

N-Octyl Chitosan- A Promising Biomaterial for Sustainable Cotton Textile Functionalization

Firoz Ahmed, Md Ibrahim H Mondal*, Joykrisna Saha and Pranab Kumar Das

Polymer and Textiles Research Lab, Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Rajshahi, Bangladesh

*Corresponding author

Md Ibrahim H. Mondal is a Professor in the Department of Applied Chemistry and Chemical Engineering at the University of Rajshahi, Bangladesh, E-mail: mihmondal@gmail.com, mihmondal@yahoo.com

Submitted: 01 Aug 2019; Accepted: 06 Aug 2019; Published: 12 Aug 2019

Abstract

The purpose of the present study is to develop a biomaterial from renewable source for its effective application on cellulosic textile fibre functionalization instead of synthetic toxic products. In this context, we have prepared a water-soluble bioactive compound N-octyl chitosan from prawn shell waste. The molecular weight of prepared chitosan and N-octyl chitosan were 139,958 Da and 162,181 Da respectively. Chitosan and N-octyl chitosan were applied on cotton fibre and characterized by various physico-chemical and instrumental techniques, e.g. FTIR, SEM, TGA, DTA, DTG, XRD etc. Thermal behavior of chitin, chitosan, N-octyl chitosan, cotton, chitosan modified cotton and N-octyl modified cotton were investigated and also followed the order cotton > chitin > chitosan > chitosan-modified cotton > N-octyl chitosan modified cotton fibers. Finally, functionality of cotton fibre was measured by dyeing performance which in turn was evaluated by controlling the percentage of the dye bath exhaustion (E %). The modified cotton fibers showed excellent dye exhaustion and colorfastness properties as well as other textile properties.

Introduction

Cotton is an abundant natural fibre, which consists of practically pure cellulose. It is popular for its several unique properties such as softness, versatility, absorbency, breathability biodegradability and high dimensional stability. Cotton fibres is subjected to modification, due to some undesirable properties like moisture sensitivity, low exhaustion of dye, susceptibility towards sunlight (UV), wrinkle and microbial degradation which all are recoverable through modification.

Nowadays, the surface modification of textile fibres is considered as the best route to obtain desire properties of textiles [1]. For this purpose, a large number of chemicals have been used including inorganic salts, iodophors, phenols, thiophenols, heterocyclics with anionic groups, nitro compounds ureas, formaldehyde derivatives and amines but most of the chemicals are toxic to humans and do not easily degrade [2]. Indeed, new types of research look for a solution and try to establish eco-friendly processes that substitute for toxic textile chemicals. In this sense, chitosan and its derivatives are an important candidate for an eco-friendly textile chemical.

Chitosan is a muco-adhesive polymer obtained by deacetylation of chitin, an abundant polysaccharide isolated from insects, crustaceans, and fungi [3]. Chemically, chitosan is a linear (1-4) linked 2-amino-2-deoxy- β -D-glucan (i.e. β -D-glucosamine) having a structure very close to cellulose. The difference from cellulose is that the hydroxyl group in C₂ of cellulose is replaced by an amino group (-NH₂) in chitosan. Chitosan is a copolymer of N-acetyl-glucosamine and

glucosamine units and the majority of any one unit is a measure of chitin and chitosan [4-6]. Due to the limited solubility of chitosan, an N-octyl chitosan derivative was prepared, to enhance the usability of the biopolymer.

Present study deals with the functionalization of cotton fibre to ameliorate textile performances using prepared bioactive chitosan and N-Octyl chitosan from prawn shell waste, which can draw attention of both textile industrialists and consumers to use these biomaterials instead of petroleum, based toxic finishing agents considering environmental and health hazardous issue. At the same time this will widen the applications of chitosan and its derivative and encourage entrepreneur has to set up chitosan production industry utilizing prawn shell waste.

Experimental

Materials

Cotton fibres were collected from Keya Spinning Mill Ltd., Dhaka, Bangladesh. The prawn (shrimp) shells used for the experiment were collected from Mongla (near Sundarban forest) in Bangladesh, which is considered as waste of prawn processing area. Sodium hydroxide, acetic acid, ethanol, sodium chloride, hydrochloric acid, acetone, Potassium bromide, octanal, sodium borohydride, etc. of the reagent, grade chemicals were procured.

