1016/j.carbpol.2018.10.069.

(129) Taheri, H.; Hietala, M.; Suopajärvi, T.; Liimatainen, H.; Oksman, K. One-Step Twin-Screw Extrusion Process to Fibrillate Deep Eutectic Solvent-Treated Wood to Be Used in Wood Fiber-Polypropylene Composites. *ACS Sustain. Chem. Eng.* **2021**, *9* (2), 883–893. https://doi.org/10.1021/acssuschemeng.0c07750.

(130) Wu, M.; Huang, Y.; Zhang, T.; Kuga, S.; Ewulonu, C. M. Cellulose Nanofibril-Based Flame Retardant and Its Application to Paper. *ACS Sustain. Chem. Eng.* **2020**, *8* (27), 10222–10229. https://doi.org/10.1021/acssuschemeng.0c02892.

(131) Wei, Y.; Zhou, M.; Yao, A.; Zhu, P. Preparation of Microfibrillated Cellulose from Wood Pulp through Carbamate Modification and Colloid Milling. *Appl. Sci.* **2020**, *10* (6). https://doi.org/10.3390/app10061977.

(132) Deng, S.; Ma, J.; Guo, Y.; Chen, F.; Fu, Q. One-Step Modification and Nanofibrillation of Microfibrillated Cellulose for Simultaneously Reinforcing and Toughening of Poly(ε-Caprolactone). *Compos. Sci. Technol.* **2018**, *157*, 168–177. https://doi.org/10.1016/j.compscitech.2017.10.029.

(133) Zhang, F.; Ren, H.; Dou, J.; Tong, G.; Deng, Y. Cellulose Nanofibril Based-Aerogel Microreactors: A High Efficiency and Easy Recoverable W/O/W Membrane Separation System. *Sci. Rep.* **2017**, *7*, 1–7. https://doi.org/10.1038/srep40096.

(134) Fang, Z.; Hou, G.; Chen, C.; Hu, L. Nanocellulose-Based Films and Their Emerging Applications. *Curr. Opin. Solid State Mater. Sci.* **2019**, *23* (4), 100764. https://doi.org/10.1016/j.cossms.2019.07.003.

(135) De France, K. J.; Hoare, T.; Cranston, E. D. Review of Hydrogels and Aerogels Containing Nanocellulose. *Chem. Mater.* **2017**, *29* (11), 4609–4631. https://doi.org/10.1021/acs.chemmater.7b00531.

(136) Tsuboi, K.; Yokota, S.; Kondo, T. Difference between Bamboo- and Wood-Derived Cellulose Nanofibers Prepared by the Aqueous Counter Collision Method. *Nord. Pulp Pap. Res. J.* **2014**, *29* (1), 69–76. https://doi.org/10.3183/npprj-2014-29-01-p069-076.

GRAPHIC ABSTRACT