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Abstract

Nowadays, cellulose nanocrystals (CNC) plays a major role in industrial processes due to their unique properties which, in turns, able to enhance the physical properties of bulk materials. The interstice properties of CNC are vary regarding to the source of the used cellulosic materials. The study aimed to characterize cellulose CNC extracted from two different genotypes of cotton slivers; Egyptian extra-long staple (G.88) and upland medium staple length (BF FK37). As per acid hydrolysis, CNC was extracted from different genotypes of cotton slivers by the use of H2SO4 6٠% (w/w) at 60 □ for 60 min. Then, the extracted CNC was characterized by making used of different tools e.g., transmission electron microscopy (TEM), Dynamic Light Scattering (DLS), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, Thermo Gravimetric analysis (TGA). Results revealed that, CNC was, successfully, extracted by acid hydrolysis of cotton slivers. Notably, the size of the obtained CNC was varied as genotypes of cotton slivers varies, which attained as shown from TEM; the average dimensions (diameter × length) of 36.46 ± 7 nm × 355 ± 98.3 nm for extra-long staple, 37.2 ± 14 nm × 284 ± 83 nm for medium staple. This fact was further supported by DLS as the size of extra-long staple was 22. 45 d.n and 35.77 d.n for medium staple. In addition, XRD results demonstrated that, both genotypes excited cellulose type I (crystalline polymorph). However, CNC extracted from extra-long showed higher crystallinity index (80%) than observed from medium staple. Moreover, the thermal stability observed for CNC of extra-long is significantly higher than obtained from medium. By varying of the source of CNC, the size of the obtained crystals was varied besides crystallinity index and their thermal stability properties. Therefore, the using of extra-long staple length cotton slivers led to reduce the crystal size with improving in both crystallinity and thermal properties.

1. Introduction

Cellulose (Latin: rich in small cells) is a biopolymer found naturally in, for example, plant cells such as cotton and wood. Cellulose nanomaterials are known as cellulose-based materials that have one or more of their external dimensions at the nano-scale, i.e. between 1 to 100 nm. Hence, the nanocellulose can be classified according to various factors such as shape, size and structure. For the shape characteristic, there are basically three types: sheet, spherical and crystal/whisker.

By and large, cellulose is defined as a macromolecule, a nonbranched chain of variable length of 1-4-linked β-D anhydro glucopyranose units. It is biosynthesized by a number of living organisms ranging from higher to lower plants, some amoebae, sea animals, bacteria and fungi **(Heux, et al. 1999)**. There are several types of cellulose, cellulose I and II are commonly found in nature. Cellulose I has a best mechanical properties and a parallel chain orientation, while cellulose II has anti-parallel chain.

George and Sabapathi (2015) reported that cellulose is a fibrous, tough٠ and water-insoluble

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polymer; it is the most plentiful natural polymer on the earth and it is an essential component of the cell wall of different plant species. Moreover, cellulose is a biocompatible, biodegradable, and renewable natural polymer and therefore it is considered an alternating to polymers derived from fossil fuel which are nondegradable **(Du et al., 2019)**. The polymerization degree of cellulose exhibit marked variability and is approximately 10,000 glucose units for wood-derived cellulose and 15,000 units for cotton-derived cellulose **(Sjostrom, 1993)**.

Cellulose nanocrystals (CNC) are nanomaterials with potential application which is promising and attracts increasing investments due to the nanoscale size and high crystallinity of CNC allow the particles to exhibit a high surface area and excellent mechanical properties **[Rusli and Eichhorn (2008) and Mariano; El Kissi and Dufresne (2014); Kose *et al.* (2019)]**. In addition, CNC cellulose has low density, abundance, high strength, stiffness, low weight and biodegradability.

Cotton is a main source of cellulose, composed of mostly 95% of long-chain carbohydrate molecule. More insight into genetic classification of cotton, physical, chemical and mechanical properties of cotton varied regarding to the genotypes that cotton belongs to *Gossypium* Genus which comprises more than fifty species, of which only four are adopted for commercial cultivation, including *G. hirsutum* (American), *G. barbadense* (Egyptian), *G. arboretum* (Asiatic/ Indian) and G. herbaceum (sub-Saharan African and Arabian) **(Wendel and Grover, 2015)**. All these four species produce unique types of fiber having distinguishable physical and mechanical properties.

