PRODUCTION OF ADVANCED FIBRILLATED CELLULOSIC MATERIAL FROM WHEAT STRAW BY REFINING PROCESS TO IMPROVE PAPER QUALITY

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In this study, a simple refining approach was tested to prepare an advanced fibrillated cellulosic material from wheat straw to avoid harmful oxidative pretreatment chemicals and to sort out cost and drainage issues. The wheat straw was delignified by pulping (soda-anthraquinone) and bleaching, and converted into advanced fibrillated cellulosic material by pretreatment with mild potassium hydroxide, followed by refining using a Valley beater. Scanning electron microphotographs analyzed by Image J software confirmed the micro-nano scale fibrillation in the prepared advanced fibrillated cellulosic material. After addition of 5% advanced fibrillated cellulosic material as a strength additive, the pulp drainability (36 °SR) was found suitable for papermaking. Paper handsheets containing 5% advanced fibrillated cellulosic material showed 4.7% reduction in bulk and 30%, 17% and 124% increment in breaking length, burst factor and double fold, respectively, when compared with the control set. Comparable tear and optical properties were also observed with better surface properties. The laboratory results confirmed the potential of the prepared advanced fibrillated cellulosic material as an appropriate additive for paper quality improvement.

Keywords: wheat straw, refining, advanced fibrillated cellulosic material, additive, drainability, strength and surface properties

INTRODUCTION

Microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC), commonly termed as cellulose nanomaterials (TAPPI standard terms and their definition, WI 3021), have been a topic of keen research interest for decades. Generally, these are extracted from cellulose, *i.e.* the most abundant organic matter on earth, and due to some inherent properties, such as renewability, biodegradability and biocompatibility, these materials are of great interest. At the nano-scale (diameter below 100 nm), almost all the materials show some entirely different physical, chemical and biological properties from their bulk form.[1] MFC and NFC (M&NFC) have many interesting properties, such as high specific surface area, high intrinsic physical strength, high cohesive energy density, hydrogen bonding potential, flexibility and strong network formation.[2-4]

Paper is a common but essential commodity for human life and it is made from cellulose. The paper industry is facing serious scarcity of wood fibres because of its use in other industries, slow growth cycle of plants, less plantation and strict forest conservation rules worldwide. Non-wood and recycled fibres are the main alternative for wood fibres, but with compromised physical properties. To overcome these strength related problems associated with the usage of non-wood and recycled fibres, the paper industry is using various chemicals, such as acrylamide, starch and long fibre fractions like softwood fibres. Research works carried out worldwide for the application of M&NFC as a strength additive in papermaking, have reported improvements in strength (tensile, burst and folding endurance), surface (barrier properties) and optical properties (brightness and whiteness). The use of M&NFC was also found favorable for filler retention and flocculation of starch and calcium carbonate in the wet end.[3] The addition of this cellulosic nanomaterial as a strength additive in papermaking can reduce the

need for higher refining of pulp and may save pulp fibres from subsequent structural damage, thus increase the life span of individual pulp fibre for recycling.[2] These properties of cellulosic nanomaterial make it valuable and in demand for the papermaking industry. However, although the application of M&NFC as a strength additive in papermaking has been established as effective, it also has some major demerits, including low water drainability and high cost at an industrial level.[5]

Lignocellulosic materials are the main source for M&NFC extraction and after a series of chemical and/or mechanical treatments, raw materials are converted into MFC or NFC (M/NFC). Firstly, lignocellulosic materials are broken into small pieces or chips by using mechanical action and then are usually delignified by pulping and bleaching mechanisms used in the papermaking process. After purification, cellulosic materials are treated by chemicals or enzymes and/or mechanical pretreatments and finally M/NFC is prepared by mechanical treatments using various mechanical devices.

In plant cells, the cellulose polymer is present as nano-dimension fibrils composed by glucan chains (up to 100) after ordered aggregation.[6] To facilitate easy separation during the mechanical treatment, various chemicals or enzymatic pretreatment strategies, such as sodium meta-periodate-chlorite oxidation, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation, deep eutectic solvents (DES), carboxymethylation, micro-emulsion treatment, quaternization and endoglucanase treatment, are used.[7,8] These pretreatments are effective and energy reducers during mechanical action, but they involve high costs, which makes them less feasible for industrial scale utilization. Some chemicals, like TEMPO and sodium meta-periodate, are also highly toxic and may be dangerous if researchers or workers are exposed to them.[9]

Under these conditions, the preparation processes for M&NFC by only mechanical treatment seem ecofriendly and less hazardous, but consume high energy, which is a matter of great concern. The most common mechanical treatments for M&NFC preparation are high pressure homogenization, ultra-grinding,[2] micro-fluidization, steam explosion,[10] ultra-sonication,[11] refining,[12] cryo-crushing,[13] and extrusion.[14] Refining is the simplest and easiest to use mechanical action for preparation of M&NFC. This industry oriented process is used by the paper industry in the papermaking process for fibrillation of pulp fibres. For preparation of M&NFC, researchers have mainly used the Valley beater and PFI mill for pre-mechanical treatments. Final mechanical treatment is generally provided by using ultra-fine grinders, high pressure homogenizers and microfluidizers. The use of refining as final or main mechanical action in the preparation of M&NFC has been reported by very few researchers.[11,15] Refining converts bulk pulp into fibrillated, collapsed, flexible, short and soft pulp fibres by frictional and shear forces.[11] The refining process is also considered an energy extensive process in the paper industry using wood as raw material. The refining energy consumption for agro residues is lower than for wood based raw material due to structural and compositional differences.

