

Elucidation of Effectiveness of Dye Absorption as a Probe to Determine The Chemical Reactivity of Cellulose Nanofibrils

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Received on 17 July 2022, Accepted for publication on 30 January 2023

ABSTRACT

Cellulose nanofibrils (CNF) has earned substantial attention as a sustainable biopolymer due to environmental consciousness and the implementation of strict regulations for the remediation of single use plastics. However, the existing processing strategies rely on intensive mechanical grinding and quality of production is often measured by physical changes such as fines which completely overlooks chemical changes such as exposure of large numbers of hydroxyls which significantly compromises desirable properties. Therefore, we use dye absorption technique to measure the chemical reactivity of the CNF. The CNF was produced from bleached hardwood kraft pulp (BHK) with different extent of fibrillation by varying the cumulative mechanical energy and then acetylation and dye absorption were used as a tool to investigate its chemical reactivity. The degree of substitution (DS) of the CNF reached a highest value and subsequently, it decreased to lesser values though the CNF were produced using higher cumulative energies. The dye absorption by CNF samples also followed the similar trend like the DS value of the CNF samples. The dye absorption was affected by the hydration shell formed by the hard-to-remove (HR) water molecules and the self-aggregation of cellulose hydroxyls at higher fibrillation, which hindered accessibility of the dye molecules to absorption sites. Therefore, this technique could be used as a new useful probing tool to determine the nanocellulose reactivity and might be a potential physicochemical strategy to produce and chemically modify CNF in an efficient and sustainable way to optimize its performance for different applications.

Key words: Cellulose Nanofibrils, Dye Absorption, Hydration Shell, Hard-to-Remove (HR) Water, Self-aggregation

1. Introduction

Cellulose, being the world's most abundant natural polymer, have garnered significant importance in the recent past as a sustainable material due to its renewability, recyclability and biodegradability.[1–4] Thus, the cellulose nanofibrils (CNF) is emerging as a potential candidate for materials science since it possesses astounding non-scalable mechanical properties, chemical tenability, biocompatibility and biodegradability, and its use in paper and tissue products, composites, membranes, flexible electronics, hygiene products, hydrogel and aerogels and so on.[5–9] Nevertheless, CNF is relatively intransigent, stable, and cannot be easily chemically manipulated, which consequently lead the researchers to come up with numerous efforts to overcome their chemical stubbornness resulting in chemically modified CNF having increased functionality which would diversify the scope of its use.[10] The occurrence of –OH groups in CNF surface leads to self-aggregation by the formation of hydrogen bonds among themselves. This behavior greatly affects its reactivity towards chemistry which still is the grandest encounter to overcome during chemical modification to improve processability and

performance.[11] Furthermore, the ratio of crystalline-to-amorphous region of its structure increases with the increase in fibrillation extent and a larger quantity of cellulosic hydroxyl groups becomes available that interact with more water hydroxyls and form hydrogen bonds to produce more HR water around the hydroxyls in the system. These HR water molecules interact with more incoming water molecules and cause closer packing of the CNF chains making it unyielding toward chemical reactions.[11] This hydrophilic nature of CNF leads to its poor miscibility in nonpolar solvents, weak interfacial compatibility in the hydrophobic polymer matrices and extensively limits its applications.[12] However, different chemical treatments could be carried out to balance the hydrophilic-hydrophobic nature of CNF, which resulted in improved interfacial properties and dispersibility in both polar and non-polar solvents and hydrophobic polymer matrices, without destroying the original morphological integrity of CNF by avoiding polymorphic conversion, and preserve pristine crystalline structure.[13] It has been reported that hardwood kraft pulp shows increase in degree of substitution (DS) with the increase of cellulose hydroxyls and after reaching a maximum value the DS

value reduced even though the fibrillation intensity was increased to produce CNF with even higher number hydroxyls.[11]

Herein, we used bleached hardwood kraft pulp (BHK) to produce cellulose nanofibrils (CNF) at varying cumulative energy consumption. We used acetylation to chemically modify the CNF samples and measured DS to validate our previous findings. We also used absorption techniques of different types of dyes, such as, congo red (CR) and methylene blue (MB), as a new probe to measure the reactivity of different CNF samples which would additionally support our previous findings. We have observed that the CNF produced from new batch of BHK showed similar DS trend like before, i.e., the cumulative energy supply used to induce higher fibrillation to CNF samples reduced the efficiency of the CNF to interact with chemistry after attaining the highest value. The dye absorption also showed that the absorption value dropped after reaching a maximum. Therefore, CNF having optimum chemical reactivity can be produced using moderate mechanical energy and the dye absorption technique can be used as simple probe to evaluate the chemical reactivity of the nanofibrils. The successful accomplishment of sustainable CNF modification by optimizing the use of chemicals is possible through manipulation of amorphous-crystalline part of CNF

and the water hydration shell around its structure. The modified CNF thus produced can be a green and ecofriendly alternative to petroleum-based products in several applications.