For instance, fiber characteristics of the two diploid (two sets of 13 basic chromosomes of A genome) species, *G. arboreum* and *G. herbaceum* are inherently short and coarse compared to the relatively longer and finer fibers of the allotetraploid (two sets each of 13 basic chromosomes of A and D genomes) species, *G. hirsutum* and *G. barbadense*.

American upland and Egyptian cotton differ remarkably from each other, where the latter yields superior quality fiber typically termed as "extra-long staple" (ELS) fiber **(Liu et al., 2015)**. ELS fibers have naturally longer lint length as compared to that produced by *G. hirsutum* and hence, Egyptian cotton fiber qualifies as a favored raw material for the textile industry in order to textile products manufactured out of genuine ELS fiber offer more value to the finished product and attract more vendors and consumers. The quality of ELS fiber from *G. barbadense* varies significantly depending upon the variety, geographical location and crop husbandry during cultivation. Many contentious cases relate to claims of 100% Egyptian ELS cotton that belongs to the species *G. barbadense*. **(Joy Das et al. 2017)**.

The cellulose chains within cotton fibers tend to be held in place by hydrogen bonding. These hydrogen bonds occur between the hydroxyl groups of adjacent molecules and are most prevalent between the parallel, closely packed molecules in the crystalline areas of the fiber. The solid state of cellulose is represented by areas of both high order (crystalline) and low order (amorphous).

The crystalline portion of cellulose can be liberated by controlled acid hydrolysis which results in CNC. The crystallinity index (CI) is defined as the volume fraction of crystallinity of one phase in a given sample and represents measure of the average crystallite size, perfection, and ordering in a sample **(Klug and Alexander (1974); Person et al (1995)**.

Cotton cellulose is highly crystalline and oriented. a-cellulose is distinct in its long and rigid molecular structure. The b-1,4-D (+)-glucopyranose building blocks in long cellulose chain are linked by 1,4-glucodic bonds. The steric effects prevent free rotation of the anhydrogluco-pyranose C-O-C link. Each anhydroglucose contains three hydroxyl groups, one primary on C-6 and two secondary on C-2 and C-3. The abundant hydroxyl groups and the chain conformation allow extensive inter-molecular and intra-molecular hydrogen bonding to further enhance the rigidity of the cellulose structure.

Cotton cellulose is remarked by having a high degree of polymerization and crystallinity. Crystallinity indicates that the fiber molecules are closely packed and parallel to one another where, the higher degree of polymerization and crystallinity are associated with higher fiber strengths.

Previous works reported that, cotton slivers have been extensively used for preparation of CNC with high crystallinity. **Hebeish et al. 2013** reported that, by using 60%w/w H2SO4, CNC was obtained at small size with high crystallinity amongst other H2SO4 concentration used. The concentrations of sulfuric acid from 45 to 65 wt. %, were recommended to obtain the high-crystalline nanoparticles having CI crystalline polymorph **(Ioelovich, 2012; Moran, 2008; Liu, 2010; Luduena, 2011)**.

In the present study, we aimed to evaluate the effect of cellulose genotypes from two different sources on the size of the extracted CNC as well as their crystallinity and thermal properties. CNC extracted by virtue of acid hydrolysis method.

To achieve the goal, two different of cotton genotypes, typically; Egyptian extra-long staple length Giza 88 (*G. barbadense*) and upland medium long

staple from Burkina Faso BF - FK37 (*G. hirsutum*) were used for extraction of CNC.

CNC were characterized in the Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS)، X-ray Diffraction (XRD), Fourier-Transform Infrared (FTIR) spectroscopy and Thermo Gravimetric Analysis (TGA).

2. Methodology

Cotton slivers of two different Cotton genotypes, extra and medium long staple length were supplied from Cotton Researches Institute. Where, Egyptian extra-long staple (*G. barbadense*) cotton variety of Giza 88; season 2017/2018 and slivers of upland medium long staple (*G. hirsutum*) of Burkina Faso cotton BF - FK37 season 2017/2018.

Sulfuric acid H2SO4 (95–98%), Sodium hydroxide (NaOH), sodium carbonate (Na2CO3), hydrogen peroxide (H2O2) and non-ionic wetting agent; Triton X – 100 were all laboratory grade reagents supplied from El Nasr Pharmaceutical Chemicals Company.

