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Modulation of the Nanostructural Characteristics of Cellulose Nanowhiskers via Sulfuric Acid Concentration

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CELLULOSE nanowhiskers (CNW) were synthesized from native cotton cellulose as per the acid hydrolysis methods. Thus Egyptian cotton slivers, after being purified, were subjected to three sulfuric acid concentrations, viz. 55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min. The yield of CNW attains values of 65%, 57% and 50%, respectively. The amorphous regions along with thinner as well as shorter crystallites spreaded throughout the cellulose structure are digested by the acid leaving CNW suspension. The latter could be freeze-dried and CNW powder could be achieved. A thorough investigation pertaining to nanostructural characteristics of CNW was performed. These characteristics could be monitored using TEM for morphology, sizes and size distribution, XRD for degree of crystallinity and crystalline structure, FTIR spectra for following the changes in functionality and TGA for studying the sample weight loss as a function of temperature. Based on the results obtained CNW prepared using 60% w/w sulfuric acid are nominated as the best candidate within the range studied in the area of reinforcement by virtue of their salient features.

Nowadays, nanotechnology is one of the most promising venues of scientific and technological development and is anticipated to grow progressively in the coming years. By and large nanotechnology is defined as creation of functional materials, devices and systems through control of matter on the nanometer length scale (1-100 nanometers) along with exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale(1,2) . Nanomaterials acquire salient properties and structures at the nanometer scale (at least one dimension is < 100 nm). This, indeed, evoked the attention of scientists and engineers in physics, chemistry, materials, information technology, and even bioscience(3) .

The use of cellulosic fibers as reinforcing elements in polymeric matrix has been the subject of a good deal of work over the last two decades. Essential reasons for this is the possibility of replacing conventional fibers such as glass by natural cellulosic fibers in reinforced composites due to the abundance,

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renewable and eco-friendly nature of cellulose[4] . As a matter of fact, a new research trend has been adopted world – wide in the recent years for synthesis of cellulose nanowhiskers (cellulose nanocrystals) from several cellulose sources[5,6] . In nature, the cellulose molecular chains are biosynthesized and self-assembled into microfibrils, which are composed of crystalline domains and amorphous domains. Amorphous domains are susceptible to and easily digested by acid attack because cellulose chains in these regions are randomly oriented in a spaghetti-like arrangement leading to a lower density in these non-crystalline regions [7] .

Synthesis of cellulose nanowhiskers from various cellulose sources has currently gained more attention by virtue of their exceptional mechanical properties including high specific strength and modulus, large specific surface area, high aspect ratio, environmental benefits and low cost[8,9]. Highly crystalline rod-like nanostructures obtained from cellulose, that is, cellulose nanowhiskers (CNW) or cellulose nanocrystals (CNC), have been regarded during the last decade as potential nano-reinforcements for different polymers [10] .

Ranby and Ribi[11] were the first to report on the production of nanowhiskers in 1949 – 1950. Nevertheless, the self-assembly of cellulose nanowhiskers into liquid crystalline phase was only reported in 1992 [12] . Since then, the production and properties of nanowhiskers from various native cellulose sources such as cotton[13,14], wood[15], tunicates (sea-squirt)[16], bacterial cellulose[17] were studied [18] .

One way to obtain cellulose nanowhiskers is by acid hydrolysis where the cellulose is treated with sulfuric acid for a modulating period of time and temperature. This treatment removes the amorphous domains of the cellulose, leaving single and well-defined crystals in a stable colloidal suspension. The negative sulfate groups on the surface of the nanowhiskers guarantee the stability of this suspension because of the electrostatic repulsion[19,20]. Thus obtained cellulose nanowhiskers (CNW) possess several advantages, namely high modulus, low density, high aspect ratio, and negligible thermal expansion. That is why they have attracted the attention of scientific working in various fields, in particular, materials scientists. CNW have been widely used as reinforcement in different polymers, such as poly (styrene-co-butyl acrylate)[21], poly (vinyl alcohol)[22], polypropylene[23] , polyethylene[4] , poly(methylmethacrylate)[24] …, etc.

The present work is undertaken with a view to modulate the nanostructural characteristics of cellulose nanowhiskers (CNW) extracted from cotton cellulose as per the acid hydrolysis using sulfuric acid. Special emphasis is placed on sulfuric acid concentration as the key factor in this state of affairs. World – class facilities, namely, TEM, XRD, FTIR and TGA are used for monitoring the nanostructural features of CNW .

Experimental

Materials

Cotton sliver, Giza 86 was kindly supplied by Cotton Research Institute, Giza. Sodium hydroxide, sodium perborate, urea and sulfuric acid (95–98%) were all laboratory grade reagents.