Agro residues (agro wastes) are non-economic parts (bark, stalk, bagasse, roots and leaves) of plants that are generated after crop harvesting. These are generally used as cattle feed, bedding for cattle, fuel (for cooking and boiler), soil mulch, home thatching and manure. In India, nearly 500-550 million tons (MT) of crop residue is generated ($1.4x10^5$ MT worldwide) each year, including 141 MT sugarcane residue, 110 MT of wheat residue (in the form of straw), 122 MT rice residue, 71 MT maize residue, 28 MT pulses residue, 26 MT millet residue and 8 MT fibre crops (cotton, jute) residue. There are around 234 MT/year of agro residues remaining as surplus after being used in the aforesaid activities. Wheat is a major crop of Haryana, Punjab and Uttar Pradesh province of India. Every ton of wheat produces 1.4 to 1.5 ton of straw, thus, it is easily available in these areas. Wheat stalk/straw is often burned in the fields by farmers before the next crop, because of the costs involved for its removal from the fields. Besides the aforesaid domestic and agricultural applications, the paper industry is also utilizing wheat straw as a raw material for papermaking. Due to abundant annual generation of surplus wheat straw, its easy availability and lower structural complexity, it has also been explored for preparation of some high-end products, such as cellulose nanomaterials and biofuels.[2,16,17]

In the present work, a mixture of cellulose fibres with fibrillation of micro- and nano-dimensions, termed as advanced fibrillated cellulosic material (AFCM), was prepared from bleached wheat straw pulp (BWSP) obtained after

pulping and bleaching of wheat straw (WS). The BWSP was converted into AFCM by mechanical treatment (refining) in a laboratory Valley beater after alkaline pretreatment. Then, this prepared AFCM was characterized and used as a strength additive in papermaking, using bleached mixed hardwood pulp (BMHWP), to investigate the suitability of AFCM in papermaking applications.

EXPERIMENTAL

Materials

WS (cellulose – 36.5%, hemicelluloses – 28.1%, lignin – 16.6%, extractives – 11.9%, ash – 6.9%) was collected from a local market and was used as a starting raw material for preparation of AFCM. It was manually screened for impurities, like pieces of plastic, stones or wires, and conserved by introducing in plastic bags. Bleached mixed hardwood pulp (BMHWP) obtained from a nearby paper mill was used to prepare paper handsheets. For preparation of AFCM, sodium hydroxide (NaOH), anthraquinone ($C_{14}H_8O_2$) and sodium chlorite ($NaClO_2$) were used. For the sake of comparison (during papermaking), cellulose nanofibrils (CNF) (solids – 3.0% slurry; fibre dimensions – width 50 nm and lengths up to several hundred microns; surface property – hydrophilic, 31-33 m^2/g (BET); density – 1.0 g/cm^3) were procured from the University of Maine, USA, and used as reference (designated as R-NFC).

Methods

Analyses were done in triplicate/duplicate. The results are presented as the mean value ± standard deviation.

Preparation of cellulose pulp

During all the treatments, chemicals were taken on equivalent basis to kg/t or g/t of oven dried (OD) material/ fibre. WS was converted to cellulose pulp (unbleached) by conventional soda pulping at 165 °C for 20 min using 150 kg/t NaOH and 500 g/t anthraquinone (AQ) with a solid to liquid ratio of 1:5 in a laboratory autoclave digester, consisting six bombs (each of 2.5 liter capacity) and polyethylene glycol as heating medium. After pulping, the digested WS material was disintegrated in a pulp disintegrator and washed with tap water to remove chemicals and other impurities. Next, the pulp was screened using a Somerville screen, with slot width of 0.15 mm, to separate out the uncooked material. Further, the unbleached pulp (~13.0 kappa number) was bleached using 50 kg/t $NaClO_2$, at 80 °C for 2 h. The pH of the pulp was adjusted to 4.0 with the help of 1 N H_2SO_4 and NaOH solutions before bleaching and pulp consistency (Cy) during the treatment was 4.0%. After the treatment, the pulp was washed with tap water until neutral pH.

Preparation of advanced fibrillated cellulosic material (AFCM)

360 g (OD basis) of BWSP (24 °SR – Schopper Riegler number; ~2.0 kappa number) was firstly treated with 6% KOH at 80 °C for 1 h, and after that refined in a laboratory Valley beater (Universal Engineering Corporation, India) at ~1.56% Cy to 87 °SR. Here, 87 °SR has been used as a threshold for refinement, since °SR of the R-NFC was 87 (obtained according ISO 5267-1 using an °SR Tester, Universal Engineering Corporation, India). After achieving the targeted °SR, the refined pulp slurry was filtered through a 300 mesh screen and the first filtrate was recycled to avoid fibril/fines loss. The prepared AFCM slurry was stored in sealed containers at 4 °C to avoid microbial contamination until further application.

