

Effects of mechanical fibrillation time by disk grinding on the properties of cellulose nanofibrils

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ABSTRACT: Cellulose nanofibrils (CNF) were successfully produced from a bleach kraft eucalyptus pulp by a supermasscolloider. Effects of grinding time on structure and properties of CNF and the corresponding CNF films were investigated. Grinding time was important to increase the optical transparency of CNF suspensions. The degree of polymerization (DP) and crystallinity index (CrI) of CNF decreased linearly with the increase in CNF suspension transparency. This suggests optical transparency of a CNF suspension can be used to characterize the degree of fibrillation. Specific tensile strength and Young's modulus of the CNF films made of CNF suspension with only 0.5 h grinding were increased approximately 30% and 200%, respectively, compared with conventional handsheets prepared by valley beating to 300 Canadian Standard Freeness (CSF). Energy input was only 1.38 kWh/kg for 0.5 h grinding. Grinding beyond 0.5 h produced negligible improvement in specific tensile and specific modulus. Opacity of CNF films decreased rapidly during the first 1.5 h of fibrillation and then plateaued.

Application: Disk milling time affects the morphology of cellulose nanofibrils as well as the optical and mechanical properties of film made of the resultant fibrils.

Cellulose nanomaterials, such as cellulose nanofibrils (CNF) derived from renewable lignocelluloses, have attracted great interest recently. Lignocelluloses are available in nature in great abundance. Cellulose nanofibrils have been used for producing a range of functional materials including films, membranes, aerogels, scaffolds, and hybrid composites [1-4] and have the potential to replace a variety of materials derived from nonrenewable petroleum. Mechanical fibrillation remains the most common approach to produce CNF from lignocelluloses. Microgrinding has the potential for large-scale CNF production and has been widely used [5-9]. Microgrinding leads to a series of dramatic changes in fibers, such as internal fibrillation, external fibrillation, and fiber shortening. Continued fibrillation resulted in fragmentation of cell wall and produced micro- and nanofibrils [10].

The dominant factors that dictate nanocellulose material strength are the fibril length and fiber bonding. The orientation of bonds between nanoparticles is an important factor in tuning the Young's modulus [11]. Increased grinding often results in increased bonding as a result of the fine materials produced that substantially increase fibril surface area. On the other hand, increased grinding time can also result in short fibrils simply because of mechanical actions. There is a trade-off between increasing bonding and reducing fibril length with extended grinding; in other words, an optimal grinding time exists for producing CNF for polymer reinforcement.

Unfortunately, such an understanding has not been well documented. The objective of the present study is to investigate the effects of mechanical fibrillation time on the properties of resultant CNF films.

MATERIAL AND METHODS

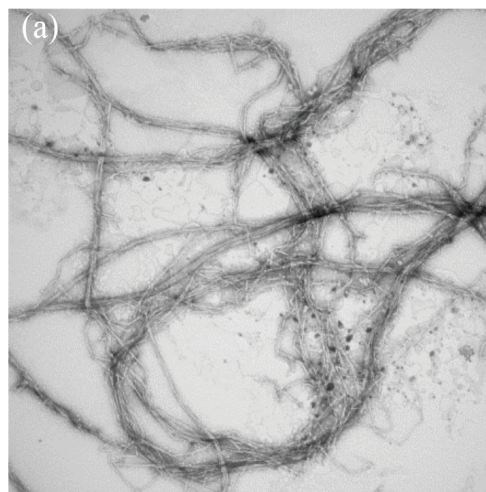
Dry lap of a bleached kraft eucalyptus pulp from Fibria (Ara-cruz, Brazil) was the same pulp used in previous studies [10,12-14], with major chemical composition of $78.1\% \pm 1.0\%$ glucan, $15.3\% \pm 0.6\%$ xylan, and $0.7\% \pm 0.1\%$ Klason lignin. The dry lap was soaked in distilled water for 24 h before disintegration in a laboratory disintegrator.