Methods

Preparation of cellulose nanowhiskers

Cellulose nanowhiskers (CNW) were prepared by subjecting the cotton sliver to three successive treatments, namely, alkali, perborate, and sulfuric acid treatments. While the first two treatments address the purification of the cotton fibres, the third treatment is concerned with conversion of the purified fibers to cellulose nanowhiskers. The experimental techniques adopted were as follows:

- *Alkali treatment* : Cotton sliver was boiled in an aqueous solution containing 2.5 g/l sodium hydroxide and 2 g/l nonionic wetting agent, under reflux for 60 min using a material to liquor ratio 1:20. The cotton sliver was then washed three times with boiling water, twice with cold water and finally air dried. This alkali treatment removes all the impurities except the natural coloring matters which are removed by subsequent treatment with sodium perborate as described below.

- *Perborate treatment* : The alkali treated cotton sliver was further purified by boiling in an aqueous solution containing 2.5 g/l sodium perborate, 0.5 g/l urea and 2 g/l nonionic wetting agent, under reflux for 60 min using a material to liquor ratio 1:20. The sliver was then washed three times with boiling water, twice with cold water and finally air dried. This purified cotton sliver will be referred to as native cotton cellulose when used for nanostructural measurements along with cellulose nanowhiskers (CNW), which were prepared as described below.

- *Sulfuric acid treatment* : The as purified cotton sliver was cut into small pieces prior to hydrolysis treatment with sulfuric acid. The hydrolysis was carried out by introducing the small pieces of the cotton into 60% (w/w) sulfuric acid (10 ml/g cotton) to form suspension. This suspension was held at 60^0C under strong mechanical stirring for 60 min to allow for hydrolysis. Immediately, following hydrolysis, the suspension was diluted five-fold with cold distilled water to stop the reaction. The suspension was then transferred into centrifuge bottles and centrifuged at 12,000 rpm for 10 min and decanted to separate the crystals. The solid aggregates in the suspension 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°C, 0.1 mbar, under such pressure cellulose nanostructure will not be affected) as powders.

Analysis and characterization

Transmission Electron Microscope (TEM)

The morphology of cellulose nanowhisker (CNW) was characterized using Transmission Electron Microscopy (TEM) (JEOL 1200, JEOL USA, Inc) with an accelerating voltage of 80 kV. The 0.1 wt% nano-crystal suspensions were dropped onto copper grids coated with a carbon support film[25] .

X-ray diffraction (XRD) analysis

The XRD patterns of dried CNW were obtained using a D500 diffractometer (SIEMENS) operated at 30 kV and 15 mA, utilising a Cu-Ka radiation source (k = 0.154). The scans were controlled by the Diffrac-AC software programme. The degree of crystallinity I_c [%] of CNW samples were calculated according to Equation (1).

$$I_c[\%] = \frac{I_{(Crys+am)} - I_{(am)}}{I_{(Crys+am)}} \qquad \text{............ Eq.(1)}$$

where $I_{(crys+am)}$ represents the peak intensity (count per second) around 22.8^0 for the crystalline and amorphous part. $I_{(am)}$ is the peak intensity around 18^0 and represents the amorphous part of the celluloses.

Fourier-transformed infrared spectroscopy (FT-IR)

FT-IR spectra were recorded using a S-100 FT-IR spectrometer (Perkin Elmer) and scanned from 4000 to 400 cm^{-1} in ATR mode and using KBr as supporting material. Characterization of samples using FT-IR technique was carried out to follow the change in the functionality of CNW[26] .

Thermogravimetric analysis (TGA)

The thermal properties of CNW are measured using thermogravimetric analysis (TGA) STD Q600. In preparation of samples for TGA, the whiskers were ground to powder form. Decomposition profiles of TGA were recorded at a heating rate of 10 ^{0}C/min between room temperature and 600 ^{0}C in nitrogen [27, 28].

Results and Discussion

Cellulose nanowhiskers (CNW) are rigid rod-like crystals or whisker shaped particles remaining after acid hydrolysis of native cellulose. The morphology of CNW is a manifestation of the origin of cellulose and the conditions of hydrolysis[29]. Acid treatment is the most promising route for the preparation of suspensions of cellulose nanomaterials. As already stated cellulose microfibres of native cellulose are composed of crystalline and amorphous domains[30]. The amorphous regions are more accessible to acid molecules and susceptible to the hydrolytic actions than the crystalline region. With sulfuric acid, for example, the amorphous regions are digested very fast. Acid hydrolysis of cellulose in sulfuric acid involves rapid protonation of glucosidic oxygen or cyclic oxygen by protons from the acid, followed by a slow splitting of glucosidic bonds induced by the addition of water. This hydrolysis process yields two fragments with shorter chains while preserving the basic backbone structure.

Formation of cellulose nanowhiskers (CNW)

Under the conditions employed for sulfuric acid hydrolysis in a previous work[31] , most of the amorphous regions were removed leaving cellulose nanowhiskers in the reaction solution. The presence of sulfate groups on the hydrolyzed cellulose surfaces results in stable negatively charged surfaces above acidic pH. The negatively charged surface groups aid in forming a stable CNW suspensions in water due to electrostatic interactions[32]. This anionic stabilization via the repulsion forces of electrical double layers was shown to be very efficient in preventing the aggregation of cellulose nanowhiskers driven by hydrogen bonding[33]. Hydrodynamic properties of neutral suspensions of cellulose crystallites are related to size and shape[34]. In the current work, bleached cotton sliver was subjected to sulfuric acid hydrolysis as described in the experimental section. The morphology of the so obtained cellulose nanowhiskers were examined using TEM. The optical photographs of cellulose nanowhiskers vis – a – vis that of the bleached sliver are shown in Fig.1. A comparison of the optical photograph of the bleached sliver (A) with those of the nanowhiskers (B and C) would indicate that digestion of cellulose (cotton sliver) by sulfuric acid creates well suspended ultrafine (nano) particles (B), meanwhile the optical photograph in (C) exhibits the cellulose nanowhiskers as white powder.

