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Preparation and Characterization of Lyocell Fabrics Coated with Cellulose Nano-Crystals and Chitosan as Functional Materials

F. Farooq[1], G. A. Baig[2], A. Latif[3], T. Sultan[4], A. Hussain[5], L. Liu[6]

[1,6] *Donghua University, Shanghai, China,*
[2,3,4,5] *Bahuddine Zakariya University, Multan, Pakistan.*

[6] lifangliu@dhu.edu.cn

Abstract- In the present study, cellulose nano-crystals (CNC) were extracted from *Ficus natalensis* bark-cloth through acid hydrolysis. Additionally, for the first time by pad curing method with different fractions of CNC weight percentage (0, 0.3, 0.6, 0.9, and 1.2) and chitosan (CS) (1%) were applied on Lyocell fabric. The durable and stable finishing material simultaneously enhanced the thermal comfort and protective performance of Lyocell fabrics. Results revealed that the mechanical properties of Lyocell fabrics increased with the addition of CNC up to 0.6 % for the sample LC0.6.

Keywords- **:** Bark-cloth; Cellulose nano-crystals; Chitosan; Lyocell fabric;

I. INTRODUCTION

The investigation of renewable materials has attracted great attention in the research world regarding a sustainable replacement of high cost, environmental-apprehension and limited availability of petroleum resources. Lyocell fibers have a unique semi micro-fibrillar structure which causes the superb comfort properties and moisture transportation. As an eco-friendly product widely used in apparel and other fashions, demand in Lyocell fabric for home textiles and apparel increased gradually due to excellent aesthetic and environmentally sustainable properties [1]. Lyocell is considered as an ideal fabric for textile apparels due to its higher crystallinity resulting in excellent strength in dry as well as wet states [2]. Similarly, the higher number of hydrogen bonds lead to good wicking properties, high strength and good absorbency, justifies the fabric (Lyocell) selection for textiles such as textile apparels [3-4]. Lyocell fabric is attracting great attention in fiber composite materials having relatively low cost and biodegradable properties compared to synthetic fibers.

Despite the fact that the basic function of the conventional textile materials is to keep the human body comfortable in hot and cold weather conditions. Numerous techniques have been utilized in manufacturing and characterization of natural and synthetic fibers to give the efficient personal thermal management to the users and assessed to represent around 47% of energy saving [5]. With the boom of nanotechnology, several improvements have stimulated in the field of textile fabric technology by applying surface finishing and coating techniques [4].

CNC produced from different ligno-cellulosic materials has been widely used in many applications in composite materials like templates, scaffold and inorganic nanoparticles due to having various qualities such as biodegradability, biocompatibility, high aspect ratio and good optical characteristics [6-8], but the isolation of CNC from the *Ficus natalensis* bark-cloth is still deficient.

Chitosan is normally obtained by de-acetylation of chitin which is a copolymer of β [1,4]-linked 2-acetamido-2-deoxy-d-glucopyranose, and 2-amino-2-deoxy-d-glucopyranose [9]. Chitosan is used in different applications such as membrane [10], wastewater treatment [11], food packaging [12], antibacterial, and electrically conductive textiles [13]. Chitosan derived from chitin and can be a good antimicrobial agent because of its biocompatibility, biodegradability and non-toxicity [14-15]. Chitosan is a pH-sensitive and cationic polymer. In the literature, many researchers discussed the antimicrobial activity of CS composite [16-17]. However, to date CNC has not been explored as a functional modifier on the Lyocell fabric to enhance the physical and functional properties in the absence of inorganic nanoparticles using *Ficus natalensis* bark-cloth cellulose nano-crystals. In this study, chitosan was employed as dispersant and binding at different contents of CNC to form nano-composite material. The Lyocell fabric was functionalized with the CS/CNC nano-composites using pad-dry-cure method. The CS/CNC modified Lyocell fabric exhibited excellent properties.

