ENERGY EFFICIENT PRODUCTION OF NANO-FIBRILLATED CELLULOSE (NFC) FROM COTTON LINTERS BY TRI-DISC REFINING AND ITS CHARACTERIZATION

A. K. BHARIMALLA,[*] P. G. PATIL,[*] S. P. DESHMUKH[**] and N. VIGNESHWARAN[*]

[*]*ICAR-Central Institute for Research on Cotton Technology, Adenwala Road, Matunga, Mumbai 400019, India*
[*]*Institute of Chemical Technology, Matunga, Mumbai 400019, India*
✉ *Corresponding author: N. Vigneshwaran, nvw75@yahoo.com*

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In this work, nano-fibrillated cellulose (NFC) with a diameter in the range of 50 to 200 nm was prepared from bleached cotton linter pulp by a combination of enzymatic and mechanical processes. To circumvent the problem of high energy consumption during mechanical processes, pretreatment with cellulase enzyme was carried out and achieved 27% energy reduction. A custom-designed recirculation setup was used with a Tri-Disc Refiner for repeated refining of the pulp. The crystallinity of the raw material (83.3%) was reduced to 81.0% in the final product (NFC) due to shearing and cutting actions involved in the processing steps (pulping, beating and refining), as could be assessed by XRD analysis. The stages of fibrillation and their corresponding size reduction were demonstrated by SEM analysis. The resultant NFC has potential applications in papers, electronics, pharmaceuticals, fuel cells and fertilizers.

Keywords: AFM, cellulase enzyme, nanocellulose, SEM, Tri-Disc Refining

INTRODUCTION

Due to advances in the field of nanotechnology, cotton fibres/linters can be converted into a novel material, nano-fibrillated cellulose (NFC), which finds varied applications due to desirable properties like low density, high specific surface area, high strength and modulus, high aspect ratio, dimensional stability, chemical functionality, thermal stability, and good optical transparency. The conversion of any cellulosic biomass to NFC makes the product more remunerative and with diversified applications in areas such as materials and manufacturing (coatings and composites for products like automobiles and building materials), electronics (displays and batteries), health care/life sciences (pharmaceutical applications) and in coating/furnish additives in papers. Though various sources of raw materials have been evaluated for preparation of nanocellulose, *viz.*, wood,[1] corn stover,[2] sisal fibers,[3] mulberry,[4] pea hull fiber,[5] coconut husk fibers,[6] sugarcane bagasse,[7] banana pseudostem,[8] citrus waste,[9] cotton is the best source, due to its purity and highest crystallinity.

Cotton linters are short fibers that remain on the surface of a seed coat after the ginning process. Because of their short fiber length and contamination with seed coat fragments during the delinting process, cotton linters cannot be used in the textile and absorbent cotton sectors. The amount of cotton linters produced worldwide is of about 2.5 MMT, considering the 25 MMT of cotton fibers produced in the year 2010 (FAOSTAT Agricultural Data, 2012). Cellulose, the building blocks of cotton linters, is the structural material of the fibrous cells with a high level of strength and stiffness per unit weight, which has a straight carbohydrate polymer chain consisting of β-1-4 glucopyranose units and a degree of polymerization of about 10,000.[10] The cellulose molecules aggregate and remain in the form of nanofibrils within the fibers. The hydroxyl (-OH) groups on the surface of cellulose play a major role in governing the reactivity and physical properties of the cellulose.[11]

The cellulose fibers can be mechanically disintegrated to basic structural components, nanoscale fibrils.[12] NFCs are defined as the fibers of cellulose with the diameter in the range of 0.1-1 μm, while the length of these materials are primarily defined by the source of the raw materials and their production process. The predominant ways of preparing NFC by mechanical means include refining/grinding, homogenization, microfluidization, cryocrushing and ultrasonication. However, one of the major challenges associated with mechanical processing for production of NFC is huge energy consumption.[13] Hence, in this work, an attempt has been made to produce NFC from enzymatically

pretreated cotton linters using a Tri-Disc Refiner (TDR) with a customized recirculating feedback arrangement for better process control and reduced energy consumption.

EXPERIMENTAL

Bleached cotton linter pulp sheets prepared from short staple cotton (variety 'Bengal Desi', India) were used as raw material for production of NFC. These sheets were shredded by hand and an amount of 4 kg of sheets was mixed with 100 L of softened water in a pulper. The pulper used was of D-type configuration for better mixing of the pulp, and was provided with three electrical coils attached around the jacket for uniform heating. This 4% consistency of the pulp was found to be optimum as a higher concentration may lead to pulp choking up in the blades. After 1 h of pulping, the shredded sheets dispersed uniformly in the water. Cellulase enzyme (Biopol®) was added at a concentration of 1% and the temperature of the pulper was maintained at 45 °C. The reaction was maintained for 1 h for partial hydrolysis (pretreatment) of the cellulosic materials. For control, the pulp was processed without enzyme addition.