2. Experimental

2.1. Materials

Bleached Hardwood Kraft (BHK) pulp was used to produce cellulose nanofibrils (CNF). Acetic acid (99%), acetic anhydride, sodium hydroxide (1N), hydrochloric acid (1N), sulfuric acid (1N), dimethyl sulfoxide, congo red, methylene blue and phenolphthalein were procured from Fischer Scientific. All the chemicals were used in the pristine form without further purification.

2.2. Methodology

CNF Preparation

Cellulose nanofibrils was produced from the BHK pulp slurry as shown in the Figure 1.[11,14] A slurry containing 3% of BHK pulp (wt%) was prepared by disintegrating the pulp using shear mixing for 15 minutes. The pulp slurry was fed into the Masuko Supermasscollider ultra-fine grinder. The revolution was kept at 2500 rpm and negative gap clearance was maintained between the two grinding stones as the slurry was passing through them. The CNF thus prepared were collected at different cumulative energies to get varying fibrillation level.

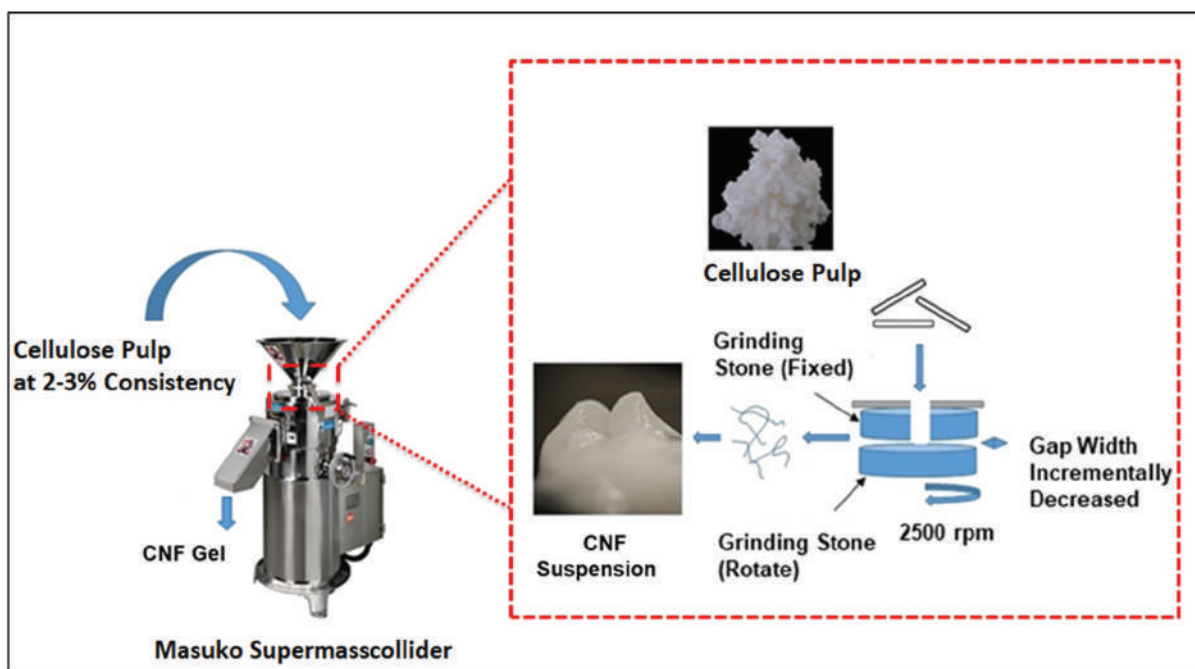


Fig. 1. CNF production using a Masuko Supermasscollider

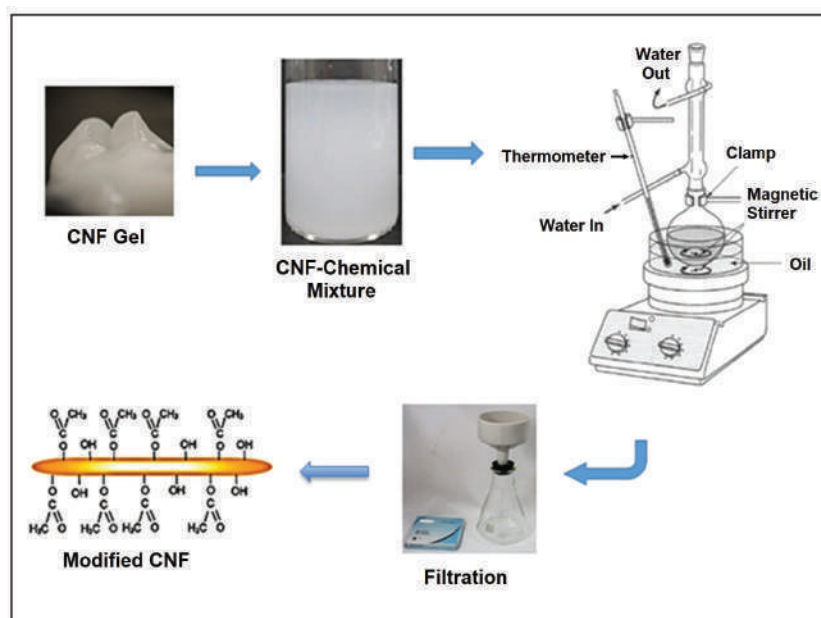


Fig. 2. Chemical modification (acetylation) of CNF

Chemical Modification of CNF

The chemical modification of CNF was carried out using acetic acid and acetic anhydride at mild conditions as shown in Figure 2.[11] CNF samples prepared at different cumulative energy were taken in such a way that each sample solution would contain 2 g of solid CNF. The water associated with the samples were calculated, and an excess (1000 mmol) of acetic anhydride relative to total water content, was added in each sample. Small amount of acetic acid (5-10 ml) was added to the CNF-acetic anhydride system for each of the reactions. The chemical reactions were conducted at ~ 80 °C for an hour. The temperature of the reaction system was maintained, and the reactants were constantly mixed throughout the time. A reflux condenser was used to supply cold water to the system so that volatiles could not leave the reaction sites due to evaporation. The reaction was stopped after one hour and the acetylated CNF was separated and collected using Whatman filter paper. The CNF thus collected was washed with water three times to remove the excess acetic anhydride and acetic acid from the sample that did not take part in the reaction.

2.3. Characterization

Fiber Quality Analysis (FQA)

Fiber length (lw), fine contents of the different CNF samples were measured by using a high-resolution fiber quality analyzer: HiRes FQA, OpTest Equipment Inc, Hawkesbury, ON, Canada. The samples were homogeneously dispersed in the water before the measurement was done and FQA was calibrated and used according to the TAPPI Standard guidelines.

