Investigation into the antibacterial and mechanical properties of cellulose nanoparticles treated cotton fabrics

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Abstract

Cellulose nanocrystals (CNC) as a reinforcing agent play a vital role in various applications. Herein, CNC was harnessed for its dual action as reinforcing and antibacterial additive biopolymers to impart cotton fabrics with mechanical as well as antibacterial properties. CNC was extracted from cotton slivers and applied to cotton fabrics with and without Polyacrylate binder. Results indicated the improvement of tensile strength, crease recovery, tearing strength and thermal properties were observed in case of CNC was mixed with polyacrylate binder at moderate ratio. In addition to this, cotton fabrics treated CNC with and without polyacrylate binder exhibited a highly efficient antibacterial activity against both pathogenic bacteria E. coli and S. aureus.

Keywords

CNC،SEM،Synwin Non Woven

الملخص

تأثير جسيمات النانوسيلولوز الكريستالية المصنوعة بالتجميد (CNC) على خصائص أقمشة القطن المنسوجة

تمت معالجة أقمشة القطن المنسوجة في ظروف مختلفة باستخدام تراكيز مختلفة من جسيمات النانوسيلولوز الكريستالية المصنوعة بالتجميد ونسب رابطة بولي أكريلات. يعتمد توصيف مثل هذه الأقمشة على الخصائص الفيزيائية التي تم تقييمها من خلال زاوية استعادة الثنية، واحتفاظ قوة الشد، والتمزق، والسمك. أظهرت جسيمات CNC تأثيرات أفضل بكثير على تحسين مقاومة التجعد لأقمشة القطن المنسوجة؛ عند مقارنتها بأقمشة القطن المنسوجة غير المعالجة، كما تعطي تأثيرات متوسطة. تم الحصول على قيم عالية لمقاومة التمزق وقوة الشد والسمك بعد استخدام جسيمات .CNC كما تم تعريض العينات المعالجة من القطن لاختبار مقاومة الحرارة، وتبين أن العينات المعالجة بجسيمات CNC تمتلك مقاومة حرارية عالية بسبب وجود النانوسيلولوز. كما تبين أن صور SEM تستخدم للتأكد من وجود جسيمات السليولوز النانوية على القماش القطني وأنه في العينات المحضرة تم تأكيد وجود الجسيمات النانوية؛ نظرًا لوجود جسيمات CNC على سطح القماش القطني. وبالتالي، يمكن الاستنتاج أن القطن عندما يتم طلاؤه بخليط من جسيمات CNC ورابطة بولي أكريلات يعطي خصائص أفضل من الفسكوز غير المعالجة.

الكلمات المفتاحية

جسيمات النانوسيلولوز الكريستالية،المسح المجهري الإلكتروني،أقمشة القطن المنسوجة غير المعالجة

1. Introduction

The most prevalent renewable polymer that has ever existed on earth is thought to be cellulose. In general, cellulose is referred to as a macromolecule, which is a nonbranched chain of 1-4-linked -D anhydro glucopyranose units that can vary in length. Numerous living things, including higher and lower plants, certain amoebae, marine animals, bacteria, and fungi, biosynthesize it [1, 2]. Among the several cellulose forms, cellulose I and II are frequently seen in the natural world. While cellulose II has an anti-parallel chain orientation, cellulose I has the best mechanical characteristics [3, 4].

Cellulose, which means "rich in small cells" in Latin, is a biopolymer that occurs naturally in things like cells of plants like cotton and wood [5, 6]. A cellulose-based material with one or more of its exterior dimensions at the nanoscale, or between 1 and 100 nm, is referred to as a cellulose nanomaterial [7, 8]. As a result, the nanocellulose can be divided into many categories based on things like shape, size, and structure. For the shape characteristic, there are basically three types: Sheet, spherical and crystal/whisker [9-14]. In the cotton fibre, hydrogen bonds frequently act as anchors for the cellulose chain, which take place between the hydroxyl groups of adjacent molecules, with parallel, closely packed molecules in the crystalline regions of the fibre. Both high-order (crystalline) and low-order (amorphous) regions can be found in the solid form of cellulose [15].

The crystalline region of cellulose can be released by the controlled acid hydrolysis resulting in CNC formation. Due to their superior mechanical properties, high surface area, high crystallinity, and nanoscale size, CNC has attracted significant investments in recent years [16]. Additionally, CNC is abundant, strong, rigid, light, low in weight, and biodegradable which allows it to be used in a variety of special applications [16].

On the other hand, cotton cellulose is notable for having a high level of crystallinity and polymerization. A higher degree of polymerization and crystallinity are related to higher fibre strengths because they show how closely packed and parallel the fibre molecules are to one another. As per pretreatment processes that were applied to cotton fabrics such as, squaring, bleaching and dyeing, strength of cotton fabrics has become a corner stone in the textile industry. Therefore, most common cotton fabrics properties such as tensile strength, contact angle, tearing, etc., are highly affected with different pretreatments process [17]. New finishes materials have been developed recently to overcome these tackles including polyacrylate binder which enhances the mechanical properties of fabric. Most recently, nanotechnology has given the textile sector amazing unique features. These include the antibacterial, UV-blocking, self-cleaning, and other properties obtained by using certain nanoparticles like Ag, Au, ZnO, TiO_2, and others [18-20].

In this regard, we herein aimed to use CNC as a unique nanomaterial for developing of functional antibacterial textile with reasonable mechanical properties. According to earlier studies, cotton slivers were frequently utilized to produce CNC with high crystallinity. According to Hebeish et al. (2013) [14], among other H_2SO_4 concentrations utilized, CNC was produced at small sizes with great crystallinity by the use of 60% w/w H_2SO_4.

2. Materials and methods

Cotton slivers and cotton fabrics were supplied kindly from Masr El-Mahalla El-kubra for spinning and weaving company, Egypt, (table 1). GB binder ETOW supplied from German Basic chemical products company. All chemicals were chemical grade.