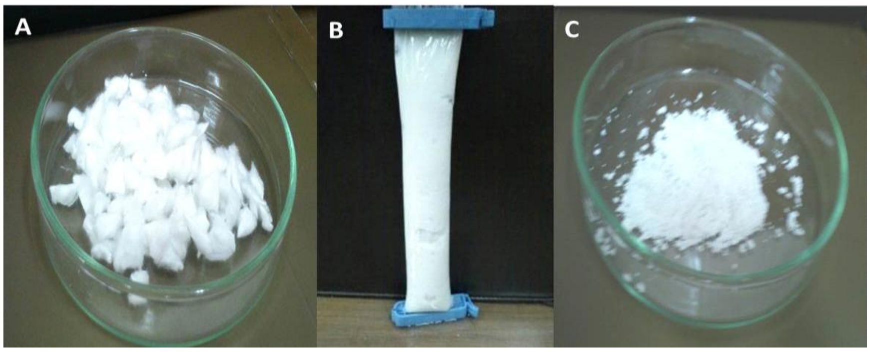

Fig. 1. Optical photograph; A) bleached cotton species before acid hydrolysis, B) dialysis bags filled with CNW suspension and C) freeze dried CNW powder.

Effect of acid concentration on the yield of cellulose nanowhiskers

Main parameters affecting the magnitude of acid hydrolysis of cellulose using sulfuric acid are concentration of the acid together with time and temperature of acid hydrolysis. Time and temperature will have a significant impact to the achieved yields as the heterogeneous diffusion of the acid to the amorphous regions of cellulose does not occur instantaneously. Basically, temperature and duration of sulfuric acid hydrolysis reaction have been early established at 60 ^{0}C for 60 min[35] . It was also shown that, the relative rate of the hydrolysis is faster in the beginning of the process when the easily accessible amorphous regions are being hydrolyzed and later slows down significantly as the acid attacks the reducing end and the surface of the residual crystalline regions.

As far as the effect of sulfuric acid concentration on hydrolysis of cotton cellulose and creation of CNW is concerned, no work has been published so far. current work is designed to fulfill the gap.

Thus, CNW preparation using different sulfuric acid concentration, viz, 55, 60, 65 and 70 % (w/w) was performed at constant time (60 min) and temperature (60 ^{0}C). Figure 2 shows the effect of sulfuric acid concentrations on the yield % of CNW formed under the influence of acid attack on cellulose during the hydrolysis process. It can be seen that, the yield % of CNW decreases significantly as sulfuric acid concentration increases up to 65% (w/w). Whereby, the yield % of CNW reaches only 50 % which is rather a very low value. Most probably, full hydrolysis of the amorphous regions of the cellulose is accompanied along with partial hydrolysis of crystalline regions. This means that, the crystalline regions also decrease as the acid concentration increases. This is strongly substantiated by the finding that, increasing the concentration of sulfuric acid to 70% (w/w) dissolves both amorphous and crystalline regions completely and cannot be separated. It is, therefore, concluded that sulfuric acid concentration above 65% (w/w) is not appropriate for preparation of CNW.

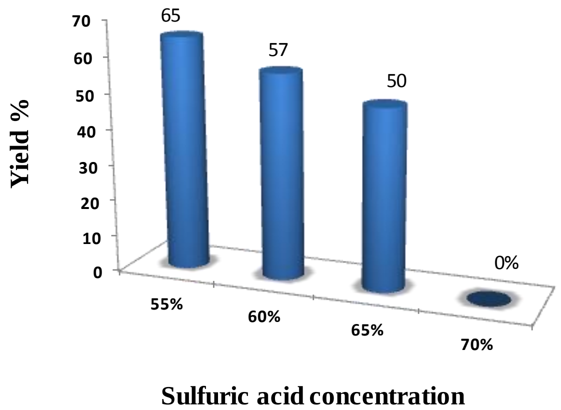

Fig. 2. CNW yield % produced using different sulfuric acid concentrations 55%, 60%, 65% and 70% (w/w) for 60 min at 60 ^{0}C.

Characterization of CNW

Transimission electron microscopy

Morphology, size and size distribution of CNW obtained from cotton cellulose using sulfuric acid at concentrations of 55%, 60% and 65% (w/w) have been investigated using TEM. Figure 3 A, B & C exhibit**s** TEM micrographs of the obtained CNW revealing the morphologies of the CNW produced from cotton cellulose under the attack of the three different acid concentrations used. In all these figures a represents TEM micrograph of cellulose nanowhiskers, while, b and c are histograms illustrating size and size distribution of cellulose nanowhiskers in diameter and in length, respectively.