Energy calculation

The energy consumed by the Valley beater for refining of BWSP to the desired °SR was calculated according to Atic *et al*.[18] (Eq. 1):

$$\text{Specific beating energy (SBEn)} = \frac{(\text{EPAn} \times \text{BTn})}{\text{FMn}} \quad (1)$$

where SBEn = specific beating energy in the process step (Wh/kg), n = sample removal step, EPA = effective power applied [TMP-NPL] (W), TMP = total motor power, NLP = no load power, BTn = beating time in step (h), FMn = oven dry fibres mass processed in the process step (kg).

Yield

The yield of AFCM was determined by using the gravimetric method (Eq. 2), using the whole AFCM mass (the yield calculation on the basis of nano-dimension fibres was not considered here):

$$\text{Yield (\%)} = \frac{\text{FW}}{\text{IW}} \times 100 \quad (2)$$

where FW= Final (OD) weight of pulp, IW= initial (OD) weight of pulp.

In this study, the main application of AFCM was in papermaking and micro-nano level fibrillation on the fibre surface may fulfill the bonding purposes during paper sheet formation.

Morphological study

Scanning electron microscopy (JEOL JSM-6510 LV) was used to study the morphology of the prepared AFCM. Specimen samples were prepared by taking 0.05% aqueous slurry of fibres. Test specimens for SEM were prepared on circular flat glass pieces and, after air drying, gold coating was applied before observation at 5000x and 30000x, using 15 kV accelerating voltage.

Fibre dispersion

Fibre dispersion and settling in aqueous solutions were observed keeping the fibre slurry (0.5% consistency) in capped glass bottles. Fibre settlement

and dispersion were observed after various time intervals, *viz.* 0 min, 30 min, 2 h and 24 h.

Water retention value

The water holding capacity of BWSP and AFCM in terms of water retention value (WRV) was determined according to standard method SCAN-C 62:00. On OD weight basis, 1.3665 g of each test sample was taken for 1700 grammage per square meter (g/m^2) pad in a G grade silica crucible. Before centrifugation at 3000 rpm for 30 min, the maximum water from the samples was removed by vacuum filtration. After centrifugation, the samples were weighed and oven dried at 105±2 °C for 12 h. The WRV was calculated using the following formula (Eq. 3):

$$\text{WRV, g/g} = \left(\frac{\text{CS}}{\text{ODS}} - 1\right) \quad (3)$$

where CS = weight (g) of centrifuged sample, ODS = weight (g) of oven dried sample.

Viscosity

TAPPI test method T 230 om-99 was used to determine the viscosity of the test samples using a capillary viscometer. In this method, 0.5M cupriethylenediamine (CED) solution was used as solvent for 0.5% cellulose solution. For viscosity measurements, 0.1250±0.0005 g (OD basis) test sample was hand torn and mixed with 25 mL of CED solution. The pulp sample was dissolved completely using a stirrer. Further, dissolved pulp solution was filled in the lower bulb of the viscometer and the viscometer was vertically placed in a water bath at 25.0±0.1 °C. The solution was drawn up with the help of a suction bulb into the measuring section of the viscometer and then allowed to drain down to wet the inner surfaces of the viscometer. The efflux time (±2.0%) was determined by drawing the solution above the upper mark and viscosity was calculated according to the following formula (Eq. 4):

$$V = C \times T \times D \quad (4)$$

where V = viscosity of CED solution at 25.0±0.1 °C, C = viscometer constant, T = average efflux time, D = density of the AFCM solution in g/cm^3.

Fourier-transform infrared spectroscopy (FTIR)

To observe the effect (if any) of the alkali and mechanical treatments on the functional groups of refined pulp, Fourier-transform infrared spectroscopy (FTIR) was carried out using a Perkin Elmer FT-IR (Frontier 104287) machine fitted with an ATR reflection accessory. The resolution of the instrument was 4 cm^{-1}. The spectra were attained from 64 scans in the 4000 to 400 cm^{-1} wavenumber range.

X-ray diffraction analysis

X-ray diffractograms (XRD) of the test samples (BWSP and AFCM) were taken by using a Malvern Panalytical X'pert Pro spectrometer, equipped with Cu-Kα radiation (λ = 1.54 Å) source (40 mA current, 45 kV voltage). XRD patterns were recorded over the 2θ range of 10-90°, at a step size of 0.0260°. After normalization of the X-ray diffractograms by the intensity (maximum) of the diffraction peak, the crystallinity index was calculated according to Segal *et al*. (1959) and by Gaussian curve fitting using amorphous fitting (AF) and amorphous subtraction (AS) methods[19] due to variation in CrI. The comparison should be made between CrI obtained following the same method for CrI estimation. Segal's method is based on the intensity of the peak 200 (I200, 2θ = 22.6°) and the minimum distance between the peaks for the planes 200 and 110 (*e.g.* Iam, 2θ = 18°) (Eq. 5):

$$\text{CrI} = \frac{\text{I200-Iam}}{\text{I200}} \times 100 \quad (5)$$

In the AF method, an individual crystalline peak was extracted from the profiles of diffraction intensity, assuming a Gaussian function for each peak by a curve-fitting process.[19] In the AS method, the amorphous fraction of cellulose was subtracted from the whole cellulose sample using the diffractogram, and CrI was determined by dividing the remaining area (crystalline part) of the diffractogram by the total area of the original diffractogram.[20] The crystallinity index obtained by Segal's method, Gaussian curve fitting using amorphous fitting and amorphous subtraction methods were denoted as CrI_S, CrI_{AF} and CrI_{AS}, respectively.