After pulping, the material was transferred to a beater and 0.05% silicone (anti-foam agent) was added to avoid foaming (which forms due to the surfactants present in the enzyme formulation). The beater was operated at 590 rpm. The gap between the bedplate and beater rolls was adjusted during the beating process for optimized size reduction. For the initial 1 h, the gap was adjusted so that it would consume 0.4 kW of energy and for the subsequent 1 h, the gap was further reduced to operate at a consumption of 0.5 kW of energy.

The beaten material was transferred to a TDR refiner using a pulp pump. The TDR has 4 refining surfaces, with a disc diameter of 32 cm. No bolting on the surface leads to a larger refining area. The TDR is attached to a 30 HP motor and the speed is 960 rpm. With a capacity of 15 TPD, it can handle a consistency of up to 6%. The TDR was attached to a custom-designed recirculating system for continuous feedback of the pulp for the required number of refining passes. It consisted of two tanks (200 L capacity) kept one over the other with the pneumatically operated valve in-between for controlled transfer of material from one tank to another. Once the first pass is completed, the refined pulp will be fed back into the feeding tank by opening the pneumatic valve. The beaten pulp was passed through this refiner 30 times and then samples were taken for further analysis. The energy consumption during the entire process was recorded with the help of energy meters. A schematic of the entire process of NFC preparation is given in Figure 1.

For atomic force microscopic (AFM) analysis, a scanning probe microscope by Veeco®, Innova, was used to characterize the surface morphology of the NFC. AFM height images of the cotton fiber samples were taken in the tapping mode at a frequency of 253 Hz using a silicon cantilever. The NFC suspension was deposited onto the surface of freshly cleaved mica and dried under an IR lamp. The scan speed (samples per line parameter for an image of 10 × 10 µm) during imaging was kept at 512 and no filtering was used during image acquisition.

Scanning micrographs of NFC samples were taken using a Phillips® scanning electron microscope operated at 10 kV. Samples were coated with gold/palladium using a vacuum sputter coater to improve their conductivity. All the samples (control and processed) were analyzed at uniform magnification (1000×) for better comparison. Pulp viscosity of the NFC in suspension (0.5% consistency) was analyzed using a Brookfield viscometer (Model DV-III Ultra Rheometer) at 25 °C temperature.

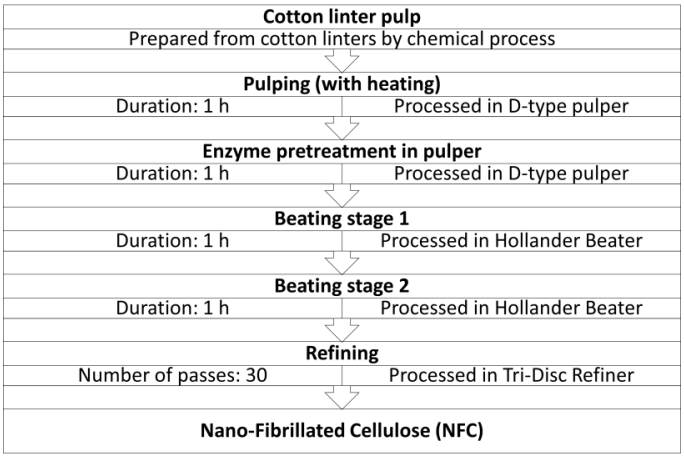

Figure 1: Scheme of NFC production from cotton linter pulp

Figure 2: Tri-Disc Refiner (TDR) opened to show the refining surfaces

Table 1
Energy requirement during production of NFC from cotton linter pulp

S.No.	Processing stage	Energy requirement (kWh) for 4 kg of pulp	
		Control pulp	Enzyme pretreated pulp
1	Pulping process including heating	8.5	8.5
2	Enzyme treatment in the pulper	3.0	3.0
3	Beating – stage 1	2.5	2.5
4	Beating – stage 2	3.5	3.5
5	Refining	12	4
6	Total	29.5	21.5

Wide angle X-ray diffraction patterns of NFC samples were obtained using a Philips® PW1710 X-ray diffractometer with nickel filtered Cu Kα (α = 1.54 A°) radiation and analyzed using automatic powder diffraction (APD) software. The diffracted intensities were recorded from 10° to 80° 2θ angles. The percent crystallinity was determined using the equation (Ic – Ia)/Ic × 100, where Ic is peak intensity of the crystal plane (0 0 2) and Ia is peak intensity of the amorphous phase (2θ = 18°).