Fourier Transform Infra-Red (FTIR) Spectroscopy

FTIR spectra of the acetylated and pristine CNF were taken

using a Perkin-Elmer Spectrum One FTIR spectroscope. The light source of the FTIR was brought into contact with the area to be analyzed for every reading. All the spectra were recorded between 4000 and 750 cm^{-1} with a resolution of 4 cm^{-1} with 16 scans per sample. The spectra were adjusted to the same baseline for accurate comparison of the data.[9]

Fiber Morphology

The morphology of CNF samples was carried out using FEI Verios 460L Field Emission Scanning Electron Microscopy SEM (FESEM). The samples were sputter-coated with AuPd coating for 10 minutes and images were taken at an accelerating voltage of 2 kV and 13 pA current.

Determination of Degree of Substitution (DS)

The DS value was measured after total dissolution of the acetylated cellulose in sodium hydroxide-dimethyl sulfoxide solution according to ISO 1597:1994. [12] The equation (1) was used to calculate the total acid value.

$$\text{CAV}(\%) = 6c(V1-V2)/m \quad (1);$$

Where, CAV is total acid, c is the concentration of sodium hydroxide, V1 is the volume of sodium hydroxide used in cellulose solution, V2 is the volume of sodium hydroxide used for blank, m is dry cellulose acetate weight, and 6 is the ration of $\text{CH}_3\text{COOH-NaOH}$ in the solution. The DS value was calculated from the total acid value using the equation 2 as shown below.[11]

$$\text{CAV} = 142.9 * x / (3.86 + x) * 100$$

$$x = 3.86 * \text{CAV} / (142.9 - \text{CAV}) \dots\dots\dots (2); \text{ where } x \text{ is DS}$$

Dye Absorption

Dye absorption experiments were performed with two different dyes to test the performance of the CNF samples. Samples having 0.1 g solid CNF were added to 50 mL of methylene blue and congo red with an initial concentration of 24 ppm and 20 ppm respectively. The system was mixed at 150 rpm on stirrer plate and observed for 20 mins, after which the CNF samples were separated from dye solution using centrifugation at 5000 rpm for 20 mins. The change in the concentration of both the dyes was assessed by UV spectrophotometer (Genesys 10S.; Methylene blue: 665 nm; Congo red: 343 nm).

Hard to Remove Water Measurement

The thermogravimetric analysis (TGA) technique was used to measure the Hard to remove (HR) water around the CNF samples.[15] The samples were taken in platinum pans and the temperature was then ramped from 30 °C to 110 °C at a rate of 10 °C/min. When the temperature reached to 110 °C isothermal drying was carried out for 15 minutes. The hard-to-remove water was determined by dividing the weight (g) of moisture content at the falling rate zone and weight (g) of CNF samples.