Table 1: Specification of the utilized fabric

Fabric type	100 % cotton
Native Fabric	1/1
Fabric Wight	140 g/m^2
Fabric width	147 cm
Bleaching	Full bleaching

- Preparation of cellulose nanoparticles (CNC)

CNC was prepared according to the acid hydrolysis approach of bleached cotton slivers which including the digestion of amorphous regions in the presence of sulfuric acid (64 % w/v). The reaction was produced at temperature 60 ^oC for 1 hr. in water bath.

- **Treating fabrics with CNC**

The coating solutions contain CNC were applied to the cotton fabric at different CNC concentrations, viz., 1.0 g/l, 2.5 g/l, and 5.0 g/l, through pad-dry-cure technique under stirring at room temperature for 30 min. The padding liquor was applied to the cotton fabric sample (size:50 cm X 40 cm) by dipping them in the dispersion for 10 min and then padded on an automatic padding mangle machine, which was running at a speed of 15 rpm with a pressure of 1.75 Kg/cm^2 using 2-dip-2-nip padding sequence at 60% expression. The padded substrates were air dried and finally cured for 3 min at 150 ˚C for treated cotton fabric.

Acrylate based binder (GB binder) was mixed with CNC at different concentration based on the most effective CNC concentration used as showed in Table 2.

Table 2: Formulation of the coating solutions CNC and binder

No.	**CNC : Polyacrylate binder ratios**
S1	0 : 100
S2	25 : 75
S3	50 : 50
S4	75 : 25
S5	100 : 0

The mixture was then stirred using magnetic stirrer at 250 rpm for 30 minutes at 60°C. Cotton fabric samples (size: 50cm × 40cm) were immerged in padding liquor at room temperature for 10 minutes and then passed through two bowl laboratory padding mangle, which was running at a speed of 15 rpm with a pressure of 1.75 Kg/cm2 using 2-dip-2-nip padding sequence at 60% expression for cottonfabric. The padded substrates were dried at 80°C. The dried samples were cured in a preheated curing oven at 150°C temperature for 2 min.

2.1. Characterizations

The extracted CNC was characterized through using Transmission Electron Microscopy (TEM, JEM-1230, JEOL, Japan), X-ray Diffraction (XRD, Philips PW3040 powder X-Ray diffractometer) and Fourier-Transform Infrared (FTIR, JASCO FT-IR 4100 spectrometer) spectroscopy analysis to affirm the chemical and morphological structure.

Tensile Strength

The fabric sample was tested for performance and comfort. Strength of fabric samples were determined according to Egyptian standard testing method EOS-1506/2007.Tensile strength and elongation at break were measured on tensile strength testing machine type tensolab strength tester.

Crease recovery

The test specimen was folded and compressed under controlled condition of defined force to create a folded angle, the specimen was suspended in an instrument for a controlled recovery and the recovery angle was measured. The test was performed as per AATCC test method 66-2003.

Tearing strength

Tear strength of fabric sample was determined by standard test method ASTM D1424 – 09(2013). By using pendulum capacity (6400 gf).

Thermal resistivity:

Thermal resistivity of fabric samples was evaluated by using standard test method ASTM D1518 – 11a with the help of Thermal resistivity tester M-259B SDL Atlas.

Thickness

The thickness was evaluated for the treated and untreated samples by using digital thickness Gauge (Mituto 40).

Surface morphology properties

The morphological properties of the treated cotton samples were examined by Scanning Electron Microscope (SEM, JSM-6400, JEOL, Japan).

Antibacterial activity

Evaluation of antibacterial activity of cotton fabrics were qualitatively evaluated against different microorganisms represent by Escherichia coli as gram-negative bacteria and Staphylococcus aureus as gram –positive bacteria (AATCC 147 – 2004). A qualitatively assessment of antimicrobial activity of treated and untreated cotton fabrics were performed using agar diffusion test.

3. Results and Discussion

Extraction of CNC from cotton slivers

Bleached cleaned and cotton slivers were exposed to sulfuric acid (64 % w/v) hydrolysis for 1 hr at 60 ^{o}C. The obtained slurry solution was then washed thrice and centrifuged before drying in freeze dried overnight. Afterward, the dried CNC was characterized using TEM, XRD and FTIR analysis as clearly represented in figure 1.