RESULTS AND DISCUSSION

The enzymatic hydrolysis of cotton linter pulp was conducted during the pulping process. Foam was formed due to the presence of surfactants in the enzyme mixture. The uniform dispersion of the sheet material indicated the completion of the pulping process. The D-type configuration of the pulper helped proper and turbulent mixing of the pulp material, which allowed speeding up the entire process, thereby reducing energy consumption. The enzymatic hydrolysis was carried out for 1 h in the pulper and the material was transferred using a pulp pump into the beater. The addition of an antifoam agent (silicone) helped avoid the formation of foam during the beating process. The beating process was carried out for a period of 2 h (in two stages).

Figure 2 shows the TDR attached to the recirculating feeding system. The pulp from the beater was transferred using the pulp pump into the feed tank of TDR from which the pulp was fed into the refiner. The gap between the rotor and the stator was adjusted by changing the current intake. The current requirement was optimized based on the number of passes required for conversion of the pulp material into NFC. In the case of the control pulp (without enzyme pretreatment), it took an average of 30 passes through the refining process to produce NFC. This result is in line with the finding of our earlier report, wherein also 30 passes of refining in the disc refiner were required to produce NFC from cotton linters.[14] In the case of the enzyme pretreated pulp, the number of required passes was reduced to 10, thereby leading to reduced energy consumption. The overall energy requirement for the stages of NFC production for 4 kg of pulp is given in Table 1. The energy consumption for all the stages, except refining, are the same for the control pulp and the enzyme treated pulp. In the case of the refining process, there is a significant reduction in energy consumption due to the diminished number of required passes.

Figure 3 shows representative scanning electron micrographic (SEM) images of fibrillation at different stages. The SEM image of bleached cotton linter pulp (Fig. 3(a)) shows the intact cotton fiber devoid of any fibrillation. The SEM image of Figure 3(b) shows the initiation of fibrillation after the

pulping stage and the extent of fibrillation increased significantly after the beating and refining processes (30 passes), as revealed by Figure 3(c) and 3(d), respectively. In the case of the enzyme pretreated pulp, the pulping process itself significantly enhanced the fibrillation, as may be noted in Figure 3(e), while the beating and refining (10 passes) processes also contributed to efficient fibrillation to form NFC, as visible from Figure 3(f) and 3(g), respectively. While NFC could be achieved from the control pulp only after 30 passes through the refiner, after the enzymatic pretreatment of the pulp, the same could be achieved in 10 passes. Because of 30 refining passes, the NFC obtained from the control pulp was mostly deformed (Fig. 3(d)), in contrast with the NFC achieved after the enzyme pretreatment, which exhibited an intact structure (Fig. 3(g)). The length could not be ascertained as both ends of a NFC could not be seen and most of the NFCs did not detach completely from the pulp fiber.

A two-dimensional AFM image of the NFC prepared from enzyme pretreated cotton linter pulp is given in Figure 4. Line analysis was carried out for three different regions and the base width and height were used to derive the diameter of NFC. The average diameter of the NFC was determined to be in the range of 50 to 200 nm. Such a wide variation is due to the non-uniformity induced during mechanical processing of the fiber. The overall yield of NFC in the case of the untreated pulp is 75%, while it is 70% in the case of the enzyme pretreated pulp, the 5% difference is attributed to the loss of cellulose because of enzymatic hydrolysis (Table 2). The remaining 25% are ascribed to losses that occurred during processing, collection, transfer and handling.

Figure 5 shows the shear thinning behavior of the NFC suspension, as determined by the viscometer at different shear rates. In the case of the NFC (refined samples), the viscosity at 5 rpm was very high (168 cP) and it reduced to 24 cP at 10 rpm. In the case of other samples (after pulping and beating), the initial viscosities were very low, since their size was not in the nanometer range. This behavior was similar for both the control and the enzyme pretreated NFC samples. This shear thinning phenomenon is an important attribute of NFC, making it suitable for applications in paints, foods and in other products requiring modified rheological properties.