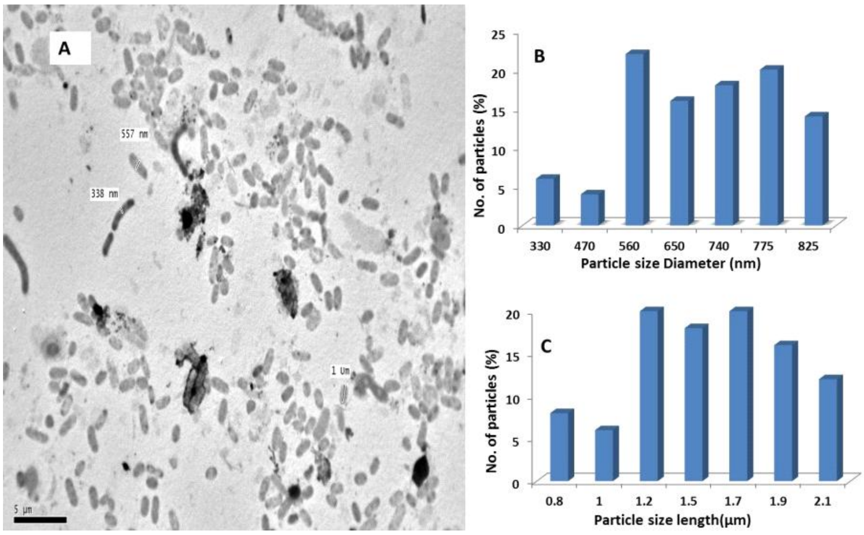

Fig. 3.:A) a TEM micrograph of cellulose nanowhiskers; b, c) histograms showing the distribution of particle size diameter and the distribution of particle size length of cellulose nanowhiskers, respectively; CNW were prepared using 55% (w/w) sulfuric acid at 60^0C for 60min.

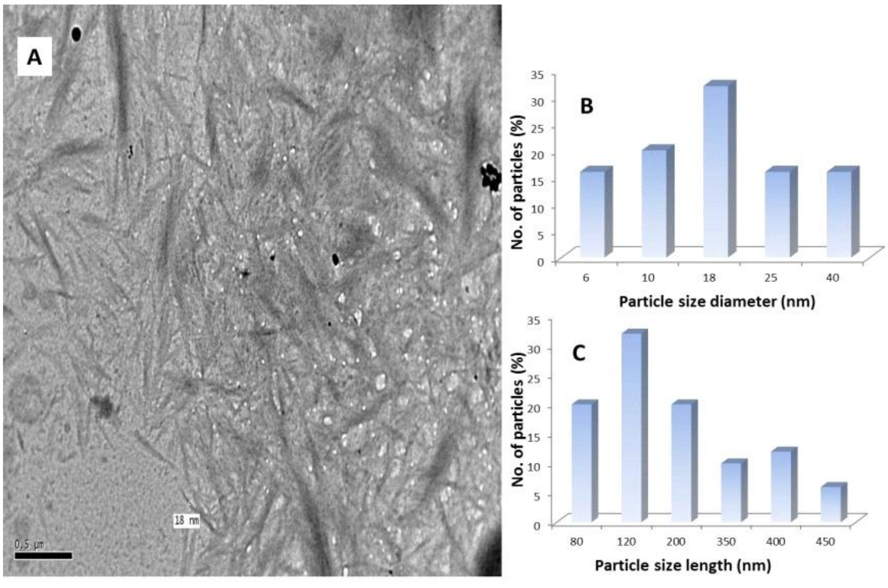

Fig. 3. B) a TEM micrograph of cellulose nanowhiskers; b, c) histograms showing the distribution of particle size diameter and the distribution of particle size length of cellulose nanowhiskers, respectively; CNW were prepared using 60% (w/w) sulfuric acid at 60^0C for 60 min.