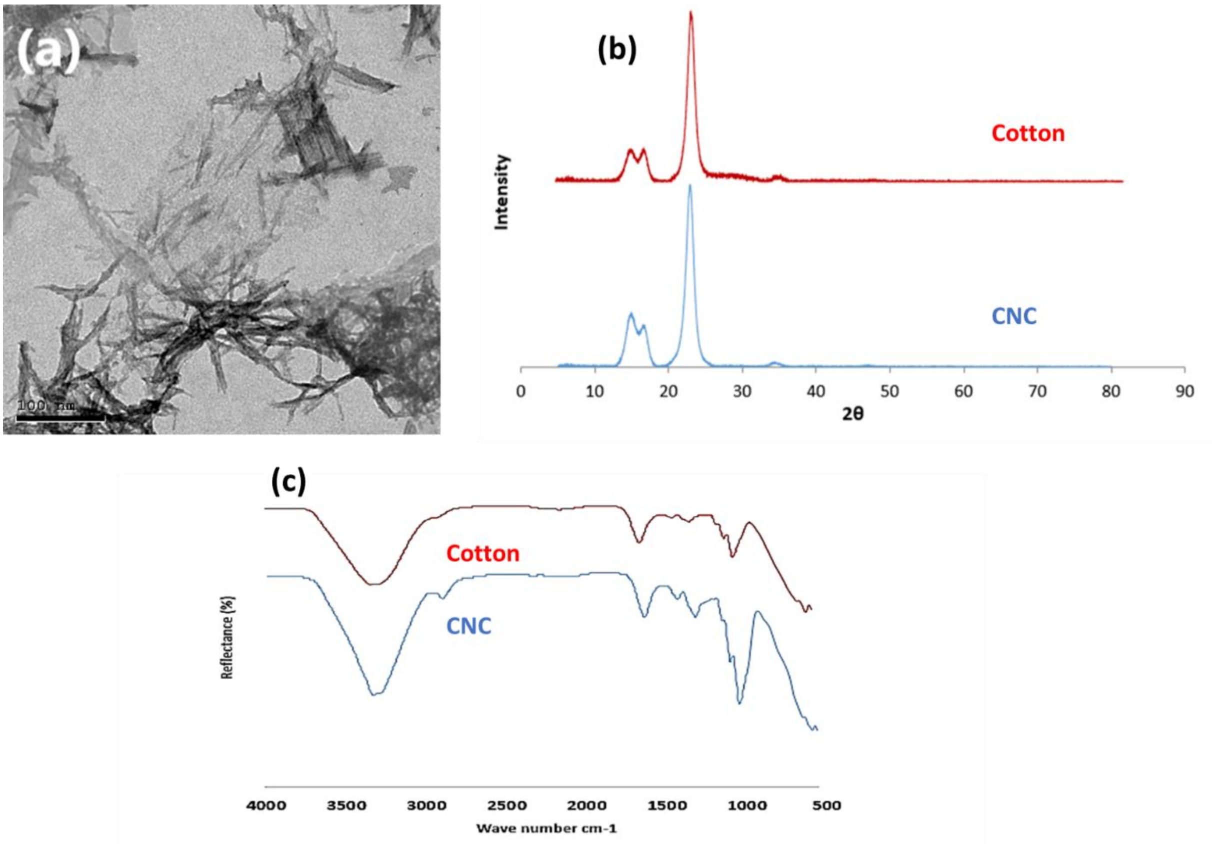

Figure 1: (a) TEM, (b) XRD and (c) FTIR of the acid hydrolyzed CNC

It can be seen from figure 1 that, CNC was successfully fabricated in crystal rode like -shape with aspect ratio (length X diameter) lied in the range of 250 ± 83 nm 35.2 ± 1.8 nm as clearly shown in TEM (figure 1A). XRD (figure 1B) also affirm the crystallographic character of CNC comparing to native cellulose sample which the major peaks were assigned at 2θ=16.5° and 22.8°, indicating the presence of CNC as cellulose I structure. Moreover, FTIR of CNC spectra showed the exact peaks from IR of the native cotton sample, where bands located at 3330.17 cm^{-1}, 2901.4 cm^{-1}, 1640.45 cm^{-1} and 1046.1 cm^{-1} were assigned to O-H stretching vibration; C-H bending vibrations, CH_2 bending vibrations, C–O vibration of C-OH and C-O-C vibration of cellulose.

CNC treating cotton fabrics

Cotton fabric samples were treated with different CNC concentration (1, 2.5 and 5 g/l). The most two factors that can judge the performance of cotton treated CNC are tensile strength and crease recovery angle (CRA). It was observed from figure 2 and figure 3 that, the strength property has improved in all the treated samples and was found to be excellent for recommended for 2.5 g/l of CNC that was used for the treatment. Also, crease recovery angle has improved in all treated samples especially, in case of 1 g/l and 5g/l. Based on the latter results, CNC of 2.5 g/l is the most adequate for further treatment for crosslinker application with CNC onto cotton fabrics.

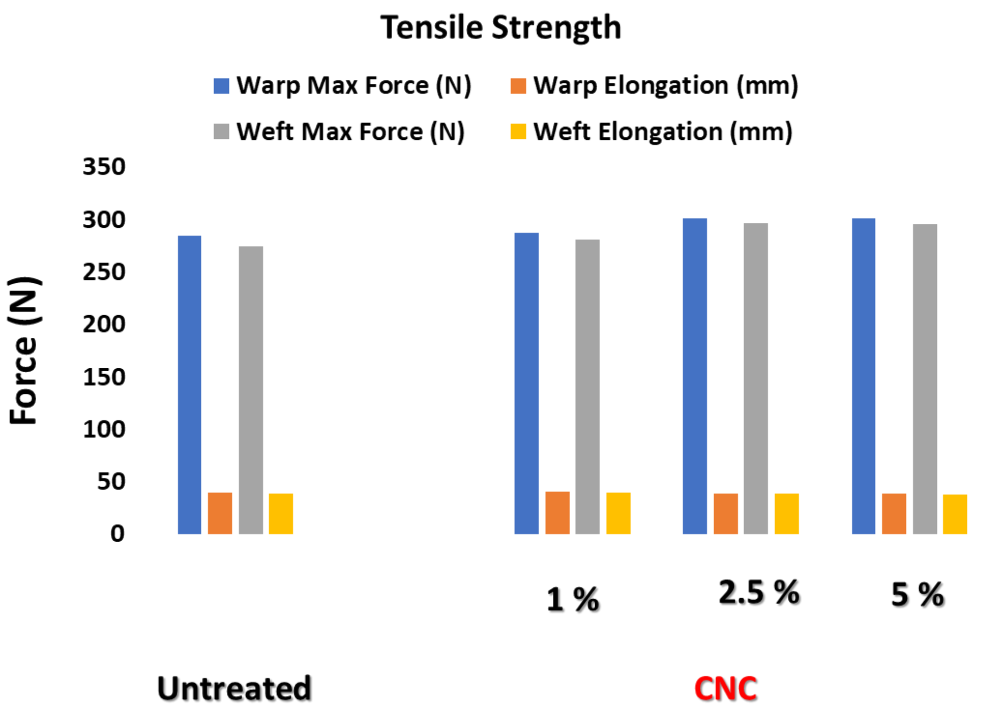

Figure 2: Strength of treated and untreated samples by CNC.

