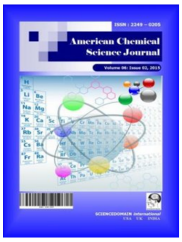

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A Morphological Study of Microfibrillated Cellulose Prepared from Waste Cotton Linter

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Authors' contributions

This work was carried out in collaboration between all authors. Authors MAAM, MR, GMAK and MSA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MHU, SMAR, JAF, MH and SR managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this work microfibrillated Cellulose (MFC) was prepared from cotton linter which was collected from a textile mills in Pabna, Bangladesh. MFC was characterized by WAXD, FTIR, SEM and OM measurements. MFC was synthesized by several steps such as alkali treatment, followed by $NaClO_2$ bleaching and acid hydrolysis. The acid hydrolysis was conducted by two different sulphuric acid (H_2SO_4) concentrations (3N and 5N). The oxidation reaction took place during the MFC preparation by using 5N of acid which was detected by FTIR spectra. The crystallinity index of MFCs were measured from the peaks at (2θ angles) 14.6 and 22.6^0 of WAXD curves. The WAXD curves show enrichment in the proportion of crystalline cellulose in MFCs, which manifests significant conversion of cellulose-I to cellulose-II. A significant change in morphology of MFC was clearly observed at SEM and OM images due to chemical treatment of cotton linter.

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Keywords: Cotton linter; microfibrillated cellulose; FTIR; WAXD; SEM; OM.

1. INTRODUCTION

Cotton linter is an important byproduct of the textile industry. It is rejected part which is produced of the different unit of textile processing industry. For example, the regular cotton fibers are extracted in the ginning process, the linter remains attached to the seed coat. The fuzzy seed needs to be subjected to an additional process that will mechanically remove the linter. The amount of linter produced worldwide is around 2.5 million metric tons, considering the 42 million metric tons of cotton lint produced in 2010 [1]. In Bangladesh there are about 7000 textile industries which produced a lot of cotton linter every year. Nanocellulose or microfibrillated cellulose (MFC) is a material composed of nanosized cellulose fibrils with a high aspect ratio (length to width ratio). Typical lateral dimensions are 5–20 nanometers and longitudinal dimension is in a wide range from tens of nanometers to several micrometers. In other words nanocellulose is a man made substance which is obtained from the naturally occurring compound i.e. cellulose. Producing cellulose nanocrystals is an interesting use for linter. Nanocrystals of cellulose, with diameters ranging from 2 nm to 20 nm and length ranging from 100 nm to 2.1 μm are called whiskers, nanowhiskers, or nanofibrils, and they can be obtained from many natural fibers [2-4]. The increasing interest in nanomaterials and their unique properties have led to intensive research in the area of nanocellulosic materials, such as cellulose nanocrystals (cellulose whiskers), electro-spun cellulose nanofibers and microfibrillated cellulose (MFC) [5-8]. On account of its small size, very high surface area and high aspect ratio, NC is a potential reinforcing material with the advantages of being derived from renewable resources, biodegradable and biocompatible. NC networks have been used in the field of biomedical applications and in transparent materials for different purposes such as, manufacture of, biocomposite for bone repair, nanoarchitechture, nanostructured foams and membranes, flexible electronic displays, magnetic films, switchable optical films novel bioplastics, additives for paints, cosmetic products, pharmaceutical products, recyclable structural and interior components for transport industry, hygiene and adsorbent products etc [9,10]. MFC can be prepared from native fibers, giving rice to highly crystalline and rigid nanoparticles [11]. Gong et al. [12] were prepared nanocellulose with high aspect ratio from wood. Abrahma et al. [13] were intended to study the extraction of nanocellulose from lignocellulosic fibers. In the preliminary analysis, they were investigated three different fibers Banana (pseudo stem), jute (stem) and pineapple leaf fiber (PALF). Cotton fiber also been used as a raw materials for NC [14]. It is mainly composed of celluluse. As like cotton and other ligonocelluloses fiber it might be a potential source of NC in the present investigation, this wastage cotton linter has been received interest as the raw materials for cellulose as well as NC. Plenty of methods have been investigated to isolate nano-cellulose for different species such as mechanical methods, enzyme hydrolysis, chemical methods etc [9,14,15]. Chemical processes were frequently practiced due to easy and quick extraction, low cost and to obtain shortest crystalline fiber diameter. Mandal and Chakrabarty [15] were isolated more crystalline nanocellulose by acid hydrolysis from sugarcane bagasse (SCB) by the acid hydrolysis of native cellulose fibers using a concentrated inorganic acid, commonly sulfuric or hydrochloric acid. Cellulose nanoparticles have been synthesized in spherical form [16], rod-like highly crystalline nanocrystals [17] which are obtained by acid hydrolysis of cellulosic fibers, and microfibrillated cellulose (MFC) resulting from disintegration of cellulose fibers under high shearing and impact forces [18]. Abrahama et al. [13] were tried to extract NC by steam explosion technique along with mild chemical treatment. Their processes were consisted usual chemical procedures such as alkaline extraction, bleaching and acid hydrolysis. However, several chemical treatment and acid hydrolysis caused the partial cleavage of the elementary crystallites and recrystallization of cellulose during hydrolysis [12]. Cellulase and Xylanase enzyme often used to find superior quality nanocellulose from cellulose [19]. Satyamurthy and Vigneshwaran [20] were established a novel process for the synthesis of spherical nanocellulose by hydrolysis of microcrystalline cellulose using anaerobic microbial consortium. Now a day, combined techniques were more popular to get homogeneous NC. Li et al. [21] were prepared of entangled nanocellulose fibers from alkaline peroxide mechanical pulp and physical ultrasonication method. Panthapulakkal and Sain [10] were prepared cellulose nano fibrils from wood pulp fibers by mechanical defibrillation, and diameter distribution of the fibers produced was in the range of 1–100 nm. Nanocelluloses are