2.1 Pretreatment for cotton slivers.

2.1.1 Scouring Process

The cotton slivers were scoured with liquor ratio 20:1 by Roaches IR machine at the laboratory of Textile Technology Center (Cairo University). Scouring bath containing 2g/l sodium hydroxide, 6g/l soda ash, 1ml/l sequestering agent and 1 ml/l wetting agent were applied at 95 ^{o}C for 60 min to remove waxes and other impurities. Afterwards, the slivers were washed, neutralized with acetic acid, and then washed with distilled water until the solution became neutral.

2.1.2 Bleaching Process

The scoured slivers were bleached in bleaching bath of Roaches IR machine at the laboratory of Textile Technology Center (Cairo University). The bleaching bath containing 1.5 g/l sodium hydroxide, 3 ml/l hydrogen peroxide (50%) and 1 ml/l wetting agent were applied by using 20:1 liquor to fiber ratio at 95 ^{o}C for 60 min to oxidize the colored natural impurities. The cotton fibers were bleached.

Afterwards, the cotton slivers were washed twice and neutralized with acetic acid, prove washing with distilled water until the solution became neutral. The obtained bleached cotton was dried gently in oven at 60 ^{o}C for 1hr.

2.2 Extraction of CNC

Bleached, cleaned and dried from bleached cotton slivers; cotton slivers from Egyptian extra-long staple (Giza 88) and upland medium staple (BF FK37) were subjected to acid hydrolysis using H_2SO_4.

For each 1gm of cotton slivers, 10 ml of 60% w/w H2SO4 was added to conical flask and then stirred at 250 rpm by using mechanical stirring at 60 ^{o}C, for 60 min to form suspension. Immediately, following hydrolysis, the suspensions were diluted five-fold with cold distilled water to stop the reaction. The suspensions were then trans-ferried into centrifuge bottles and centrifuged at 12,000 rpm for10 min and decanted to separate the crystals.

The solid aggregates in the suspensions were disrupted by sonication. The residual materials were then washed with distilled water and the mixture was centrifuged again to remove traces of sulfate groups. Dialysis against distilled water was performed to remove free acid in the dispersion using dialysis tubing (MWCO 12,000 – 14,000). This was verified by neutrality of the dialysis effluent. The resultant CNW suspension was frozen. After freezing, samples were freeze-dried (-60 ^{o}C, 0.1 mbar, under such pressure cellulose nanostructure will not be affected) as powders.

The extracted nanocrystals from different cotton genotypes extra-long staple and medium are labeled as CNCe and CNCm, respectively.

2.3 Characterization of CNC.

2.3.1 Yield % of CNC

The yield of CNC was determined by weighing a 10 ml aliquot of suspensions after standing overnight to dry in freeze drying. Yield (%) and concentration (g/ml) were calculated from the difference between initial and final weight as Equation (1).

$$\%\ Yield = (wa/wb) \times 100 \quad \text{(1)}$$

Where: wb= weight of raw-material and wa= weight of product after acid hydrolysis.

Nanocrystalline cellulose has been characterized by Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), X-ray Diffraction (XRD), Fourier-Transform Infrared (FTIR) Spectroscopy, and Thermo Gravimetric Analysis (TGA).

2.3.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) (JEOL 1200, JEOL USA, Inc) was used to determine the

dimensions and morphology of hydrolyzed cellulose (CNC) which obtained from the cotton cellulose fibers.

A drop of diluted CNC was deposited on the surface of copper grid and allowed to dry at room temperature. The analysis carried out with an accelerating voltage of 80 kV.

Aspect ratios of length to diameter (L/D) of treated samples (CNC) were calculated based on the TEM measurement.

2.3.3 Dynamic Light Scattering (DLS)

Particle Size analyzer (z-average-size) and the polydispersity index (PDI) of CNC has been performed using the Dynamic Light Scattering (DLS) techniques. The Dynamic Light Scattering (DLS) measures the sizes of grains or particles in the sample. Under TEM, the shape and the size of polyacrylamide grafted onto nano-cellulose whiskers cannot be identified. To fully characterize the suspensions, the average sizes of synthesized CNW – PAAm copolymer particles were determined by Dynamic Light Scattering (DLS). The measurements were conducted using a Malvern Instruments Zetasizer Nanoseries.

The samples were measured at a constant temperature of 25±1 ^{o}C. The results were averaged over 30 runs. Each value was obtained by averaging measurements of three samples.