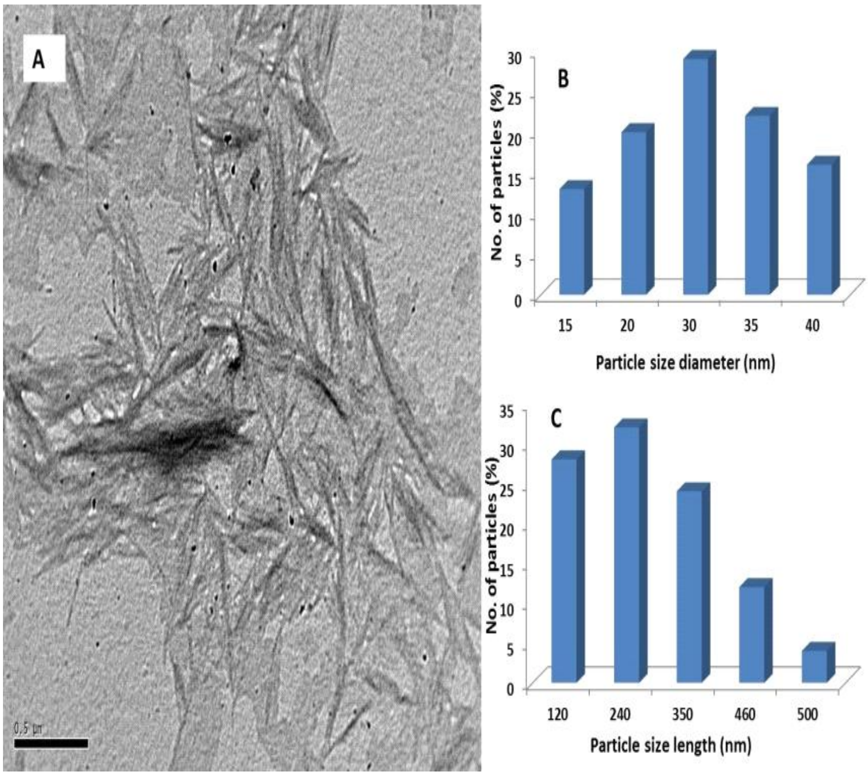

Fig. 3. C) a TEM micrograph of cellulose nanowhiskers; b, c) histograms showing the distribution of particle size diameter and the distribution of particle size length of cellulose nanowhiskers, respectively; CNW were prepared using 65% (w/w) sulfuric acid at 60^0C for 60min.

TEM examination (Fig. A, B & C) discloses that, the original cotton cellulose successfully undergoes acid hydrolysis to bring about well stabilized polydispersed cellulose nanoparticles having needle–or short rod–like structure. This is observed regardless of the concentration of the acid used. However, size and size distribution of the CNW are significantly affected by the acid concentration.

Table 1 summarizes the effect of sulfuric concentration on the CNW yield % and size and size distribution of CNW obtained from TEM and histograms. As is evident, increasing the sulfuric acid concentration decreases the crystallite sizes as clarified by diameter size and length size of CNW. For example, when 55% (w/w) of sulfuric acid was used, longer and wider crystallites were formed with an average diameter size of 650 – 825nm and length of 2.1 µm up to 2.1 µm.

TABLE 1. Effect of sulfuric acid concentration on CNW yield %, size diameter and size length.

Sulfuric acid concentration (w/w)	Particle size diameter (nm)	Particle size length (nm)	Yield % of CNW
55%	650 - 825	1200 - 2100	65
60%	10 - 25	80 - 200	57
65%	20 - 35	120 - 350	50

This is in contrast with the characteristics of CNW obtained with 60% and 65% (w/w) sulfuric acid. When the latter two concentrations were used a smaller needle – like shape nanocrystals / nanowhiskers are formed with narrow size distribution. The CNW produced using 60% (w/w) sulfuric acid display diameter ranging from 6 – 40nm and length in the range of 80-450nm, while, CNW obtained by using 65% (w/w) sulfuric acid acquire a diameter ranging from 15 – 40nm and length in the range of 120 – 500 nm. It is certain, however, that the majority of the nanowhiskers diameter size produced using 60% (w/w) sulfuric acid are ranging from 10 – 25 nm with a length range of 80-200 nm. Meanwhile, the majority of nanowhiskers diameter size produced using 65% (w/w) sulfuric acid ranges from 20 – 35 nm with length range of 120 – 350 nm.

Differences in size diameter, size length and the yield of CNW upon using various sulfuric acid concentrations could be interpreted in terms of greater availability of hydronium ions in the vicinity of glucosidic linkages of the cellulose chain molecules. It is understandable that acid hydrolysis with consequent digestion and removal of the amorphous regions along with surfaces of crystallites occurs through molecular chain scission of the glucosidic linkages. Higher concentration of sulfuric acid (65% w/w) seems to create a reaction environment containing great amount of hydronium ions thereby inducing more progressive acid attack in comparison with moderate (60% w/w) and low concentration (55% w/w) sulfuric acid. As a result, the yield of CNW obtained thereof differs significantly being the lowest with the higher sulfuric acid concentration; the CNW yield follows the order: 65% > 60% > 55% (w/w).

The above order holds good for sizes (diameter and length) of CNW except that the CNW obtained with 65% (w/w) sulfuric acid exhibits larger sizes than for 60% and 50% (w/w). In other words, the sizes of diameter and length of CNW prepared using 65% (w/w) sulfuric acid do not cope neither with its lower yield nor with the severity of the acid attack under which this CNW is created. Hence, it is logical to assume that at higher sulfuric acid concentration (65% w/w) cellulose crystalline domains undergo fast decomposition / disintegration to yield crystallites the sizes of which are even smaller than those found with 60% (w/w) sulfuric acid. But such crystallites are liable for aggregation and recrystallization to produce ultimately CNW based on crystallites with larger sizes of diameter and length than those obtained when 60% (w/w) sulfuric acid was used.

X-ray diffraction (XRD) analysis

XRD was used to investigate the changes of phase structures of cellulose before and after acid hydrolysis. X-ray diffraction patterns of cellulose nanowhiskers prepared using different sulfuric acid concentrations (55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min) compared with cotton cellulose (blank) are presented in Fig.4.