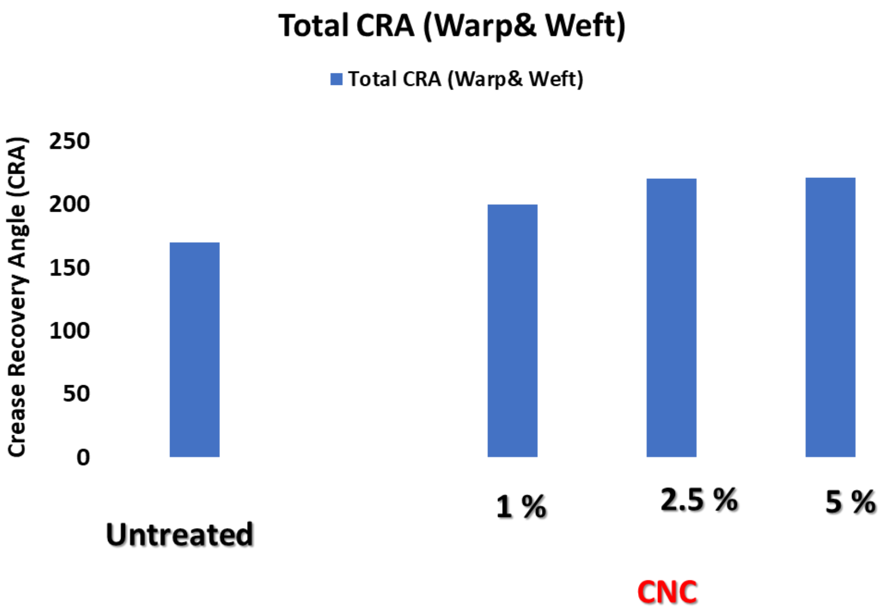

Figure 3: Crease recovery angle properties of treated and untreated samples by CNC

Treating cotton fabrics with CNC/binder

Tensile strength

It is manifested from figure 4 that, the tensile strength in warp and weft direction for untreated cotton is lower than treated samples due to CNC crystallinity which reinforces the chain of cellulosic cotton structure, which makes it higher in the strength (Stana-Kleinschek 2003).

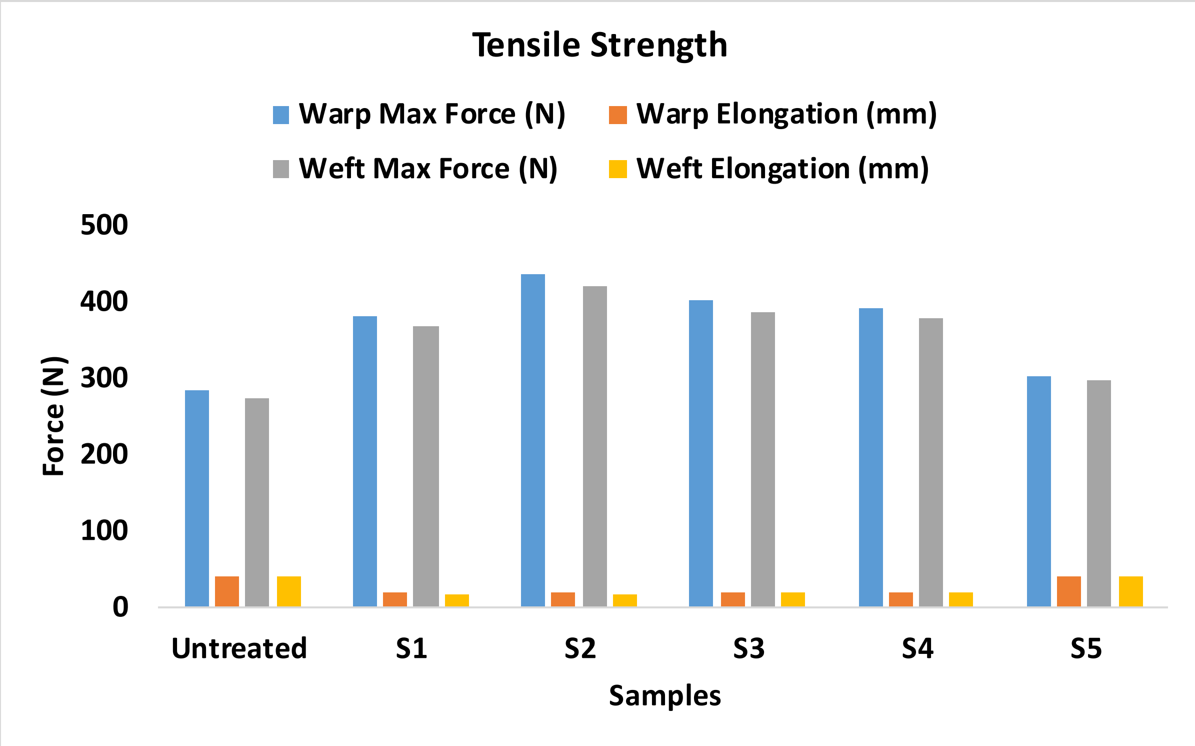

Figure 4: Tensile strength property of untreated and treated cotton samples

The results of breaking Tensile strength and associated elongations in both warp and weft directions at break are plotted in figure 4. The average highest strength for warp and weft directions follows the order of S2, S3, S4, S1and blank with maximum force value of 435.43 N, 401.46 N, 390.56 N, 320.32N and 284.3N, respectively.

The presence of CNC in both warp and weft directions gives better strength than untreated cotton. However, untreated cotton gives the lowest strength and elongation at break (%) as the max force value is much lower than that of treated cotton by different concentrations of CNC with/without binder as treated cotton samples are expected to reach to high values due to presence of binder along with CNC.

The results indicated the presence of CNC enhanced the strength of cotton fabric due to CNC extracted from cotton which is strong where wet strength is 3.7 times stronger than pulp and 1.3 times stronger than rayon.

Crease recovery

There are three broad groups of fabric parameters which affect the crease recovery of fabrics: 1) the physical properties of the fiber, 2) fabric construction and history, and 3) finish. This application focused on the effect of finishing and coating by using CNC nanoparticles.

The crease recovery behavior of all fabrics treated with CNC and binder is observed to be very good. Data represented in figure 5 illustrate that, the crease recovery angle (CRA) for untreated cotton fabric was at lowest value as expected (170°) while for CNC with or without binder treated, it ranges between 220° to 234°.