2.3.4 Zeta Potential Measurement of CNC

The z-potentials (surface charge) were determined in an electrophoretic light scattering ZetaPlus apparatus (Malvern Instruments, Malvern, UK) to examine nanocellulose colloidal stability and charge. The electrophoretic determinations of z potentials were made in aqueous media at moderate electrolyte concentration. Each value was obtained by averaging measurements of three samples.

2.3.5 X-ray diffraction (XRD).

The XRD patterns of dried CNC were obtained using a D500 diffractometer (SIEMENS) operated at 30 kV and 15 mA, utilizing a Cu-Ka radiation source (k = 0.154). The scans were controlled by the Diffrac-AC software programme. The degree of crystallinity Ic [%] of CNW samples were calculated according to Segal's method in Equation (2).

$$I_c[\%] = \frac{I_{(Crys+am)} - I_{(am)}}{I_{(Crys+am)}} \quad \text{..... (2)}$$

Where, I (crys+am) represents the peak intensity (count per second) around 22.80 for the crystalline and amorphous part. I (am) was the peak intensity around 180 and represents the amorphous part of the celluloses.

The method based on the intensity IC which measures the orientation of the crystals in cellulose to the cellulose axis.

2.3.6 Fourier transformed infrared (FTIR) spectra

FTIR experiments were performed using a S-100 FT-IR spectrometer (Perkin Elmer) and scanned from 4000 to 400 cm−1 in ATR mode. Thermo Scientific Spectrophotometer with KBr pellets.

The samples were mixed with potassium bromide (KBr), and then pressed into ultra-thin transparent pellets for analysis.

CNCe and CNCm were oven-dried at 65 ℃ overnight and pelletized. The spectra were recorded in the range from 4000 to 400 cm^{-1} at 4 cm^{-1} resolutions.

2.3.7 Thermogravimetric Analysis (TGA).

The thermal stability properties of CNCe and CNCm are measured using thermogravimetric analysis (TGA) STD Q600. In preparation of samples for TGA, the CNC were ground to powder form. Decomposition profiles of TGA were recorded at a heating rate of 10 ℃/ min between room temperature and a hold temperature is 800 ℃.

3. Results and Discussion

Bleached and cleaned cotton slivers, as obtained from subjecting to pretreatment processes, particularly notable scouring and bleaching process as described in method, were utilized as a precursor for acid extraction of CNC. Two different genotypes of cotton were used in this study. Typically, extra-long, medium staples length was two domains under investigation for study their effect on the chemical, physical, mechanical properties of the obtained CNC. Extraction of CNC was performed regarding to the acid hydrolysis process.

Briefly, the extraction condition of CNC by concentrated sulfuric acid (60%, w/w) at 60 ℃, for 60 min.

3.1 Yield % of CNC

The yield % of CNC extracted from each genotype of cotton was calculated according to the equation 1. Yield % of CNCe and CNCm were represented in table 1, which the loss of their weights after sulfuric acid was attack due to dissolve of their amorphous domains.

Table: 1. CNC yield % produced using sulfuric acid concentration 60% (w/w) for 60 min at 60 ℃.

Variety	Yield %
CNC*e*	60%
CNC*m*	63%

From table 1, it can be seen CNCe was lower than those of CNCm. This indicates the great loss in the weight of cotton during extraction of CNCe. This could be attributed to the reactivity of cotton genotype extra-long is relatively higher than of cotton genotype medium staple. This may cause rapid attack of H2SO4 on the amorphous regions in extra-long than happened in another genotype (medium staple length). As a result, the loss is higher in case of genotype extracting than of medium staple length.

3.2 Transmission electron microscopy (TEM)

The morphological shape of the formed CNC was determined by using TEM as seen in figure1. Crystals like rod shape distinguish the presence of CNC. Hence, figure1 showed obviously the TEM micrographs obtained from CNCe and CNCm, which indicating the successful disintegration of cotton fibers to individual crystals after decomposition of amorphous regions.

Also, size and shape of the obtained CNCe and CNCm can be determined clearly from TEM in figure1a and 1b, respectively.

