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Side selective surface modification of chitin nanofibers on anionically modified cotton fabrics

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ABSTRACT

Chitin nanofibers have been prepared from crab shell as a chitin source using ultrasound assisted fibrillation. Atomic force microscopy (AFM) study showed that the prepared nanofibers were having diameters and lengths primarily in the range of 2–20 nm and 0.3–4 μm respectively. These nanofibers were selectively grafted on one side of a 100% cotton fabric using a special apparatus. Prior to the grafting, cotton fabrics were modified with partial carboxymethylation to encourage cotton fiber nanofiber interactions. The surface modification was confirmed by Fourier transform infrared spectroscopy (FT-IR) peaks at 1594 cm^{-1} and 1735 cm^{-1} due to the presence of carboxylic acid functionality in modified cotton fabrics. Scanning electron microscope (SEM) study of the nanofiber grafted cotton fabrics showed that nanofibers were adhered to the cotton fabrics. Elemental analysis confirmed that side selective grafting of nanofiber has taken place due to the peak at 0.394 keV which attributes to the presence of nitrogen element in chitin nanofibers. This peak was absent in the other side of the fabric which was not coated with chitin nanofibers. Amount of adhered nanofibers was seen to increase with the increase of nanofiber concentration used in grafting as confirmed by Kjeldahl analysis. A possible mechanism of cotton fiber–nanofiber interactions is introduced.

1. Introduction

Chitin, a biopolymer primarily extracted from exoskeleton of crustaceans is under intensive research due to its unique advantages in many fields. Chitin is a linear amino-polysaccharide and known to consist of 2-acetamido-2-deoxy-β-D-glucopyranose through a β(1 → 4) linked structure. Availability of hydroxyl, primary and secondary amine groups in the polymeric structure suggests that intermolecular hydrogen bonding between polymer chains can be very significant in determining chitin properties (Song, Shang, Ratner, Matyjaszewski, & Möller, 2012; Tokura, Tamura, & Kamerling, 2007). Chitin and its deacetylated counterpart: chitosan has stirred great interest across number of different scientific fields due to many of their favorable properties (Muzzarelli, 2010; Muzzarelli, Boudrant, Meyer, Manno, DeMarchis, & Paoletti, 2012; Muzzarelli, 2012).

In crab shells, chitin is organized in a well-defined hierarchical arrangement primarily made of $CaCO_3$, protein and chitin. Above composite structure is very complex and follows twisted plywood structure which is commonly known as Bouligand structure (Chen, Lin, McKittrick, & Meyers, 2008; Khor, 2001; Raabe, Sachs, & Romano, 2005). In this structure chitin exists as chitin nanofibers with average diameters approximately 3–5 nm. These nanofibers arrange themselves into much larger bundles with average diameters ranging from 60 nm to 70 nm. But in many conventional chitin extraction processes, chitin nanofibers collapse to sheets so that the observation of small nanofibers is impossible. Many researches have published various preparation methods of chitin nanofibers. High water binding capacity is one of the many interesting properties shown in these nanofibers. High surface area and high concentration of sites available for Hydrogen bonding to take place can increase absorption capacity of water (Rodrigues et al., 2014).

Cotton by far is the most significant natural fiber used in the textile industry. It is the purest form of cellulose and 90% of the weight of the fiber is α-cellulose (Goldwaith & Guthrie, 1954). Although many types of synthetic fibers are available today, it is generally agreed that no other fiber type can match with cotton as far as the comfort requirements are concerned. As a natural fiber it is inherently heterogeneous and has many favorable mechanical, thermal, electrical and optical properties. Cotton is the first choice for most of the apparel applications since it has excellent comfort character.

Despite of many advantages, cotton fabrics may show poor performance when it comes to moisture management. Human body

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gives away moisture in the form of perspiration and sweat. The fabric act as a buffer between the skin and the environment and its properties will finally decide the conditions of the microclimate between skin and the fabric. For this microclimate to be comfortable enough for the wearer, fabric must have improved performance especially in wicking property, moisture vapor transmission (breathability), sorption of water and faster drying. But unfortunately regular fabrics made out of cotton does not perform up to the required level especially when wearer engages in works that require intense body activity like sporting and exercising. Therefore it is very common that garments made out of cotton fabrics show performance issues such as heaviness when wet, uncomfortable hotness, clinginess to the skin, excessive slacking and longer drying time. Many factors can affect the moisture vapor transmission and other thermal properties of fabric such as fiber blending, spinning method, fabric structure, yarn count, yarn twist, combing method, softeners use etc. (Oglakcioglu, Celik, Ute, Marmarali, & Kadoglu, 2009; Özdil, Marmaralı, & Kretzschmar, 2007; Raj & Sreenivasan, 2009).