II. Experimental Work

Materials

Biomass raw material was obtained from bark-cloth of *Ficus natalensis* tree from Uganda after special extraction techniques as mentioned in [18]. The other chemicals including sodium bromide, sodium chlorite, sodium hydroxide and acetic acid were used and purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Bleached Lyocell fabric (100%) was acquired from Hangzhou Xinsheng Printing & Dyeing Co., Ltd., China. The Lyocell fabric in plain weave; 30x30/128x128; 160 g/m^2 and chitosan with degree of acetylation (95%) was used.

Methods

Pretreatments of Ficus Natalensis Bark-cloth

Bark-cloth fabric was cut into small pieces of 2-4cm and ground to pass through 60-mesh. The obtained powder was boiled for 1 hour at 100 ℃ to remove impurities such as oil, waxes, dirt and dust from the raw material. Residue was dried in an oven at 60 ℃ for 1 hour and labeled as BC-R. The residue was also immersed in 15% (w/w) NaOH solution for 2h at 100℃. The samples were quenched with deionized water and dried in oven at 70℃ for 5h. After that, residue was treated with 2.5% (w/v) sodium chlorite at 90 ℃ and pH ~ 4.5 at material to liquor ratio 1:20. The mass was washed with boiling water to remove the excessive and untreated chemicals and finally dried in oven.

Extraction of Cellulose nano-crystals

Cellulose nano-crystals were isolated from *Ficus natalensis* bark-cloth by acid hydrolysis method. Briefly, bark cloth material was chopped into small pieces and treated with 1M sodium hydroxide for 3h at 95 °C and material to liquor ratio was 1:50. Fibers were then washed with distilled water (pH 7), dried in oven at 70 °C for at least 2h and ground to powder form using a blender (Green Mix, model DA700-G). The dry scoured residue in powder form was subsequently bleached with 30% (w/v) hydrogen peroxide (30ml) in the presence of 0.25M NaOH for 2h at 70°C. Bleached residue (5g) was placed in round bottom flask and 60% pre-heated sulfuric acid (H_2SO_4) was added drop wise at 50°C for 90min under strong stirring (speed: 900 rpm) at material to liquor ratio of 1:25. Cellulose nano-crystals solution was quenched by mixing cold water with the suspension. The resulted solution was then cooled at room temperature. Acidic contents in the solution were removed by washing with distilled water, where the excess water was removed using centrifugation for 5 min at 4000 rpm on the neutral CNC suspension. The supernatant was poured off and the precipitates were later on oven-dried at 60 °C for 12h and weighed. The dried CNC materials in the form of a white powder were stored for analysis.

Lyocell Fabric Treatment

Chitosan (1g) was dissolved in 2ml solution of acetic acid using homogenizer; the mixture was stirred for 30 min to produce a homogeneous solution. The cellulose nano-crystals (CNC) at different concentrations (0, 0.3, 0.6, 0.9, 1.2 wt%) were separately added to 100 ml water and homogenized at 8,000 rpm for 10 min. Chitosan solution was added to every solution to make a suspension. To obtain the functional finishing formulation, the mixtures were stirred at 60 ºC for 2 h. Lyocell fabrics was soaked in the alkali solution (NaOH, 10%w) for 30 min at 60°C and then oven dried at 60ºC for 20 min. Lyocell swatches were made and soaked in the prepared solutions for 1 hr., and padded in a laboratory wringer by two dips and two nips method to get a wet add-on of 80 wt%.. The swatches were dried afterward by putting into oven twice; once for 40 min at 60 ºC and then secondly for 15 min at 90ºC.

Characterization of CNC

Cellulose content was determined by a calorimetric method by using anthrone reagent [19] and chemical composition investigation was done by gravimetric method[20].

For CNC imaging, a transmission electron microscope (Philips CM120) was used at 120 kV. For this purpose CNC samples from its aqueous dilute suspension were precipitated on a micro-grid covered with a thin carbon film. Scanning electron microscope (JSM-6360LA, Jeol, Japan) was used for BC-NC and LC-NC fabrics. The samples were mounted on the stabs and gold coated by the sputtering method.