This clearly shows that presence of a mixture of CNC and binder has imparted better recovery behavior specially in case of S4 and S3 with similar value of 232° N.

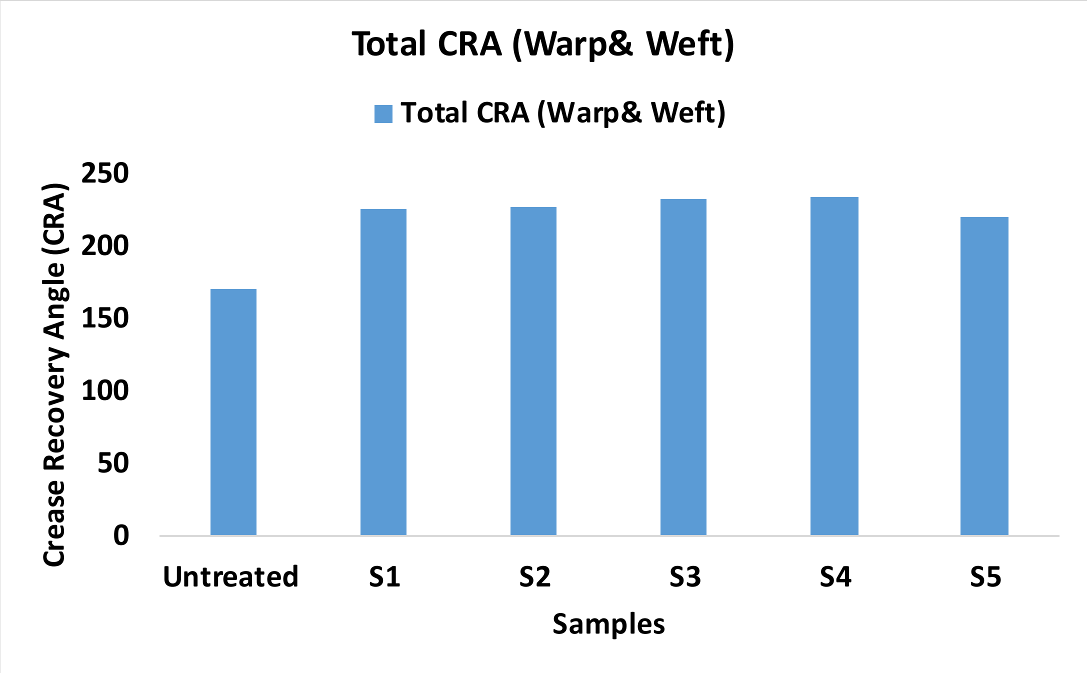

Figure 5: Crease recovery property of untreated and treated cotton samples.

The results show that the crease recovery angle has improved in all the cases and the improvement was found to be excellent for cotton fabric, with the exception of untreated cotton, in all the other cases, the crease recovery angle was changed slightly. Thus, CNC treatment is strongly recommended for cotton woven fabric as it is found to improve crease resistance without causing any deterioration in strength.

Tearing strength

Tearing strength is highly sensitive to slight variation in finishing filling and lubrication. The different finishing process can affect tearing strength by altering the properties as thickness. The effect on tearing strength of changes in different parameters wet processing has also been studied.

As shown in figure 6, there is a difference between dry tear strength of untreated and treated cotton. Initially, untreated cotton had dry strengths 27kg and 17kg respectively. After applying CNC with or without binder coating, the tearing strength of cotton was gradually increased to be 37 kg, 35 kg, and 34 kg for S3, S4 and S2, respectively. Further a treatment with binder and CNC, separately, decreased the tearing strength as seen from S1 and S5.