Preparation of paper handsheets

To investigate the effect of AFCM addition on paper properties (strength, optical and surface), paper handsheets (target grammage – 70 g/m^2) were prepared according to TAPPI test method T 205 sp-02, using a British handsheet former machine (Universal Engineering Corporation, India). All the chemicals or fibre components were taken on equivalent basis to kg/t or g/t of OD pulp fibre and mixed into the pulp slurry using a laboratory disintegrator (Universal Engineering Corporation, India). Per ton of OD pulp fibres, 50 kg (equivalent) AFCM/R-NFC was mixed into 950 kg (equivalent) BHWP. In the control set, 1000 kg (equivalent) BHWP was taken. The other components, like Alcofix 169 (polydiallyl dimethyl ammonium chloride-cationic polyDADMAC obtained from BASF, India, molecular weight – 3X10^5 g/mol): 200 g/t; cationic starch T 85 (obtained from Bluecraft Agro Pvt. Ltd., India, molecular weight – 825.5 g/mol, degree of substitution – ~0.035 mol/mol, Brookfield viscosity – 500 cps min): 5 kg/t; alkyl ketene dimer (AKD), (obtained from IVAX Paper Chemicals Ltd, India, wax – 9.1%, charge demand – 111 µeq/l anionic): 3.0 kg/t (*i.e.* 20 kg/t on such basis, having ~15% solids) and Percol 47 (cationic polyacrylamide flocculant obtained from BASF India Ltd., molecular weight – 6.12±0.45 X 10^{12} g/mol; pH 4.5) as retention aid: 200 g/t, were mixed one by one into the BHWP

slurry. The order of addition of the aforesaid additives was: (i) pulp, (ii) Alcofix 169, (iii) cationic starch T85, (iv) AKD, (v) adjusted to 0.33% Cy and (vi) Percol 47. R-NFC and the control sets were used only for comparison purposes.

Measurement of strength, optical and surface properties of paper handsheets

The prepared paper handsheets were examined for various properties, such as strength, optical and surface characteristics. Before examination, paper handsheets were conditioned for 24 h at 65±5% humidity and 27±1 °C temperature (ISO 187). Thickness and strength properties, such as breaking length, burst index, tear index and folding endurance, were measured according to IS 1060 Part I-1966, IS 1060 Part I-1966, IS 1060 Part I-1966, IS 1060 Part I-1966, ISO 5626-1993, respectively, by using AB Lorentzen & Wettre equipment. An Elrepho 070E instrument was used to measure the optical properties, namely, brightness (IS 1060 Part II-1960), whiteness (IS 1060 Part II-1960), yellowness (IS 1060 Part II-1960) and opacity (IS 1060 Part I-1966). The surface properties, *i.e*., average contact angle and surface energy (using a Drop Shape Analyzer DSA 10Mk2, Kruss GmbH, Germany, with DSA1 program for surface energy), smoothness (using a L&W Bendtsen Tester SE 164), porosity (using an L&W Air Permeance Tester SE 166), wax pick and $Cobb_{60}$ of paper handsheets were measured according to TAPPI T458 cm-04, IS 9894-1981, IS 4006 (Part I)-1985, IS 1060 (Part III), and IS 1060 (Part I), respectively.

RESULTS AND DISCUSSION

AFCM preparation using refining process as main mechanical treatment

The aim of the present study was to investigate the possibility of AFCM preparation from WS by using a simple and energy efficient process, and to test the efficacy of AFCM as a strength additive in papermaking. Therefore, WS was delignified by conventional soda-AQ pulping and bleaching (using sodium chlorite). The delignified WS pulp (BWSP) was treated with an optimized dose of KOH (equivalent to 60 kg/t) to swell and purify the fibres, and further it was refined using a laboratory Valley beater till the attainment of the targeted °SR – the targeted °SR (*i.e.* 87 °SR) was achieved after refining for 30 min. During chemical pretreatment in the AFCM preparation process, only mild alkaline treatment was given to BWSP and traditional oxidation treatments using TEMPO or periodate *etc*. were not applied. This makes the process eco-friendly as oxidation chemicals have certain harmful effects on the environment. These oxidative chemicals are also toxic for the research personnel, if exposed.[9] The use of a Valley beater as the only mechanical action device makes the process more facile and industrially feasible, as other mechanical action devices such as high pressure homogenizers, microfluidizers, ultra grinders, ball mills and ultrasonication devices, are costly and not compatible with industrial scale processing. Refining is a common practice in paper mills and is used for fibrillation of pulp fibres. Refining is an important mechanical action and it not only breaks down the intact fibre into micro-nano fibrillated fibres, it also exposes the indigenous functional groups of the cellulose.[21] To some extent, these functional groups have a repulsive effect, which helps in the separation of fibres.