Effective moisture management of the fabric will depend mainly on its ability to transport moisture away from the inner side of the fabric to outer surface where more spreading and evaporation occurs. This will significantly enhance the drying rate while providing cool and dry feeling to wearer. For such effect to happen fabric should demonstrate enhanced wicking power while having more absorbent capacity of water in the outer surface of the fabric than in the inner side. It should also have the ability to transport moisture vapor more effectively through the fabric, so that humidity equilibrium between skin and environment is kept at a point which is not uncomfortable to the wearer. For any practical application, durability of the treatment is also important. Hence if a treatment method is employed it should sustain at least several washes. Chemical treatment that will not significantly change favorable properties of the fabric is preferred than a method that relay merely on physical adhesion and adsorption of the modifying agent.

The present work is aimed at improving the above mentioned properties of the cotton fabric by incorporation of high water absorbent (Supplementary data: Fig. 1) chitin nano fibers (CNF) into the cotton fiber assembly of the fabric.

2. Experimental

2.1. Materials and methods

Raw crabs (*Portunus pelagicus*) were obtained from fish market. Once received, they were thoroughly washed and separated according to their size. Crab shells having carapace length of only 14 ± 1 cm was selected for the experiments since this length usually corresponds to the fully grown species. Cotton (100%) fabrics which were previously scoured, bleached and having 1×1 rib structure with a weight of 196 g/m^2 was obtained from Textured Jersey Lanka Ltd. Sodium hydroxide, hydrochloric acid, acetic acid, sulfuric acid, boric acid, sodium acetate, hydrogen peroxide and monochloro acetic acid (MCAA) were reagent grade and purchased from Sigma Aldrich (USA). Double distilled water was used in all the experiments.

2.2. Preparation of chitin nano fibers

Modified version of general methods available in preparation of chitin nanofibers was used in this research (Fan, Fukuzumi, Saito, & Isogai, 2012; Fan, Saito, & Isogai, 2008, 2010; Ifuku, Morooka, Morimoto, & Saimoto, 2010; Ifuku et al., 2009, 2011; Shams, Ifuku, Nogi, Oku, & Yano, 2011). Detailed procedure is given in Supplementary data. Prepared nanoparticles were dispersed in distilled water using ultrasonic tip sonicator when required.

2.3. Partial carboxymethylation of cotton fabrics

First cotton fabrics were anionically modified by slight carboxymethylation of cellulose using monochloroacetic acid treatment in alkali medium (Hashem, Hauser, & Smith, 2003; Rácz, Borsa, & Bodor, 1996; Rácz, Deák, & Borsa, 1995; Xiquan, Tingzhu, & Shaoqui, 1990). Briefly, a fabric was dipped in a solution containing 2 M NaOH and 1 M MCAA and set to wet pickup of 200%. Then the fabric was transferred to sealed polyethylene bags and let for the reaction to occur at 75–80 °C for 30 min. Once completed fabric was first washed with 0.1% acetic acid solution for removal of excess alkali in the fabric followed by thorough wash with water. Partially carboxymethylated cotton fibers will be referred to as pCMC from here on.

2.4. Grafting chitin nano fibers (CNF) to cotton fabrics

Fabrics were grafted with CNF through wet exhaustion process similar to dyeing. Experiment was carried out in such a way that material to liquor ratio is 15 (for 1 g of fabric 15 ml of solution). Special apparatus (Supplementary data: Fig. 2) is used in the experiment to facilitate the side selective grafting of CNF. Fabric to be grafted with CNF was wrapped one cycle around a Teflon lined solid cylinder secured with a rubber ring and edge closed with a rubber stripe. Then the solid cylinder was placed concentrically inside a beaker. Chitin dispersion having 0.25 g/l, 0.50 g/l and 0.75 g/l concentrations were prepared during the experiment from fully dried CNF obtained after fibrillation. Before treating fabrics with CNF dispersions, pH was adjusted to be at the range of 5.0–5.5 using 0.1 M HCl and 0.1 M NaOH solutions. For grafting, solutions were poured into the assembly until the fabric is totally immersed in chitin dispersion. Then the solution was heated up to 80 °C for 1 h followed by washing and air drying at room temperature. Samples prepared using 0.25 g/l, 0.5 g/l and 0.75 g/l concentrations are referred as pCMC-0.25, pCMC-0.5 and pCMC-0.75 respectively from here on.

2.5. Characterization

Fourier transform infrared spectroscopy (FTIR) measurements were taken for CNF, cotton and modified cotton using (Bruker FT-IR Vertex 80). CNF Sample was placed inside the ATR chamber on top of the ZnSe crystal. Special tightening unit comes with the instrument was used to ensure the maximum contact between crystal and the sample. For the fabrics, since they are having irregular surface, diffuse reflectance assembly was used as it provides more intense signals. FTIR spectra were recorded between 4000 cm^{-1} and 600 cm^{-1} with the resolution of 4 cm^{-1} in the absorbance mode for 128 scans at room temperature.

X-ray diffraction (XRD) measurements were carried out using (Brucker D8 Focus X-ray Diffractometer) with Cu-Kα radiation using diffraction tube operated at 30 kV and 25 mA as the X-ray source for finely ground chitin powder and for chitin nanofiber powder. Samples were dried 2 h at 60 °C for removal of any excess moisture and immediately after taking from the oven, diffraction pattern was recorded at room temperature.