Methods

Fibre preparation

The fibres were at first washed thoroughly with 0.2% Na₂CO₃

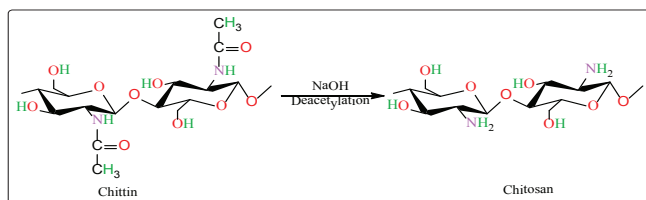
solution at 75 °C for 30 min in fibre- liquor ratio of 1: 50 [7, 8]. After treatment, the fibres were washed with distilled water. Finally, process samples were air dried and stored in a desiccator.

Processing of shrimp shells

Firstly, the collected shrimp (prawn) shells were separated from the head and legs. The shrimp shells were washed several times with hot water, and then dried in a hot oven at 105 °C for 72 h. The dried shells were ground to a fine powder.

Preparation of chitin and chitosan

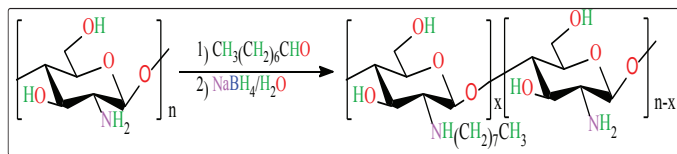
The shrimp powder was treated with 1 mol/L HCl with chitin to HCl solution ratio of 1:50 at 100°C for 4 h, and then washed with distilled water. The alkali-treated solid was then treated with 1 mol/L NaOH with chitin to NaOH solution ratio of 1:50 at 100°C for 4 h followed by washing with distilled water [9-11]. The resultant solid was washed to neutral and dried in a vacuum oven at 50°C for 20 h that was known as chitosan. The deacetylation of chitin is shown in Scheme 1.



Scheme 1: Preparation of chitosan from chitin

Preparation of N-octyl chitosan

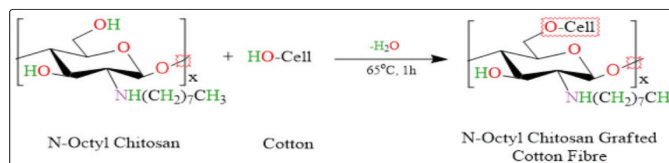
In the present study, N-alkyl chitosan was prepared in several steps, Chitosan (1g) was suspended in a water-methanol 1:1 mixture (100 mL), and then octanal (1g) was added and stirred for 30 min. The reduction was carried out with sodium borohydride solution (0.5 g dissolved in 10 ml of water) under continuous stirring at room temperature. After adjusting of pH to 8-10 with NaOH solution, the preparation was left overnight. The reaction mixture was then neutralized with 2M HCl solution and N-octyl chitosan was precipitated with methanol. The precipitate was then filtered and washed with methanol, then with water and dried at 60°C for 12 h under reduced pressure [12-14]. The alkylation reaction is shown in Scheme 2.



Scheme 2: Preparation of N-octyl chitosan

Modification of cotton fibre

The washed cotton fibre treatment was carried out with chitosan and chitosan derivative containing solution. Firstly, required amount of chitosan or its chitosan derivative solution was dissolved in 2% acetic acid solution where the fibre to liquor ratio was maintained at 1:50. Then cotton fibre was dipped in the solution and allowed to stand at 60°C for 1h. The pH of the solution was maintained at 3.5 - 4.0 using 0.2M acetic acid [15]. The modified fibres were washed with distilled water and subsequently dried in hot air at 60°C until constant weight. The proposed grafting reaction is shown in Scheme 3.



Scheme 3: Grafting of N-octyl chitosan on cellulose

Cotton fibre dyeing with reactive dyes

Three reactive dyes, e.g. Reactive Brown 10, Reactive Orange 14 and Reaction Red were selected for the dyeing of washed cotton, chitosan and N-octyl chitosan modified cotton fibre. Reactive dye was dissolved, at first, by making a paste with little warm distilled water and then, by adding cold distilled water.

The dyeing sequence of washed and modified cotton fibres are shown in Figure 1. The dye bath was prepared by taking (5g/L) NaCl as an electrolyte solution based on the weight of fibre. The fibre-liquor ratio was maintained at 1:50. Dyeing was carried out using 0.3% dye (on the weight of fibre) in a dyeing machine (DYSIN). During dyeing 5g of washed cotton, fibre was immersed in the dye pot. Exhaustion was done at 80°C for 120 min. After 1 h, the pot was taken out and then Na₂CO₃ solution (2g/L) was added based on the weight of fibre [7]. The fixation of dye was continued for a further 60 min.

