Preparation and characterization of cellulose nanofibers from bleached pulp using a mechanical treatment method

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ABSTRACT: Cellulose nanofibers from three types of bleached pulp fibers were prepared using a mechanical method. In this method, bleached bagasse, hardwood, and softwood pulps were refined to a very high degree (~ 90°SR) using a laboratory PFI mill. The effectiveness of the method used to isolate nanofibrils was studied by field emission scanning electron microscopy and atomic force microscopy. The micrographs showed large numbers of nanosized fibrils and broken fibers with diameters ranging from 30 nm to 100 nm in the refined pulps. Laboratory paper sheets were prepared from the highly refined pulps and evaluated for various mechanical and optical properties, such as tensile index, tear index, burst index, tensile energy absorption, bending stiffness, porosity, apparent density, opacity, scattering coefficient, and absorption coefficient. The nanopaper sheets made from bleached softwood pulp showed higher strength properties than those made from bleached hardwood and bagasse pulps. At 90°SR refining, the maximum enhancement of the strength properties was observed in the bagasse pulp.

Application: Mechanically prepared nanofibers used with other pulps in suitable proportions may enhance paper properties and reduce energy consumption.

Nanomaterials from natural resources such as cellulose are a growing area for research because of their exclusive properties. Nanofibrillated cellulose isolated from the cell wall of lignocellulosic fibers is a potential natural nanomaterial. Researchers are working extensively with nanocellulosic materials such as microfibrillated cellulose [1–2], electrospun nanofibers [3–5], and cellulose nanocrystals (cellulose whiskers) [6–7]. Various techniques, without and with use of chemicals, have been used to achieve the results. Cellulose nanofibers have high aspect ratios and very high surface areas when compared with normal cellulose fibers. Nanofibrillated cellulose is a highly prospective reinforcing material in nanocomposites that are biocompatible, biodegradable, and renewable.

Nanofibrillated cellulose matrices have been used for manufacturing advanced nanocomposites such as surgical materials in biomedical applications, high toughness nanocomposite membranes in ultrafiltration, and transparent materials [8–15]. The plant fibers are made up of microfibrillar bands, microfibrils, and elementary fibrils [16]. The structural dimensions of these units is >100 nm for microfibrillar bands, between 10 nm and 30 nm for nanofibrils, and between 2 nm and 4 nm for elementary fibrils [17]. The length of microfibrils is on the order of more than a few hundred nanometers; these are surrounded in the matrix of lignin and hemicellulose.

Very high mechanical energy is required to fibrillate nanofibers from the cell wall. Much work is being done on producing nanofibrillated cellulose using different methods. These methods include mechanical treatments, such as grinding [18], cryocrushing [19–20], high pressure homogenizing [21], ultrasonication [22], and mechanical treatment preceded by a chemical or enzymatic treatment [23–24]. In a previous study, Iwamoto et al. [25] used a high-shear ultrafine friction grinder to generate nanosized cellulose fibrils. The pulp was passed several times through the grinder to obtain the required high degree of fibrillation. The nanofibrillated fibers could be used for reinforcing transparent resins without losing transparency. The nanocomposites exhibited low thermal expansion (as good as can be found with silicon crystal), high strength comparable to that of soft steel, and ease of bending similar to that of plastics. Hassan et al. [26] prepared nanofibers using a chemical treatment with an alkali followed by a mechanical treatment with the help of a super mass colloider. From the handsheets made in the laboratory, they observed that the paper made from nanocellulosic fibers had wet strength about 12 times greater than that of normal papers. Lindgren and Wennberg [27] prepared nanofibers using TEMPO-mediated oxidation followed by a mild mechanical treatment and made handsheets in the laboratory. They observed that the strength properties of the paper sheets were enhanced as the level of nanofibers increased.

We felt that this strengthening of the paper sheets could also be achieved, in the case of Indian wood pulp, by mixing the pulp with requisite amount of nanofibered pulp. However, there seems to be no investigation performed on nanofibrillation of wood or nonwood pulp of Indian origin. Therefore,

work was planned to investigate the possibility of nanofibrillation of wood and nonwood species of Indian origin. We started with the aim of preparing nanofibrillated fibers from chemical bleached bagasse, hardwood, and softwood pulp (all of Indian origin) using a mechanical treatment method. Another aim was to try to find correlation between the constituents of the pulp, degree of beating, and the extent of nanofibrillation. Lastly, we also attempted to evaluate and analyze the change in the strength, optical, and other properties of the sheets made from nanofibrillated pulp. This paper is a report of our work.