The microstructures of the CNF coatings were characterized using field emission scanning electron microscope (SEM) using Hitachi SU6600 Analytical Variable Pressure FE-SEM. SEM characterization of untreated and treated cotton fabrics was also carried out after sputter-coating with gold for 30 s at 15 mA prior to the observation. Energy-dispersive X-ray spectroscopy (EDEX)

measurements were also carried out on the two sides of the fabric to confirm the differential grafting of the CNF.

Morphological characterizations of CNF and CNF coatings were performed using atomic force microscope (AFM) using Park Systems, XE-100 microscope. Imaging was carried out using non contact mode cantilever, having a tip radius less than 10 nm operating at a frequency of 0.5 Hz. CNF was first dispersed in water using ultrasound tip. Then a drop of the solution is casted on to a mica piece which is later mounted on the scanning stage of AFM. For imaging of fiber surfaces, untreated and treated fabrics were tightly mounted on to sample holder using a double scotch tape which is then flattened using a load placed horizontally on top of the fabric. Then the fabric was mounted on the scanning stage.

Nitrogen content of the samples was analyzed using Kjeldahl method. Fabric pieces having the weight of approximately 5 g were first digested with sulfuric acid. After digestion, ammonia was distilled into 4% boric acid solution and titrated with 0.01 N HCl using methyl-red as an indicator (Ma & Zuazaga, 1942). Following equation was used to calculate the percentage of nitrogen:

$$A = \frac{(V_s - V_b) \times N_a \times 1.4007}{W_s} \quad (1)$$

where V_s, volume of standard acid solution used to titrate the distillate; V_b, volume of standard acid solution used to titrate the blank; N_a, normality of the acid; W_s, weight of the sample.

3. Results and discussion

3.1. Atomic force microscopy characterization of CNF

AFM image analysis reveal that nanofibers are having diameter range starting from 2 nm to 20 nm (Supplementary data: Fig. 3(a)). Majority of nanofibers have lengths in the range of 300 nm–4 μm. Having very small nanofibers with diameters between 2 and 5 nm in abundance indicates that complete fibrillation of chitin matrix has occurred during CNF preparation process. Much larger nanofibers observed are possibly due to fibers that are not fully fibrillated. Width and height of the nanofibers were analyzed using a cross sectional line profile analysis. It is possible to identify that with the cross sectional analysis, width of the nanofiber is very large compared to the height. This is possibly due to the AFM tip-convolution effect (Sedin & Rowlen, 2001). In our case significant amount of obtained nanofibers are smaller than the radius of the tip, hence appropriate correction must be employed for more accurate result if the diameter is to be estimated using the AFM image width. Here we have estimated the diameters from fiber height to avoid tip convolution effect (Supplementary data: Fig. 3(b)).

Further, we could also observe that fibers arrange themselves into a random mesh like formation lying on top of each other. This type of interpenetrating arrangement is favorable since the CNF mesh will be able to deform and stretch freely with the fabric movement. Continuous film will increase effective transport of moisture through the surface of the cotton fiber and will enhance absorbance of moisture by CNF. Both of these factors are important to improve moisture management performance of the fabric (Supplementary data: Fig. 4).

3.2. X-ray diffraction spectroscopic characterization

In the XRD spectrum, four major diffraction peaks were identified and they are located around 9.5°, 19.5°, 20.9°, and 23.4° (Supplementary data: Fig. 5). These peaks correspond to the 0 2 0, 1 1 0, 1 2 0, 1 3 0 crystal planes respectively, and are inline with typical crystal patterns of α-chitin (Waldemar Maniukiewicz, 2011; Zhang, Xue, Xue, Gao, & Zhang, 2005). Peaks closely coincide with chitin powder XRD peaks indicating that the crystal structure has been maintained even after the chemical and mechanical treatment. Crystallinity of prepared CNF is lower than that of the chitin nanofibers. Marked difference in intensity of peak located at 9.5° was observed for CNF for normalized XRD spectra. This indicates that fibers may have some preferential orientation on the sample film or CNF maintain particular crystal direction during fibrillation.

3.3. Fourier transform infrared spectroscopic characterization of CNF

The FTIR spectrum (Supplementary data: Fig. 6) for CNF is in accordance with previously published work (Gopalan Nair & Dufresne, 2003; Ifuku et al., 2009, 2010, 2011). First the broad and weak absorption bands which lie within 3600–3000 cm^{-1} are due to the combined absorption by N—H and O—H groups in the polymer. This broad absorption band can further be resolved into several minor peaks. The absorption band at 3252 cm^{-1} can be attributed to the N—H secondary amine stretch. The evidence for existence of NH—CO group in the chitin structure can be provided with the absorption band at 3101 cm^{-1}. The weak absorption in the region of 2961–2829 cm^{-1} is due to the presence of methylene and methyl group in the chitin structure. Spectra show the presence of two bands in the region of 1660–1620 cm^{-1}. Both these bands are due to the C=O stretching vibration of the Amide I bonds. Splitting of the peak into two characteristic bands at 1658 cm^{-1} and 1618 cm^{-1} is due to the influence of hydrogen bonding in the polymeric structure. The absorption at 1553 cm^{-1} occurs due to the presence of N—H of Amide II bond structure in the polymer.