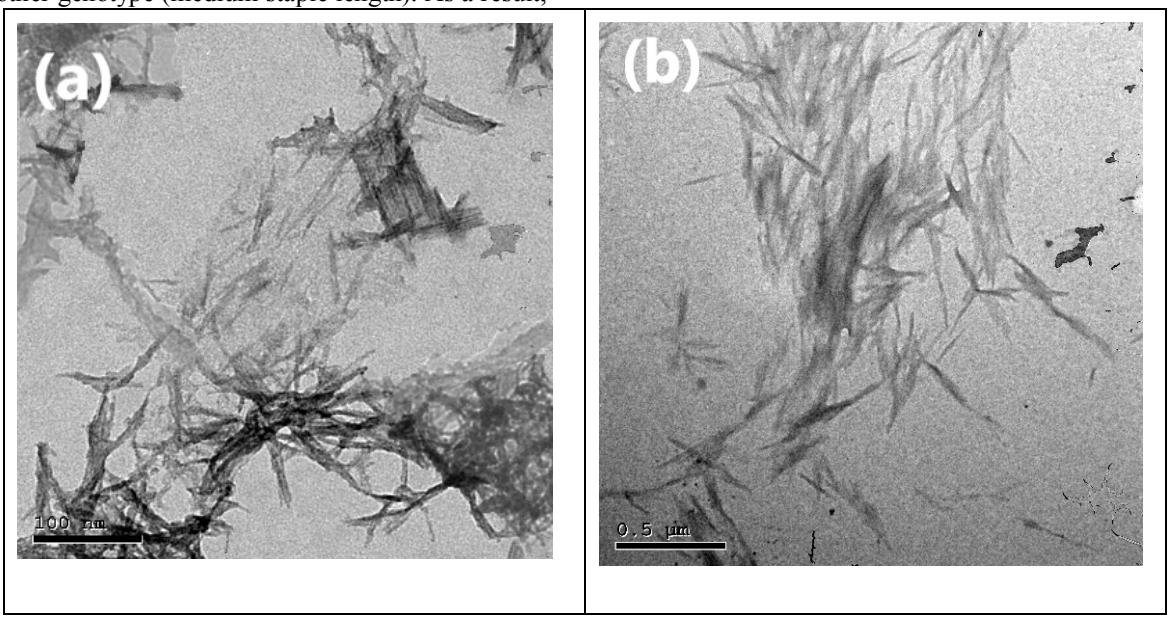

Figure: 1. Transmission electron micrographs of CNC; (a) CNCe; (b) CNCm.

It can be observed from TEM micrograph that, the aspect ratios (length × dimension) of both CNCe and CNCm are in the range of 355 ± 98.3 nm× 36.46 ± 7 nm and 284 ± 83 nm× 37.2 ± 14 nm, respectively. These finding revealed that, the size and shape of the formed crystals of CNCe and CNCm are in the same range which emphasized that, 60%(w/w) sulfuric acid is adequate to produce uniform size and shape of crystals regardless their genotypes used.

The data from figure1, disclosed that, CNC was successfully extracted from cotton slivers undergoes sulfuric acid treatment which was motivated by heating in continuous stirring for 60 min.

3.3 Dynamic Light Scattering (DLS)

The results of zeta potential showed that the formed nanocrystals were quite staple displaying an absolute value of 25.35±1.5 mV (Fig. a). A value of 25 mV is widely reported in literature and it is considered the minimum value for staple nanocellulose dispersions. (Olszewska, et al. 2013) The particle size distribution of the instrument of Zetasizer Nanoseries is remarkably monodisperse showing a single sharp peak in intensity with sizes between 30 and 75 nm for CNCe and CNCm, respectively.