EXPERIMENTAL

Materials

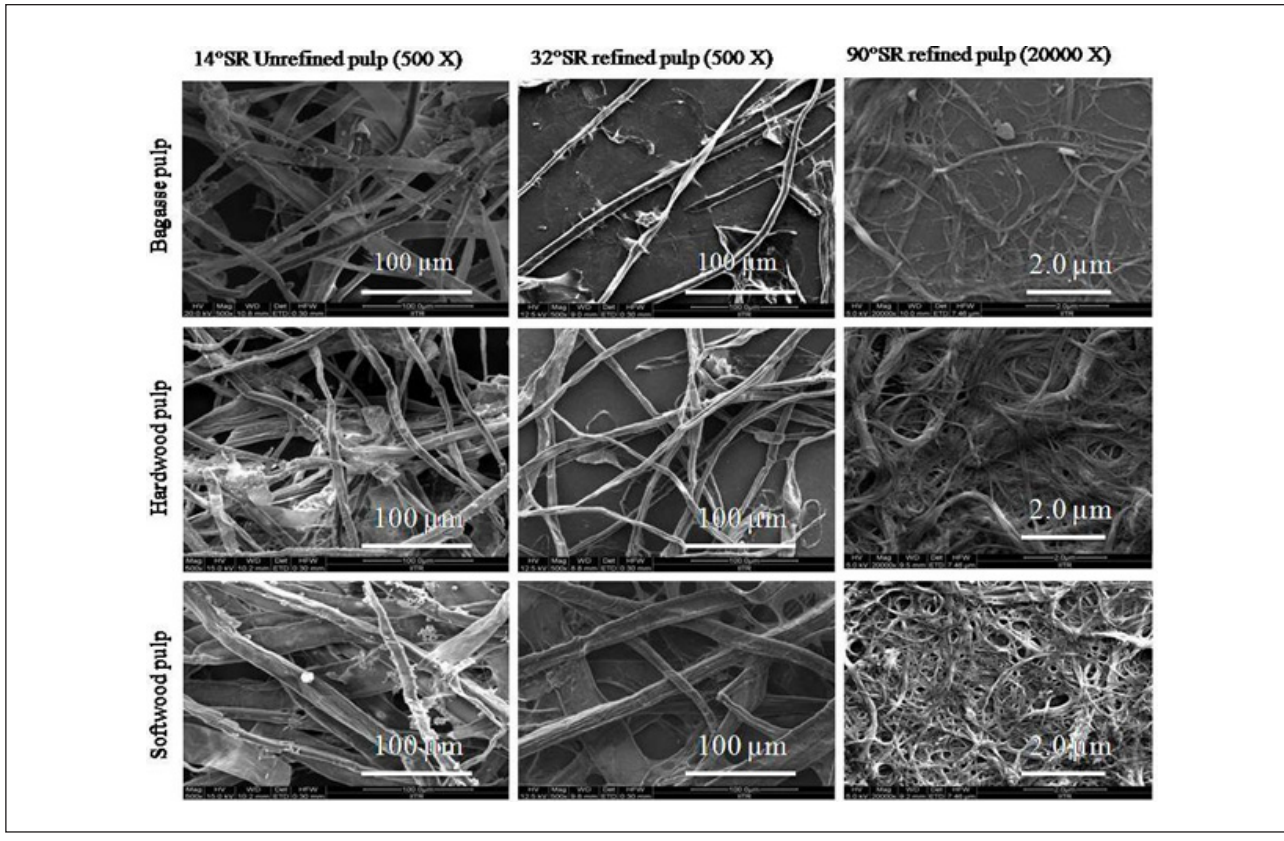
For the present study, the bleached bagasse pulp was obtained from a bagasse-based integrated pulp and paper mill (Century Paper Mills; Lalkuan, Nainital, India), and the bleached hardwood pulp was obtained from a mixed hardwood-based integrated pulp and paper mill (Star Paper Mills; Saharanpur, India). The bleached softwood pulp was also obtained from Star Paper Mills' stored pulp imported from North America. The bagasse and hardwood pulps were received wet (≈20% solid content) and were air dried in the laboratory and stored at room temperature. The softwood pulp was available in the form of dried sheets. The composition of the three pulps (especially alpha cellulose and hemicellulose) was determined using TAPPI standard method T 203 cm-09 "Alpha-, beta- and gamma-cellulose in pulp"; these are presented in **Table I**. All the AR-grade laboratory chemicals were used in the determination of pulp composition.