Yield and energy consumption

The approximate gravimetric yield of AFCM was ~98% (352 g), which was a good yield. In this study, 360 g BWSP was taken as starting material for AFCM preparation to explore the scaling-up possibility and the positive results (~98% yield) confirmed the possible scale-up of the AFCM production.

During the mechanical conversion process, the specific beating energy consumed by the Valley beater was 116 kWh/t, with total energy consumption of 865 kWh/t. The total energy consumed during the refining was lower than the energy consumption reported in previous studies (6000 to 30,000 kWh/t), using other high-end mechanical action devices for preparing nano-fibrillated cellulose.[22,23] The main purpose of this study was to investigate the suitability of this simply prepared AFCM as strength additive in papermaking. The low energy consumption makes the process convenient for the industry. However, the AFCM prepared in this study was inferior to other superior quality preparations requiring higher energy consumption reported previously.

Characterization of AFCM

Morphology

The morphology of AFCM was explored using scanning electron microscopy. Micro-nano level fibrillation on the backbone of fibres and intertwined individual fibrils having micro-nano diameter were observed in the micrographs. These SEM images confirmed the successful conversion of BWSP into AFCM (Fig. 1). The main objective of this study was to prepare AFCM that could be useful for the paper industry (able to maintain an

appropriate drainage rate) and thus mechanical action was applied to the pulp to a level that would ensure fibrillation of BWSP fibres in the mico-nano range (*i.e.* AFCM) rather than getting all fibrils in the nano-dimension range.

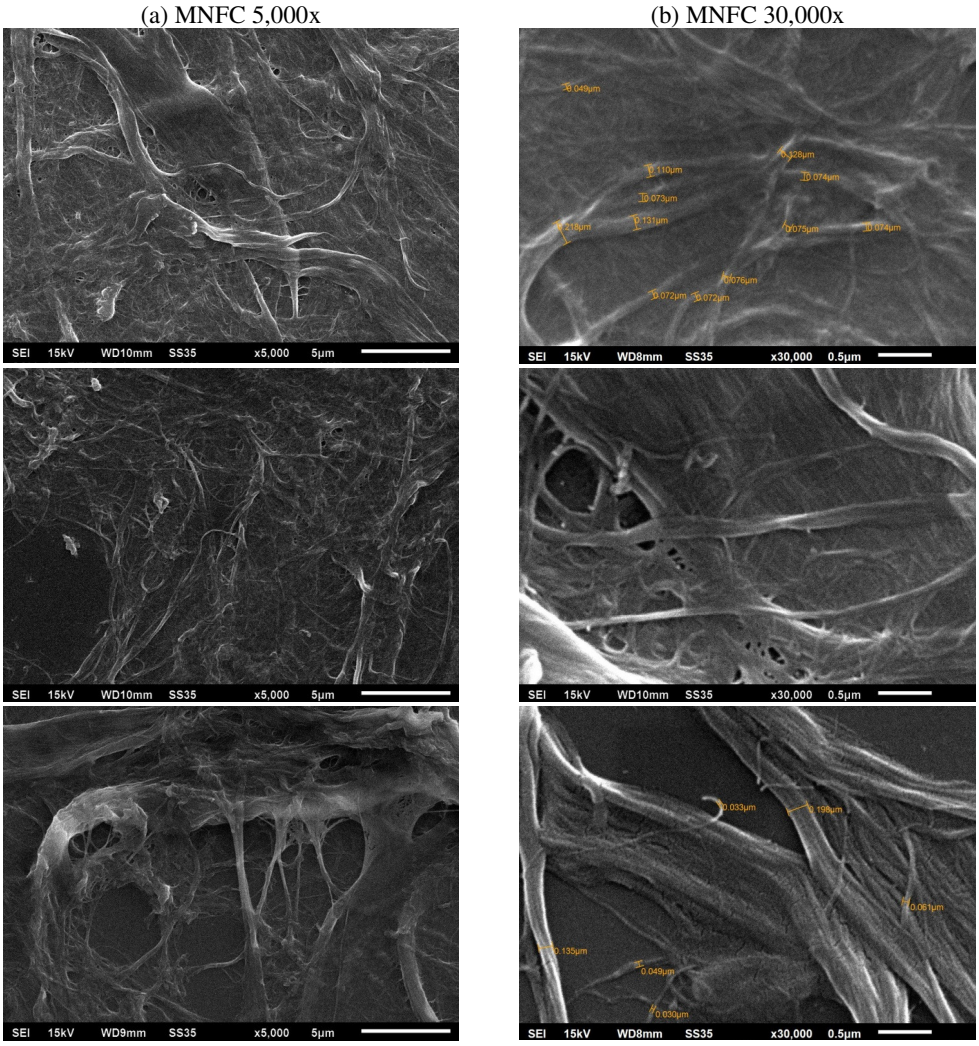

Figure 1: SEM micrographs of laboratory prepared AFCM (a) at 5,000x and (b) at 30,000x

Figure 2: Fibre dispersion and settling of BWSP and AFCM

Fibre dispersion and settling

To examine the fibre dispersion and settling visually, 0.1% fibre slurry of each sample was prepared and observed for 24 h. The slurry of BWSP and AFCM test samples were kept in capped glass tubes (Fig. 2). The fibre slurry of BWSP settled very fast and separated into a fibre fraction and clear supernatant just after 10 min.

