

**CHARACTERIZATION OF MICROFIBRILLAR CELLULOSE
(MFC) OBTAINED FROM CORN STALK, SUNFLOWER
STALK, REED AND SESAME HUSK**

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ABSTRACT

Microfibrillar cellulose (MFC) samples from different agricultural resources and their wastes were characterized and compared in this study. MFCs were prepared from corn stalk, sunflower stalk, reed and sesame husk by two different methods. Hydrochloric acid (HCl) was used in Method 1, while formic acid (CH₂O₂) and sulphuric acid (H₂SO₄) were used in Method 2. SEM, FTIR, XRD and TGA analyses were conducted to determine the morphological, physical and thermal properties of the MFCs. The widths of the MFCs varied between 2.35 μm – 7.96 μm depending on the treatment methods and the raw materials. The crystallinity index of the lignocellulose increased after the chemical treatment, and the highest crystallinity index was found to be 82.0% for the sesame husk treated by Method 2. FTIR results indicate the presence of cellulose (~1640 cm⁻¹), hemicellulose (1740 cm⁻¹), lignin (1510 cm⁻¹) and the other components in the MFCs. The TGA results show that the decomposition temperatures for the treated samples were higher than those for the untreated samples, indicating that the chemical treatments increased the thermal stability of the MFCs. As a consequence, it was seen that agricultural resources and their wastes can be an effective raw material in production of MFCs.

KEYWORDS: Microfibrillar cellulose, agricultural resources, chemical treatment.

INTRODUCTION

Currently, there is a global interest in replacing petroleum-based products with bio-based products which are obtained from bioresources such as wood, agricultural sources etc. to solve the environmental problems associated with the use of petroleum-based products, such as global warming and pollution of plastics. Bio-based products are carbon neutral, and thus are good alternatives to petroleum-based products to protect environment. In this regard, cellulose is a sustainable natural resource for the production of bio-based materials and bio-products.

Cellulose is biodegradable, renewable, non-toxic and the most abundant organic compound in the world. The amount of cellulose produced by plants each year is approximately 1010 tons. 33% of annual plants, 50% of wood and 90% of cotton are cellulose. By mass, cellulose is composed of 44-45% carbon, 6-6.5% hydrogen and approximately 50% oxygen (Granström 2009).

Cellulose has many traditional applications in paper production (Jonoobi et al. 2015), textile industry (Mansouri et al. 2015), pharmaceuticals and cosmetics (Olaru et al. 1998), food industry (Mansouri et al. 2015) and adhesive (Khiari et al. 2011) etc. Nonetheless, cellulose has found nanotech applications recently (Kallel et al. 2016). Especially, nanotech applications of cellulosic fibres are preferred in paper industry, regenerative medicine, coating, transparent and barrier films because of their bio-degradable and renewable properties (Cha et al. 2012). In general, the micro and nano-sized cellulosic materials are produced with different chemical and mechanical methods. In the literature, these materials are termed micro/nanocrystalline cellulose (MCC, NCC), micro/nanofibrillar cellulose (MFC, NFC), cellulose nanowhiskers (CNW) etc. MCC and NCC are like needle-shaped, while MFC and NFC are like cobweb or spaghetti-shaped. Fig. 1 shows different types of nanocellulosic materials according to new TAPPI Standard WI 3021 (Osong et al. 2016).

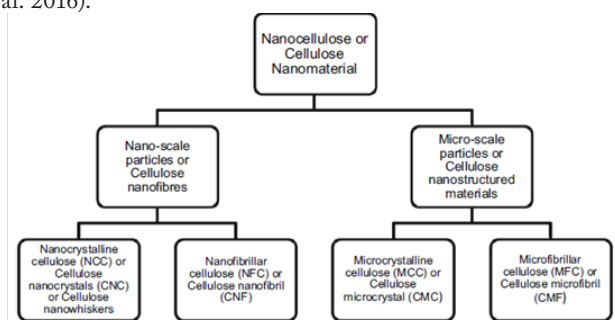


Fig. 1: Different types of nanocellulosic materials (Osong et al. 2016).

In the literature, it is seen that researchers have utilized various cellulosic raw materials in nanocellulose production. Because of wide availability and high cellulose content, wood is commonly used as the raw material. However, the production of nanocellulose from wood involves multi-stage treatment (Osong et al. 2016). Bleached kraft pulp (Kekäläinen et al. 2014a,b), bleached sulphite pulp (Henriksson et al. 2007), sulphite pulp (Wägberg et al. 2008) and wood powder (Uetani and Yano 2011) were also used as the raw materials in these processes.

Annual plants, their wastes, animal sources and bacteria can be good natural cellulosic resources for nanocellulose production. Sugar beet pulp (Habibi and Vignon 2008), wheat straw and soy hulls (Alemdar and Sain 2008a,b), coconut husk (Rosa et al. 2010), potato root (Dufresne et al. 2000), banana rachis (Zuluaga et al. 2009), flax (Cao et al. 2007), jute (Jahan et al. 2011), hemp (Wang et al. 2007), cotton (Elazzouzi-Hafraoui et al. 2008), sisal (Morán

et al. 2008), mulberry (Li et al. 2009b), corn stalk (Reddy and Yang 2005), sugar cane bagasse (Bhattacharya et al. 2008), rutabaga (Bhatnagar and Sain 2005), palm (Bendahou et al. 2010), tunicate (Elazzouzi-Hafraoui et al. 2008) and herbal-animal bacteria (Yano et al. 2008) were used for obtaining of nanocellulose.