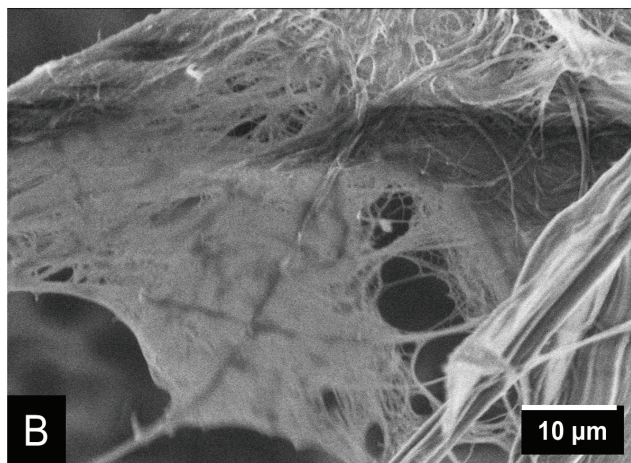
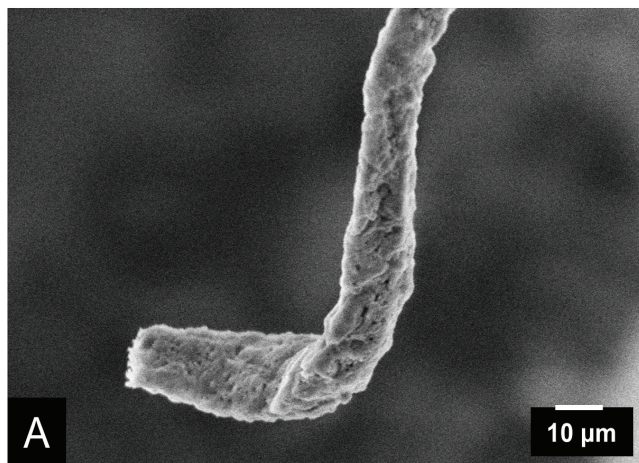
3. Results and discussions

The physical properties of the CNF produced at different energy consumption were investigated and are represented in Table 1.

The above Table 1 shows that fines percentage increased with the increase energy supply to produce nanofibrils with greater fibrillation which consequently increased the associated available surface area having more cellulosic hydroxyls for chemical reaction. The shear and frictional forces caused inner delamination of the fiber resulting in cellulose nanofibrils having greater level of fibrillation which was also clearly seen in the SEM images as depicted in Figure 3.[16] The SEM images supports the fact that cellulose fibers changed from macro to nano size with the supply of cumulative mechanical energy, and CNF samples with different extent of fibrillation were prepared by changing the mechanical energy supply. This relation between fines content and extent of fibrillation of CNF with increased energy has already been studied and established before.[11]

Table 1: Cumulative Energy supplied to generate of CNF having different fibrillation extent

Name of the Sample	Total Energy (kWh/Tonne)	Solid Percentage (%)	Fines (%)
CNF_0CE (Cellulose)	0	3.0	38.1
CNF_1CE	970	2.9	47.5
CNF_2CE	2160	2.7	83.0
CNF_3CE	3050	2.4	89.1
CNF_4CE	3980	2.1	93.2
CNF_5CE	4910	1.9	95.0



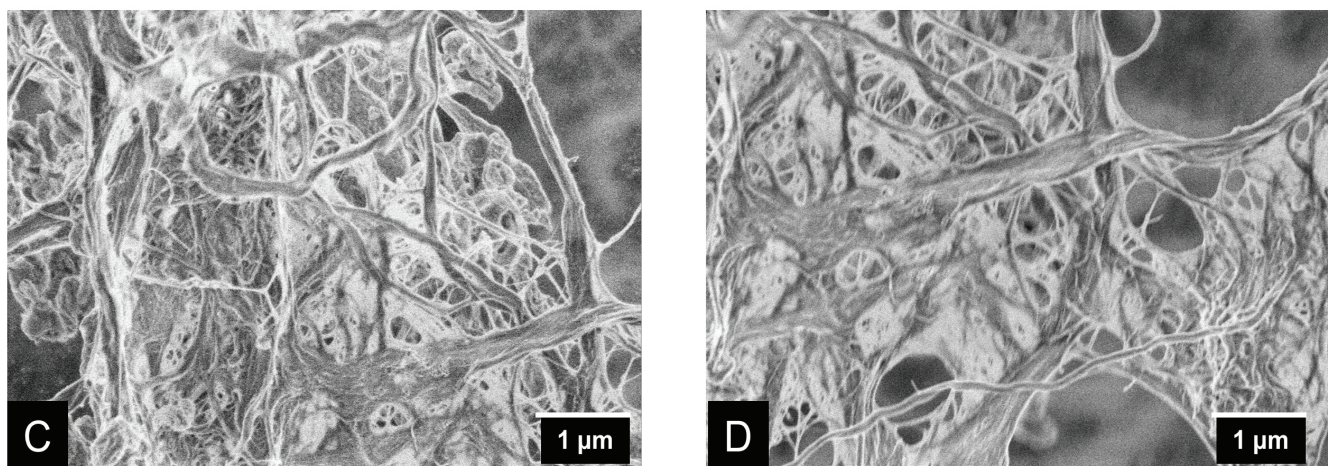


Fig. 3. Surface morphology of A) cellulose fiber before fibrillation (0 kWh), B) initial stage of fibrillation (CNF_1CE) at ~1K kWh, C) CNF_3CE at ~3K kWh, and D) CNF_5CE having greater fibrillation at increased energy supply (~5K kWh)