Mechanical fibrillation

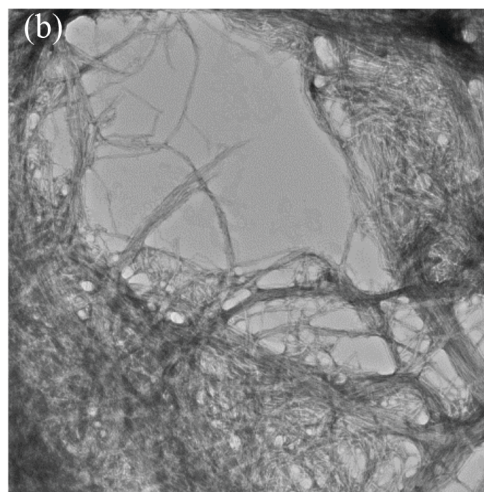
For the experiment, 140 g of o.d. bleached kraft eucalyptus pulp was fibrillated at 2 wt% consistency using a supermass-colloider (model MKZA6-2, Masuko Sangyo; Kawaguchi, Japan) at 1500 rpm as described previously [10]. Approximately 130 g was beaten in a Valley beater (Valley Laboratory Equipment, Voith; Appleton, WI, USA) to approximately 300 mL Canadian Standard Freeness (CSF) as a control sample.

Fractionation of CNF by centrifuge

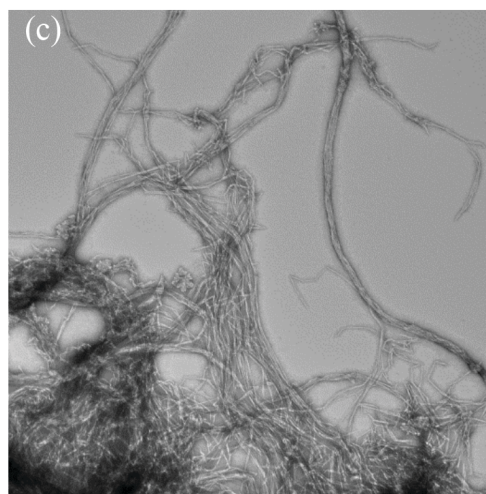
An attempt was made to fractionate large networked CNF from small ones by centrifuge. Cellulose nanofibrils solution from 11 h of fibrillation was diluted to 0.2 wt% and continuously stirred for 1 h and then centrifuged at 1000 rpm for 15



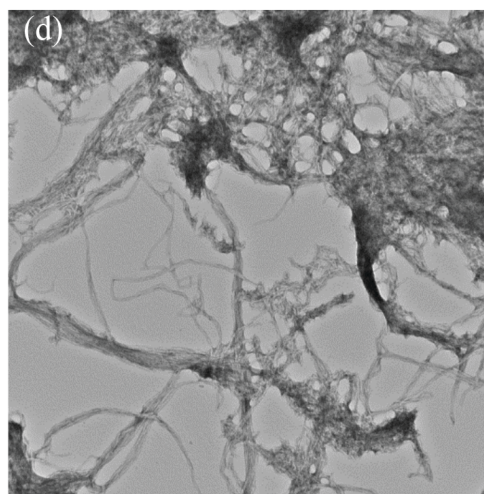
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EM Lab (H-7600 Bottom Mount)



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EM Lab (7650 Bottom Mount)

1. Transmission electron microscopy images of cellulose nanofibrils (CNF) samples at different fibrillation times: (a) 0.5 h, (b) 3 h, (c) 7 h, and (d) 11 h; scale bar = 500 nm.

min in a Sorvall Superspeed RC2-B 5.75-in. rotator (Ivan Sorvall; Norwalk, CT, USA). The supernatant liquid was carefully removed with a pipette from the precipitation layer.