Materials	Alpha Cellulose (%)*	Hemicellulose (%)*
Bagasse pulp	71.6	28.4
Hardwood pulp	84.4	15.6
Softwood pulp (pad)	89.7	10.3
*All values represented as an average of three measurements.		

I. Composition of the pulp fibers.

Refining of the fibers

All pulp samples were beaten in a laboratory PFI mill that was charged with 30 g of pulp at 10% consistency for beating. The pulp samples were beaten to two levels of freeness: 32°SR and 90°SR. For beating to 32°SR, it was required to operate the PFI-mill for about 3500 revolutions for bagasse and hardwood pulp and for about 10000 revolutions for softwood pulp. For beating to 90°SR, 100000 revolutions in the PFI mill were required for the bagasse and hardwood pulps and 125000 revolutions were required for the softwood pulp. More revolutions



1. Field emission scanning electron microscope (FE-SEM) micrographs of three bleached pulps at different °SR refining.

in the PFI mill likely were required for softwood pulp than for the bagasse and hardwood pulps because of the lower content of hemicelluloses in the softwood pulp. In the PFI mill, a cylindrical rotor with narrow axial bars on its curved surface rotates in a smooth housing. During the operation of the mill, the rotor is pushed to one side of the housing. The pulp fibers remain in contact with the inner surface of the mill housing because of centrifugal force and are repeatedly subjected to high shear stresses as they are carried into the narrow gap formed between the housing and the rotor bars.

Microscopic studies

All beaten pulp samples were examined using a field emission scanning electron microscope (FE-SEM, Quanta 200 F, FEI Company; Hillsboro, OR, USA) to observe the effect of refining on the fiber dimensions. A dilute suspension of pulp fibers and fibrils was spread on a glass slide in a thin layer and allowed to dry. These fibers and fibrils were coated with gold by an ion sputter coater. The coated samples were observed under the FE-SEM operating at 12.5 kV. Morphology of the isolated cellulose nanofibers was also observed using an atomic force microscope (AFM, NTEGRA, NT-MDT; Zelenograd, Russia). A drop of the diluted fiber suspension was dried onto a glass slide surface for AFM examination. The dimensions of pulp fibers were measured using ImageJ (Java version) image processing software on the results obtained from FE-SEM and AFM.

Preparation of sheets

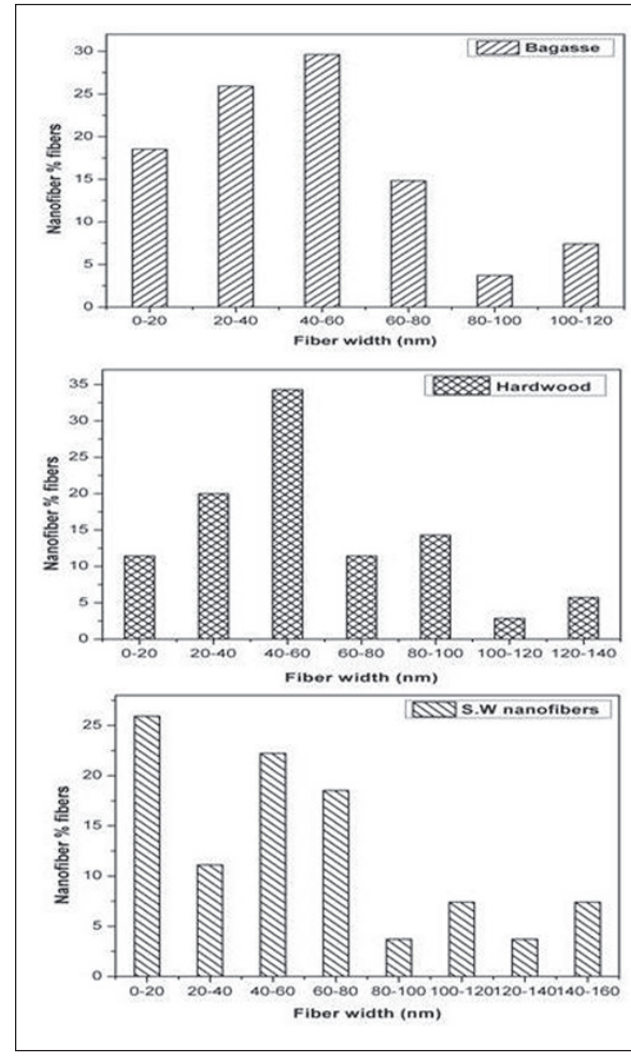
Paper sheets from mechanically refined nanofibers could not be made using the normal procedure due to the smallness of the fibers. Therefore, sheets were made by the vacuum filtration method; nanofibered pulp at 0.5% consistency was placed on filter paper (MN615A) over a Buckner funnel. The nanopaper sheets were dried for 3 h at 100°C and then kept for 8 h at 60°C. These sheets were preconditioned at 23°C±1°C temperature and 50%±2% relative humidity (RH) according to TAPPI Standard T 402 sp-08, "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products," before undertaking different tests.