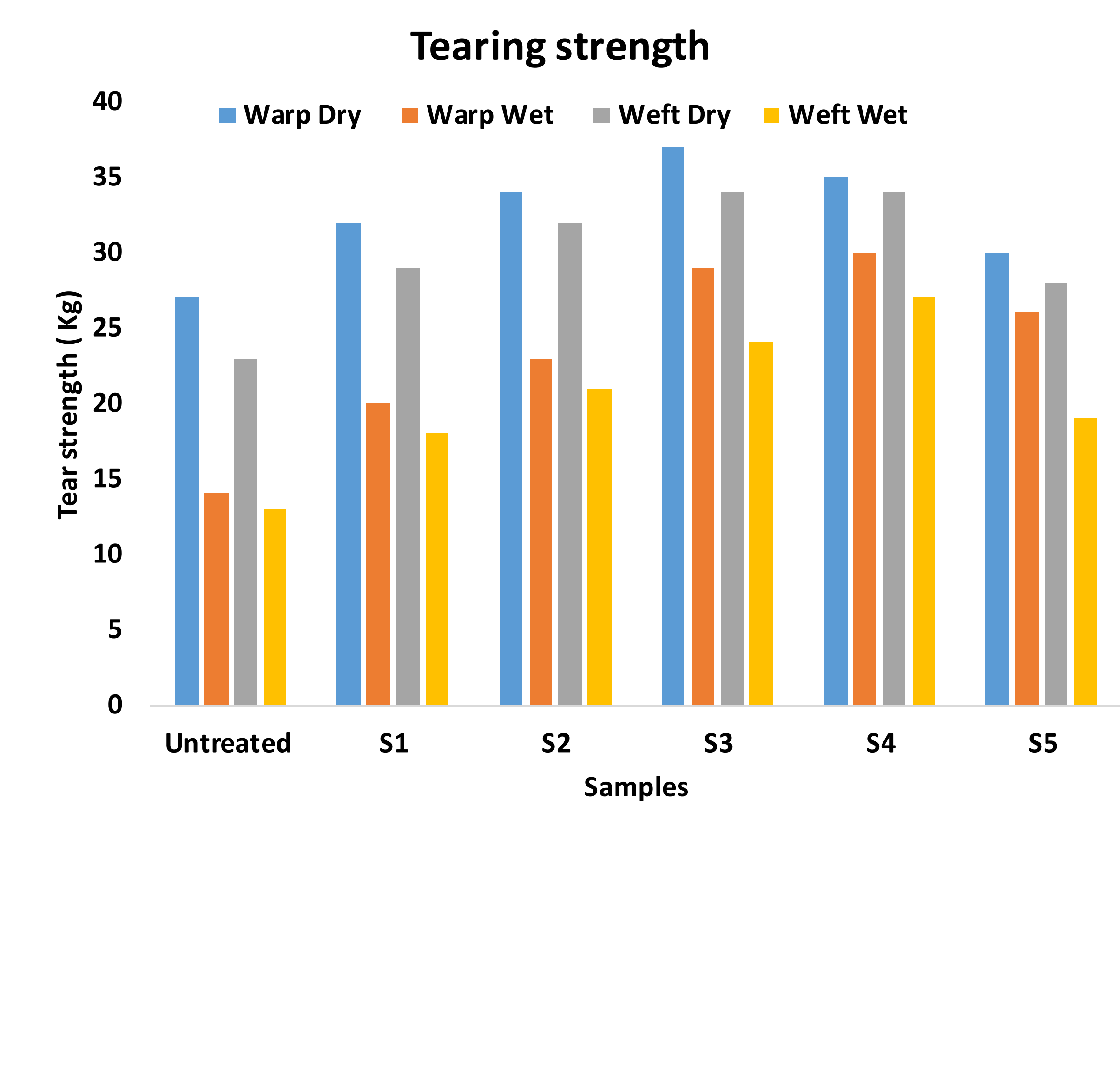

Figure 6: Tearing strength "Tearing Load 6400 g" of untreated and treated cotton (dry and wet conditions)

Cotton has a very high effect by binder and CNC at dry or wet conditions. For combination recipe between binder and CNC, it is seen that cotton has better dry and wet strength than untreated one. Cotton is naturally stronger when wet than dry lending enhanced tear resistance to all wet wipes even those used for tough household cleaning jobs.

Thickness

The data given in Figure 7 showed the thickness of untreated cotton was lower (0.33mm) than those of treated cotton samples with CNC and CNC/binder (0.34mm), revealing the presence of coated layer on the fabric surface.

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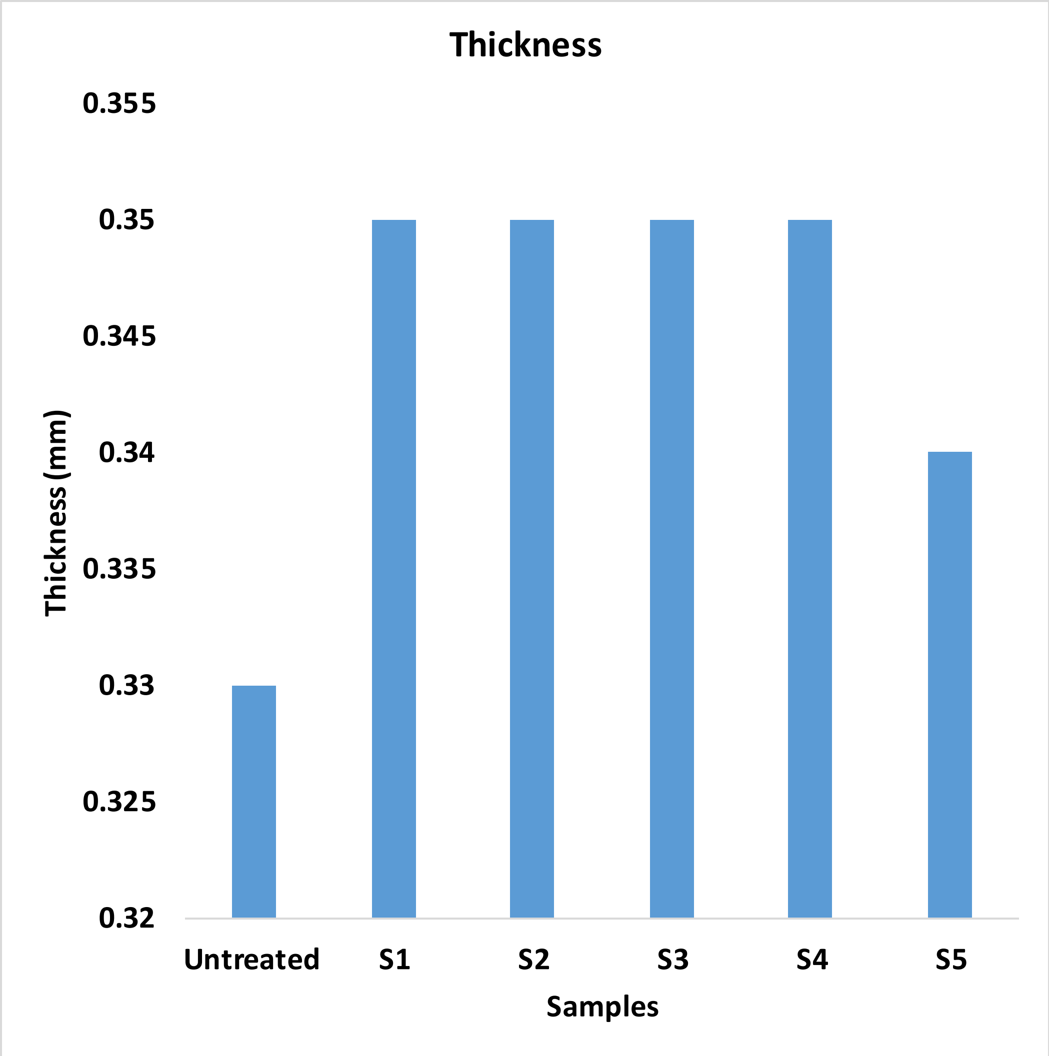


Figure 7: Thickness of untreated and treated cotton fabric

Increased the thickness after treatment led to increase the tearing, crease recovery and tensile strength. This is observed with other properties and could be tackled on similar lines.