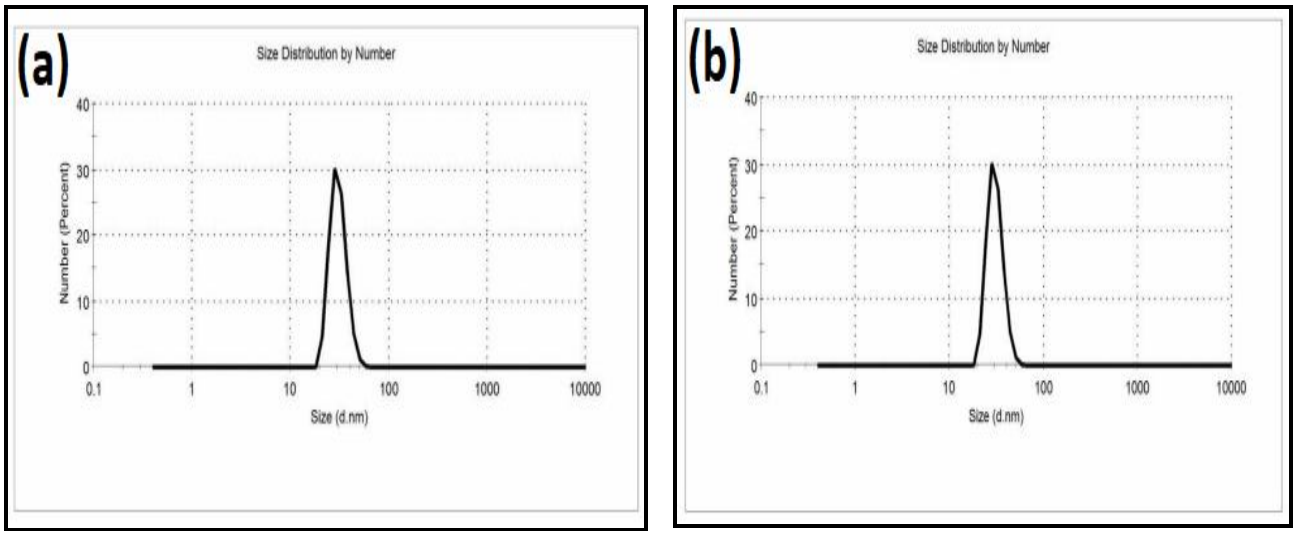

Figure: 2. Particle size distribution of CNCe (a) and CNCm (b).

Figure 2(a) shows the average diameter of CNCe which found to be 22.45 nm with poly-dispersity index of 0.437and the size average of CNCm was at 35.77 nm with poly-dispersity index of 0.437.

Therefore, the poly-disperisty index (PdI) represents the molecular weight distribution of the polymer. The PDI value of CNCe was similar to CNCm to be 0.437, which clearly indicating the uniformity of the chains length of CNC.

3.4 X-ray diffraction (XRD)

XRD analysis was conducted to investigate the crystalline behavior of CNCe and (b) CNCm. The XRD patterns of all samples showed major peaks at around 2θ=16.5° and 22.8°, which indicated the presence of cellulose as cellulose I structure (Figure 3). The crystallinity index (CrI) was used also to indicate the order of crystallinity for CNCe and CNCm.