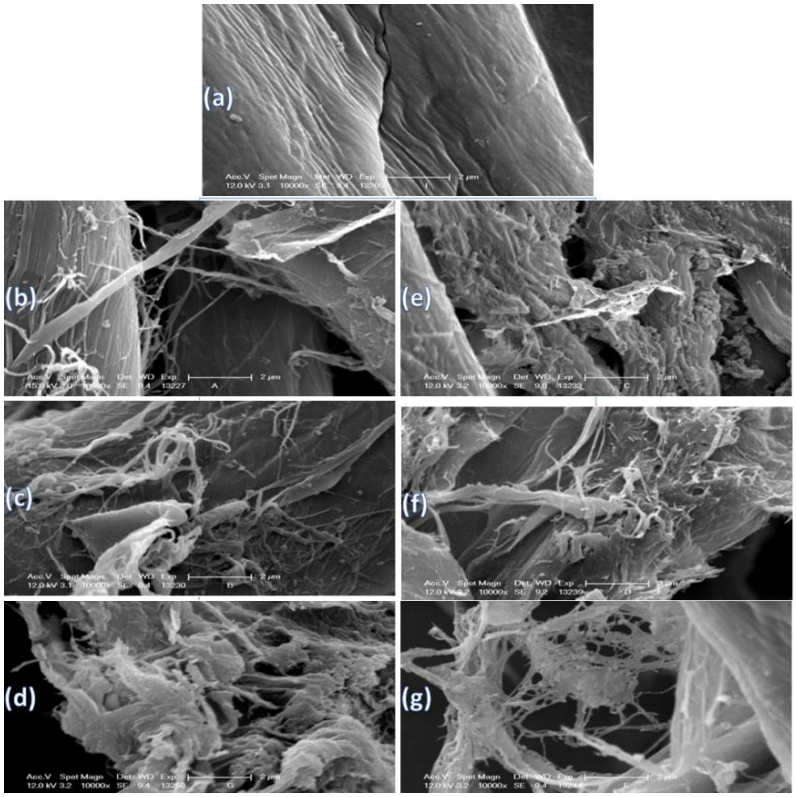

Figure 3: SEM images of control cotton linter pulp (a), subjected to pulping (b), beating (c) and 30 refining passes (d); and cotton linter pulp subjected to enzyme pretreatment pulping (e), beating (f) and 10 refining passes (g)

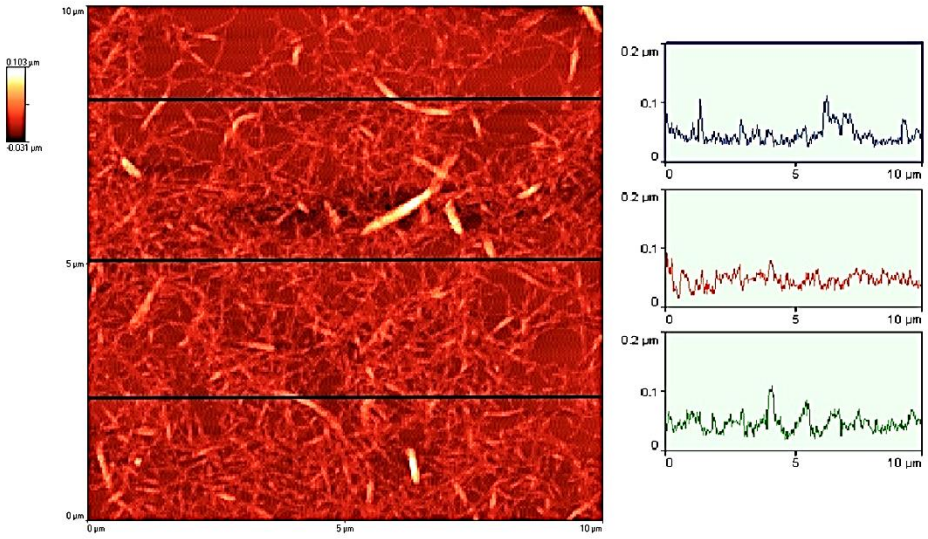

Figure 4: Two-dimensional AFM image of NFC prepared from enzyme pretreated cotton linter pulp and its corresponding line analyses at three identified regions marked by dark lines on the AFM image

Table 2
Crystallinity and yield analyses of NFC during various processing stages

S.No.	Processing stage	Crystallinity (%) by XRD		Yield (%)	
		Control pulp	Enzyme treated pulp	Control pulp	Enzyme treated pulp
1	Initial linter pulp	83.3	83.3	100	100
2	Enzyme treated pulp	Not applicable	83.5	Not applicable	95
3	Beating – stage 1	82.0	82.8	89	85
4	Beating – stage 2	81.3	82.0	81	77
5	Refining	80.8	81.0	75	70