In this study, microfibrillar cellulose (MFC) was produced with two different methods from corn stalk, sunflower stalk, reed and sesame husk. MFC samples were characterized with SEM, FTIR, XRD and TGA. According to the results of analyses, the samples were compared.

MATERIALS AND METHODS

Materials

Corn stalk, sunflower stalk, reed and sesame husk were obtained from different regions in Turkey. The chemicals used in MFC production were supplied by the laboratories in Kastamonu University and University of New Brunswick. Experimental analyses were conducted at the Faculty of Forestry of Kastamonu University, the Limerick Pulp and Paper Centre, Department of Chemical Engineering, Department of Geological Engineering and Department of Biology of the University of New Brunswick.

Methods

Preparation of MFCs

The raw materials were ground with Wiley Mill and screened with a 60-mesh fine sieve to remove the fine particles. The materials retained on the sieve were dried in an oven at $103\pm 2^\circ\text{C}$ to constant weight. In the first method, the raw material was extracted with 96% ethanol ($\text{C}_2\text{H}_5\text{OH}$) in a Soxhlet extractor for 5 hours, with six solvent recirculations per hour. The ratio of ethanol to sample was $80:1 \text{ ml}\cdot\text{g}^{-1}$. After the extraction, the samples were dried at $103\pm 2^\circ\text{C}$ to constant weight. Then the procedures reported by Alemdar and Sain (2008 a, b), were followed. 5 g of the sample was mixed with 400 ml of 17.5% sodium hydroxide (NaOH) solution, and stirred for 2 hours at 1000 rpm. Then the mixture was filtered and washed a few times with distilled water in a glass crucible. The solid was then mixed with 400 ml of 1 M hydrochloric acid (HCl) solution, and stirred with a magnetic stirrer on a hot plate at 80°C for 8 hours. It was then filtered and washed again. After the acid treatment, a second alkali treatment of the material was performed with 400 ml of 2% NaOH solution at 80°C for 2 hours with magnetic stirring. It was then filtered and washed with distilled water.

The second method was based on the method of Nuruddin et al. (2011), and extraction treatment was applied as in the first method. 5 g of extracted corn stalk, sunflower stalk, reed or sesame husk were mixed with 300 ml of 90% formic acid (CH_2O_2) solution and were stirred at boiling temperature ($\sim 100.8^\circ\text{C}$) for 2 hours. Then the mixture was filtered and washed 5 times with distilled water and in a glass crucible. After that, the sample was treated with 300 ml peroxyformic acid (CH_2O_3) solution at 80°C for 2 hours. The peroxyformic acid solution was prepared by mixing 90% formic acid with 4% hydrogen peroxide (H_2O_2) at a ratio of 2:1. Then the sample was filtered and washed, and then treated with 300 ml of 17.5% NaOH solution at 80°C for 1 hour and again the samples were filtered and washed with distilled water, and then treated with 300 ml of 16% sulphuric acid (H_2SO_4) solution at 45°C for 2 hours, followed by filtration and washing.

The treated sample was then soaked in liquid Nitrogen for 5 min to freeze the cell wall water, and pressed at 100 psi on a Labtech 400-1 Automatic Sheet Press for 10 min. Then the sample was treated with a sonicator (Model Q Sonica, 6000 kJ and 1375 W) at 20 kHz for 30 min in a beaker with water, and then filtered with a 0.45 micron membrane filter.

Characterisations of the MFCs

Morphology of MFCs

Secondary electron images of the MFC samples were recorded at the University of New Brunswick Microscopy and Microanalysis Facility with a JEOL JSM-6400 Scanning Electron Microscope (SEM) using an accelerating voltage of 15 kV and a working distance of 14 mm. Images were acquired using a Digiscan II controlled by Gatan Digital Micrograph software. Samples were trimmed to size, attached to mounting stubs. For conductivity, the samples were coated with carbon by evaporation using an Edwards E306A carbon coater, and gold using an Edwards S150 sputter coater. Average widths of the untreated and treated samples were measured with Fiji Software Programme. A total of 120 measurements, 10 for each samples, were performed.

Fourier transformed infrared (FT-IR) spectroscopy analyses of MFCs

FT-IR spectra were recorded using a Spectrum 100 Series (PerkinElmer Ltd, Beaconsfield, BUCKS, United Kingdom) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high linearity lithium tantalate (HLLT) detector in the range of 500-4500 cm^{-1} . KBr powder (Specpure grade, Aldrich) was used as the background.

X-Ray diffraction and crystallinity measurements of MFCs

X-ray diffraction was measured using a Bruker D8 Advance Spectrometer. The diffractometer was equipped with a two circle (θ and 2θ) goniometer housed in a radiation safety enclosure. The X-ray source was a sealed, 2.2 kW Cu X-ray tube, maintained at an operating current of 40 kV and 30 mA. The goniometer was computer controlled with independent stepper motors and optical encoders for the θ and 2θ circles with the smallest angular step size of $0.0001^\circ 2\theta$. Samples were scanned in the range of $5-60^\circ 2\theta$. A step size of 0.02° and a step time of 1.0 sec were used during the measurements. A peltier-cooled solid-state [Si(Li)] detector (Sol-X) with a useful energy range of 1 to 60 KeV was used as the detector. No correction was made for $K\beta$ radiation. A set of 2° Soller slits were used in order to lower horizontal beam divergence.