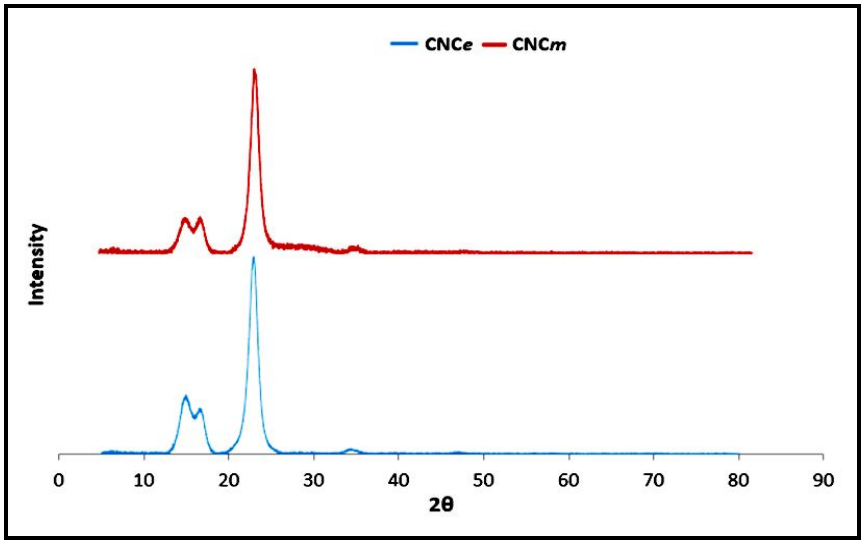

Figure: 3. XRD patterns of CNC; (a) CNCe and (b) CNCm

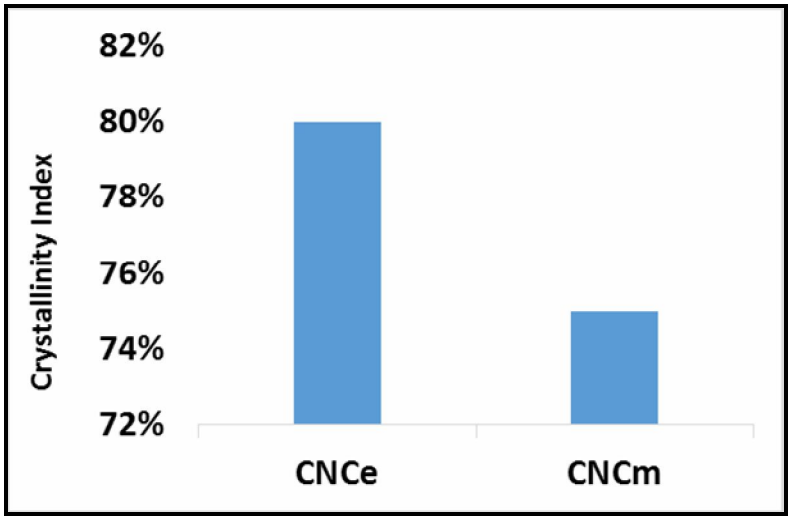

Figure: 4. Crystallinity Index of CNCe and CNCm

Figure 4 indicates that, the CrI of CNCe was higher than that obtained from CNCm, which was calculated from CNCe and CNCm to be, 80%, 75% respectively using Segal's empirical method (Segal et al. 1959). It was as well to emphasize that the results of the above XRD analysis declared that, the crystallinity of the obtained CNC was highly depending on their genotypes, in which, CNCe from extra-long staple length has higher crystallinity comparing with medium staple. Therefore, extra-long staple cotton was distinguished with low amorphous than medium staple and hence, medium staple was high sensitively towards acid attack which interpenetrating the high loss of weight than extra-long staple.

3.5 Fourier Transforms Infrared (FTIR) Spectroscopy

The infrared spectroscopy was carried out to characterize the samples by identifying the presented functional groups. Figure 5 shows the FTIR spectra of the CNCe cellulose and CNCm, respectively.

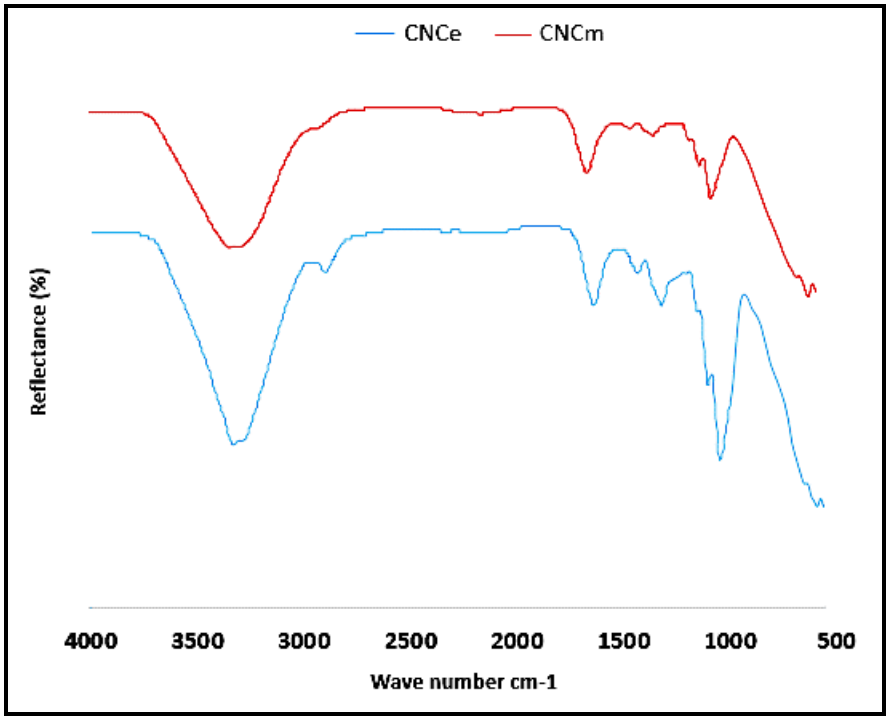

Figure: 5. Fourier transform infrared (FTIR) spectroscopy of CNCe and CNCm.

Bands at 3332.17 cm^{-1}, 2900.50 cm^{-1}, 1640.40 cm^{-1} and 1046 cm^{-1} were assigned to O-H stretching vibration; C-H bending vibrations, CH2 bending vibrations, The C–O vibration of C-OH and C-O-C (ether) groups yield peaks. From figure 5, there was no significant difference between the beaks allocated from CNCe and CNCm. As consequence, regardless their genotypes, the hydrolysis process with sulfuric acid had no remarkable effect on the chemical structure of the prepared CNC.