The AFCM slurry started to settle after 30 min and clearly settled after 2 h. The settling was observed in the form of height of the fibre fraction and, in the case of AFCM, it was higher than the BWSP. After 24 h, the height of the fibre fraction in the case of AFCM decreased, but remained higher than the height of BWSP fibre fraction. This experiment shows the dispersion behavior of the fibres in water suspension. The higher height of the fibre fraction indicates a low agglomeration tendency between the fibres, possibly due to the repulsion effect of the negatively charged groups on fibre surfaces. The good dispersion behavior of the AFCM fibres in the pulp slurry is supportive for bonding of the pulp fibres during the papermaking process.[24]

Water retention value

The water retention value of AFCM (5.98±0.62 g/g) was found to be higher than that of BSWP (2.18±0.24 g/g). WRV shows the water holding capacity or water retaining capacity of pulp fibres or micro-nano fibrils, directly, and the volume of fibre pores, indirectly. After centrifugation, the amount of water adhered within the thin layers and the ridges of fibre outer surfaces and within fibre pores indicates the water retention value.[25] The WRV of advanced fibrillated cellulosic material is mainly influenced by chemical or enzymatic pretreatments and the final mechanical action.[26] Fibre swelling, originating due to delamination or internal fibrillation of fibres induced by beating or refining treatment, also has a positive impact on WRV. External fibrillation on the fibre surfaces was also found responsible for increased WRV, as enormous inter-fibril spaces are present between the fibrils and they might hold water.[27,28] These aforesaid factors may be main contributors to an increased WRV of AFCM.

Viscosity

The viscosity of AFCM was observed to be lower (6.8 cP) than the viscosity of BWSP (10.7 cP). The measurement of viscosity is an indirect method for the evaluation of cellulose chain length and the effects of various chemical, enzymatic or mechanical treatments on the chain length of cellulose can be investigated.[29] A decrement in the viscosity of AFCM may occur because of length shortening of cellulose fibres and fibrils during the extensive refining action in the Valley beater. The short length fibres and fibrils are dissolved easily in CED solution and are unable to create a strong network during the flow.[30]

FTIR analysis

To investigate the effect of the pretreatment and mechanical action on the chemical structure of AFCM, FTIR analysis of BWSP and AFCM was carried out (Fig. 3). In both samples, two main absorption areas (regions), one ranging around 3336-2899 cm^{-1} and the second ranging around 1651-522 cm^{-1}, were observed. A large peak at 3336 cm^{-1} represented the O-H stretching band and the peak at 2899 cm^{-1} showed the presence of the C-H stretching band.[31] The absorption peaks near 1150 cm^{-1}, 1110 cm^{-1}, 1060 cm^{-1}, 1028 cm^{-1} and 895 cm^{-1} in both samples showed the cellulose structure (C-H glycosidic deformation of cellulose).[10,16,32] However, no significant differences were observed in the pulp samples and can be explained by the absence of any kind of chemical pretreatment.

XRD analysis

The effect of refining on the crystallinity of AFCM was investigated by X-ray diffraction analysis. The diffractogram contained typical (characteristic) peaks around 15.8, 21.1 and 34.4, denoting cellulose I reflection planes (1 1 0), (2 0 0), and (0 0 4), respectively.[33] During a comparison between the crystallinity index (CrI) values following the same method, it was observed that the CrI of AFCM (CrI_S = 59.2%; CrI_{AS} = 15.1%; CrI_{AF} = 29.0%) was found to be lower than the CrI of BWSP (CrI_S = 78.2%; CrI_{AS} = 26.1%; CrI_{AF} = 35.7%) (Fig. 4). A possible reason of this decrement in the CrI of AFCM may be due to the breakup or fragmentation of cellulose crystals because of the collapse of the crystalline domain by extensive refining of fibres.[2,34]

Application of AFCM to improve quality of paper handsheets

Strength properties

The effect of AFCM addition on paper handsheet properties (strength, optical and surface) was evaluated by adding AFCM into BMHWP. Table 1 shows the effect of AFCM and R-NFC addition on the strength properties of paper handsheets. The breaking length increased by 30.5% (from 4418±190 m to 5764±224 m) and 30.8% (from 4418±190 m to 5777±221 m) after addition of AFCM and R-NFC, respectively. A 17.7% (44.0±1.20 to 51.8±1.31) increment was observed

in burst factor in the case of AFCM addition and a 23.4% (44.0±1.20 to 54.3±1.38) increment – after addition of R-NFC. The addition of AFCM (88.5.±1.70 to 91.0±1.90) and R-NFC (88.5.±1.70 to 92.9±2.10) positively affected the tear factor.