Thermal characterisation of MFCs

Thermogravimetric analysis was done by SDT Q600 from TA Instrument. This was performed under inert conditions in order to obtain pure thermal decompositions of the samples by heating under N_2 gas at a flow rate of $100 \text{ ml}\cdot\text{min}^{-1}$. Approximately between 5-10 mg of each sample was heated from around 20°C to 600°C at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

Morphology of MFC samples

SEM (Scanning Electron Microscope) images which display fibre morphologies of untreated and treated corn stalk, sunflower stalk, reed and sesame husk samples are shown in Figs. 2, 3, 4 and 5. It is noticed that lignin and extractives were removed in the chemical and mechanical treatments. The acid hydrolysis crumbled hemicellulose, and in addition to this, the cryo-crushing and ultrasonification processes disintegrated the fibres from each other. It can also be seen that the fibres of the samples treated by Method 1 separated well from each other without splintering (Figs. 2b, 3b, 4b and 5b), whereas the fibres of samples treated by Method 2 separated from each other by splintering (Figs. 2c, 3c, 4c and 5c).

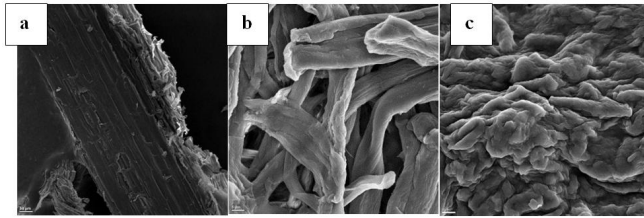


Fig. 2: Scanning electron micrographs of the (a) Untreated corn stalk (b) Treated corn stalk with Method 1 (c) Treated corn stalk with Method 2.

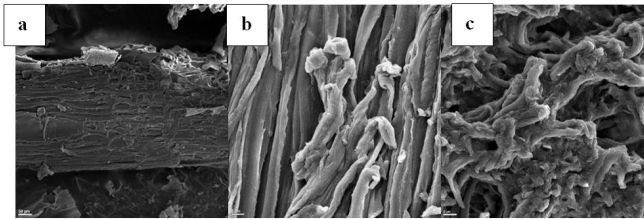


Fig. 3: Scanning electron micrographs of the (a) Untreated sunflower stalk (b) Treated sunflower stalk with Method 1 (c) Treated sunflower stalk with Method 2

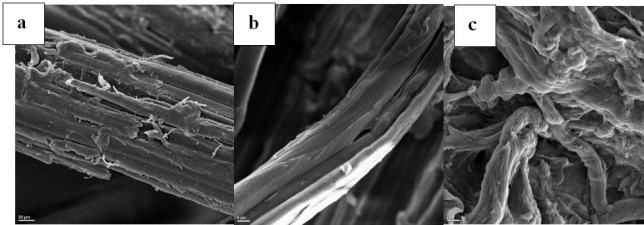


Fig. 4: Scanning electron micrographs of the (a) Untreated reed (b) Treated reed with Method 1 (c) Treated reed with Method 2.

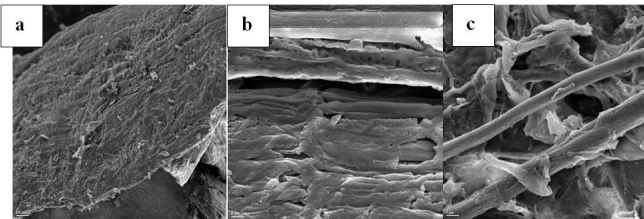


Fig. 5: Scanning electron micrographs of the (a) Untreated sesame husk (b) Treated sesame husk with Method 1 (c) Treated sesame husk with Method 2.

According to results in Tab. 1, the width of the MFC obtained by Method 2 was smaller than the width of the MFC obtained by Method 1. The chemical treatment in Method 2 leads to the fibre cell wall penetration and thus had more effect on the fibres.

Tab. 1: Average widths of the untreated and treated samples (μm).

Samples	Untreated	Method 1	Method 2
Corn stalk	144.59	6.56	4.94
Sunflower stalk	128.66	5.15	2.35
Reed	120.60	7.96	4.98
Sesame husk	150.79	4.21	3.48

According to Figs. 2, 3, 4, 5 and Tab. 1, various chemical and mechanical treatments reduced the dimensions of cellulosic fibres and they transformed the fibres to micro and nano-scale fibres such as MFC, NFC, MCC and NCC. There are many works in the literature about obtaining of micro/nano-scale fibers. Frone et al. (2011) obtained NCC with mean particle sizes of 37 nm and 32.6 nm from MCC with a mean particle size of 20 μm by using two different methods. Nuruddin et al. (2011) produced microfibrils from dhaincha, rice straw, wheat straw and corn stalks with chemical treatment. Average diameters were determined as 6.8 μm for dhaincha, 8.7 μm for rice straw, 9.3 μm for wheat straw and 6.6 μm for corn stalks in their work. Wang et al. (2013) stated that the diameter range of the obtained cellulose nanofibrils from waste papers were between 30-100 nm in their report. Xu et al. (2013) reported that when acid hydrolysis time was increased from 25 min to 30 min, the average diameters of NCCs decreased from 22.85 nm to 19.43 nm. Pereira et al. (2017) found average length and diameter of wheat straw cellulose nanocrystals as 180 nm and 9 nm, respectively in their work. Similarly Kumar et al. (2017) stated that diameters and lengths of cellulose nanocrystals obtained with sulfuric acid hydrolysis were within the range of 5-35 nm and 40-290 nm, respectively.

Spectroscopic analysis of the MFC samples

The FT-IR spectra of the untreated and treated samples by different methods were shown in Fig. 6.