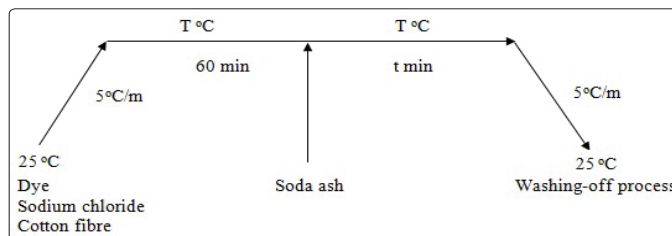


Figure 1: Dyeing sequence of washed, chitosan modified and N-octyl chitosan modified cotton fibre

Characterization

Degree of deacetylation (DDA) of chitosan

Various methods have been used for the determination of the degree of deacetylation of chitosan. Among all the methods elemental analysis is a simple, suitable and rapid method to determine the degree of deacetylation (DDA) value of chitosan. The degree of deacetylation was calculated from the carbon/ nitrogen ratio (C/N). It varies from 5.15 (X) in completely N- deacetylates chitosan (C₆H₁₁O₄N per unit) to 6.86 (Y) in chitin, the fully N-acetylated polymer (C₈H₁₃O₅N repeat unit). The degree of deacetylation (DDA) value of chitosan was determined by the following equation [16].

$$DDA = \{1 - (C/N - X)/(X - Y)\} \times 100$$

Where, C is the mass of carbon in chitosan sample and N is the mass of nitrogen in chitosan sample.

Molecular weight

For the determination of viscosity-average molecular weight (Dalton), the chitosan and its derivative were dissolved in a mixture of 0.1 M acetic acid and 0.2 M NaCl, and then the intrinsic viscosity (η) was measured by using an Ubbelohde Capillary Viscometer. The Mark-Houwink equation relating to intrinsic viscosity with empirical viscometric constants $K=1.81 \times 10^{-3} \text{ cm}^3/\text{g}$ and $a=0.93$ for chitosan

was used to calculate the molecular weight using “Mark- Houwink-Sakurada” equation [17,18].

$$[\eta] = KM^a$$

Measurement of tensile strength

The experiment was performed using a “Portable Electronic Single Yarn Strength Tester-YG021J” Fanyuan Instrument (HF) Co. Ltd, China, for quick and reliable tensile strength measurement. The breaking load of unmodified and modified fibre was shown on the scale of the tensile tester in N/yarn.

Moisture absorption study

The modified and washed cotton fibres were placed on a humidity chamber at room temperature (70°C) for a week where humidity was maintained at the saturation level [19]. After that moisture analyzer, using the following formula analyzed the fibres:

$$\text{Moisture Content (\%)} = \frac{W_f - W_i}{W_i} \times 100$$

Where W_f is the weight of wet sample and W_i is the weight of dry sample.

Swelling behavior study

Swelling behavior of the modified and washed cotton fibres were determined by dipping into water at room temperature for 24 h. The percent swelling was calculated according to the following equation [20].

$$\text{Percent Swelling (\%)} = \frac{W_f - W_i}{W_i} \times 100$$

Where, W_i is the initial weight of fibre and W_f is the final weight of fibre.

FTIR analysis

FTIR spectroscopy analysis of chitin, chitosan, N-octyl chitosan, cotton, chitosan modified and N-octyl chitosan modified cotton fibres was performed by using a “Shimadzu IR-8900” spectrophotometer (Shimadzu, Kyoto, Japan). The examined samples and KBr (potassium bromide) were dried in an oven at 105°C for moisture free. Then fine powder was made using mortar pestle. The powder sample was mixed with KBr in the ratio of 1:25 and a pellet were prepared. The IR-spectra of this KBr pellets were recorded with the FTIR spectrophotometer. The scanning range was between 400-4000 cm^{-1} and a resolution of 4 cm^{-1} .

Thermal analysis

The experiments were performed using a Seiko-Exstar-6000, TG/DTA-6300 (Seiko Instruments Inc., Chiba, Japan). The tests were conducted between 25-550 °C under an inert atmosphere (Argon). The heating rate and the air (nitrogen) flow rate were 10°C/min and 200 ml/min respectively.