For X-ray diffraction (XRD) patterns to obtain diffractometer; D500, Siemens was used. The fiber samples were scanned in the 2θ angle ranging from 10 to 60° at scanning time of 5 min. using a Ni-filtered Cu Kα radiation (λ=0.15406 nm) at room temperature of 25°C. The crystallinity index (CI) was calculated using (1)[21].

$$CrI(\%) = 100 \times \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

where I_{002} is maximum intensity at plane 002, and I_{am} is the minimum intensity at plane 110.

The tensile properties of all the samples were carried out according to the standard (GB/T3923.1), using fabric tensile strength tester (HD-026-510, Hongda, Instr. Co., China). Five composite specimens were cut into 100 × 3 × 20 mm^3 (longitudinal × radial × tangential) and average value was listed to measure the elongation at break and tensile strength.

III. Results and Discussion

Chemical Compositional Analysis of Bark Cloth fabric

To determine the chemical composition of the *Ficus*

natalensis bark-cloth standard methods were used, three samples from the bark-cloth were taken and average value was calculated to evaluate the precise value of all the components. The contents of α-cellulose were noted to be 34.5±1, hemicellulose as 23.5±.8, lignin, and ash contents were determined as 19.5±0.9, and 4±0.5 respectively.

Morphological Investigation BC-NC

The macroscopic evaluation of the *Ficus natalnesis* bark-cloth CNC materials during preparation at every stage is shown in Fig. 1. After chopping and converting into powder form the reddish-brown color of the bark cloth fabric is turned into brown color (Fig. 1c) after alkali treatment. The bleached samples can be seen clearly different and white in color as shown in Fig. 1d. The change in color was majorly due to removal of lignin, hemicelluloses, pectin and wax from the bark-cloth by the chemical treatment. The obvious white color of the prepared sample is an indication of almost pure cellulosic material. SEM images showed that bark-cloth consists of microfibers that are naturally bonded and aligned at an angle as shown in Fig. 2a. As alkali treatment contributed to remove the non-cellulosic impurities, which led to reduce the fiber proportions and the dispersion of micro-fibrils, so the Fig. 2b shows the samples turned into fibrous shape and more separated and aligned as chemical treatments contributed to break the inter-molecular hydrogen bonding which caused to remove more non-cellulosic materials. Fig. 2c shows the cellulose nano-crystals after freeze drying of the cellulosic materials.

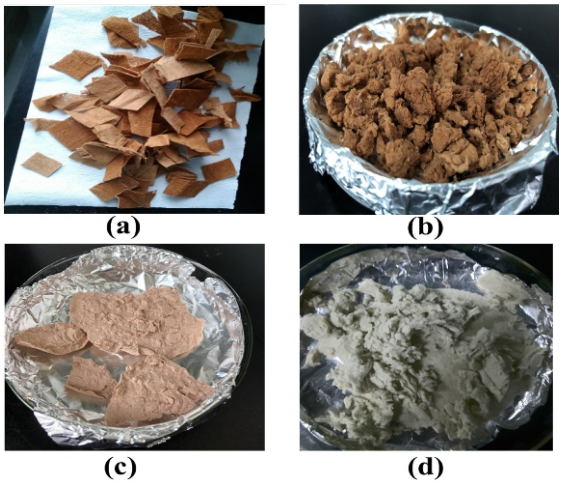

Fig. 1. Photographs of bark cut pieces: (a) chopping of the samples (b) sample washing to remove impurities (c) alkali-treated samples, and (d) cellulose fibers after bleaching

Images of transmission electron microscope obtained for CNC resulted from acid hydrolysis of *Ficus natalensis* bark-cloth are shown in Fig. 3a. Under controlled conditions, the action of treatment was expected to slash the amorphous regions of cellulosic materials. Transversely, the change in fiber size from the micron to the nano meter scale was recorded as shown as Fig. 3a. Most of the nanoparticles showed diameter in the range of 20-25 nm and a length of several hundred nanometers. The histogram in Fig. 3b exhibited that diameter of the CNC was ranging from 10 nm to 35 nm.