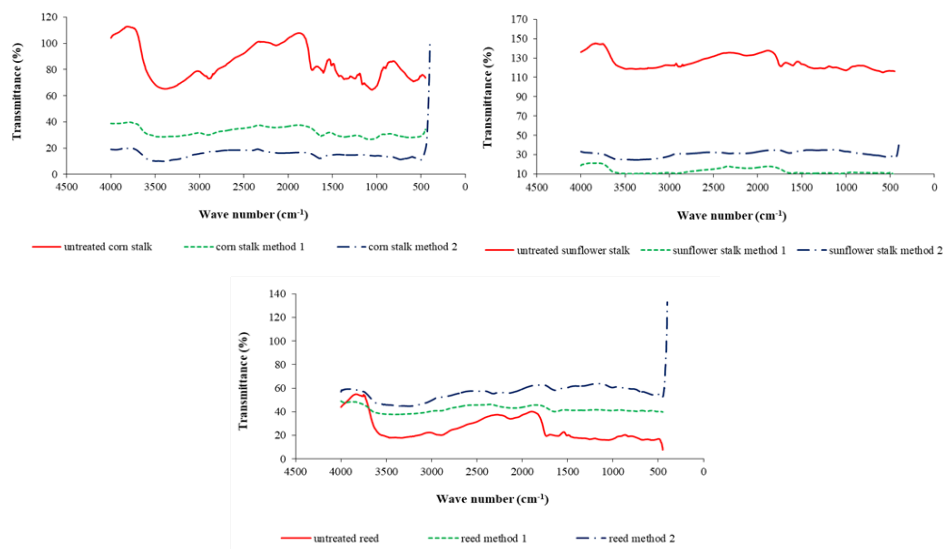


Fig. 6: FT-IR spectra of the untreated and treated the samples (a) Corn stalk, (b) Sunflower stalk, (c) Reed.

The peaks in the region between 3600 cm⁻¹ and 3000 cm⁻¹ for all samples reflect the vibrations of intermolecular hydrogen bonds of –OH groups (Wong et al. 2004, Ndazi et al. 2007, Wang et al. 2017). For the untreated samples and samples treated by Method 1, the peaks between 3000 cm⁻¹-2800 cm⁻¹ are attributed to H-C-H asymmetric and symmetric stretch for alkane bonds. For all untreated samples the bands between 2200 cm⁻¹-2100 cm⁻¹ are –C≡C– (alkyne) stretches, and the peak of ~1640 cm⁻¹ for treated samples by Method 1 and Method 2 demonstrates vibrations of hydrogen bonds of the OH groups of cellulose and absorbed water (Rosa et al. 2010, Fahma et al. 2010). A peak around 1740 cm⁻¹ was observed for the untreated samples, which was attributed to the acetyl and uronic ester groups of hemicelluloses, ester bonds of carboxylic group of ferulic and p-coumaric acids of lignin and/or hemicelluloses (Trejo-O'Reilly et al. 1997, Sun et al. 2005; Jasmani and Adnan 2017) or to natural fats and any extractives (Ndazi et al. 2007). The shoulder at around 1510 cm⁻¹ for the untreated samples represents the aromatic C=C bonds in aromatic ring of lignin (Sun et al. 2005, Wang et al. 2017). All peaks and shoulders in the region 1400 cm⁻¹-1000 cm⁻¹ for untreated samples were associated with cellulose. The vibration peak between 2160 cm⁻¹ and 2000 cm⁻¹ for the treated samples by Method 1 was attributed to –C≡C– (alkyne) bonds. The peaks in the region of 1200–950 cm⁻¹ for the untreated and treated samples by Method 1 attributed to C–O bonds (Xiao et al. 2001). The peaks in this region were lost for treated samples by Method 2. The acid treatments in Method 2 probably removed the C–O bonds.

X-Ray diffraction of the MFC samples

The crystalline lattice of cellulose is monoclinic. Individual fibres involve both regular zones (crystallites) and irregular zones (amorphous). Chemical and mechanical treatments influence the crystallinity of the cellulosic fibres. For example, the crystalline regions can withstand the attack of dilute acid, whereas the amorphous parts are crumbled and removed (Fengel and Wegener 1984).

Crystallinity index (CI) gauges the orientation of the cellulose crystals in a fibre to the fibre axis. The crystallinity index was specified by using the wide angle X-ray diffraction (WAXD) counts at 2θ angle close to 22° and 18°. The sharp peak at 22° reflects the crystalline zone, while the peak intensity at 18° betokens to the amorphous zone in cellulosic materials. In light of this information, the crystallinity index is calculated using Eq.1.

$$CI = \frac{I_{22} - I_{18}}{I_{22}} \quad (1)$$

where: I_{22} and I_{18} represent the counter readings at 2θ close to 22° and 18°, respectively (Reddy and Yang 2005).

Fig. 7: Indicates the crystallite and amorphous zones of the MFCs.