Thermal resistivity:

Thermal properties are the properties of materials that change with temperature. They are studied by thermal analysis techniques. Thermal resistivity of untreated and treated cotton woven fabric samples was evaluated by thermal resistivity tester.

Figure 8 represents the thermal resistance of cotton treated fabrics. Treated Cotton with CNC 100% exhibits high thermal resistivity in comparison to CNC/binder. Untreated cotton was found to has a least thermal resistivity value (0.005m^2K/W) which means it conducts mostly when it is in pure form. Whilst, the variation of CNC/binder concentrations leads to gradual increase in the resistance by increasing the CNC ratio, which could be due to insulation properties of CNC.

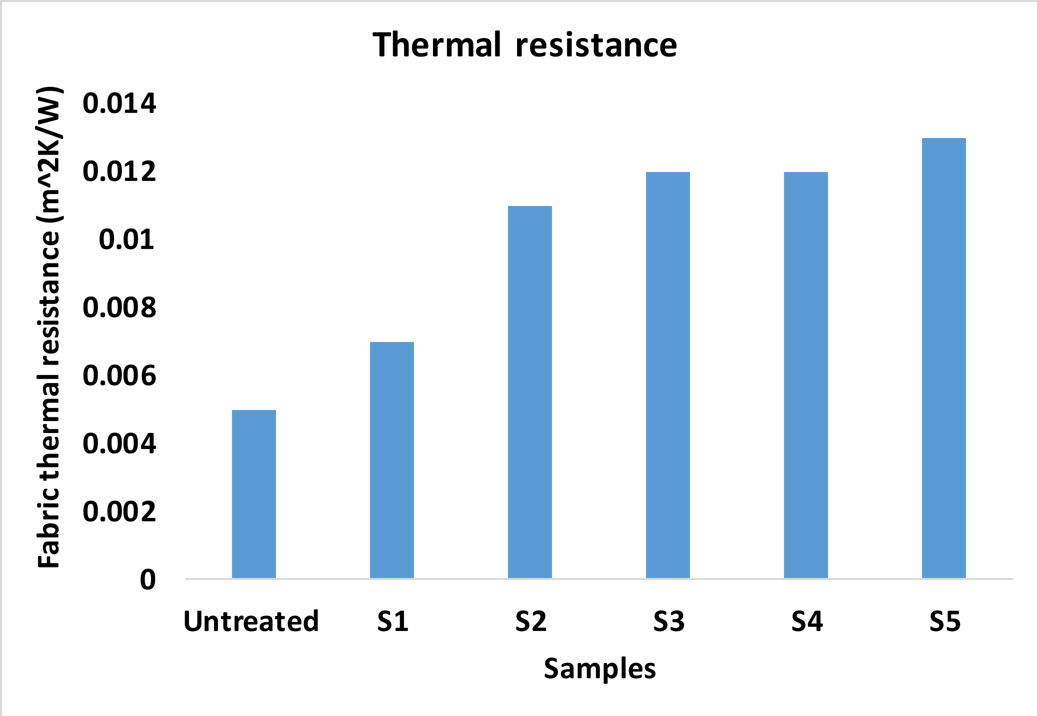
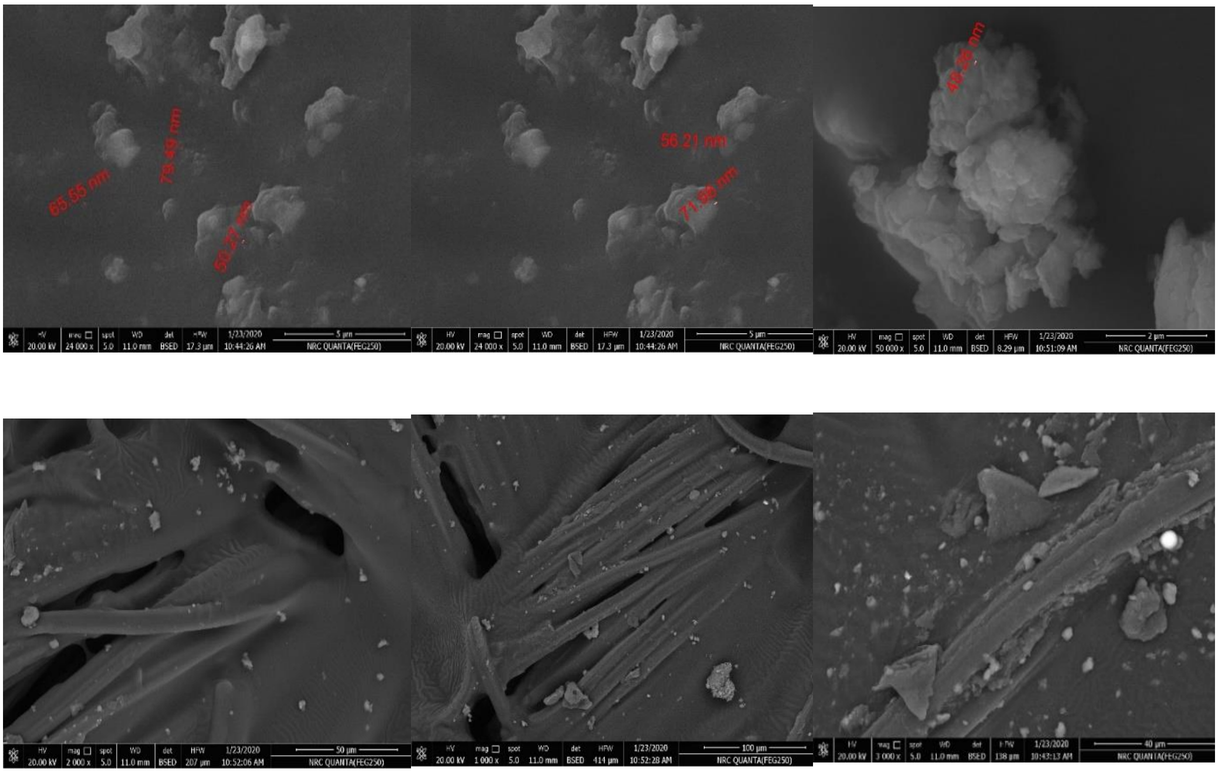