Scanning electron microscopy (SEM) analysis

The Scanning Electron Microscopy (SEM) was studied to analyze the morphology of unmodified, chitosan modified and N-octyl chitosan modified cotton. Morphological investigation of unmodified, chitosan modified and N-octyl chitosan modified cotton fibres was performed using a Scanning Electron Microscope, (FEI Quanta Inspect, Model: S50, Netherlands). The micrographs were taken at a magnification of 2000 times using 40 kV accelerating voltage.

XRD analysis

X-ray diffraction (XRD) patterns of washed and modified cotton fibres were recorded using Bruker D8 Advanced Germany, X-ray Diffractometer that generated Cu-K α radiation. Powdered samples were exposed to X-ray beam at the operating voltage and current of 40 KV and 30 mA respectively. Data were collected at a scanning rate of 2°/min with the scan angle from 2 to 40°.

Dye bath exhaustion

The dye bath exhaustion was determined spectrophotometrically. The absorbance of each dye bath solution was measured using a 1 cm path length quartz cell housed in a UV spectrophotometer (WPA Model S104-D Digital Spectrophotometer, UK) both before and after the dyeing process. The bath exhaustion percentage E (%) was calculated according to the following equation [21,22].

$$\text{Exhaustion of dye, \%} = \frac{(A_0 - A_r) \times 100}{A_0}$$

Where, A_0 and A_r are the absorbance of the dyeing bath before and after dyeing respectively.

Statistical analyses

All the experiments were carried out in triplicate and the data were expressed as mean \pm standard deviation (SD, n=3) for reproducibility. Significant difference analysis was determined using Schiffe’s multiple range test considering statistically significant values.

Results and Discussion

Yield

Table 1 shows extraction percentage (on weight of raw basis), colour and odour of yield of chitin and chitosan at various reaction stages of preparation. The yield percent of chitin from dry prawn shells modified with 1 mole/L NaOH and 1 mole/L HCl was 29.4 wt%, 25.62 wt% and 24.12 wt% on the first, second and third reaction steps respectively and obtained yields of chitosan were 15.56 wt.%, 11.26 wt.% and 9.80 wt.% on the first, second and third successive reaction steps. In general, the results were similar to those found by Alimuniar et al [23]. The yield was dependent on the size of shell powder and on the reaction step. Percent yield decreases with respect to the reaction step due to the removal of protein, pigment, lipids, inorganic salts and acetyl groups (-COCH₃) present in chitin. Some carotenoid pigment remaining in the chitin powder caused a brown colour in the first step product and light brown in both the second and third step products, with little or no odour. For the first step, about 50% of the acetyl groups, with pigments and lipids, were removed by alkali treatment. On the second and third steps, a trace amount of acetyl group was removed with no remaining pigments. The final product obtained was white and odourless [24].

Table 1: The yield of chitin and chitosan at various reaction stages

Parameters	Chitin extracted at different extraction stages		
	1 st Stage	2 nd Stage	3 rd Stage
Extraction, %	29.40	25.62	24.00
Colour	Brown	Light Brawn	Light Brawn
Odour	Weak	None	None
Chitosan extracted at different extraction stages			
Extraction, %	15.56	11.26	9.80

Colour	Off-white	Light Brawn	Brown
Odour	Weak	None	Weak

Degree of Deacetylation of Chitosan

The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with a high degree chemical reactive amino group (-NH₂). This makes the degree of deacetylation an important property in chitosan production as it affects the physicochemical properties, hence focuses its appropriate applications [25]. Deacetylation also affects the biodegradability and immunological activity [26]. The degree of deacetylation mainly depends on the method of purification. Also, reaction conditions, such as temperature, alkaline concentration and reaction time, are also important [27]. From Figure 2, it is seen that the degree of deacetylation maximized at 85% at 80°C temperature. To produce this, 50% alkaline solution was used in the solid to liquor ratio of 1:50 (w/v) for 4 h refluxing the reaction mixture in the presence of ethanol.