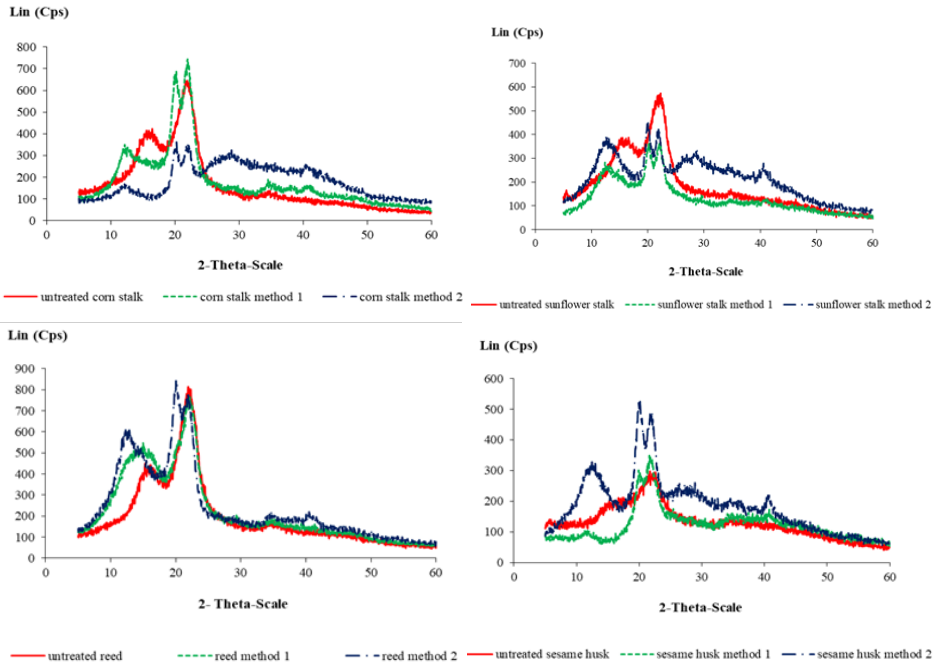


Fig. 7: X-Ray diffraction of the untreated and treated the samples (a) Corn stalk, (b) Sunflower stalk, (c) Reed, (d) Sesame husk.

In Tab. 2, the crystallinity indexes of the untreated and treated samples are shown. The crystallinity indexes of the treated samples were higher than those for the untreated samples. Furthermore it was found that the crystallinity indexes of the treated samples by Method 2 are higher than those for the samples treated by Method 1. The highest crystallinity index of 82.0% was observed for the sesame husk sample treated by Method 2, and the lowest crystallinity index of 42.2% for the untreated sesame husk. The XRD results indicated that Method 2 was more effective than Method 1 in removing the amorphous materials from the fibres.

Tab. 2: Crystallinity index of the untreated and treated samples (%).

Samples	Untreated	Method 1	Method 2
Corn stalk	50.6	68.1	72.9
Sunflower stalk	47.0	52.7	54.5
Reed	53.5	55.8	58.4
Sesame husk	42.2	68.9	82.0

When Tab. 2 was researched, it was seen that the crystallinity index of the untreated samples increased by acid hydrolysis treatments and the similar results are found in the literature. Tonoli et al. (2012) found that when acid hydrolysis time was increased from 30 min to 60 min, the crystallinity index of cellulose whiskers increased from 76% to 82%. Yu et al. (2012) determined the crystallinity of bamboo NCCs as 71.98% after sulfuric acid hydrolysis and high

intensity ultrasonication. Neto et al. (2013) used soy hulls in cellulose nanocrystal production with different acid hydrolysis times and they found that the crystallinity indexes of cellulose nanocrystals increased from 26.3% to 64.4%, 67.2% and 73.5%. Chan et al. (2013) reported that the crystallinity index of kenaf core powder increased from 48.1% to 75% as a result of sulfuric acid hydrolysis. Likewise Wang et al. (2017) determined that crystallinity indexes of mulberry raw material and cellulose nanowhiskers isolated from mulberry pulp were 67.6% and 92%, respectively. Cudjoe et al. (2017) found the crystallinity index of CNCs obtained from *Miscanthus giganteus* with sulfuric acid hydrolysis as 78%.

Thermal characterisation of the MFC samples

The thermal properties of MFCs are important to their applications in composite materials. Fig. 8 shows the TGA curves of the MFCs obtained from different agricultural wastes by different methods. The graphs show that the thermal decomposition of the untreated corn stalk, sunflower stalk and reed started at about 250°C, while the untreated sesame husk began to decompose at about 200°C. The initial weight losses of the samples treated by Method 1 were observed between 0°C and 100°C owing to moisture loss. The main decomposition of the treated samples by Method 1 took place between 270°C - 300°C, whereas the main decomposition of the samples treated by Method 2 occurred between 300°C - 320°C. These decompositions continued until 360°C - 380°C. These results indicated that by Method 2, better thermal properties of the MFCs were achieved, compared with Method 1.