To investigate the reactivity of the CNF samples produced, acetylation reaction was done following the method as described in the experimental section. The accomplishment of the chemical modification was verified by doing FTIR of the pristine and acetylated samples to observe the presence of the acetyl group in the CNF as represented in Figure 4. The appearance of characteristic peak of carbonyl ($>C=O$) stretching at $\sim 1750\text{ cm}^{-1}$ confirms the successful acetylation of nanofibrils. The peaks at 1362 and 1240 cm^{-1} also appeared which represents methyl in-plane bending and C–O stretching vibration mode, respectively, and are distinctive signatures of the acetyl functional group.[11] This result is quite similar to that of our previous findings.[11]

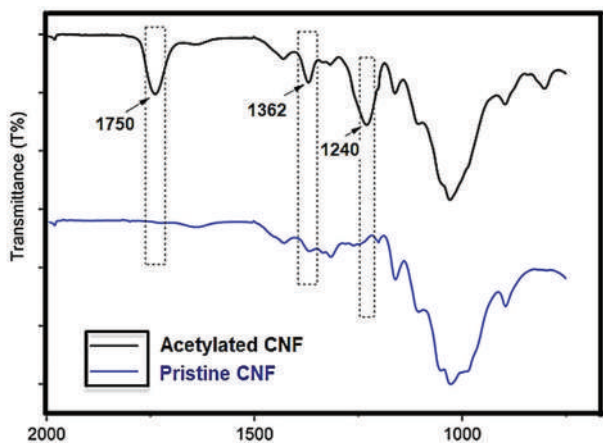


Fig. 4. FTIR spectra of pristine and acetylated CNF samples.

The chemical reactivity of the produced CNF samples was investigated by measuring the degree of substitution (DS) value for all the samples as shown in Figure 5A. The DS was the lowest for the cellulose samples before fibrillation. The DS improved for CNF_1CE and CNF_2CE as the fibrillation increased with the energy supply and reached the highest value for CNF_3CE when the total mechanical energy supply was $\sim 3000\text{ kWh/Tonne}$. The further fibrillation of

CNF, i.e., energy supply resulted in decreased in DS value for CNF_4CE and CNF_5CE. Initially the delamination of the cellulose fiber to nanofibrils increased the surface area and hence exposed more and more cellulose hydroxyls for reaction with acetyl group.

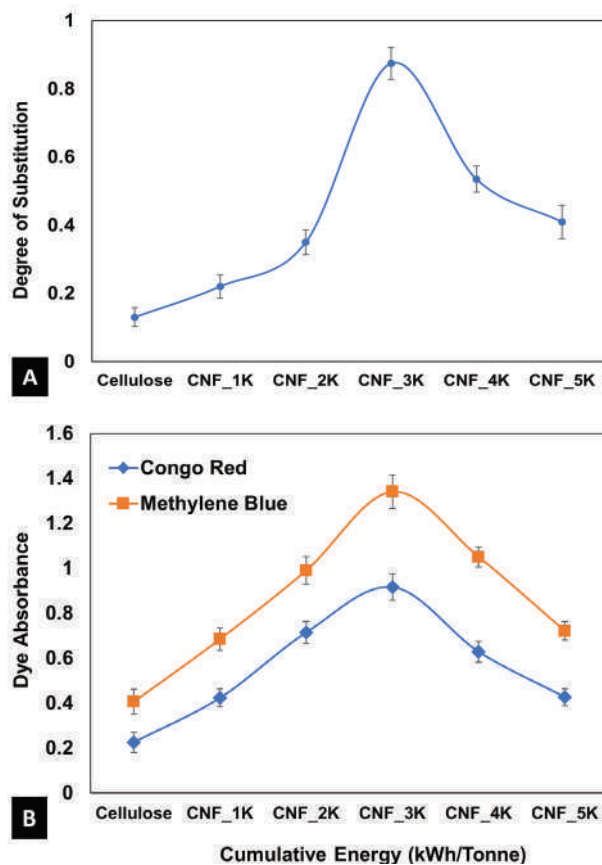


Fig. 5. A) Degree of substitution value and B) Dye absorption of CNF samples prepared at varying cumulative mechanical energies.