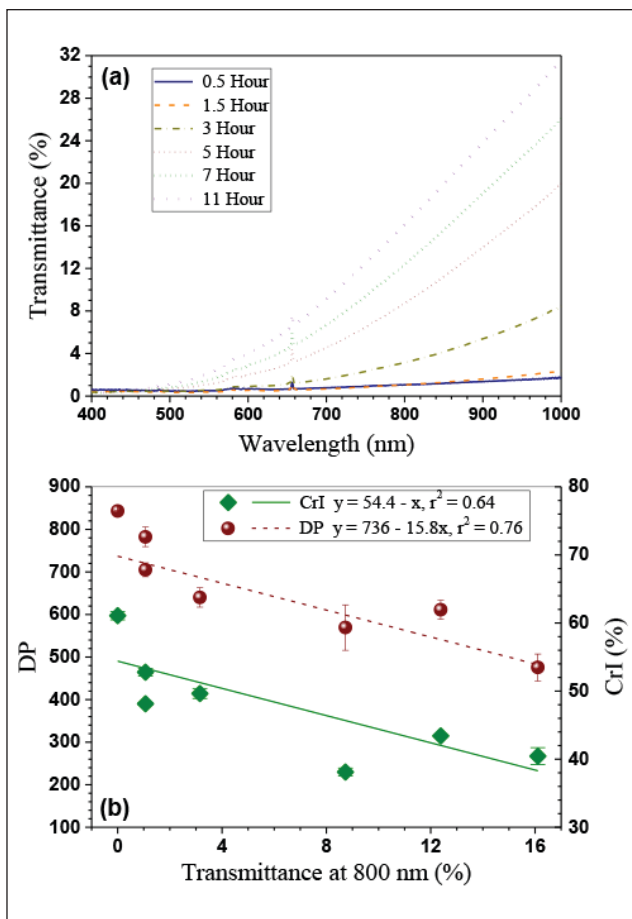
Preparation and testing of CNF film

Solutions of CNF were diluted to 0.1 wt% and mixed for 4 h using a magnetic stir. A 9-in. vacuum filtration system with a 0.45- μ m Durapore membrane (Millipore; Billerica, MA, USA) was used to prepare CNF film. Wet films together with blotting paper were pressed at 206 and 345 kPa for 3 min and then dried in a copper dry ring. Film opacity, basis weight, and thickness were measured according to TAPPI T519 om-06 “Diffuse opacity of paper (d/0 paper backing),” T410 om-08

“Grammage of paper and paperboard (weight per unit area),” and T411 om-10 “Thickness (caliper) of paper, paperboard, and combined board,” respectively. Strain-stress testing was determined using an Instron 5865 Advanced Mechanical Testing System (Instron; Norwood, MA, USA). Conventional hand-sheets as control were also made using the Valley-beaten pulp (control sample) and tested using the same procedure.

Analyses

CNF samples were imaged using a Hitachi H7650 microscope (Hitachi; Tokyo, Japan) at 80 kV with a 2k x 2k charge coupled device camera under ultrahigh vacuum conditions. Transmittance of CNF suspensions were measured by a Model 8453UV-



2. (a) Variation of spectral transmittance of CNF suspensions at 0.1% consistency with grinding time and (b) correlation of CNF degree of polymerization (DP) and crystallinity (CrI) with optical transmittance of CNF suspensions at 0.1% consistency at 800 nm.

Vis spectrophotometer (Agilent Technologies; Santa Clara, CA, USA) with a quartz cuvette (optical path length of 10 mm) at 0.1 wt% consistency.

Degree of polymerization (DP) of CNF samples was calculated from their viscosities determined according to TAPPI T230 om-99 "Viscosity of pulp (capillary viscometer method)." Crystallinity indices (CrI) of CNF samples were measured by a Bruker RFS 1000 Raman Spectrometer (Bruker Instruments; Billerica, MA, USA). The method is based upon the band intensity ratio 380/1096 obtained from the FT-Raman spectrum of the sample [15].

RESULTS AND DISCUSSION

Morphological properties of CNF

The morphologies of CNF samples after grinding for 0.5, 3, 7, and 11 h were revealed by transmission electron microscopy images (**Fig. 1**). Complex CNF networks together with individualized fibrils were observed. Diameters of the smallest nanofibrils were in the range of 3–5 nm. It appears that the diameters of the fibrils decreased with grinding time in general. Highly kinked, twisted, and entangled networks with



3. Visual images of CNF films made of CNF-0.5 h (right) and CNF-11 h (left). Diameter and thickness of the films were approximately 15 cm and 30 μ m, respectively.