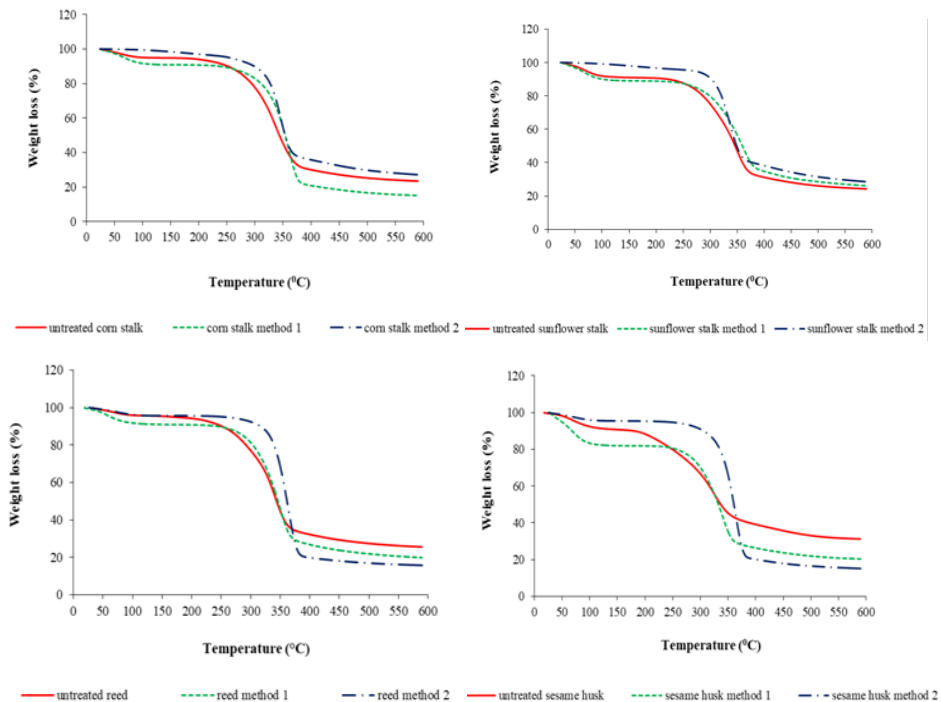


Fig. 8: TGA characterisation of untreated and treated samples (a) Corn stalk, (b) Sunflower stalk, (c) Reed, (d) Sesame husk.

The improved thermal stability of the MFCs was attributed to the removal of hemicelluloses and lignin from the fibres considerably in the chemical treatments and these results are in agreement with those reported in the literature. Chen et al. (2011) stated that the starting decomposition temperature of cellulose nanofibres was at nearly 350°C in their report. De Morais Teixeira et al. (2011) obtained nanofibres from sugarcane bagasse by using two different acid hydrolysis times. They found that the decomposition of nanofibres happened between 235°C – 365°C and 200°C – 370°C.

He et al. (2013) reported that the decomposition temperature of *Bambusa rigida* raw material was 223°C, whereas the decomposition temperature of *Bambusa rigida* cellulose nanofibres was 315.2°C, increasingly. Bano and Negi (2017) stated that the main decomposition of CNC isolated from groundnut shells occurred within the range of 210°C – 340°C. Likewise Khanjanzadeh et al. (2018) determined that the main decomposition happened in the range of 258°C – 322°C for unmodified CNCs and in the range of 268°C – 341°C for modified CNCs with 3-aminopropyltriethoxysilane.

CONCLUSIONS

In this study, microfibrillar cellulose (MFC) was successfully prepared from four different agricultural residues. The results show that the acid treatment decreased the widths of the fibres significantly. The minimum MFC width of 2.35 µm was obtained with sunflower stalk by Method 2. The crystallinity index increased after the acid treatment, and the maximum crystallinity index of 82% was observed for the sesame husk samples treated by Method 2. Method 2 was more effective than Method 1 in reducing the width and increasing the crystallinity. The FTIR Figs. showed peaks of intermolecular hydrogen bonds of –OH groups between 3600 cm⁻¹ - 3000 cm⁻¹ in all samples. The shoulders which were seen around 1510 cm⁻¹ for the untreated samples demonstrated the aromatic C=C bonds in the aromatic rings of lignin, and all peaks and shoulders between 1400 cm⁻¹-1000 cm⁻¹ for the untreated samples belonged to the typical cellulosic bonds. The main decomposition temperature increased from about 250°C to 270°C – 300°C for the samples obtained by Method 1, and to 300°C – 320°C by Method 2, indicating that Method 2 was superior to Method 1 in improving the thermal properties of the obtained MFC samples.

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REFERENCES

1. Alemdar, A., Sain, M., 2008a: Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties, *Composites Science and Technology* 68: 557–565.