rod like highly crystalline particles with a regular cross-section and their dimensions depend on 1) The native cellulose source material, 2) Hydrolysis time and 3) Temperature. Jiang and Hsieh [22] were isolated from pure rice straw cellulose through sulfuric acid hydrolysis, mechanical blending and TEMPO-mediated oxidation to 16.9%, 12% and 19.7% yields, respectively. Hassan et al. [23] were isolated of nanofibers from bleached bagasse and rice straw pulps using high-shear ultrafine grinder. The pulps were refined using high-shear ultrafine grinder and then homogenized using high-pressure homogenizer and resulted in nanofibers with diameters ranging from 3.5 to 60 nm.

In this work, bleached cotton linter was used as cellulose source to prepare MFC. Waste cotton linter obtained from textile mills as a byproduct which is used as pulp and paper industry. High cellulose and low lignin percentage of cotton linter can be the potential raw material for MFCs production. The aim of this work is to isolated MFC from bleached cotton linter by acid hydrolysis and thereafter ultrasonication. The MFCs were characterized by FTIR, WAXD, SEM and OM measurement.

2. EXPERIMENTAL

2.1 Materials

The cotton linter was collected from I-man Textile Industries at Pabna in Bangladesh. All the chemicals used in the present investigation were analytical reagent grade purchased from Sigma Aldrich.