3.6 Thermo-gravimetric analysis (TGA).

Thermo gravimetric analysis (TGA) provides information on sample weight loss as a function of temperature. Figure 6 shows TGA curves of native cellulose of G.88, BF. FK37, CNCe and CNCm prepared using sulfuric acid concentrations 60% (w/w) at 60 ℃ for 60 min. The thermo-gravimetric analysis carried out within the temperature range 25- 650 ℃ for native cellulose and the extracted CNC.

The initial stage of weight loss began at the temperature range 56-120 ℃ and 50-116 ℃, respectively for CNCe and CNCm. (Figure 6).

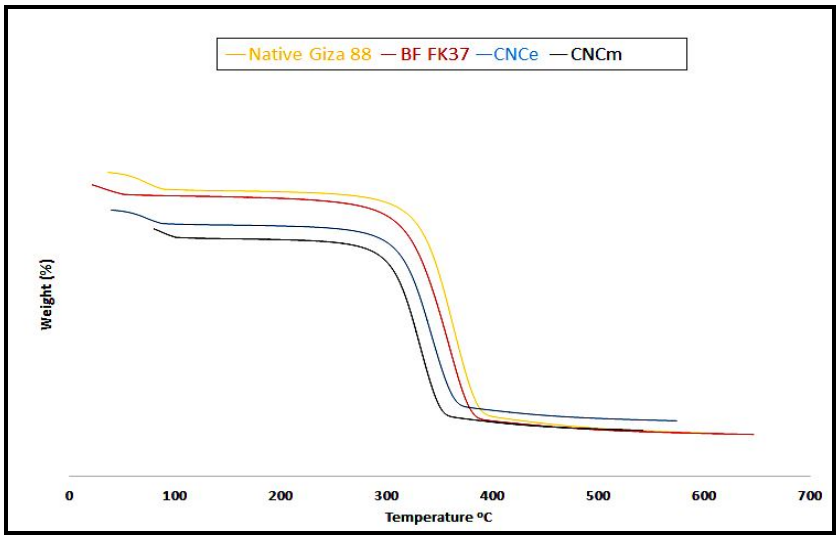

Figure: 6. Thermo-gravimetric curves of (native Giza 88, BF. FK37, CNCe and CNCm).

This could be described as dehydration reaction which was due to evaporation of bonding water associated with the moisture content of cellulose. And thereafter, weight loss started from the onset temperature, approximately, 296 ℃ and 243 ℃ for CNCe and CNCm, respectively as illustrated in Figure 6. Surprisingly, at this stage CNCe displayed superior thermal stability to CNCm; this might be ascribed to some remnant inherent impurities of the delignified cellulose since it was in unbleached state. 50% degradation (T50) of both samples was achieved at 343.16 ℃ and 340.60 ℃ for G.88 and BF FK37, respectively.

The weight loss here as also reported was attributed to breakdown of organic volatile matters due to decarboxylation and depolymerization. The peak temperature of weight loss in the samples was observed at 327 ℃ and 306 ℃ for G.88 and BF FK37, respectively.

4. Conclusion

Cellulose nanocrystal (CNC) was successfully generated from two different genotypes of cotton slivers; Egyptian extra-long staple G.88 (*Gossypium barbadense*) and upland medium long staple Burkina Faso cotton BF-FK37 (*Gossypium hirsutum*) with the performance of chemical treatment to obtain native cotton fibers, the extraction was performed by 60% w/w of H2SO4 rendered active effect for acid depolymerisation of cellulose at 60 ℃ and 60 min of time with high crystallinity (>70%). The TEM images indicated that acid hydrolysis is able to depolymerize cellulose micro chain into nanocrystallites in which CNC60 rendered average dimensions in nanoscale (<100 nm); the average dimensions (diameter × length) of 36.46 ± 7 nm × 355 ± 98.3 nm for extra-long staple, 37.2 ± 14 nm × 284 ± 83 nm for medium staple. This fact was further supported by DLS as the size of extra-long staple is 22.45 d.n and 35.77 d.n for medium staple. In addition, XRD results demonstrated that, both genotypes excited cellulose type I (crystalline polymorph). However, CNC extracted from extra-long

showed higher crystallinity index (80%) than observed from medium staple. Moreover, the thermal stability observed for CNC of extra-long is significantly higher than obtained from medium. By varying of the source of CNC, the size of the obtained crystals was varied besides crystallinity index and their thermal stability properties. Therefore, the using of extra-long staple length cotton slivers led to reduce the crystal size with improving in both crystallinity and thermal properties.

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