Figure 8: Cotton fabric thermal resistance for untreated and treated fabric

4.5 Surface morphology properties



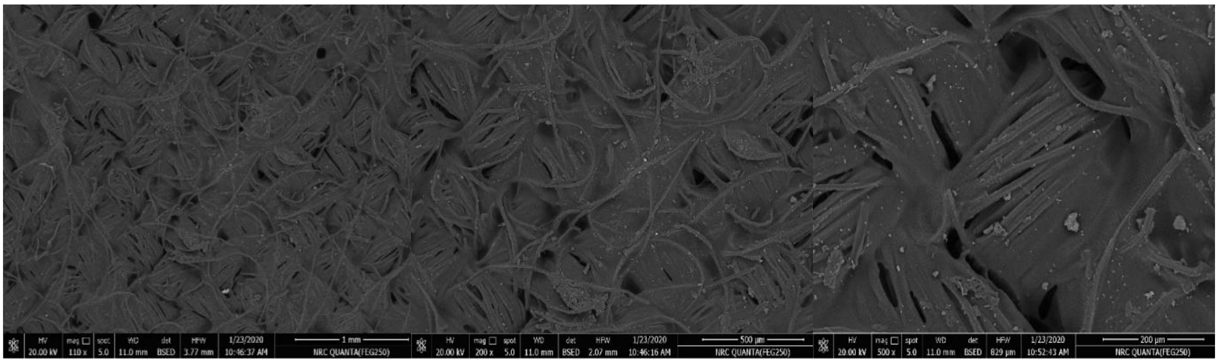


Figure 9: SEM images of CNC and CNC/binder loaded cotton fabrics

It was observed that the CNC was formed with spherical particles that presented in very small size. In addition, the particles are well dispersed as displayed from the upper figures. Via taking these nanoparticles and applied for treating fabric as shown from SEM images (lower images), it can be clearly seen that, the particles are well dispersed onto the surface of the cotton fabrics). The images are taken at low and high magnification, in order to illustrate the existence and distribution of CNC onto the cotton fabric surfaces.

Antibacterial Activity

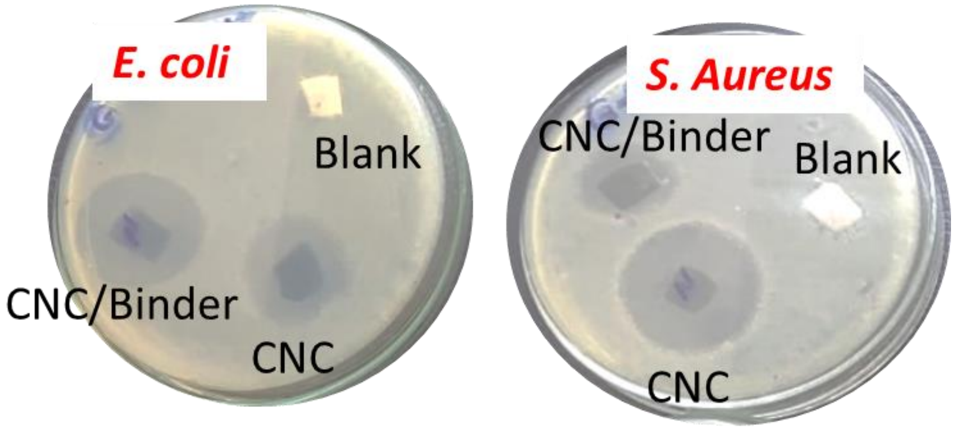


Figure 11: Antibacterial activity of cotton treated CNC and CNC/Binder

Figure 11 represents the antibacterial activity of the treated cotton fabrics with CNC and CNC/binder. The results signified the effect of treatment of CNC on the resistance of bacterial activity with average inhibition zone diameter range of 3.43 mm and 2.15 mm for E. coli and 2.5 mm and 3.17 mm for S. aureus respectively for CNC and CNC/binder treated cotton fabrics, which render them antibacterial activity with high performance and mechanical properties.

Finally, it can be clearly seen that, CNC has Positive role in treating the cotton fabrics to impart multifunctional properties. The antibacterial properties of treated cotton fabrics become superior. In addition, the other properties such as tensile strength and thickness has been improved. Taking in mind, the utilized concentration is very small when compared with other traditional finishing agents. Thanks to the nanotechnology science which has positive impact on reducing chemical and materials that used for textile finishing. The fascinating multifunctional properties can be mainly attributed to the high surface area of. Nanoparticles that give superior properties without affecting the properties of cotton fabrics. Additionally, due to their very small size, it is expected that, the durability of properties of cotton fabric after treatment is expected to be durable for a long time attributable also to the effect of binder.

3. Conclusion

Cotton woven fabrics are treated in different conditions with various concentrations of CNC and Polyacrylate binder ratios. The characterization of such fabric is dependent on physical properties, which were evaluated by the crease recovery angle, tensile strength retention, tearing, thickness. In trials CNC particles showed much better effects on the crease-resistant finish of cotton woven fabrics; when comparing the untreated cotton woven fabric, also gives moderate effects. High values of tearing resistance, tensile strength and thickness were obtained after using CNC. Also, the treated samples of cotton were subjected to thermal resistivity tester, it was found that the treated samples with CNC have high thermal resistance due to presence of nanocellulose. Also, it is found that SEM images are used to ensure the presence of cellulose nanoparticles on cotton fabric that in prepared samples the presence of nanoparticles is confirmed; because there are particles of CNC on the surface of cotton fabric. Therefore, it can be concluded that cotton when coated with a mixture of CNC and Polyacrylate binder gives better properties than untreated cotton fabric. So, in order to optimize the mechanical, physical and thermal properties of cotton woven fabrics, it is acceptable to add CNC additive with the ratio of polyacrylate binder. Eventually, CNC conferred the antibacterial activity to cotton fabric against both Gram +Ve and Gram -Ve bacteria.

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