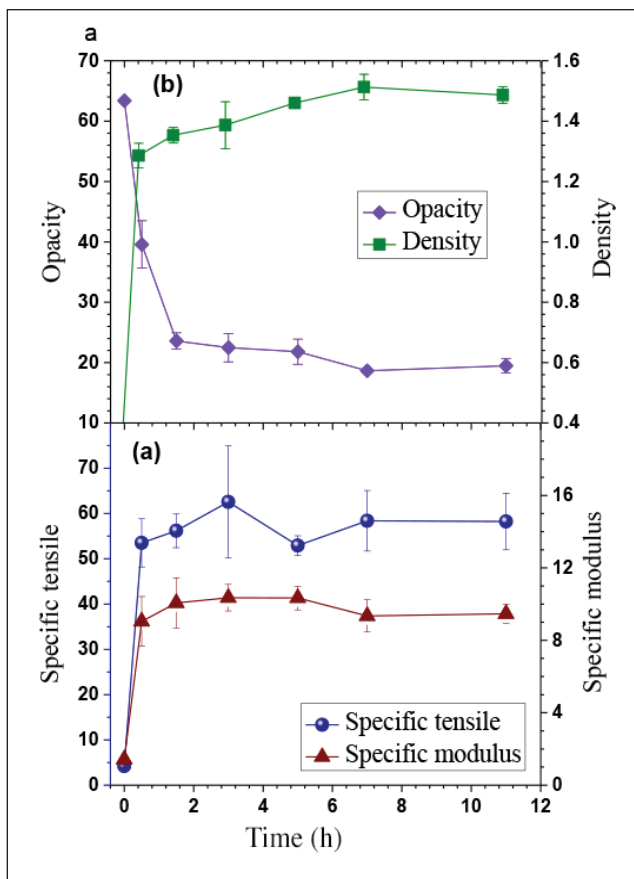
fibril diameters ranging from tens of nanometers to microns were the major structures of CNF produced by grinder [10]. It was difficult to achieve uniform individualized nanofibrils using grinding in the time range studied.

Transparency of CNF suspension, DP, and degree of crystallinity of CNF

Light transmittance of CNF suspensions was evaluated at wavelengths between 400 nm and 1000 nm as an indirect estimate of the size of the fibrils and fibril networks (**Fig. 2**). As expected, CNF at 0.5 h and 1.5 h of fibrillation gave the lowest transmittance, which was barely above zero, while CNF fibrillated for 3 h exhibited slightly higher light transmittance at 400–1000 nm. Transparency of CNF increased steadily with fibrillation time, especially in the infrared region (>700 nm). The highest light transmittance was recorded with 11-h grinding. Maximal transmittance at 1000 nm was at 26.0% for CNF at 7 h and 31.5% for CNF at 11 h. In addition, DP and CrI were good indicators for degree of fibrillation and were plotted against light transmittance at 800 nm (**Fig. 2**). Overall reduction in DP and CrI was in the order of 7%–43% and 13%–37%, respectively, after 11-h fibrillation. Both DP and CrI decreased linearly with light transmittance in a range of wavelengths. Degree of polymerization was reduced from 843 to 475, while CrI decreased from 61 to 40, suggesting that continuous mechanical force in disk grinding destroyed cellulose crystalline structure and shortened cellulose chain length.

Properties of CNF films

At least five CNF films were prepared from each sample. Visual appearance of the films demonstrated relatively good light transparency. The CNF film from 11-h fibrillation has higher transparency than the one from 0.5 h (**Fig. 3**). CNF film prepared by ultrafiltration with copper ring dry technique was flat with no wrinkles and was as foldable as conventional paper.



4. Optical and strength properties of CNF films as a function of fibrillation time: (a) film opacity and density, and (b) specific tensile strength and Young's modulus.