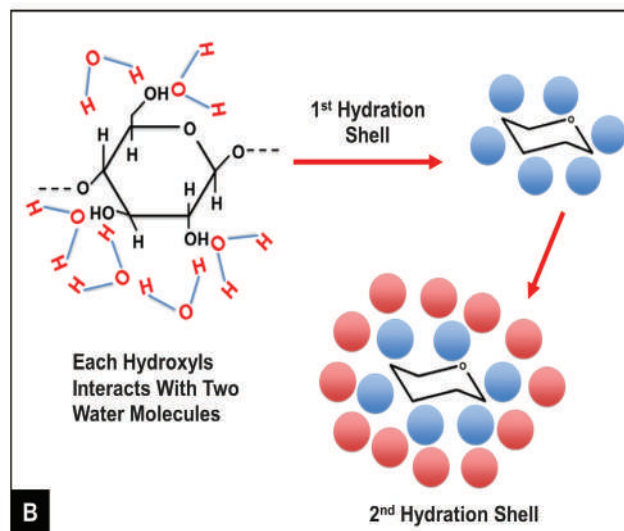
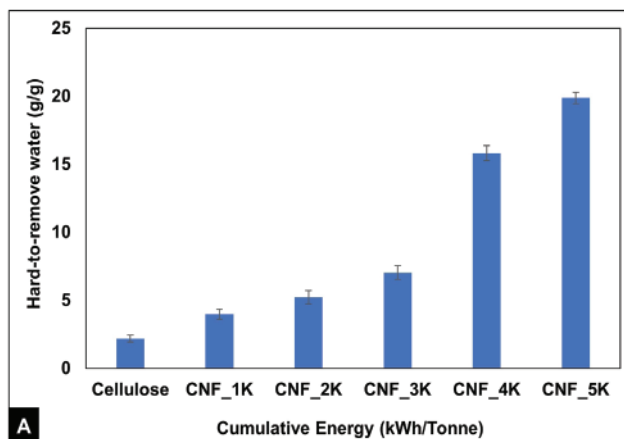
This higher accessibility of the acetyl group resulted in the highest DS for CNF_3CE with the increase of energy supply.

However, further delamination, i.e., fibrillation of CNF led to decreased DS value though it is expected otherwise. This phenomenon of CNF with respect to energy supply is not new and was already reported.[11] This finding shows that the reactivity of CNF increases with fibrillation, i.e., energy supply, to a certain level and then drops to lower value and validates our previous results.[11] To reassess our findings, we used two different dye, congo red (CR) and methylene blue (MB) and measured the absorption by the CNF samples having varying fibrillation level as represented in Figure 5B.

It could be observed that the dye absorption of CNF samples also followed the similar trend like the degree of substitutions of CNFs at different energy. The absorption in both cases increased initially with the energy supply and reached the maximum for CNF_3CE and then dropped to lower values though the energy supply was increased to get higher fibrillation. The methylene blue being cationic in nature, interacted more with the cellulose nanofibrils and therefore, showed higher absorption through more dye exhaustion from the solution. However, in both cases, acetylation and dye absorption phenomenon, similar trend could be observed which validates and supports our previous claims and we can state from these results that CNF reactivity first increases to reach a global maximum, followed by a drop to lower values with the increase in fibrillation through energy supply.

This drop in reactivity of CNF was because of presence of hard-to-remove (HR) water around the nanofibrils and self-aggregation of nanofibrils which was discussed already. [11] Here we also measured the HR water of the CNF samples to validate our hypothesis. The delamination of the CNF exposes the hydroxyls to the surrounding water and interact with the water by forming hydrogen bonds. Figure 6A clearly depicts that the HR water around the cellulose nanofibrils surface and its vicinity increased with increase in extent of fibrillation, and it was due to the greater cellulose-water interaction around the nanofibril surface. This water first saturates all the hydroxyl sites available and then water-water interaction kicks off. The hydration shell around the CNF is formed due to interaction of the each glycosyl ring with two water molecules. Each subsequent hydration shell is formed by two outer water molecules interacting with an inner water molecule and thus resulted in layers of hydration shell around the CNF as shown in the schematic in Figure 6B. So, in the first layer, one mole of glycosyl ring interact with six moles water molecules. Each subsequent water molecule interacts with two more water molecules, i.e., six moles of water interact with twelve moles of water in the next layer. The next of hydration shell is formed when 12 moles of water interact with 24 moles of water and this interaction goes on where each layer of water interact with double number of water in the next layer and results in hydration shells where

the water molecules are arranged as follows: (6)(12)(24)(48)(96)(192).[17] Therefore, the hydration shell around the cellulose chains exhibited greater stiffness since the water molecules around them were more closely packed through formation of hydrogen bonds and hence acts as a barricade to the diffusion of acetic anhydride and dye molecules to the reaction site and decreased the reactivity.[18] The self-aggregation tendency of the CNF also increased with the increase in fibrillation due to the creation of hydrogen bond between the CNF hydroxyls and therefore, CNF_5CE showed more aggregation tendency (Figure 6C). Thus, DS and dye absorption of CNF_4CE and CNF_5CE dropped to lower value due to an expanding water network which reduced the availability of surface area (Figure 6C). As a result, the reactivity of CNF diminished for CNF_5CE and CNF_4CE samples having greater fibrillation than that for CNF_3CE. The results validated that there is an optimal fibrillation level for CNF at which the reactivity of cellulose nanofibrils was maximum. Beyond this fibrillation level, the reactivity reduced to a lesser value albeit the degree of fibrillation is much greater.