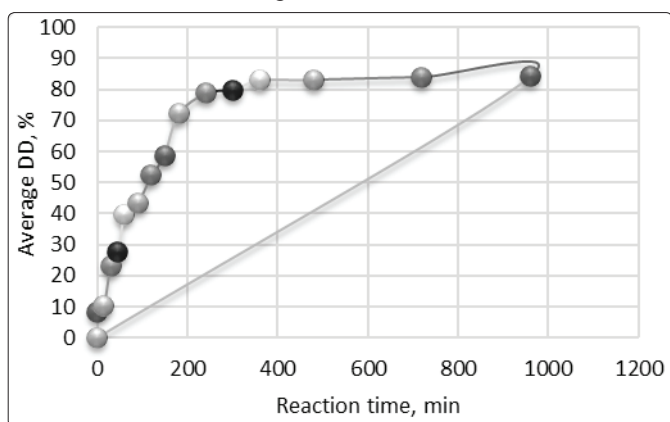


Figure 2: Effect of time on deacetylation percent

Molecular weight

Chitosan is a biopolymer of high molecular weight (MW) and varies with the sources and the methods of preparation [28]. The MW of native chitin is usually larger than one million Daltons while commercial chitosan products fall between 1.0×10^5 to 1.2×10^5 an average MW of 1.20 - 1.50×10^5 Da [27, 29]. The molecular weight of shrimp chitosan obtained in this study was 1.40×10^5 Da. On the other hand, the molecular weight of N-octyl chitosan was 1.60×10^5 Da. This molecular weight is higher than chitosan as hydrogen of the amine group in chitosan was replaced by octyl radical.

Physico-chemical properties of unmodified and modified fibres

Moisture absorption, swelling test, tensile strength, % elongation, and biodegradation reports of washed and modified cotton fibres are shown in Table 2. From the Table, modified cotton fibres showed improved physico-chemical properties. The covalent bond formation between cellulose of cotton fibre and modifier (chitosan and N-Octyl chitosan) reduces hydroxyl groups (-OH) on fibre backbone which ultimately reduces the moisture uptake by the cotton fibre. Similarly, for this reason swelling activity of modified fibres decreases than that of unmodified or washed cellulosic cotton fibre. In case of tensile strength and elongation tests, we saw that both tensile strength (N/yarn) and elongation (%) of modified fibres were improved due to chemical bonding between fibre and modifier as well as modification.

The biodegradation rate in terms of weight loss (%) modified and unmodified cotton fibres was more or less similar because the used chitosan and its derivative N-Octyl chitosan are totally ecofriendly bioactive compounds which do not affect the natural biodegradation of cotton fibre. So, the modified cotton fibres will be more suitable for textile application with blazing properties.

Table 2: Physico-chemical tests of washed and modified cotton fibre

Serial No	Types of tests	Unmodified cotton	Chitosan modified	NOCh modified
01	Moisture absorption (%)	17±0.4	13±0.7	11±0.6
02	Swelling (%)	118±0.6	97±0.8	88±0.5
03	Tensile Strength (N/yarn)	173±2	190±1.75	197±2
04	% Elongation	9±0.06	10±0.03	10.5±0.01
06	Biodegradation (% wt loss at 28th day)	71±1	72±1	69±2

Fourier transform infrared spectroscopic analysis (FTIR)

Fourier-transform infrared spectra were used to identify the presence of functional groups. The FTIR spectra of chitin, chitosan, N-octyl chitosan, unmodified cotton, chitosan modified and N-octyl chitosan modified cotton fibres are shown in Figure (a-f) respectively. The peak intensity at 1660 cm^{-1} gradually decreased while that at 1600 cm^{-1} increased, indicating the prevalence of -NH₂ groups and at 1600 cm^{-1} displayed a greater intensity than the one at 1660 cm^{-1} which demonstrated the effective deacetylation of chitin. Obvious changes of the FTIR spectrum are observed after chitosan alkylation, suggesting that substitution has occurred on the amino groups of chitosan. Peak intensity at 1600 cm^{-1} decreases, due to the conversion of -NH₂ to N-alkyl substituent, a new peak appearing at 1520 cm^{-1} corresponding to asymmetrical stretching of C-H in the methyl groups. Figure 1(d-f) is clearly seen that cotton, chitosan modified cotton and N-octyl chitosan modified cotton are more or less near about same except at the band of 1600 cm^{-1} and 1520 cm^{-1} due to the incorporation of chitosan and N-octyl chitosan respectively on the cotton fibre.