Evaluation of sheets

Tensile index of nanopaper sheets was measured using a universal testing machine according to TAPPI T 494 "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)." The specimen dimensions were taken as 15-mm width and 50-mm length. Because the sheets were prepared by a different method, the size of the filter paper limited the length of the sheet to 50 mm. Tear index and burst index were measured according to method TAPPI T 414 om-04 "Internal tearing resistance of paper (Elmendorf-type method)" and TAPPI T 403 om-02 "Bursting strength of paper," respectively. Porosity of the paper sheets was measured by the Gurley method (TAPPI T 460 om-11 "Air resistance of paper [Gurley method]") using a Lab Permi porosity analyzer (ACA Systems; Sotkuma, Finland). Opacity, scattering, and absorption coefficients were measured according to TAPPI T 425 om-11 "Opacity of paper (15/d geometry, illuminant A/2°, 89% reflectance backing and paper backing)" using a CM3630 brightness tester (Konica Minolta; Tokyo, Japan). The results have been presented as an average of at least six measurements.

Pulp Samples	Width of Fibers (μm)		Width of Fibers (nm)
	14°SR	32°SR	90°SR
Bagasse	2.5–22.5	2.5–12.5	10–120
Hardwood	2.5–27.5	2.5–17.5	10–140
Softwood	2.5–52.5	2.5–37.5	10–160

II. Fiber width distribution of pulp fibers.



2. Pulp fiber distribution graphs for bagasse, hardwood, and softwood pulps.

RESULTS AND DISCUSSION

Morphological properties

Figure 1 shows FE-SEM images of bagasse, hardwood, and softwood pulp fibers at different levels of refining. The micrographs for 14°SR and 32°SR pulps are at a magnification of 500X while the micrographs for 90°SR pulps are at a magnification of 20000X.