2.2 Methods

2.2.1 Isolation of cellulose from cotton linter

Cotton linter was subjected several physical methods to remove small particles like as sand, mud and other dirty then washed with distilled water. It was dried in air. The washed cotton linter was immersed in 17% (w/v) sodium hydroxide solution at room temperature for 3 h with occasional stirring by glass rod where liquor ratio was maintained at 1:50 (w/v). The alkali treated cotton linter was washed several times thoroughly by distilled water and neutralized with very dilute acetic acid. The alkali treated cotton linter was dried in air filled by an electric oven at 105°C for 6 h and stored in poly bag. The alkali treated fibers were bleached with 1 wt% sodium chlorite solution for 90 min at 85-95°C. The fiber-liquor ratio was maintained at 1:50 (w/v). In this process the pH was controlled at 4. A buffer mixture of pH 4 (acetic acid-sodium acetate) was prepared and added to the chlorite solution in the proportion of 1 ml of buffer solution for every 10 ml of chlorite solution. After treatment, bleached cotton linters were filtered over a sintered funnel and washed thoroughly with distilled water. The pulp was then treated with 0.2% (w/v) sodium meta-bi-sulfite ($Na_2S_2O_5$) solution for 20 min with fiber-liquor ratio 1:20 (w/v). The pulps were filtered and washed thoroughly with distilled water and finally dried in an electric oven.

2.2.2 Preparation of microfibrillated cellulose from cotton linter

An aqueous suspension of MFC was prepared as our previous paper [24]. The cellulose as obtained earlier was acid hydrolyzed by refluxing with 3N and 5N sulphuric acid solutions. 10 g of each bleached cotton linters were added in the solutions of 3N and 5N sulfuric acid. The fiber-liquor ratios were maintained at 1:50 (w/v). The pulp suspensions were then placed on a magnetic stirrer and continued stirring up to 6 h by a magnetic bar. After 6 h acid hydrolysis, the white powder like MFCs were formed and then MFCs were filtered and washed thoroughly with distilled water. The obtained MFCs are insoluble in water, ethanol, DMF and other organic solvents. MFCs were kept in acetone and sonication was performed for 12 h in an ultrasonic bath.

3. CHARACTERIZATION

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the cellulosic samples were recorded on an instrument (Shimadzu FTIR 8400, Japan) in the range of 500–4000 cm^{-1} with a resolution of 4 cm^{-1}. The samples were ground into powder by a fiber microtome and then blended with KBr followed by pressing the mixture into ultra-thin pellets. The pellet was prepared by mixing approximately 0.5 mg of powder cotton linter and 100 mg of dry KBr in small agate mortar pestle. For better resolution 30 times scans were taken.

3.2 Wide-Angle X-ray Diffraction (WAXD)

WAXD pattern of cellulose samples were obtained with BRUKER D8 ADVANCE wide

angle X-ray diffractometer using Cu Kα radiation (α=0.154 nm), voltage of 50 KV and current of 40 mA with 2θ ranges from 5 to 45° increased in step of 2º/min. The data was analyzed by origin 8 software.

3.3 Scanning Electron Microscopy (SEM)

SEM photographs of virgin cotton linter and MFCs surfaces were captured using JSM-6490LA, Japan. In this case, the samples were coated with gold using the sputtering technique.

3.4 Optical Microscopy (OM)

OM was carried out by an NMM-800TRF machine using a drop of dilute suspension of the fibers in order to study the effectiveness of the refining process for fiber size reduction.

4. RESULTS AND DISCUSSION

The morphological structures of MFC was prepared from cotton linter have been studied by FTIR, WAXD, SEM and OM. The FTIR spectra of bleached cotton linter, MFC-3N and MFC-5N as shown Fig 1. The FTIR spectra of fibers contain the typical vibration bonds of the components mainly corresponding to cellulose, hemicellulose and lignin. The hydrophilic tendency of the cellulose and MFC are reflected in the broad absorption bond in the 3500-3000 cm^{-1} region, which is related to the – OH groups present in their main components. In the 1600–900 cm^{-1} region, it is possible to appreciate in fibers vibrations of chemical components of the lignin at frequencies of 1514 cm^{-1} for guaiacyl and 1428, 1372 and 1325 cm^{-1} associated with syringyl. These absorptions are consistent with those of the typical cellulose backbone. Furthermore, almost the same absorption peaks as shown in