2. Alemdar, A., Sain, M., 2008b: Isolation and characterization of nanofibers from agricultural residues-wheat straw and soy hulls, *Bioresource Technology* 99: 1664–1671.
3. Bano, S., Negi, Y. S., 2017: Studies on cellulose nanocrystals isolated from groundnut shells, *Carbohydrate Polymers* 157: 1041-1049.
4. Bendahou, A., Kaddami, H., Dufresne, A., 2010: Investigation on the effect of cellulosic nanoparticles' morphology on the properties of natural rubber based nanocomposites, *European Polymer Journal* 46: 609–620.
5. Bhatnagar, A., Sain, M., 2005: Processing of cellulose nanofibre-reinforced composites, *Journal of Reinforced Plastics and Composites* 24: 1259–1268.
6. Bhattacharya, D., Germinario, L.T., Winter, W.T., 2008: Isolation, preparation and characterization of cellulose microfibrils obtained from bagasse, *Carbohydrate Polymers* 73: 371–377.
7. Cao, X. D., Dong, H., Li, C. M., 2007: New nanocomposite materials reinforced with flax cellulose nanocrystals in waterborne polyurethane, *Biomacromolecules* 8: 899–904.
8. Cha, R., He, Z., Ni, Y., 2012: Preparation and characterization of thermal/pH-sensitive hydrogel from carboxylated nanocrystalline cellulose, *Carbohydrate Polymers* 88: 713–718.
9. Chan, C. H., Chia, C. H., Zakaria, S., Ahmad, I., Dufresne, A., 2013: Production and characterization of cellulose and nanocrystalline cellulose from kenaf core wood, *BioResources* 8: 785–794.
10. Chen, W.S., Yu, H.P., Liu, Y.X., Chen, P., Zhang, M.X., Hai, Y.F., 2011: Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments, *Carbohydrate Polymer* 83: 1804–1811.
11. Cudjoe, E., Hunsen, M., Xue, Z., Way, A. E., Barrios, E., Olson, R. A., Hore, M. J. A., Rowan, S. J., 2017: *Miscanthus giganteus*: A commercially viable sustainable source of cellulose nanocrystals, *Carbohydrate Polymer* 155: 230-241.
12. de Moraes Teixeira, E., Bondancia, T.J., Teodoro, K.B.R., Correa, A.C., Marconcini, J.M., Mattoso, L.H.C., 2011: Sugarcane bagasse whiskers: Extraction and characterizations, *Industrial Crops and Products* 33: 63–66.
13. Dufresne, A., Dupuyre, D., Vignon, M. R., 2000: Cellulose microfibrils from potato tuber cells: Processing and characterization of starch-cellulose microfibril composites, *Journal of Applied Polymer Science* 76: 2080–2092.
14. Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J. L., Heux, L., Dubreuil, F., Rochas, C., 2008: The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose, *Biomacromolecules* 9: 57–65.
15. Fahma, F., Iwamoto, S., Hori, N., Iwata, T., Takemura, A., 2010: Isolation, preparation and characterization of nanofibers from oil palm empty-fruit-bunch, *Cellulose* 17: 977–985.
16. Fengel, D., Wegener, G., 1989: Walter de Gruyter. *Cellulose*. 4, 66-69, Berlin, New York.
17. Frone, A. N., Panaitescu, D. M., Donescu, D., 2011: Some aspects concerning the isolation of cellulose micro- and nano- fibers, *University Politehnica of Bucharest Scientific Bulletin-Series A* 73: 134–152.
18. Granström, M., 2009: *Cellulose Derivatives: Synthesis, Properties and Applications*. Master Thesis, University Of Helsinki, Finland.
19. Habibi, Y., Vignon, M. R., 2008: Optimization of cellouronic acid synthesis by TEMPO-mediated oxidation of cellulose III from sugar beet pulp, *Cellulose* 15: 177–185.
20. He, W., Jiang, S., Zhang, Q., Pan, M., 2013: Isolation and characterization of cellulose nanofibers from bambusa rigida, *BioResources* 8: 5678–5689.

21. Henriksson, M., Henriksson, G., Berglund, L. A., Lindström, T., 2007: An environmentally friendly method for enzyme-assisted preparation of microfibrillar cellulose (MFC) nanofibers, *European Polymer Journal* 43:3434–3441.
22. Jahan, M. S., Saeed, A., He, Z., Ni, Y., 2011: Jute as raw material for the preparation of microcrystalline cellulose, *Cellulose* 18: 451–459.
23. Jasmani, L., Adnan, S., 2017: Preparation and characterization of nanocrystalline cellulose from *Acacia mangium* and its reinforcement potential, *Carbohydrate Polymers* 161: 166–171.
24. Jonoobi, M., Oladi, R., Davoudpour, Y., Oksman, K., Dufresne, A., Hamzeh, Y., Davoodi, R., 2015: Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: A review, *Cellulose* 22: 935–969.
25. Kallel, F., Bettaieb, F., Khiari, R., García, A., Bras, J., Chaabouni, S. E., 2016: Isolation and structural characterization of cellulose nanocrystals extracted from garlic straw residues, *Industrial Crops and Products* 87: 287–296.
26. Kekäläinen, K., Liimatainen, H., Niinimäki, J., 2014a: Disintegration of periodate–chlorite oxidized hardwood pulp fibres to cellulose microfibrils: Kinetics and charge threshold, *Cellulose* 21: 3691–3700.
27. Kekäläinen, K., Liimatainen, H., Illikainen, M., Maloney, T. C., Niinimäki, J., 2014b: The role of hornification in the disintegration behaviour of TEMPO-oxidized bleached hardwood fibres in a high-shear homogenizer, *Cellulose* 21:1163–1174.
28. Khanjanzadeh, H., Behrooz, R., Bahramifar, N., Gindl-Altmutter, W., Bacher, M., Edler, M., Griesser, T., 2018: Surface chemical functionalization of cellulose nanocrystals by 3-aminopropyltriethoxysilane, *International Journal of Biological Macromolecules* 106: 1288–1296.
29. Khiari, R., Mauret, E., Belgacem, M. N., Mhemmi, F., 2011: Tunisian date palm rachis used as an alternative source of fibres for papermaking applications Palmrachis fibers for paper, *BioResources* 6: 265–281.
30. Kumar, A., Lee, Y., Kim, D., Rao, K. M., Kim, J., Park, S., Haider, A., Lee, D. H., Han, S. S., 2017: Effect of crosslinking functionality on microstructure, mechanical properties, and in vitro cytocompatibility of cellulose nanocrystals reinforced poly (vinyl alcohol)/sodium alginate hybrid scaffolds, *International Journal of Biological Macromolecules* 95: 962–973.
31. Li, R., Fei, J., Cai, Y., Li, Y., Feng, J., Yao, J., 2009b: Cellulose whiskers extracted from mulberry: A novel biomass production, *Carbohydrate Polymers* 76: 94–99.
32. Mansouri, S., Khiari, R., Bettaieb, F., El-Gendy, A. A., Mhenni, F., 2015: Synthesis and characterization of carboxymethyl cellulose from Tunisian vine stem Study of water absorption and retention capacities, *Journal of Polymers and the Environment* 23: 190–198.
33. Morán, J. I., Alvarez, V. A., Cyras, V. P., Vazquez, A., 2008: Extraction of cellulose and preparation of nanocellulose from sisal fibers, *Cellulose* 15: 149–159.
34. Ndazi, B. S., Karlsson, S., Tesha, J. V., Nyahumwa, C. W., 2007: Chemical and physical modifications of rice husks for use as composite panels, *Composites Part A: Applied Science and Manufacturing* 38: 925–935.
35. Neto, W. P., Silverio, H. A., Dantas, N. O., Pasquini, D., 2013: Extraction and characterization of cellulose nanocrystals from agro-industrial residue-soy hulls, *Industrial Crops and Products* 42: 480–488.
36. Nuruddin, M., Chowdhury, A., Haque, S. A., Rahman, M., Farhad, S. F., Jahan, M. S., Quaiyyum, A., 2011: Extraction and characterization of cellulose microfibrils from agricultural wastes in an integrated biorefinery initiative, *Cellulose Chemistry and Technology* 45: 347–354.