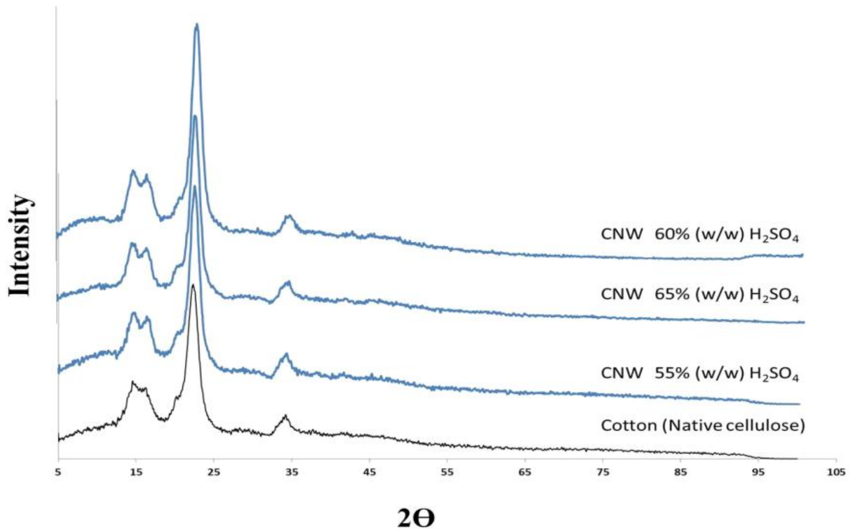

Fig. 4. XRD patterns of native cotton cellulose and cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations; 55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min.

The principal peaks from XRD patterns (Fig.4) are at 2θ values 14^0, 16^0, 22^0, and 35^0. These four peaks correlate respectively, with [101], [101]$^-$, [200] and [400] crystal lattice planes which were assigned to typical cellulose I crystalline structure [(36)]. This confirms that CNW have mainly the crystalline structure of cellulose I. It also confirmed that CNW species are identical to their neat, untreated cellulose source. The sharp intensity of diffraction peak for the [200] plane at 2θ=22^0 speaks of a quite high degree-of-order structure indicating almost high perfection of the crystal lattice[(37)]. In contrast, differences among the degrees of crystallinity of the CNW samples under investigation are observed as shown below.

Table 2 demonstrates the degree of crystallinity brought about by XRD patterns for native cotton cellulose and cellulose nanowhiskers (CNW) prepared thereof using different sulfuric acid concentrations viz. 55%, 60% and 65% (w/w). It is observed that CNW display higher degree of crystallinity than native cellulose and the highest value for the degree of crystallinity is pertaining to CNW prepared using 60% w/w sulfuric acid. At this particular concentration, cotton cellulose seems to get rid of most of the amorphous regions as previously stated and, as a result, crystallinity increases.

TABLE 2. Degree of Crystallinityof native cotton cellulose and cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations.

Conc. Of sulfuric acid (w/w)	Degree of Crystallinity%
0	80.3
55%	80.6
60%	90
65%	81.53

It is further observed (Table 2) that CNW prepared using sulfuric acid of 65% (w/w) reveal a degree of crystallinity which is lower than those prepared using 60% (w/w) sulfuric acid. This might have occurred because the acid treatment at high acid concentration causes corrosion which not only removed the amorphous portions of the cellulose fibers but also partly destroyed the crystalline portions. This kind of damage in the cellulose crystalline regions may decrease the flexibility of the nanowhiskers. This is one of the reasons which advocate preparation of CNW using 60% (w/w) sulfuric acid. At any event, however, the degree of crystallinity – based on sulfuric acid concentration (w/w) follows the order: 60% > 65% > 55% > cotton cellulose.

It is as well to emphasize that the results of the above XRD analysis are in accordance with the results of CNW yield and their sizes as examined by TEM. The crystallinity of cotton cellulose, as shown above, amounts to 80.3%. When amorphous regions are completely removed from this cellulose using the most appropriate conditions for preparation of CNW (60% w/w sulfuric acid at 60 ^{0}C for 60 min.), the yield of CNW attains practically – as previously shown – a value of 57%. This indicates that current acid hydrolysis removes not only the amorphous regions but also much of the crystalline domains through dissolution of the thinner as well as shorter crystallites which are randomly distributed and spreaded throughout the cellulose structure.

Fourier-transformed infrared spectroscopy (FT-IR)

Figure 5 assembles FT-IR spectra of cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations as compared with the spectra of native cotton cellulose. FTIR spectra recorded for all samples show an intense broad band in the higher energy region (3400 cm^{-1}) which is assigned for O–H stretching vibration of cellulose molecule. Moreover, the spectra of all samples show the characteristic peak that appears just below 3000 cm^{-1} due to alkyl C–H stretching vibration. The CH_2 bending vibrations occur just below 1,500 cm^{-1}. The C–O vibration of C-OH and C-O-C (ether) groups yield peaks just above 1000 cm^{-1}.