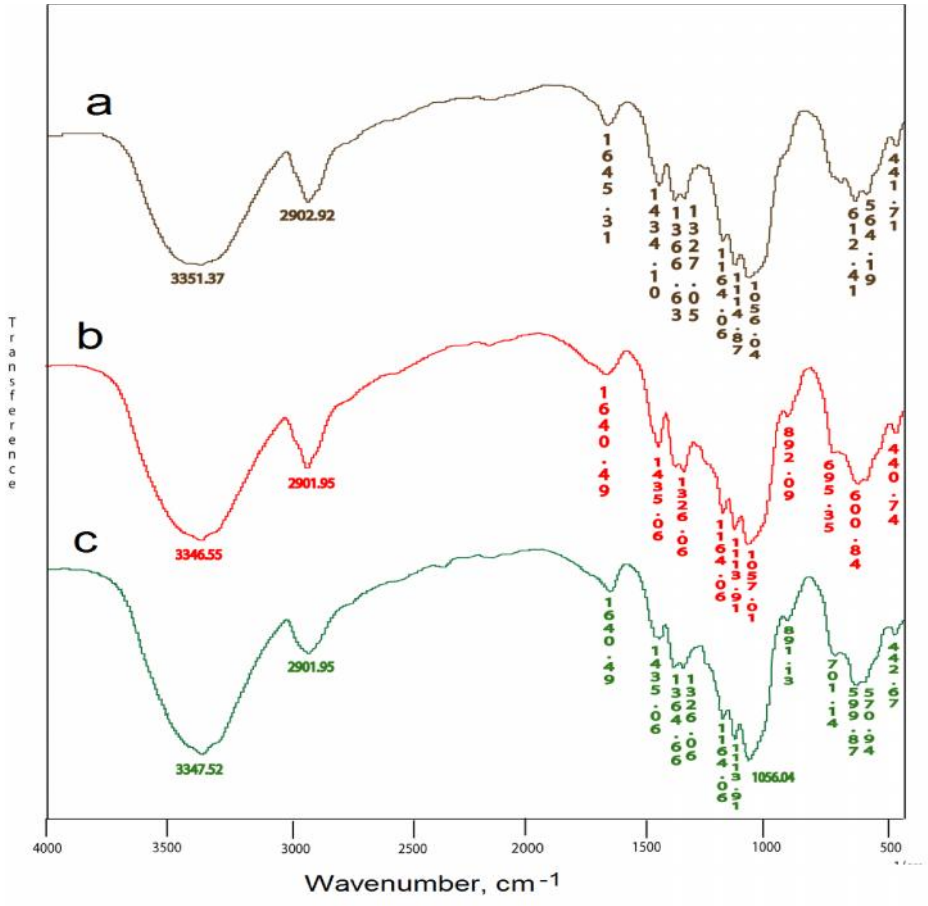

Fig. 1. FTIR spectra of (a) cotton linter, (b) MFC-3N and (c) MFC-5N

the cellulose fibers were observed in the spectrum of the MFCs. This indicated that the structure of celluloses have not been damaged after the treatments. On acid hydrolysis, the hydroxyl group of cellulose is oxidized to aldehyde (-CHO) or carboxylic acid (-COOH) group thus gives the identical peak at 1736 cm^{-1}. As the concentration of acid hydrolysis increases, the intensity of the peak at 1736 cm^{-1} of the samples increases. From the Fig. 1, it is observed that the very low intensity of the peak which negligible for cotton linter, but it gradually increases in case of MFC-3N and MFC-5N. On the other hand, the peak centered at 1643 cm^{-1} in the FTIR spectrum of cellulose and MFC may be due to the C=O bond of hemicellulose. The intensity of the peak decreases from cellulose to MFC as the hemicellulose is removed gradually by acid hydrolysis.