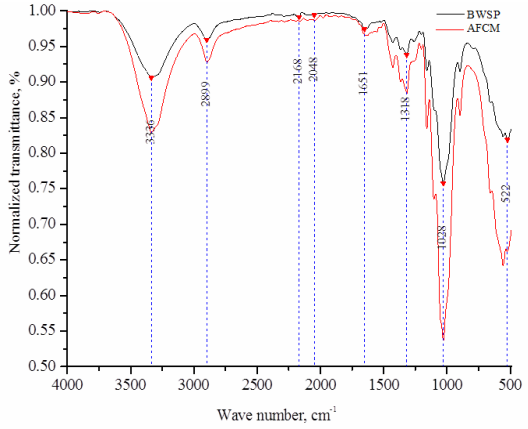

Figure 3: FTIR spectra of BWSP and AFCM

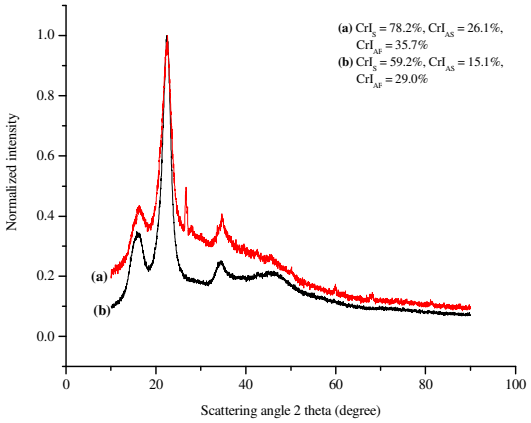

Figure 4: XRD diffractograms of (a) BWSP and (b) AFCM

After the addition of AFCM, the double fold (58±4 to 130±6) of paper handsheets was found increased (124%) and a similar outcome (increment of 131%) was also observed in the case of R-NFC (58±4 to 134±5). Comparable drainability (36 °SR) was also observed in the case of AFCM addition (Table 1). The water holding capacity of the pulp was found increased after the addition of AFCM and the reason of this increment is the binding of water molecules with the OH^- groups of AFCM by hydrogen bonds.[2] Moreover, the AFCM enhances clogging of pores between the fibres and may reduce the drainability.[5]

An increment in tensile strength (breaking length) after addition of AFCM was observed mainly due to the role of AFCM as promoting agent of adhesion between the pulp fibres by making hydrogen bonds.[35] AFCM has a small diameter and large specific surface area, and when it is mixed with ordinary pulp fibres, it provides more linkable points to fibres, thus it enhances bridging and entanglement between fibres. The same chemical structure of AFCM also helps in creating strong affinity towards pulp fibres.[28]

Paper handsheets having AFCM showed reduction (4.8%) in bulk (Table 1). The bulk is calculated from the thickness of paper sheets. The main reason for a reduction in the thickness of paper handsheets might be the increment in sheets' compactness due to closeness of pulp fibres. The adhesion between pulp fibres caused by increased hydrogen bonding due to AFCM is the main factor for fibre closeness.

Table 1
Strength properties of paper handsheets having AFCM and R-NFC

Particulars		Control	AFCM	R-NFC
BMHWP, kg		1000	950	
NFC, kg		0	50	
°SR		30±1	36±1	44±1
Drainage time, s	600 mL	11±1	17±1	30±1
	700 mL	19±1	26±1	45±1
	800 mL	29±1	39±1	60±1
Grammage, g/m^2		72.8±0.8	72.5±0.7	72.0±0.6
Bulk, cc/g		1.47±0.04	1.40±0.02	1.39±0.02
Breaking length, m		4418±190	5764±224	5777±221
Burst factor		44±1.2	51.8±1.3	54.3±1.4
Tear factor		88.5±1.7	91.0±1.9	92.9±2.1
Double fold, no.		58±4	130±6	134±5

Table 2
Optical properties of paper handsheets prepared with the addition of AFCM and R-NFC

Particulars	Control	AFCM	R-NFC
BMHWP, kg	1000	950	
NFC, kg	0	50	
ISO brightness, %	77.8±0.7	76.2±0.5	77.9±0.3
CIE whiteness	62.2±0.2	59.0±0.5	61.2±0.5
Yellowness	8.88±0.07	9.45±0.08	8.78±0.07
Opacity, %	79.6±0.4	79.2±0.4	80.0±0.6

Moreover, AFCM may also act as fines and may reduce the meniscus radius of the pulp suspension and finally, may intensify the pressure gap between water and the fibre suspension, ultimately helping fibres to come together.[36]

An improved tear factor (tear resistance) for the control set was observed after the addition of AFCM. The main reason for this preservation in tear index may be the unaffected or somewhat improved union between pulp fibres due to the presence of AFCM.[37] The tear resistance of paper sheets depends on average fibre length, strength of individual pulp fibres, bonding and amount of fibres participating in a rupture. In the present case, the mixing of AFCM positively affected these factors and helped in maintaining the tear resistance of paper sheets.[36]

The addition of AFCM imposed a positive effect on the burst factor of the paper handsheets and a possible reason for this increment may be the formation of a highly bonded fibre network in the paper sheets by AFCM. The nano-level fibrillation on fibre surface participates in fibres' connectivity and binding.[38]

After mixing of AFCM into BMHWP, double fold numbers were also found to increase. Double fold shows the number of folding and unfolding times of paper sheets at the same point before final breakage of the sheet. The double fold number of a paper sheet usually depends on fibre length, fibre bonding and brittleness or flexibility of fibres. The presence of AFCM in paper sheets is supposed to enhance these factors and positively affect double fold numbers.