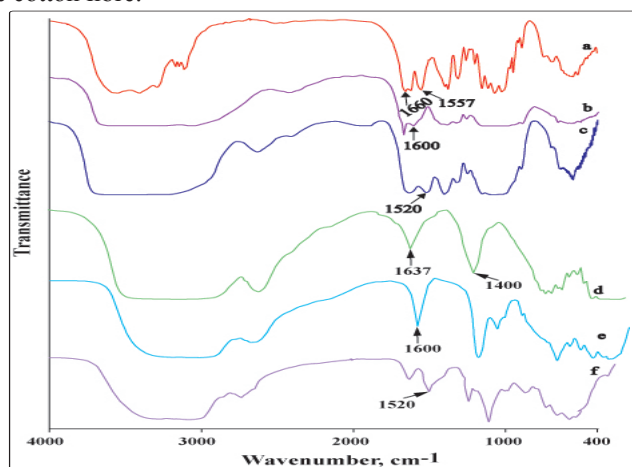


Figure 3: FTIR spectra of (a) Chitin, (b) Chitosan, (c) N-octyl chitosan, (d) Cotton, (e) Chitosan modified and (f) N-octyl chitosan modified cotton fibres

Thermal analysis

The TGA, DTG and DTA profiles of chitin shown in Figure 4(a), it is observed that the loss in weight is around 65.3% at 346.6°C-400.7°C due to loss some protein and minerals. The DTA curves indicate two endothermic peaks at 70.6°C and 389.7°C due to moisture and thermal degradation respectively. DTG curves show two peaks at 57.4°C and 266.5°C. The initial peak is due to the elimination of moisture and the second peak is due to one-step degradation of chitin. The maximum peak is at 387°C. On the other hand, in Figure 4(b) it is seen that the DTA curves indicate two endothermic peaks at 72.3°C and 392.6°C due to moisture and thermal degradation respectively. DTG curves show two peaks at 66.6°C and 294.4°C. The initial peak is due to the elimination of moisture and the second peak is due to one-step degradation of chitosan. The maximum peak is at 389.9°C.

Figure 4(c-e) shows the thermal behavior of unmodified cotton fibre, chitosan modified cotton fibre and N-octyl chitosan modified cotton fibre, respectively. From Figure 4(c-e) it can be seen that the weight loss of cotton fibre, chitosan modified cotton fibre and N-octyl chitosan modified cotton fibre are 69.3% at 388.5°C, 54% at 350°C and 29.7% at 306°C, respectively. The initial decomposition temperature of raw cotton fibre, chitosan-modified cotton fibre and N-octyl chitosan- modified cotton fibre are 300°C, 250°C and 215°C and the corresponding char yield are 15%, 27% and 35%, respectively. Based on initial decomposition temperature, the thermal stability of that compounds and fibre follows the order, chitin > chitosan > cotton > chitosan modified cotton > N-octyl chitosan modified cotton. The DTA curve indicates two endothermic peaks at different temperatures due to moisture and thermal degradation of cotton fibre, chitosan and N-octyl chitosan-modified cotton fibres respectively. The DTG curve represents the decomposition rate at different temperature ranges. So, it can be said that the thermal stability of chitosan and N-octyl chitosan-modified fibres are decreased compared to that of unmodified fibres. This might be the result of the incorporation of chitosan and its derivative with the cotton fibres.