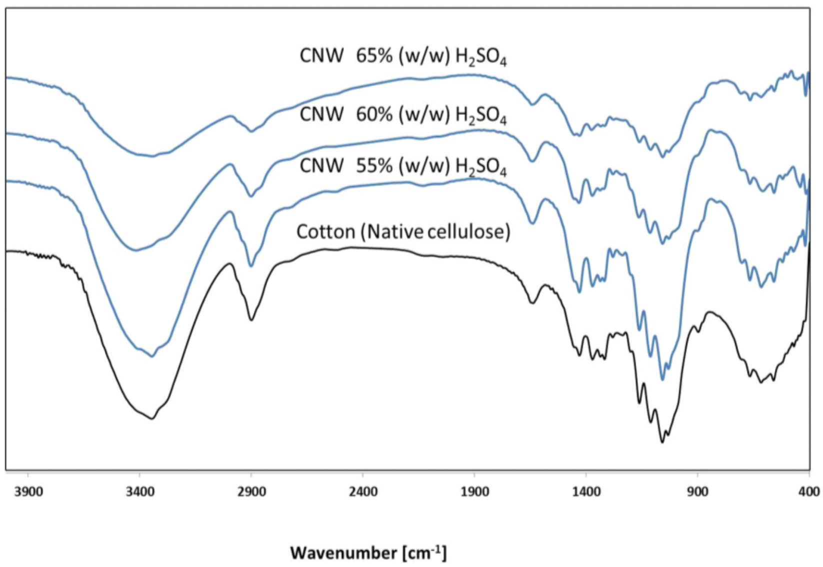

Fig.5. FT-IR spectra of native cotton cellulose and cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations; 55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min.

Besides, the absorbance peaks observed in the spectra of native cotton cellulose and the cellulose nanowhiskers in the region 1645–1641 cm^{-1} are attributed to the O–H bending of the adsorbed water. The peak observed in the spectra of all samples at 1058 cm^{-1} is due to the C–O–C pyranose ring (antisymmetric in phase ring) stretching vibration.

The region of 800-1500 cm^{-1} is a unique fingerprint region for cellulose where the majority of peaks in that range are found for all samples, indicating that regardless of acid treatment, cellulose maintained a similar chemical structure to the original untreated species. The data obtained from FTIR spectra are in full agreement with those obtained from XRD analysis.

Thermo – gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) provides information on sample weight loss as a function of temperature. Figure 6 shows TGA curves of native cotton cellulose and cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations; 55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min. On the other hand, Table 3 summarizes the decomposition temperature (peak maximum for the first derivative) and the peak onset (T_o) and endset (T_∞) temperatures and the residue (%) of all samples. Results depict that CNW exhibit a typical degradation profile of native cotton cellulose but with significant different thermal behavior than the native cotton cellulose

The thermal degradation of cellulose involves de-polymerization, dehydration and decomposition of glycosyl units followed by the formation of a charred residue, which typically occurs between 250°C and 350°C. The small shoulder above 325°C is ascribed to the oxidation and breakdown of the charred residue to lower molecular weight gaseous products [31] . Whereas, the first weight loss up to 100 ^{0}C is due to water evaporation. It was reported that the decrease of the moisture loss could be attributed to the strong hesion of water molecules to the large surface of whiskers [38].

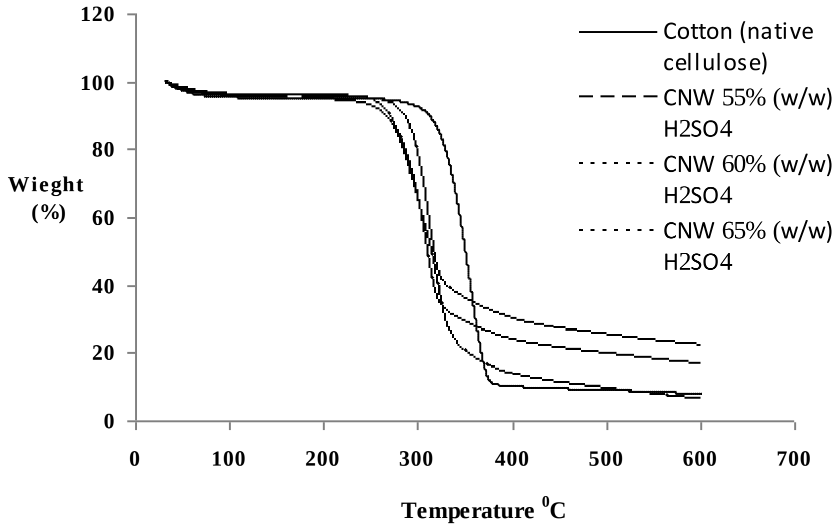

Fig. 6. TGA curves of native cotton cellulose and cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations; 55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min.

TABLE 3. Weight loss % of native cotton cellulose and cellulose nanowhiskers (CNW) prepared using different sulfuric acid concentrations; 55%, 60% and 65% (w/w) at 60 ^{0}C for 60 min.