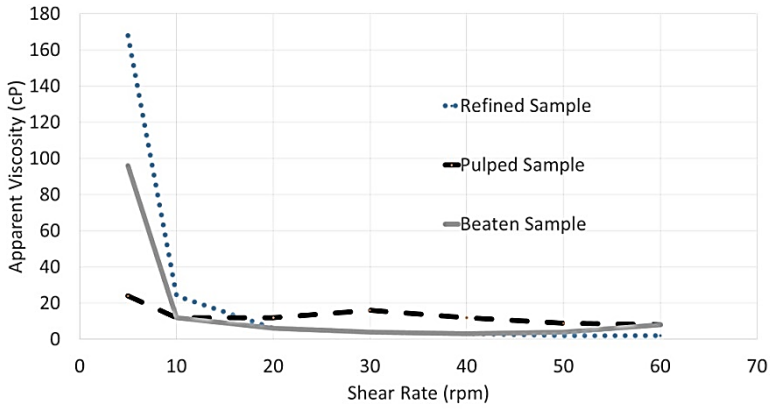

Figure 5: Shear thinning behavior of NFC as analyzed by the viscometer at different shear rates (the apparent viscosity was reduced significantly once the shear rate was increased from 5 to 10 rpm)

The XRD analysis of NFC was carried out to determine the percent crystallinity, also called degree of order. XRD has been found to be sensitive to well-ordered regions in cellulose larger than 1.0 nm. However, some areas of the lattice contain unstructured regions that are caused by the presence of amorphous cellulose, or which arise as a result of small crystalline units being imperfectly packed together.[15] As given in Table 2, the initial linter pulp crystallinity was 83.3% and it was increased marginally to 83.5% after the enzyme treatment. This is attributed to the preferential hydrolysis of the amorphous region by the cellulase enzyme. In all other processing stages, the crystallinity was reduced significantly because of the various mechanical actions to which the pulp was subjected in the line of

production (pulping, beating and refining). No significant difference in crystallinity was noted among the final products (NFC) prepared from the control pulp and the enzyme treated pulp.

Figure 6 shows the concentrated NFC prepared by squeezing the excess of water from the NFC suspension. Since the water retention capacity of NFC is very high, complete removal of water by the draining process could not be achieved. The NFC (30% concentration) is stored and under study for evaluating its suitability for use in two different applications, *viz*., improving the compressive strength of concrete and improving the tensile strength of paper.

The entire process was carried out at ICAR-CIRCOT, Mumbai, in its recently established nanocellulose pilot plant. The comparison of this pilot plant with other similar units in the world is given in Table 3. Though the capacity is low, ICAR-CIRCOT pilot plant's unique advantage is its capacity to process both NCC and NFC. Moreover, it allows processing of a wide variety of raw materials, such as pulp from cotton linter, softwood, hardwood, bagasse and so on.

Figure 6: NFC prepared from cotton linter pulp

Table 3
Nanocellulose pilot plants available in the world[16]

Organization	Country	Unit	Type*	Capacity
FP Innovation	Canada	Pilot plant	NCC	10 kg/week
US Forest Services Forest Products Laboratory	USA	Pilot plant	NCC	35-50 kg/day
Alberta Innovates – Technology Futures	Canada	Pilot plant	NCC	100 kg/week
Celluforce Inc.	Canada	Demonstration plant	NCC	1 tonne/day
Biovision Technologies Inc.	USA	Pilot plant	NCC	4 tonnes/year
Innventia	Sweden	Demonstration plant	NFC	100 kg/day
The Us Forest Service	USA	Demonstration plant	NFC	500 kg/day
ICAR-CIRCOT, Mumbai	India	Pilot plant	NFC/NCC	10 kg/day

*NCC – Nanocrystalline cellulose; NFC – Nanofibrillated cellulose

CONCLUSION

The present study has allowed drawing the conclusion that the combination of enzymatic pretreatment with traditional mechanical processes helps hasten the NFC production process (in an energy efficient way) from cotton linter pulp. The enzymatic pretreatment contributed to a reduction of the energy consumption in the overall process by 27%. Also, the use of enzyme as a pretreating agent ensures the avoidance of toxic effluents, in contrast to using chemical pretreating agents. The size reduction trend during various processing steps was demonstrated with the help of scanning electron microscopy. The shear thinning behavior of NFC, as revealed by viscosity analysis, at different shear rates, makes it a potential candidate for application in paints and foods. The potential of the thus produced NFC from cotton linters is being explored for application as reinforcing agent in

concrete to increase its compressive strength and as a coating/furnish additive in paper preparation to improve its printability/strength.

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