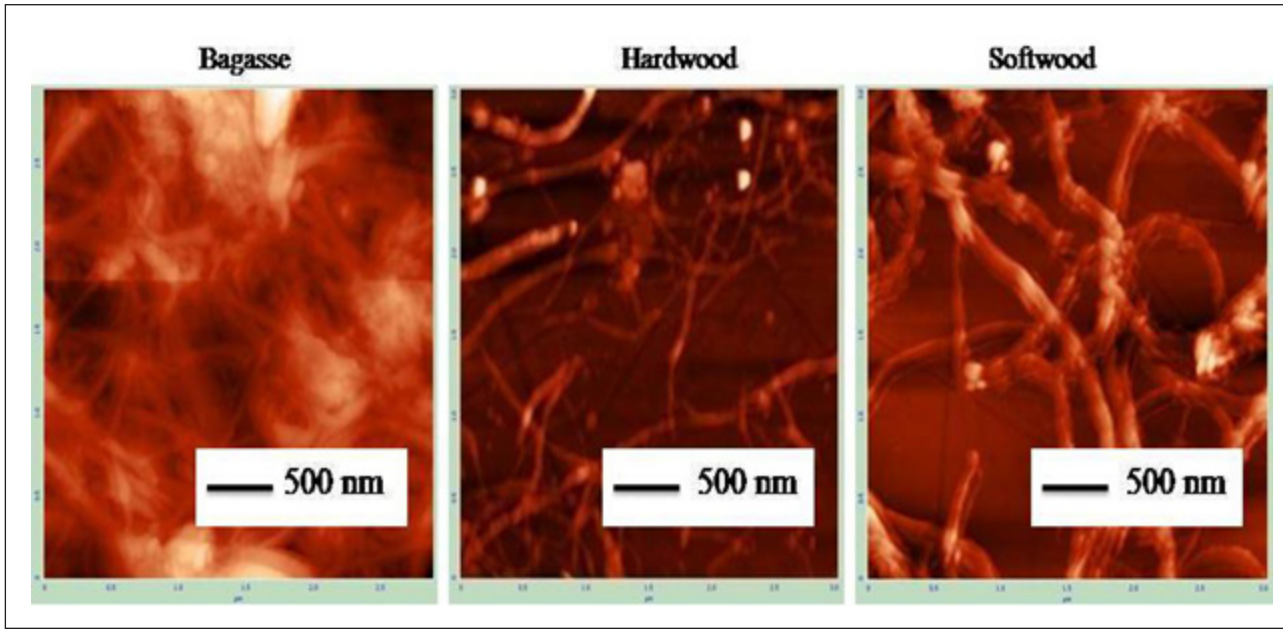
Extra refining of the pulps showed a decrease in the fiber width for all three types of pulp. For 14°SR and 32°SR refined pulps, there seems to be little external disintegration of the fibers. The decrease in freeness of the pulp appears largely due to the internal fibrillation and imbibing of water in the cell wall. Continuous refining up to 90°SR causes disintegration of the fiber wall and separates the nanosized fibrils from the fibers. **Table II** and **Fig. 2** show the width distribution of fibers refined to different extents. The fiber width of 14°SR and 32°SR pulps is in the micron range, whereas the fiber width falls in the nanometer range (<160 nm) when the pulps are beaten to 90°SR level. The comparison of different pulps shows a larger extent of refinement on beating for the bagasse and hardwood pulps than for the softwood pulp. At 90°SR refining level, nanosized fibrils were separated from the fibers that could be easily observed in the FE-SEM micrographs. Fig. 2 also shows a similar pattern. For all the pulps studied, approximately 85%–90% of fibers were formed in the nanosized range (<100 nm) during the prolonged refining.

Figure 3 shows AFM images of three types of pulp fibers refined to 90°SR. These are isolated nanofibrils with diameter ranges of 12–75 nm, 16–80 nm, and 21–97 nm for bagasse, hardwood, and softwood pulp fibers, respectively. These are nearly in the same ranges as determined from the FE-SEM images. For all pulps, microfibrillar bands with diameters in the range of 55–160 nm were observed.

Strength properties

Because the difference between the pulps beaten to 14°SR and 32°SR does not appear large in terms of degree of fibrillation (Fig. 1), they were not expected to differ significantly in strength properties. Because the aim of the present investigation was to see how nanofibrillation affects various properties of the resulting pulp vis-à-vis the normal beaten pulp, strength properties (tensile index, tear index, burst index, tensile energy absorption [TEA] index, and stiffness) were compared for only 32°SR and 90°SR beaten pulp shown in **Table III**.

The refining process has three primary effects on the fibers: (1) internal fibrillation, (2) external fibrillation resulting in decrease of fiber width and therefore overall larger surface area, and (3) production of fines. Results of the present tests indicate effect 2 only. When the refining of the pulp was continued up to 90°SR, tensile index and burst index values increased very significantly whereas tear index decreased with respect to normally beaten pulp (Table III). Tensile and burst strength increased primarily due to increased specific surface area of the fibers. Due to very high surface area, intra- and intermolecular hydrogen bonding capability for all the three types of pulp fibers were increased at 90°SR. Therefore, the fiber-fiber interaction at 90°SR refined pulp was more than that of 32°SR refined pulp. As per usual understanding, the tear index decreases as fiber-fiber bond strength increases. Also, TEA index was increased for all three types of pulp. To some extent, decrease in tear strength could also be due to shortening of fibers. Stiffness of nanofiber paper sheets was decreased significantly for all types of pulps. Stiffness is inversely proportional to the cube of paper density; therefore, the nanofiber paper sheets were less stiff (more flexible) than conventional paper sheets. The