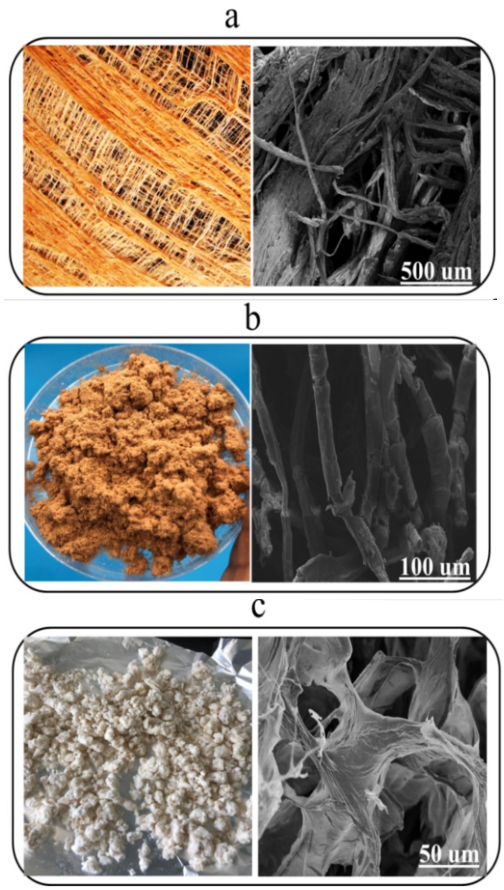

Fig. 2. Scanning Electron Micrographs at various stages of *Ficus natalensis* bark-cloth during cellulose extraction process (a) bark-cloth without any treatment, (b) after converting into powder form (c) Freeze dried cellulose nano-crystals.

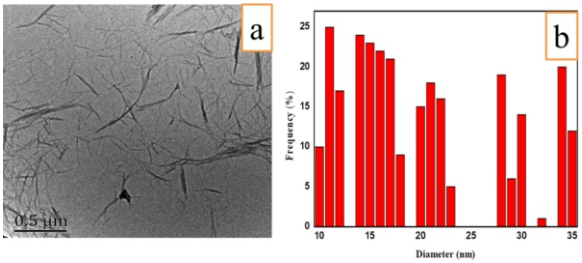

Fig. 3. (a) TEM image for the cellulose nano fibers prepared with 2 h TEMPO oxidation (b) Diameter-frequency histograms of cellulose nano-crystals

Characterization of Modified Lyocell Fabric

Morphologic study of all the samples was conducted with the help of scanning electron microscopy (SEM). The images (Fig. 4 a) showed smooth and clean surface of the untreated Lyocell fabric which distinctly contrasts with that of control modified fabrics. While after coating with chitosan and CNC the images show that surface of Lyocell fabrics have a smoother coverage of coated material which is distributed on the surface and fixed in the fiber spacing due to the cross-linking of polar groups of CS, CNC and Lyocell fabric (Fig. 4 c,d,e,f). As the percentage of CNC in the finishing coating is increased, the roughness and uneven coverage of the interlocking bonds are also increased that can be clearly observed on the sample LC0.9 Fig. 4 e. The images provide further evidence to confirm the coating of CS and CNC on Lyocell fabric. The SEM micrographs further confirmed that the chitosan and CNC was coated onto the surface of Lyocell fabrics and nanoparticles are evenly covered along the fabric surface which obviously further improve surface nanoscale roughness. SEM images (Fig. 4) showed smooth and clean surface of the untreated Lyocell fabric which markedly contrasts with treated samples LC/CS, LC0.3, LC0.6, LC0.9 and LC1.2.