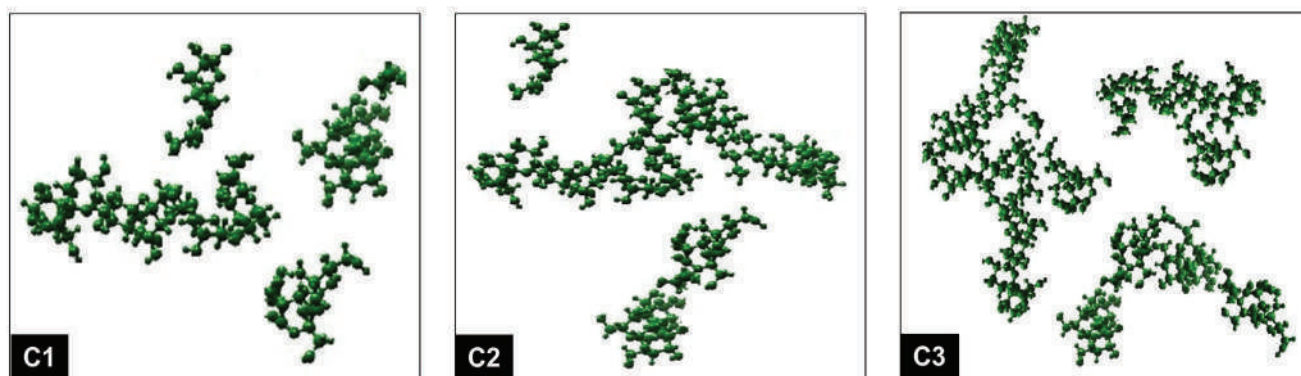


Fig. 6. A) Hard-to-remove water of various CNF samples, B) Graphical presentation of water hydration shell around the CNF, C) Self-aggregation behavior of CNF samples as a function of fibrillation extent (C1, C2 and C3 represents CNF produced at 2K, 3K and 5K kWh/Tonne of cumulative energy)

4. Conclusion

CNF samples having varying fibrillation levels were successfully produced by delamination using different cumulative mechanical energy supply. Acetylation reaction using acetic anhydride and acetic acid and dye absorption were used as a probe to investigate the reactivity of CNF samples prepared at different energy supplies. The DS values of the modified CNF gels were measured and compared to validate the consequence of the fibrillation level on the reaction dynamics. It was made sure that the fiber strength and native crystalline structure remains unaffected due to acetylation by keeping the DS below one where only the surface hydroxyls are substituted by the acetyl group. It was observed that there was an optimal fibrillation level beyond which the DS and dye absorption showed lower value. This reduction in DS and dye absorption at greater fibrillation level after reaching the highest value was due to the presence of larger amount of hard-to-remove water molecules around the nanocellulose and increased interaction of the hydroxyl groups which resulted in greater order of self-aggregation. The HR water molecules at and around the CNF surface behave as a barricade due to the dynamics of cellulose-water interactions, while the self-aggregation reduces the availability of the nanofibril hydroxyl groups; these two factors acting simultaneously lead to lower DS and dye absorption. Therefore, one understanding which is unswerving with the observations is that the fibrillation level regulates the cellulose-water dynamics and the extent of self-aggregation nanofibrils, which eventually regulates the reactivity of the CNF. In summary, this work has validated our previous findings by using surface acetylation as a probe for CNF made from different batch of bleached hardwood pulp. This work also used different types of dyes as a new probing tool to explore the dye absorption of CNF samples to determine the nanocellulose reactivity and could be a potential sustainable approach for efficient preparation and chemical alteration of CNF having optimum performance for numerous uses.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors gratefully acknowledge funding support from Ministry of Science and Technology (Project ID: SRG-222388) while carrying out the work partially in the Department of Applied Chemistry and Chemical Engineering, University of Dhaka. The work was also partially carried out at North Carolina State University in the Department of Forest Biomaterials and in the Department of Biological and Agricultural Engineering. This work was performed in part at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure.