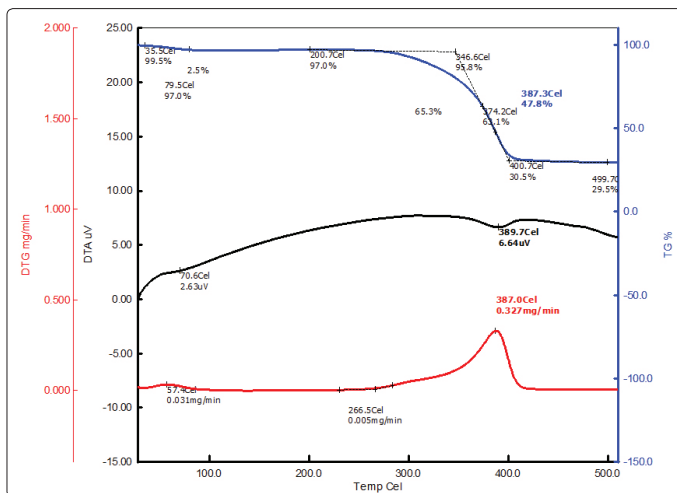


Figure 4(a): TG, DTA and DTG curve of chitin

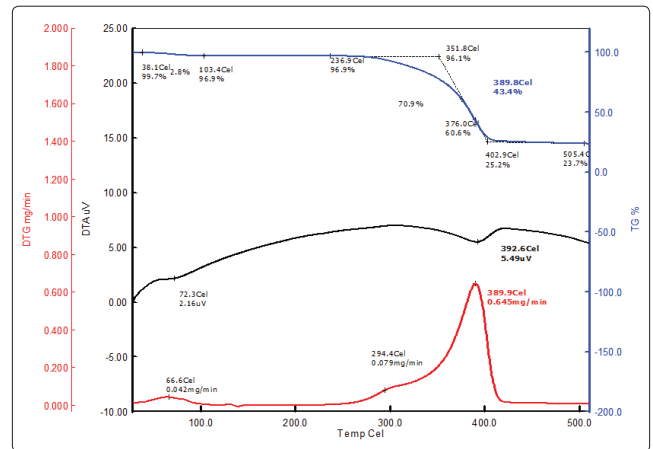


Figure 4(b): TG, DTA and DTG curve of chitosan

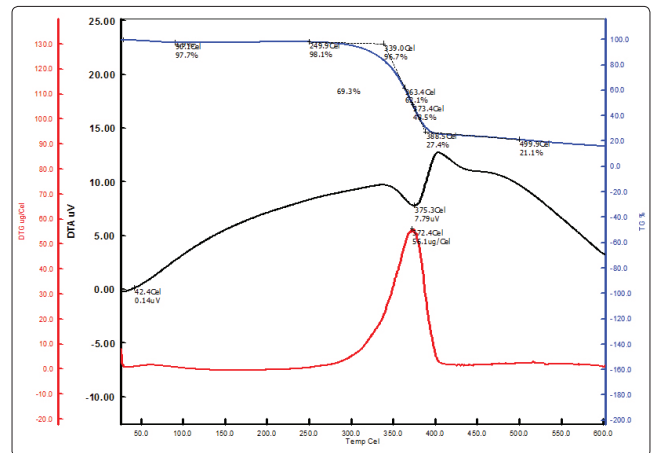


Figure 4(c): TG, DTA and DTG curve of unmodified cotton fibre

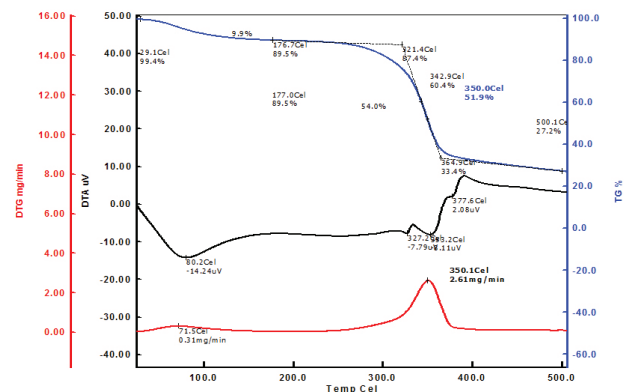


Figure 4(d): TG, DTA and DTG curve of chitosan modified cotton fibre

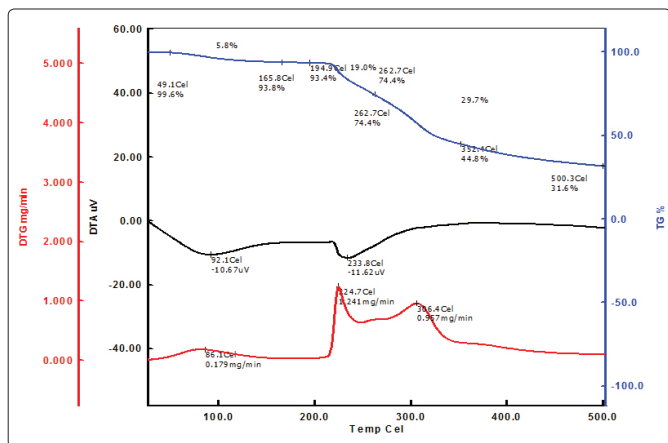


Figure 4(e): TG, DTA and DTG curve of NOCh modified cotton fibre

Surface Morphology

The SEM images of unmodified cotton fibre, chitosan modified cotton fibre and N-octyl chitosan modified cotton fibres are shown in Figure 5 (a-c). It can be clearly observed that the surfaces of the unmodified cotton fibres are relatively smooth and clean with many tiny projecting fibres Figure 5(a). After treatment with chitosan and N-octyl chitosan, the surfaces of the modified cotton fibres were coated with a film of granular substances and dispersed with some agglomerated particles Figure 5(b-c). Yet, the chitosan- and N-octyl chitosan-modified cotton fibres exhibits smoother surfaces, due to the absorption of chitosan and N-octyl chitosan on the fibre. The micrograph of the surface of the chitosan-modified fibre indicates that it is smoother than that of the N-octyl-chitosan-modified fibre. This is because chitosan tends to form more film than does N-octyl chitosan. Chitosan exhibits an inherent property of film formation, which is clearly seen as a gloss on the fibre surface. According to the micrograph, chitosan is spread on the fibre in a homogeneous way, without agglomerated deposition on the fibre surface. Such agglomeration occurs on the N-octyl chitosan-modified fibre.