The opacity, density, specific tensile strength, and Young's modulus of CNF films made at different grinding times were measured (**Fig. 4**). Between 12 and 16 strips were used for testing mechanical strength. Opacity data agreed with the ultraviolet-visible transmittance measurements. The opacity of handsheets prepared with bleached kraft eucalyptus pulp was 63%. Opacity decreased rapidly to 20% in the first 1.5 h of nanofibrillation followed by very slow reduction. The opacity decreased only slightly, from 24% to 19%, with additional 9.5 h grinding. Film density increased abruptly to 1.3 g/cm³ in contrast to handsheets made from bleached kraft eucalyptus pulp without grinding. Density increased steadily and reached a maximum at 7 h with minimal change thereafter. The highest density of CNF films was approximately 1.51 g/cm³, close to the density of cellulose (1.59 g/cm³), indicating near complete removal of voids in the films [16]. The increased density improved the strength properties of CNF films; however, the increase in tensile strength is much more substantial than the increase in density. This can be observed from the increase in specific tensile stress of 309% after 1.5 h grinding over the control handsheet. Similar results were also reported from enzyme-treated CNF films [17] and nanofiller paper produced by grinding mixed office paper [18]. This suggests that the

main contribution to film tensile strength was by increased bonding resulting from the increased surface area facilitated by nanofibrillation. No significant difference was detected between CNF films prepared with 0.5 h grinding and 11 h grinding. This clearly indicates that grinding beyond 0.5 h is not beneficial for increasing film tensile strength, which is important to reduce energy consumption for nanofibrillation.

Previous studies indicated that DP and CrI strongly affect mechanical properties of the resultant cellulose materials [19,20]. However, the reductions in DP and CrI in this study did not cause deterioration in the strength or stiffness of CNF films, probably because of the relatively high DP level as compared to leveling-off DP [21].

Energy inputs for nanofibrillation by grinder were between 1.38 kW·h/kg and 30 kW·h/kg, while energy consumption was only approximately 0.4 kW·h/kg to beat the control pulp sample (300 mL CSF) using a Valley beater [10,22]. The 12- to 74-fold increases in energy consumption only resulted in 30% and 200% increases in specific tensile strength and Young's modulus, respectively. The low-intensity Valley beating produced mainly internal fibrillation of fiber, whereas high shear and friction energy intensity of nanofibrillation by disk milling caused both internal and external fibrillation [10,23]. Energy consumption was linearly proportional to grinding time using the supermasscolloider [6,10], suggesting the majority of the energy input was not efficiently used for fibrillated fibers.

CONCLUSIONS

The properties of films made of CNF produced from a bleached kraft eucalyptus pulp at different grinding times were evaluated. The opacity of the CNF films decreased rapidly within the first 1.5 h grinding and was proportional to the reductions in DP and CrI degree of polymerization and crystallinity. Specific tensile strength and Young's modulus increased by 30% and 200%, respectively, with just 0.5 h grinding with energy input of 1.38 kW·h/kg compared with those of the control handsheet prepared using a Valley-beaten pulp at 300 mL CSF. This energy consumption of 1.38 kW·h/kg is not expensive from a cost point of view but yields substantial improvement in strength properties. Further grinding beyond 0.5 h produced negligible benefits in terms of film opacity and mechanical properties. The results reported indicate that minimal grinding to the point of achieving gel formation through visual inspection is sufficient for producing high strength CNF films. **TJ**

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ABOUT THE AUTHORS

Cellulose nanomaterials have been identified with many unique mechanical and optical properties for a variety of applications. We specifically studied the diminishing effect of disk milling time on the properties of resultant cellulose nanofibrils (CNF), because energy cost is proportional to disk milling time.

The most difficult aspect of this work was characterizing the morphological properties of CNF because of its small physical dimensions. An interesting finding was that for the existing disk milling equipment, long milling time has limited effect on the properties of resultant CNF. Thus, mills can benefit from short milling time to produce microfibrils.

The next step is to evaluate dewatering properties when applying cellulose nanomaterials.



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