3. AFM images of bagasse, hardwood, and softwood pulps refined at 90°SR.

Sample No.	Properties	Bagasse Pulp*		Hardwood Pulp*		Softwood Pulp*	
		32°SR	90°SR	32°SR	90°SR	32°SR	90°SR
1	Tensile index, Nm/g	32±1.9	64±5.2	36±2.1	55±3.0	45±3.0	78±5.2
	Relative change due to extra refining, %		+100		+53		+73
2	Tear index, mNm^2/g	7±0.5	3±0.7	8±0.2	4±0.5	14±0.9	6±0.8
	Relative change due to extra refining, %		-57		-50		-57
3	Burst index, $KPam^2/g$	3.0±0.3	7±0.9	4±0.3	6±0.5	5±0.3	10±0.8
	Relative change due to extra refining, %		+133		+50		+100
4	TEA index, J/g	0.66±0.06	2.39±1.64	0.55±0.03	1.21±0.18	1.21±0.18	2.59±2.29
	Relative change due to extra refining, %		+398		+120		+114
5	Stiffness, Nmm	0.73±0.09	0.36±0.01	1.09±0.18	0.22±0.07	1.96±0.94	0.41±0.07
	Relative change due to extra refining, %		-103		-395		-378
*Standard deviations are shown by ± values.							

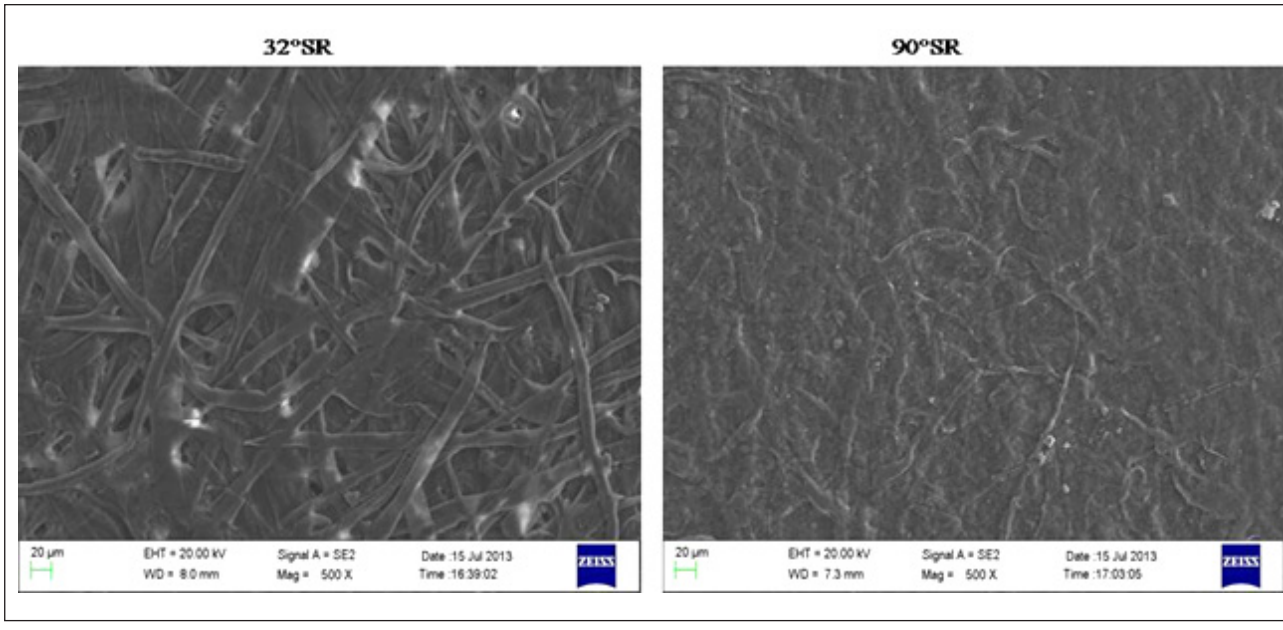
III. Effect of the refining process on strength properties of conventional paper and nanopaper sheets made from refined bagasse, hardwood, and softwood fibers.

Sample No.	Properties	Bagasse Pulp*		Hardwood Pulp*		Softwood Pulp*	
		32°SR	90°SR	32°SR	90°SR	32°SR	90°SR
1	Opacity, %	91±2	39±2	92±2	43±3	88±3	54±4
2	Porosity , Gurley, s/100 mL	193.3	Infinity	201.1	Infinity	85.2	Infinity
3	Scattering coefficient, m^2/kg	28±1	2±0.4	28±0.3	3±0.4	28±0.8	7±0.6
4	TEA index, J/g	0.65±0.02	0.32±0.06	0.64±0.01	0.28±0.06	0.56±0.02	0.29±0.31
5	Stiffness, Nmm	0.67±0.05	1.24±0.08	0.66±0.10	1.18±0.10	0.78±0.11	1.11±0.10
*Standard deviations are shown by ± values.							