3.4. Fourier transform infrared spectroscopic characterization of fabrics

We have carried out FTIR for untreated cotton fabrics as well as for all the other fabrics including fabrics modified with MCAA and CNF. Fig. 1(a)–(c) shows FTIR spectra for cotton fabric, pCMC and coated side of CNF grafted pCMC fabric respectively. Major peak assignments of cotton fabric, partially carboxymethylated cotton fabric and CNF are listed in Table 1. The peaks at 1594 cm^{-1} and 1735 cm^{-1} in partially carboxymethylated cotton indicate the carboxylate and carboxylic functionality respectively in pCMC (Fig. 1(b)). These peaks are absent in untreated cotton (Fig. 1(a)).This clearly indicates the partial carboxymethylation of cotton cellulose. We could also observe that transformation of carboxylate to carboxylic and vise-versa when FTIR spectra were taken for samples which were treated with dilute acid and alkali solutions. At appropriate pH values, carboxylic acid groups will be anionized to carboxylate groups rendering a negative charge to the cotton surface (Chowdhury & Neale, 1963; Heinze & Koschella, 2005). Even though amine groups in the CNF surface is fairly low compared to acetyl amine groups, employing an acidic reaction medium will produce cationic charge on the surface of the chitin nano fiber (Fan et al., 2010; Revol & Marchessault, 1993; Shams et al., 2011). This will serve two purposes. First the CNF will repel each other due to surface charge thus improving its stability in dispersion medium. Second, in aqueous medium the opposite charges on cotton fiber and CNF will produce mutual attractive force making CNF more affinitive to the fabric. In Fig. 1(c), peak at 1627 cm^{-1} is an evidence for such coating formation. This peak is due to the combined absorption of Amide I and its hydrogen bonded counterpart of CNF coated into the pCMC surface.

3.5. Scanning electron microscopic analysis

Deposition of CNF layer on the cotton fiber surface can be proven by using SEM and AFM imaging. Fig. 2 shows SEM images