Conc. of sulfuric acid	Evaporation		Main decomposition					Residual content Wt.%
			Decomposition temp.		Remaining Weight %		Weight loss %	
	Wt. %	Temp.	T_0	T	W_0	W		
Cotton	4.51	100	307.74	350.16	89.62	37.94	51.68	8.24
55%	4.63	100	267.21	313.59	89.43	50.13	39.3	6.23
60%	3.87	100	288.41	316.77	91.11	59.21	31.9	27.79
65%	4.05	100	272.81	314.13	89.97	46.99	42.98	22.25

Table 3 discloses that, cotton cellulose shows the typical decomposition with onset temperature just above 300 °C and endest temperature at 350 ^{0}C (weight loss 51.68 %) and this coincides with a massive weight loss leaving only 8.24 % ash at 600 ^{0}C. The cellulose nanowhiskers, on the other hand, shows a lower T_o and T_∞ occurred around 250 ^{0}C and 310 ^{0}C, respectively, which are much lower than the expected degradation temperature of native cotton cellulose. These major thermal behavioral differences between the cellulose nanowhiskers and the native cotton cellulose may involve different decomposition gasification process. Cellulose is known to decompose to levoglucosan (1,4-anhydro-β-d-glucopyranose) at around 180^{0}C which then gasifies efficiently at 300^{0}C [(38)].

The gradual mass loss of the cellulose nanowhiskers in the 150-300°C temperature range suggests a different decomposition mechanism, possibly direct solid-to-gas phase transitions catalyzed by surface sulfate groups. It has been reported that the activation energies of the degradation of cellulose nanowhiskers were significantly lowered by introducing sulfate groups via sulfuric acid hydrolysis[(39)]. It was argued that the lower degradation temperature of nanowhiskers with sulfate groups was due to the increasing numbers of free end chains and sulfate groups at the surface, which were liable to earlier decomposition.

Obviously, then, the thermostability of cellulose nanowhiskers is compromised by sulfate groups, agrees well with the above TGA results. Furthermore, the high surface area of CNW might also play an important role in diminishing their thermostability due to the increased exposure surface area to heat. Moreover, the decomposition of CNW occurring at lower temperatures from (150 to 300°C) might also indicate faster heat transfer in cellulose nanowhiskers. The cellulose nanowhiskers have been reported to function as efficient pathways for phonons, leading to their higher thermal conductivity[(40)]. The better thermal conductivity of cellulose nanowhiskers might be ascribed to smaller phonon scattering in the bundle of crystallized cellulose chains in the cellulose nanowhiskers than the amorphous random chains in cellulose powder.

Of particular interest is the thermal stability of CNW samples which could be achieved from Fig. 6 and Table 3. With reference to both decomposition temperature and residual content % the thermal stability of CNW follows the order; 60 % > 65% > 55% (w/w) sulfuric acid. Accordingly, CNW prepared using 60% (w/w) sulfuric acid undergoes more gradual thermal transitions than that reported for others including the native cellulose, which loses about 42% of its mass in 150 - 316 ^{0}C region followed by another 30% mass loss between 316 ^{0}C and 600 ^{0}C leaving significantly highest residue, nearly 27%, at 600 ^{0}C.

Conclusion

Modulation of nanostructural characteristics of cellulose nanowhiskers (CNW) was achieved via synthesis of the latter from native cotton cellulose using three different sulfuric acid concentrations. Of these, 60% (w/w) sulfuric acid was found the most adequate. When this particular concentration was used at 60 ^{0}C for 60 min to extract CNW from the native cotton cellulose, the resultant CNW display salient features. Specially, thus obtained CNW are characterized by 57% yield (based on dry weight of cellulose), size diameter of 10 – 25 nm and size length of 80 – 200 nm, degree of crystallinty of 90% while maintaining the crystalline structure of cellulose I, similar functionality and typical profile like the native cotton cellulose but with significantly different thermal behavior. Indeed, these characteristics advocate the CNW in question as a good candidate in the area of reinforcement and applications.

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تحديد وتنظيم الخواص النانوتركيبية للألياف النانومترية عن طريق تركيبات حمض الكبرتيك

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يهدف البحث الي تحضير وتوصيف دقائق السليولوز النانومتريه باستخدام تركيزات مختلفه من حامض الكبريتيك المركز. تم استخدام القطن كمصدرللسليلوز حيث يعتبر القطن من اهم المحاصيل السليلوزيه الرئيسيه وتاتي اهميه في المقام الاول بالنسبه للانسان حيث يستخدم في صناعة الملابس والمنسوجات المختلفه كما يدخل ايضا في اغلب الصناعات المختلفه الغذائية منها والصناعيه.

تم تحضير دقائق النانو سيليوز من خلال تفاعل القطن مع اربعة تركيزات من حامض الكبريتيك المركز وكانت كالتالي 55٪ و 60٪ و65٪ و 70٪ ، وتم دراسة القياسات المختلفه علي العينات المحضرة مثل TEM و XRD وFTIR. ومن النتائج يتضح ان افضل تركيز يمكن الحصول من خلاله علي اصغر حجم وافضل كميه من دقائـــق النانـــو سليلوزهــو تركير الحــامض عند 60٪ لمـــدة ساعه عند 60 درجه مئويه.