IV. Optical and structural properties at different levels of refining.

fiber diameter was positively correlated to the strength properties of the paper. The maximum strength improvement was seen in bagasse pulp because of the large amount of nanofibers obtained. For bagasse pulp, surface area was higher and more hydroxyl groups were exposed compared with hardwood and softwood pulps.

Generally, nanopaper sheets prepared from softwood nanofibers were characterized by higher strength properties than sheets made from hardwood and bagasse pulp nanofibers. This effect was due to the presence of a greater amount of alpha cellulose in the softwood pulp than in the hardwood and bagasse pulps. The strength properties were dependent on the cellulose content of the raw materials. High alpha cellulose content material required more energy for the fibrillation of fibers during the refining process as compared to materials with less alpha cellulose content.



4. FE-SEM images (500X magnification) of bagasse pulp refined at 32°SR and 90°SR.

Optical properties

Table IV shows the optical and structural properties of handsheets made from pulps refined at 32°SR and 90°SR. Refinement to nanosize range (90°SR) results in a very significant decrease in the specific scattering coefficient of the pulp. The reduction is relatively lower in softwood pulp than in hardwood and bagasse pulps. The effect of reduced scattering is also apparent in opacity values; the sheets made of 90°SR refined pulps were quite translucent. The decrease in scattering coefficient is due to reduced scattering surfaces caused by increased fiber-fiber bonding in the sheets made from nanofibrillated pulps. As expected, the absorption coefficient does not change as significantly as the scattering coefficient because it depends more on the chemical nature of the constituent materials. In contrast the scattering coefficient depends, to a great extent, upon the sheet structure.

Structural properties

Apparent density of the paper sheet is very significantly increased on refining the pulp fibers, and consequently the porosity is decreased for all three pulps. The air permeance of nanopaper sheets as measured by the porosity analyzer was found to be 0.0 mL/min (equivalent to Gurley porosity of infinity seconds). The results indicated that the paper sheets made from nanofibers were practically impervious to air passage. In **Fig. 4**, the FE-SEM images (500X magnification) show a very close structure for the sheets made from nanofibrillated pulps.

CONCLUSIONS

1. In the laboratory method using PFI mill, we can easily produce cellulose nanofiber within a 30–100 nm range. No chemicals were used in the refining method, which is one of its main advantages. Thus, the method is an environmentally friendly treatment.
2. Fibrillation was observed to be incomplete during normal refining (32°SR). A high degree of refining (90°SR) was required for fibrillation of fibers in the nanoscale range.
3. A high degree of refining of bagasse, hardwood, and softwood pulps resulted in paper sheets having significant increases in tensile index, burst index, and TEA index but decreases in tear index and stiffness.
4. Improvement in strength properties of nanopaper sheets was much greater in sheets made of bagasse pulp fibers than in sheets made of hardwood and softwood pulp fibers. This was due to of a higher proportion of nanosized fibrils in the highly beaten bagasse pulp.
5. Nanofibrillation resulted in decreased opacity, absorption coefficient, and scattering coefficient of the paper sheets. The nanopaper sheets were highly translucent. **TJ**

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ABOUT THE AUTHORS

We wanted to study how nanofibers with such exclusive properties as high aspect ratio, high mechanical strength, and high specific surface would behave when formed into a paper sheet. In our present study, we used the conventional PFI mill to produce nanofibrillated pulps. We included bagasse pulp, which is made from an agricultural residue.

Preparation of sheets from the slow-draining nanofibrillated pulp was quite difficult. We overcame this challenge by preparing the handsheets using vacuum filtration. An interesting finding was that nanofibrillation of fibers resulted in the greatest improvement in strength properties of agricultural residue pulps, which are otherwise weak pulps.

Nanofibers can be blended with other pulps to enhance paper properties, reduce energy consumption, or achieve more favorable combinations of paper properties. For industrial application of nanofibers in paper, it is necessary to develop a low energy process by combining mechanical, chemical, and biochemical treatments.

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