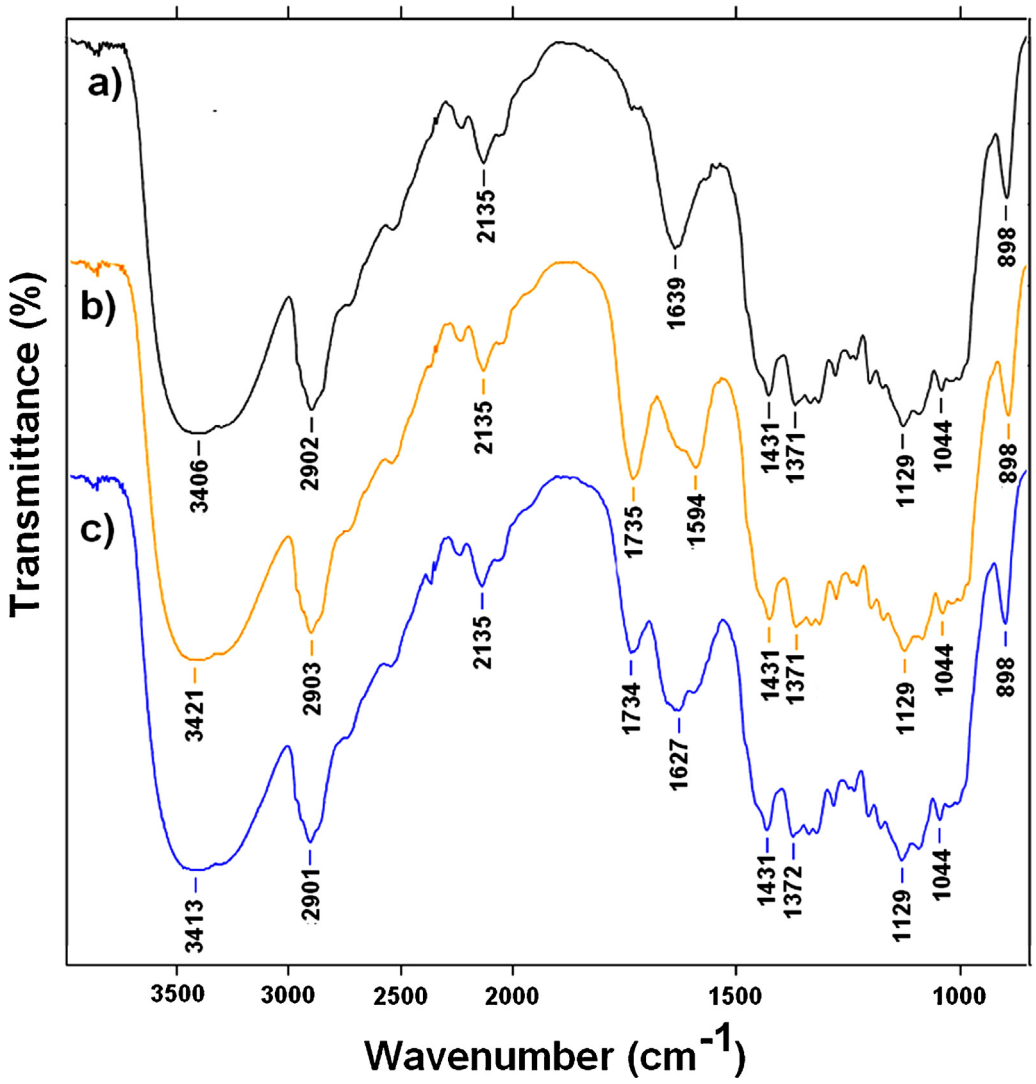


Fig. 1. FTIR spectrum of (a) normal cotton, (b) partially carboxymethylated cotton and (c) CNF grafted surface of the partially carboxymethylated cotton.

of untreated cotton fiber surface and cotton fiber surface treated with 0.5 g/l solution of CNF. SEM images of untreated cotton taken at two magnifications are given in Fig. 2(a) and (b). It is very easy to identify the twisted and wrinkled structure of cotton fiber with the characteristic concave groove spiraling around the fiber with an angle to the axis of the fiber. Surface of the untreated cotton fiber is comparatively smooth with many ridges situated parallel to each other.

Table 1
Major FTIR peak assignments for Cotton, pCMC and CNF.

Cotton		pCMC		CNF	
Peak (cm^{-1})	Assignment	Peak (cm^{-1})	Assignment	Peak (cm^{-1})	Assignment
3406	Alcoholic —OH stretching	3421	Combined absorption of carboxylic —OH stretch and alcoholic —OH stretch	3430	Combined stretching absorption of —N—H and —OH
2902	Aliphatic —CH_2 stretching	2902	Aliphatic —CH_2 stretching	3252	—N—H stretch of secondary amines only with trans-configuration
1430	Aliphatic —CH_2 bending	1735	—C=O stretch of carboxylic group	3101	Trans configured NH—CO stretch
1338	—OH in plane bending	1594	—C=O stretch of carboxylate anion	2871	Aliphatic —CH_2 absorption
1642	—OH bending of absorbed water	1642	—OH bending of absorbed water	1658 & 1618	Absorption of Amide I vibration, 1618 due to hydrogen bonding
1110	—C—O—H bending of secondary alcoholic	1337	—OH in plane bending	1559	Bond absorption of Amide II
1043	—C—O stretching	1044	—C—O stretching	1379	Symmetric deformation of —CH_3 group
900	Asymmetric out of plane β-glucosidic bond stretch	898	Asymmetric out of plane β-glucosidic bond stretch	1420–700	Presence of —CH_x, —C—O—C, —OH groups attached to pyranose ring