The crystallography of cotton linter and MFCs have been detected by WAXD. From the Fig. 2, it is seen that all the cellulose peaks near 2θ = 14.6, 22.6, and 34.2°. Comparing with the bleached cotton linter, there is no crystalline transformation of the crystalline structure in the MFC samples due to invisible changes in the diffraction angle (2θ). It is also observed that after acid treatment the crystalline peak intensity 22.6° at of MFC was increased. The increase of the intensity indicated that the acid hydrolysis induced the *crI%* due to the removal of amorphous materials like hemicellulose, lignin, and some other non-cellulosic materials. It can be noted that the increases orientation of cellulose along a particular axis with the non-cellulosic polysaccharides which are removed by hydrolysis and the amorphous zones are dissolved. It can be also noted that peak intensity ratio between the peaks 22.6 and 14.6° is increase with the increase of acid concentration. This may be due to higher acid concentration; degradation of cellulose occurs which may decreases the crystallinity index in case of MFC-5N (Table 2). Some WAXD data of cotton linter, MFC-3N and MFC-5N is shown in Table 2.

Fig. 3 shows that the SEM micrographs of the (a) original cotton linter cellulose, (b) MFC-3N and (c) MFC-5N. The diameter of the original cotton linter fiber was much bigger and each fiber appears to be composed of several microfibrils. Each elementary fiber possesses a compact structure, exhibiting an alignment in the fiber axis direction. The micrograph of the original cotton linter also displays a lot of non-fibrous components scattered over the fiber surface. On treating firstly with $NaClO_2$ lignin is removed through complex formation and depolymerization. On subsequent treatment with NaOH hemicellulose is hydrolyzed and becomes water soluble. These help in defibrillation of the fibrils and result in micrograph Fig. 3(c) whereby the diameter of the fibrils is reduced to a great extent, also possibly because of removal of non-cellulosic constituents.

Fig. 4 shows the optical micrograph of cotton linter and MFCs. It is apparent that, dimension of cellulose decreased with acid hydrolysis of cotton linter cellulose. In addition, between two microfibrilled cellulose MFC-5N shows lowest dimension.

Table 1. Infrared band assignment for cotton linter and MFCs [25-28]

Peaks	Characteristics present
3351	–OH bond stretching in cellulose
2901	C–H bond stretching present in cellulose
1736	C=O group present in fatty acid
1643	C=O bonds of hemicellulose
1597	Aromatic skeletal vibration and C=O bond stretching present in lignin
1503	Aromatic skeletal vibration present in lignin
1465	C–H bond asymmetrical deformation of cellulose
1428	C=C bond aromatic ring of lignin
1372	C–H bond symmetrical deformation of cellulose
1325	C–O bond stretching associated with syringil ring
1244	C–O bond stretching of primary alcohol present in guaiacyl lignin, cellulose an hemicellulose
1157	C–H bond stretching of cellulose
1116	C–H bond stretching of lignin
1059	C–O bond of secondary alcohol
897	β–glycosidic linkages of glucose ring of cellulose