Optical properties

In the AFCM addition sets, a slight decrement was observed in brightness (1.6 pts) and whiteness (5.2%). The yellowness was found slightly increased (6.4%) in comparison with the control set (Table 2). The addition of some contaminants into the AFCM slurry during the refining process in the Valley beater may be a possible reason for this decrement in whiteness and the increment in yellowness. Comparable opacity with that of the control and R-NFC set was also observed in the case of AFCM addition. Gonzalez *et al*.[39] and He *et al*.[28] observed unaffected opacity after the addition of NFC, while some researchers, for example, Eriksen *et al*.[40] and Boufi *et al*.,[3] reported a decrement in opacity and brightness after MFC and NFC addition.

Surface properties

Better surface properties than those of the control set were observed in paper handsheets containing AFCM and R-NFC (Table 3). Improved smoothness with decreased porosity was seen in sets containing AFCM and R-NFC. The Gurley porosity (air resistance in seconds for 100 mL air flow through the paper sheet) was found increased by 129% for AFCM and by 395% for R-NFC addition, compared to the control. Porosity represents the pores or empty spaces present in a paper sheet. The increment in Gurley porosity (air resistance, indirectly) shows increased compactness of paper handsheets as a result of gaps and empty spaces occupation by AFCM or R-NFC fibrils between the large fibres.[2,37]

The effect of the addition of AFCM on water penetration resistance or hydrophobicity of the paper sheet surface was assessed by the methods of contact angle measurement and $Cobb_{60}$. In the contact angle method, a single drop of water was poured on the paper sheet surface by injection and the angle between the drop and the paper sheet surface was measured. In the $Cobb_{60}$ method, the paper sheet surface was wetted with 100 mL of water for 60 seconds and the quantity of absorbed water was calculated using the gravimetric method. An increment in contact angle was observed from that of the control (96.1±1.0º) to

AFCM (121±1.4º) and R-NFC (123.5±1.1º) addition sets, and a decrement in $Cobb_{60}$ after AFCM addition (21.4±0.2 to 15.1±0.2 g/m^2) indicates the positive effect of AFCM addition on the water resistance of the paper surface (Table 3).

Table 3
Surface properties of paper handsheets containing AFCM and R-NFC

Particulars	Control	AFCM	R-NFC
BMHWP, kg	1000	950	
NFC, kg	0	50	
Smoothness, mL/min (top/bottom)	170/570	140/540	100/520
Gurley porosity, s/100 mL	15.8±1.01	36.3±4.11	78.3±6.20
Average contact angle, º	96.1±1.0	121±1.4	123.5±1.1
Surface energy, mN/m	25.4±0.2	10.6±0.2	9.8±0.3
$Cobb_{60}$, g/m^2	21.4±0.2	15.1±0.2	14.5±0.3
Wax pick (clear)	16	18	18

After addition of AFCM, a decrement in surface energy was observed (control – 25.4±0.2 mN/m, AFCM – 10.6±0.2 mN/m), and it also indicates the hydrophobic nature of paper sheets. Water (having low surface energy) can be easily absorbed onto the paper surface, if the paper surface has high surface energy.[41] After mixing AFCM, the surface energy of the paper was reduced, and this was also supported by decreased $Cobb_{60}$ values.

Higher Wax pick (clear) numbers (18 clear) were observed in the set with AFCM addition, compared to the control set (16 clear) (Table 3). Wax pick numbers show the strength of the paper sheet surface and a positive effect was induced by the addition of AFCM. Thus, the application of AFCM as additive showed an improvement in the surface properties of the paper. As a result, the prepared paper will be compatible for improved printing speed and printing with tacky inks.

CONCLUSION

The study proposes a facile approach of alkaline pretreatment, followed by refining as the main mechanical action for the production of AFCM from bleached pulp of wheat straw. This process may also be considered as economical and eco-friendly due to the use of a low-energy demanding refining process, without using oxidative chemicals during BSWP pretreatment. Fruitful application of the Valley beater for refining as final mechanical treatment made the process simple and mill-compatible. The current laboratory study showed the successful preparation of AFCM from BWSP with ~98% gravimetric yield. The prepared AFCM delivered positive effects on the strength and surface properties of paper handsheets, with comparable optical properties. This laboratory AFCM also provides compatible drainage rate to pulp and its application may not affect the productivity of mills. Overall, the prepared AFCM was found suitable for improvement of paper qualities. Based on laboratory findings, it can be concluded that the AFCM may be prepared by paper mills on site and applied in the same mill using existing facilities.

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