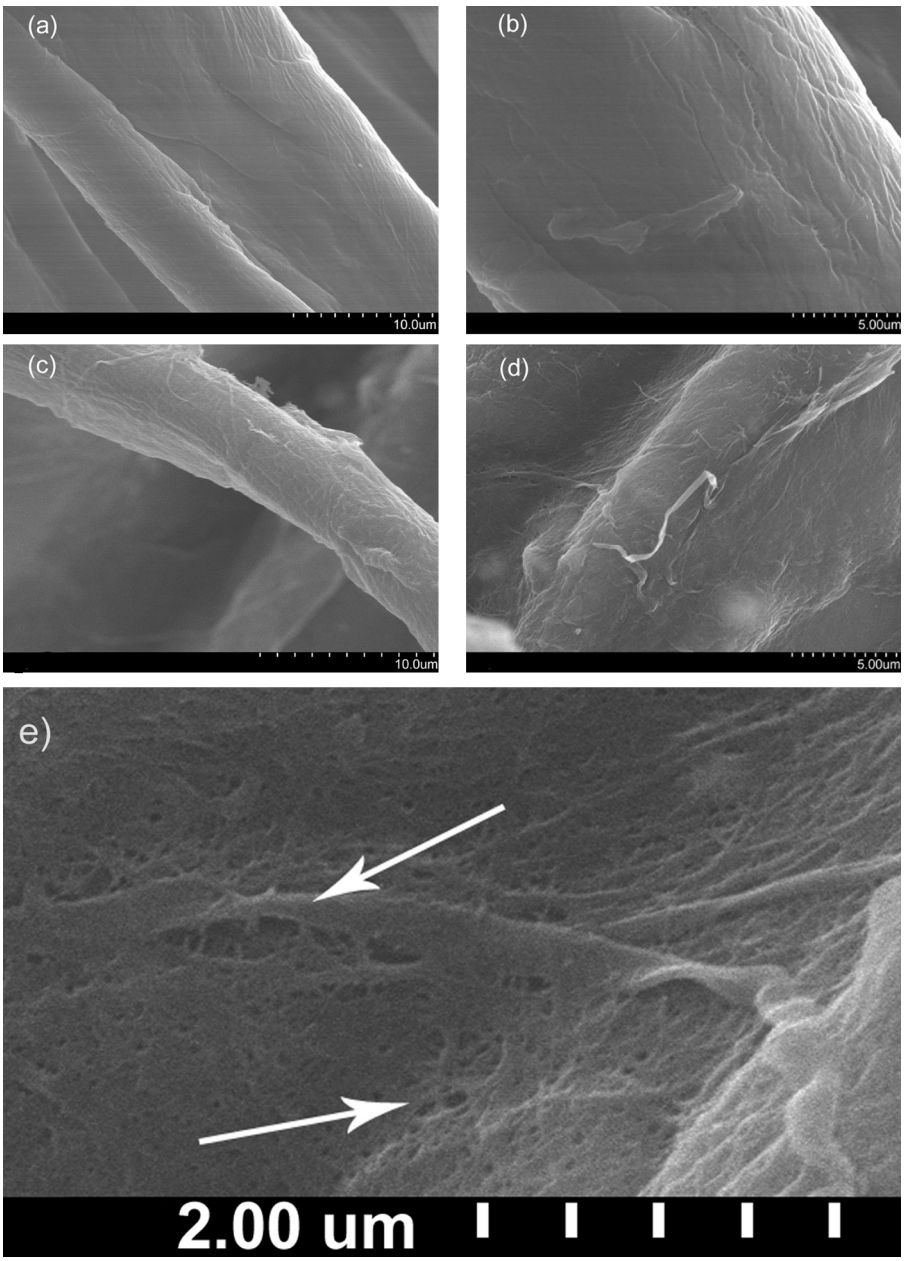


Fig. 2. Scanning electron microscope images of (a) untreated cotton fiber, (b) untreated cotton fiber surface, (c) CNF grafted pCMC fiber, (d) surface of CNF grafted pCMC fiber and (e) porous CNF coating on grafted pCMC fibers.

On the other hand a remarkable difference can be observed with the fabrics treated with CNF dispersion. Fig. 2(c) shows a single fiber of CNF treated fabric, where continuous coating on the surface of the fiber is clearly visible. Parallel ridges on the surface of the untreated cotton fiber are not visible any more in the treated cotton fibers. Instead they are covered with randomly oriented ridges indicating a development of secondary structure on the fiber surface. By analyzing the thickness of the coating where the splitting has taken place, it was possible to evaluate the coating thickness to be somewhere between 50 and 150 nm. Fig. 2(d) shows more magnified image of the fiber surface. By analyzing such images, it was possible to conclude that the observed coating is a construction of many smaller fibers which are typically in the dimensions below 100 nm. Most importantly, the coating is continuous and consists of randomly oriented mesh like formation as expected. Close investigation of coating surface reveals that it is not compactly filled. Fig. 2(e) shows indication of such porous coating development on the fiber surface. Porous structures having diameters in the range of 80–200 nm are clearly visible (indicated by arrows). It is very reasonable to expect coating to be porous since CNF are randomly oriented. Development of porous coating offers an additional advantage since they can retain more water than a compact coating.

3.6. Energy-dispersive X-ray spectroscopic analysis

The grafting procedure used in the experiment was especially employed to encourage the grafting of CNF to one side of the fabric only. The existence of side selective grafting of CNT on cotton fabrics can be best demonstrated using EDEX by taking the spectra on two sides of the fabric. Fig. 3 shows the SEM images and the respective EDEX spectra. Fig. 3(a) shows the SEM and EDEX spectrum of the cotton fibers that were facing the Teflon cylinder. The fibers appear almost similar to the untreated cotton fibers and there was