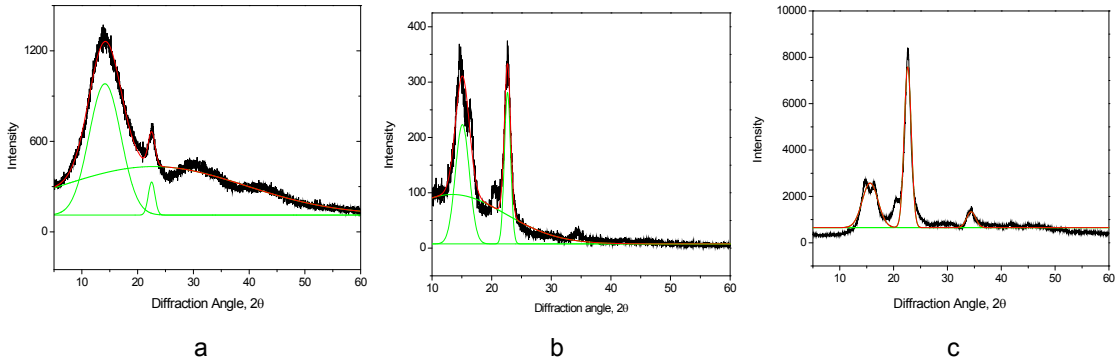

Fig. 2. WAXD spectra of (a) cotton linter, (b) MFC-3N and (c) MFC-5N

Table 2. WAXD data of (a) cotton linter, (b) MFC-3N and (c) MFC-5N

Sample name	Full width of half maximum of 2θ =22.6° peak (unit)	Similar peak position (Diffraction angle, θ)^0	Peak height	Peak wide	Peak area	Crystalliniy index, %
Cotton linter	1.9	14.6 22.6	10.0 4.7	9.5 4.6	660.9 211.5	62
MFC-3N	0.9	14.6 22.6	10.6 10.9	6.1 4.5	222.0 168.0	83
MFC-5N	0.8	14.6 22.6	3.4 11.0	4.2 4.4	78.0 165.0	51

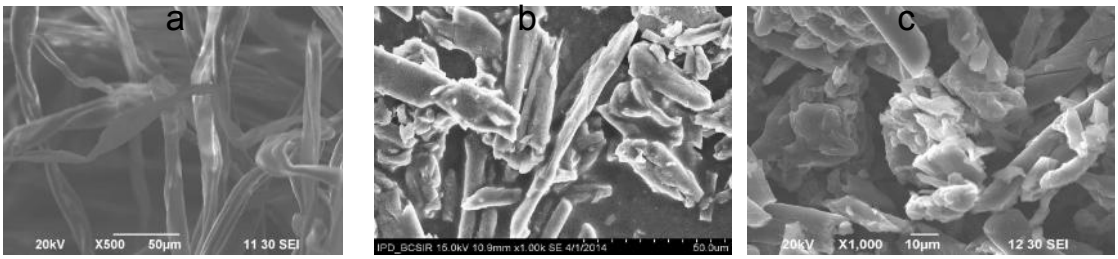

Fig. 3. SEM images of (a) cotton cellulose (magnification 500X), (b) MFC-3N (magnification 500X) and (c) MFC-5N (magnification 1000X)

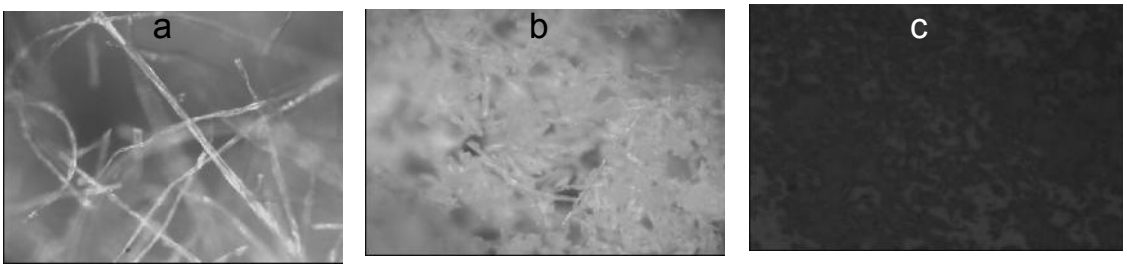

Fig. 4. Optical microgram of (a) bleached cotton linter, (b) MFC-3N and (c) MFC-5N

5. CONCLUSION

Cotton linter, the byproduct of textile industry has no economic value now that can be used to produce valuable microfibrillated celluloses (MFCs). Morphological and data revealed that the prepared MFC has identical characteristics and quite different to cellulose. The concentration

of acid during hydrolysis reaction of bleached cotton linter is affected on the dimension as well as crystallinity of MFC. The further work would attempt to do to modify the MFC for suitable industrial application.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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