References

1. M. Kropat, M. Liao, H. Park, K.S. Salem, S. Johnson, D.S. Argyropoulos, "A Perspective of Lignin Processing and Utilization Technologies for Composites and Plastics with Emphasis on Technical and Market Trends," *BioResources*, vol. 16, pp. 2084, 2021.
2. S. Agate, P. Tyagi, V. Naithani, L. Lucia, L. Pal, "Innovating Generation of Nanocellulose from Industrial Hemp by Dual Asymmetric Centrifugation," *ACS Sustainable Chemistry and Engineering*, vol. 8, no. 4, pp. 1850–1858, 2020.
3. P. Tyagi, L.A. Lucia, M.A. Hubbe, L. Pal, "Nanocellulose-based multilayer barrier coatings for gas, oil, and grease resistance," *Carbohydrate Polymers*, vol. 206, pp. 281–288, 2019.
4. M. Debnath, K.S. Salem, V. Naithani, E. Musten, M.A. Hubbe, L. Pal, "Soft mechanical treatments of recycled fibers using

- a high-shear homogenizer for tissue and hygiene products,” *Cellulose*, vol. 28, no. 12, pp. 7981–7994, 2021.
5. Y. Habibi, A.-L. Goffin, N. Schiltz, E. Duquesne, P. Dubois, A. Dufresne, “Bionanocomposites based on poly(ϵ -caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization,” *Journal of Materials Chemistry*, vol. 18, no. 41, pp. 5002–5010, 2008.
 6. T. Li, C. Chen, A.H. Brozena, J.Y. Zhu, L. Xu, C. Driemeier, J. Dai, O.J. Rojas, A. Isogai, L. Wågberg, L. Hu, “Developing fibrillated cellulose as a sustainable technological material,” *Nature*, vol. 590, no. 7844, pp. 47–56, 2021.
 7. P. Tyagi, K.S. Salem, M.A. Hubbe, L. Pal, “Advances in barrier coatings and film technologies for achieving sustainable packaging of food products – A review,” *Trends in Food Science & Technology*, vol. 115, pp. 461–485, 2021.
 8. X. Sun, S. Agate, K.S. Salem, L. Lucia, L. Pal, “Hydrogel-Based Sensor Networks: Compositions, Properties, and Applications—A Review,” *ACS Applied Bio Materials*, vol. 4, no. 1, pp. 140–162, 2020.
 9. K.S. Salem, V. Naithani, H. Jameel, L.A. Lucia, L. Pal, “Lignocellulosic Fibers from Renewable Resources Using Green Chemistry for a Circular Economy,” *Global Challenges*, vol. 5, no. 2, pp. 202000065, 2020.
 10. S.S. Ahankari, A.R. Subhedar, S.S. Bhadauria, A. Dufresne, “Nanocellulose in food packaging: A review,” *Carbohydrate Polymers*, vol. 255, pp. 117479, 2021.
 11. K.S. Salem, H.R. Starkey, L. Pal, L. Lucia, H. Jameel, “The Topochemistry of Cellulose Nanofibrils as a Function of Mechanical Generation Energy,” *ACS Sustainable Chemistry and Engineering*, vol. 8, no. 3, pp. 1471–1478, 2020.
 12. K.S. Salem, V. Naithani, H. Jameel, L. Lucia, L. Pal, “A systematic examination of the dynamics of water-cellulose interactions on capillary force-induced fiber collapse,” *Carbohydrate Polymers*, vol. 295, pp. 119856, 2022.
 13. Y. Habibi, L.A. Lucia, O.J. Rojas, “Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications,” *Chemical Review*, vol. 110, no. 6, pp. 3479–3500, 2010.
 14. F. Zambrano, Y. Wang, J.D. Zwillig, R. Venditti, H. Jameel, O. Rojas, R. Gonzalez, “Micro- and nanofibrillated cellulose from virgin and recycled fibers: A comparative study of its effects on the properties of hygiene tissue paper,” *Carbohydrate Polymers*, vol. 254, pp. 117430, 2021.
 15. S. Park, R.A. Venditti, H. Jameel, J.J. Pawlak, “Hard to remove water in cellulose fibers characterized by high resolution thermogravimetric analysis - methods development,” *Cellulose*, vol. 13, no. 1, pp. 23–30, 2006.
 16. L. Yuan, J. Wan, Y. Ma, Y. Wang, M. Huang, Y. Chen, “The Content of Different Hydrogen Bond Models and Crystal Structure of Eucalyptus Fibers during Beating,” *BioResources*, vol. 8, no. 1, pp. 717–734, 2013.
 17. S.B. Pillai, R.J. Wilcox, B.G. Hillis, B.P. Losey, J.D. Martin, “Understanding the Water-in-Salt to Salt-in-Water Characteristics across the Zinc Chloride: Water Phase Diagram,” *Journal of Physical Chemistry B*, vol. 126, no. 11, pp. 2265–2278, 2022.
 18. H. O’Neill, S.V. Pingali, L. Petridis, J. He, E. Mamontov, L. Hong, V. Urban, B. Evans, P. Langan, J.C. Smith, B.H. Davison, “Dynamics of water bound to crystalline cellulose,” *Scientific Reports*, vol. 7, no. 1, pp. 1–3, 2017.