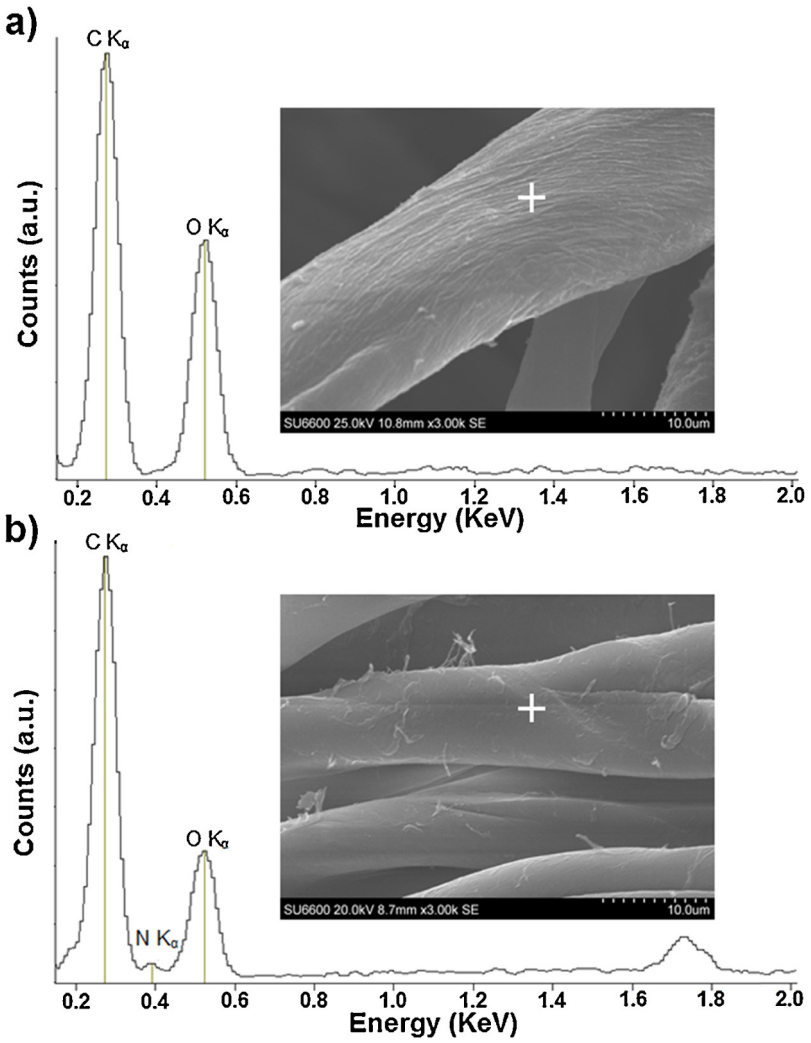
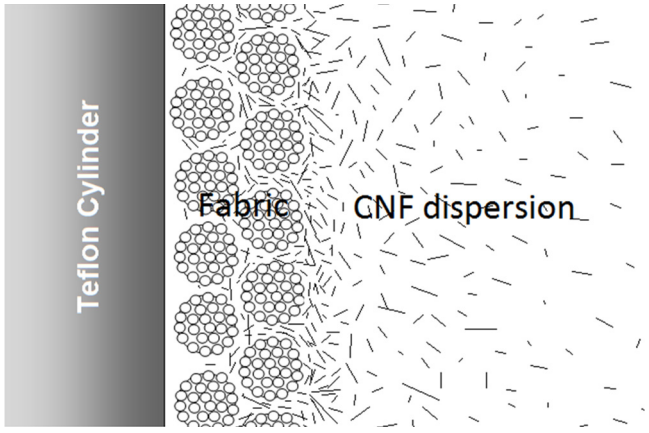


Fig. 3. EDEX spectrum and respective SEM image of (a) cotton fibers that faced Teflon cylinder during grafting and (b) cotton fibers faced the CNF dispersion during grafting.

no significant grafting of nanofibers. However in certain places, isolated patches can be seen on the fiber surface which may be due to the deposition of aggregated CNF. EDEX analysis shows absence of nitrogen element on the surface of the cotton fiber which indicates no significant grafting has taken place on the fibers. However, when SEM and EDEX were analyzed, significant difference could be observed in the fibers that were directly exposed to the CNF dispersion. Development of a thin coating was clearly visible and EDEX spectrum shows the presence of nitrogen element on the fiber surface confirming the grafting of CNF fibers. When the fabric is treated in CNF dispersion, nanofibers can approach the fiber in both sides of the fabric. However, special grafting apparatus used in the experiment allows CNF fibers to approach the fabric only in one direction since Teflon cylinder surface works as a barrier. Hence CNF has to diffuse through the fibrous structure of the cotton fabric leaving a concentration gradient of CNF through the fabric structure. This renders significant CNF coating on one side of the fabric and little or no CNF coating on the other side. Proposed grafting mechanism for CNF on cotton is illustrated in Scheme 1.

3.7. Atomic force microscopic analysis

Although SEM can be used to characterize CNF coating development and distribution, AFM data can be used to further complement the information obtained. It is a very well adopted technique especially in surface topology imaging and for surface roughness calculations. Fig. 4 shows AFM topology image of unmodified cotton fiber surface and fiber modified with CNF. It can be noticed in Fig. 4(a) that for the case of raw fiber, fibrils are visible which are parallel to each other and spiraling around the fiber in an angle to fiber axis. In Fig. 4(b), which presents the surface of a cotton fiber modified with CNF. These fibers can easily be located as



Scheme 1. Illustration of the side specific grafting mechanism of CNF on fabric

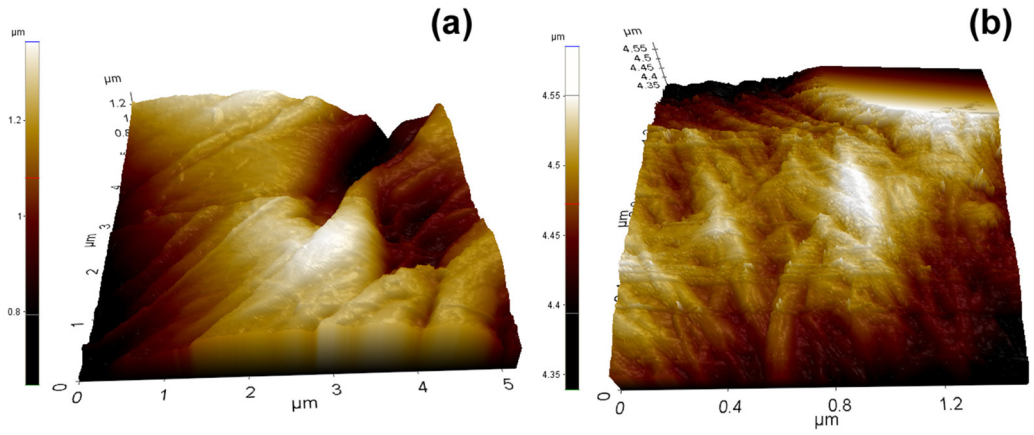


Fig. 4. Atomic force microscope images of (a) untreated cotton fiber surface and (b) pCMC fiber surface grafted with CNF.