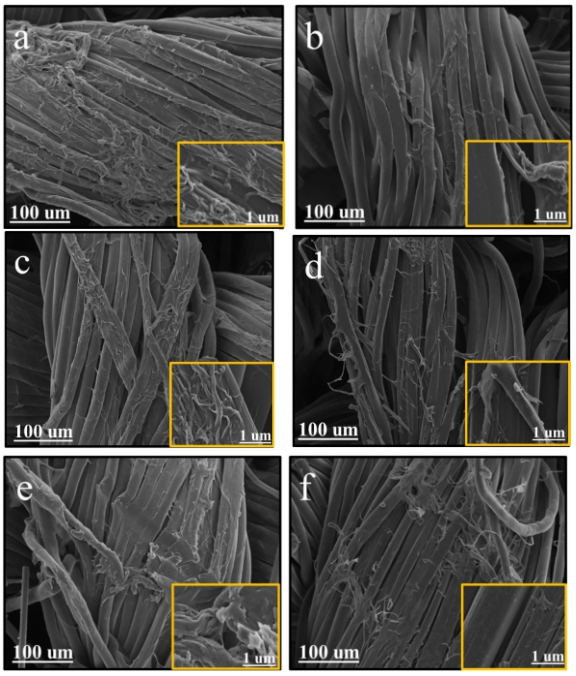

Fig. 4. SEM images of (a) Lyocell fabric, (b) LC/CS, (c) LC0.3, (d) LC0.6, (e) LC0.9 and (f) LC1.2.

Breaking Strength and Elongation at Break

To examine the effects of composite coatings on the mechanical properties of pristine, Lyocell fabric cross-linked with 1% CS, 1% CS 0.3%CNC, 1%CS 0.6% CNC, 1% CS 0.9% CNC and 1% CS 1.2%CNC, their breaking strength and elongation at break properties were evaluated using universal tensile strength tester as shown in Fig.5. At a constant concentration of chitosan, the tensile strength and elongation at break of Lyocell fabric was increased first with the increasing cellulose nano-crystals content till it reached its maximum value at the sample LC0.6 having 0.6 wt% CNC content. Mechanical properties were enhanced, can be attributed to linkages developed among the polar groups of chitosan, nano-crystals and Lyocell fabric. At higher concentration of CNC in the finishing solution before coating, the accumulation of the cellulose nano-crystals happened that created defects in the coating smoothness of the Lyocell fabric. So, the breaking strength and elongation at break show descending values at higher concentration of CNC as compared to lower content of CNC (LC0.6). However, at lower concentration chitosan perfectly dissolved the CNC. It is also worth noting that, all the modified samples of the Lyocell fabrics have higher mechanical properties as compared to pristine Lyocell fabric.

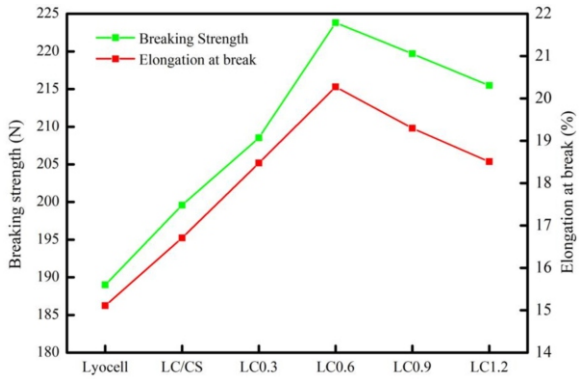

Fig. 5. Tensile strength and elongation at break of pristine and modified Lyocell fabrics with constant chitosan and varied fractions of CNC

IV. Conclusions

Cellulose nano-crystals were extracted, using acid hydrolysis, from *Ficus natalensis* bark-cloth were characterized through various techniques. CNC in the presence of chitosan, were applied on Lyocell fabrics by pad-cure technique to modify functional properties of the fabrics. The results proved that the tensile strength and elongation of the treated Lyocell fabrics increased with the increase in CNC concentration up to 0.6% by weight. This strategy for fabricating CNC and chitosan on Lyocell fabric would be a guide for the development of functional textiles that might have promising potential for various applications in the future work.

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2	Dr Gulzar Ahmad Baig (2nd Author)	Interpretation of results etc.	
3	Dr. Abid Latif (3rd Author)	Literature review	
4	Dr. Tahir Sultan (4th Author)	Methodology and manuscript writing	
5	Dr. Azmat Hussain (5th Author)	Data Collection and statistical analysis	
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