37. Olaru, N., Olaru, L., Stoleriu, A., Timpu, D., 1998: Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone, *Journal of Applied Polymer Science* 67:481–486.
38. Osong, S. H., Norgren, S., Engstrand, P., 2016: Processing of wood-based microfibrillar cellulose and nanofibrillated cellulose and applications relating to papermaking: A review, *Cellulose* 23: 93–123.
39. Pereira, P. H. F., Waldron, K. W., Wilson, D. R., Cunha, A. P., de Brito, E. S., Rodrigues, T. H. S., Rosa, M. F., Azeredo, H. M. C., 2017: Wheat straw hemicelluloses added with cellulose nanocrystals and citric acid. Effect on film physical properties, *Carbohydrate Polymers* 164: 317–324.
40. Reddy, N., Yang, Y., 2005: Structure and properties of high quality natural cellulose fibers from cornstalks, *Polymer* 46: 5494–5500.
41. Rosa, M.F., Medeiros, E.S., Malmonge, J. A., Gregorski, K. S., Wood, D.F., Mattoso, L.H.C., Glenn, G., Orts, W.J., Imam, S.H., 2010: Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behaviour, *Carbohydrate Polymers* 81: 83–92.
42. Sun, X., Xu, F., Sun, C., Fowler, P., Baird, M., 2005: Characteristics of degraded cellulose obtained from steam-exploded wheat straw, *Carbohydrate Research* 340: 97–106.
43. Tonoli, G. H. D., de Moraes Teixeira, E., Corrêa, A. C., Marconcini, J. M., Caixeta, L. A., Pereira-da-Silva, M. A., Mattoso, L. H. C., 2012: Cellulose micro/nano from Eucalyptus kraft pulp: preparation and properties, *Carbohydrate Polymers* 89: 80–88.
44. Trejo-O'Reilly, J. T., Cavaille J. Y., Gandini, A., 1997: The surface chemical modification of cellulosic fibres in view of their use in composite materials, *Cellulose* 4:305–320.
45. Uetani, K., Yano, H., 2011: Nanofibrillation of wood pulp using a high-speed blender, *Biomacromolecules* 12: 348–353.
46. Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., Axnäs, K., 2008: The build-up of polyelectrolyte multilayers of microfibrillar cellulose and cationic polyelectrolytes, *Langmuir* 24: 784–795.
47. Wang, B., Sain, M., Oksman, K., 2007: Study of structural morphology of hemp fiber from the micro to the nanoscale, *Applied Composite Materials* 14: 89–103.
48. Wang, H., Li, D., Zhang, R., 2013: Preparation of ultralong cellulose nanofibers and optically transparent nanopapers derived from waste corrugated paper pulp, *BioResources* 8: 1374–1384.
49. Wang, L. F., Shankar, S., Rhim, J. W., 2017: Properties of alginate-based films reinforced with cellulose fibers and cellulose nanowhiskers isolated from mulberry pulp, *Food Hydrocolloids* 63: 201–208.
50. Wang, Z., Yao, Z., Zhou, J., Zhang, Y., 2017: Reuse of waste cotton cloth for the extraction of cellulose nanocrystals, *Carbohydrate Polymers* 157: 945–952.
51. Wong, S., Shanks, R., Hodzic, A., 2004: Interfacial improvements in poly(3-hydroxybutyrate)-flax fibre composites with hydrogen bonding additives, *Composites Science and Technology* 64: 1321–1330.
52. Xiao, B., Sun, X. F., Sun, R. C., 2001: Chemical, structural, and thermal characterization of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw, *Polymer Degradation and Stability* 74: 307–319.
53. Xu, Q., Gao, Y., Qin, M., Wu, K., Fu, Y., Zhao, J., 2013: Nanocrystalline cellulose from aspen kraft pulp and its application in deinked pulp, *International Journal of Biological Macromolecules* 60: 241–247.

54. Yano, S., Maeda, H., Nakajima, M., Hagiwara, T., Sawaguchi, T., 2008: Preparation and mechanical properties of bacterial cellulose nanocomposites loaded with silica nanoparticles, *Cellulose* 15: 111–120.
55. Yu, M., Yang, R., Huang, L., Cao, X., Yang, F., Liu, D., 2012: Preparation and characterization of bamboo nanocrystalline cellulose, *BioResources* 7: 1802–1812.
56. Zuluaga, R., Putaux, J. L., Cruz, J., Velez, J., Mondragon, I., Ganan, P., 2009: Cellulose microfibrils from banana rachis: Effect of alkaline treatment on structural and morphological features, *Carbohydrate Polymers* 76: 51–59.

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