Table 2
Surface roughness data of untreated cotton fiber surface and pCMC surface grafted with CNF.

Samples	R_a	R_{ms}	R_{sk}	R_{ku}
Untreated cotton	102.3 ± 22	117.6 ± 32	0.181 ± 0.073	2.006 ± 0.42
pCMC grafted with CNF	13.1 ± 3	16.3 ± 3	−0.318 ± 0.121	2.572 ± 0.145

R_a: average roughness in nm; R_{ms}: root mean square roughness in nm; R_{sk}: skewness; R_{ku}: kurtosis.

randomly oriented small fiber network. Individual fiber width is in the range of 40–150 nm. Table 2 lists the surface roughness values of the untreated cotton fiber and fiber modified with CNF. Data suggest that the surface roughness has increased significantly with the CNF modification. This data further strengthen the fact that a CNF layer has been grafted on the surface of the cotton.

3.8. CNF loading of fabrics

The CNF loading of the cotton fabrics was evaluated using the Kjeldahl method and is shown in Fig. 5. It could be observed that nitrogen content of unmodified cotton fibers and pCMC without any CNF grafting approaches to a value near to 1.5 mg/g and 1.2 mg/g respectively. However, with the surface modification, an increase in nitrogen content could be observed. This increase in nitrogen content can be related to higher loading of CNF on the cotton fibers as chitin is a nitrogenous polysaccharide. The nitrogen loading also increased with CNF dispersion concentration. The maximum nitrogen loading of 3.6 mg/g was observed in the sample treated with highest concentration of CNF (0.75 g/l). Nitrogen loading of the samples in pCMC-0.25, pCMC-0.5 and pCMC-0.75 are

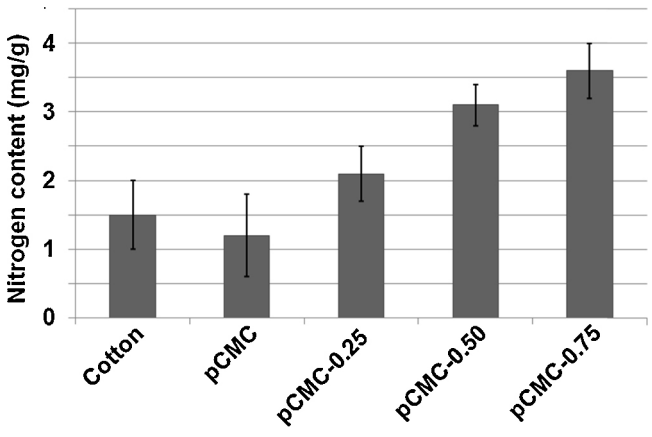


Fig. 5. Nitrogen content of fabric samples as analyzed by Kjeldhal method.

2.1 mg/g, 3.1 mg/g and 3.6 mg/g respectively. This corresponds to a theoretical CNF loading of 3.3% (w/w), 4.9% (w/w) and 5.7% (w/w) for the sample systems of pCMC-0.25, pCMC-0.5 and pCMC-0.75 respectively.

We can expect the presence of different types of interactions between CNF and surface carboxylic acid groups on pCMC fibers which will lead to higher adhesion. We suggest that the binding is through a combination of different forms including weak anion–cation type attractions, hydrogen bonding and physical attractions (Supplementary materials: Fig. 6). We can hypothesize that, initially the protonated surface amine groups of CNF and surface carboxylic acid groups in pCMC surface are forming ionic type attractions leading to CNF adsorption on pCMC surface. This adsorption process may be followed by much stronger hydrogen type bonding between adsorbed CNF and pCMC surface via number of functional sites of two polymer systems.

4. Conclusion

Chitin nanofibers can be prepared with complete fibrillation using ultrasound technique. Thus obtained nanofibers can be used as a novel coating material for cotton fibers. MCAA can be used to modify the cotton fiber surface to have carboxylic acid groups which can be ionized to carboxylate ions at appropriate pH values. These ionized anionic groups can attract CNF producing uniform porous coating made of randomly oriented network of nanofibers on the fiber surface. By using special grafting process described in the paper, CNF grafting can be encouraged to occur only in one side of the fabric. Nano coating significantly enhances the surface roughness of the cotton fabrics. Loading of CNF on cotton depended on the concentration of the CNF dispersion.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.03.035.

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