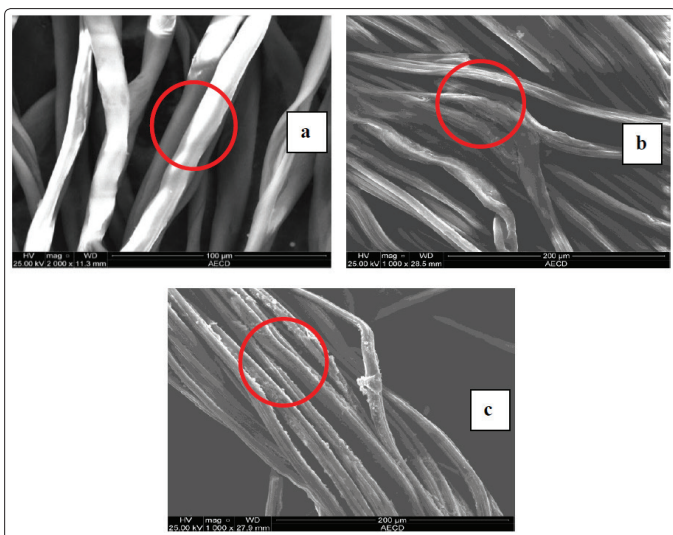


Figure 5: SEM of a) Unmodified, b) Chitosan modified and c) N-octyl chitosan modified cotton fibres

XRD analyses

The degree of crystallinity of unmodified and modified (with chitosan and NOCh) cotton fibres were investigated through X-ray diffractometry and the X-ray diffractograms are shown in Figure 6. From the figures it can be concluded that the order of crystallinity of the modified and unmodified cotton fibres is as follows: Washed > chitosan modified > NOCh modified cotton fibres.

The XRD profile of unmodified cotton fibres exhibits comparatively well resolved and intense peaks, while broad diffuse scattered and less intense peaks are found for modified fibres. This indicates that modifier affects the crystallinity of cotton fibre with their incorporation.

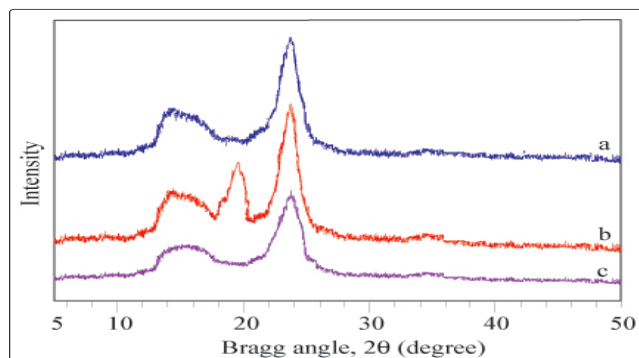


Figure 6: XRD pattern of a) Washed, b) Chitosan modified and c) N-Octyl chitosan modified cotton fibre

Dye bath exhaustion

The dyebath exhaustion and colour of unmodified and modified cotton fibres are represented in Table 3 and Table 4 respectively. The exhaustion of dye by the fibres was increased by treating them with chitosan and N-octyl chitosan prior to dyeing. Generally, reactive dyes formed a covalent bond with fibre polymer [30]. The reactive system of this dye enables it to react with the hydroxyl groups in cellulose by nucleophilic addition reaction. As the reactive dyes are anionic and cotton fibres gain anionic surface charge in water, the charge repulsion adversely affects the dye bath exhaustion. For this reason, unmodified fibre shows low exhaustion of dye. Their exhaustion behavior is shown in Figure 7. Chitosan and N-octyl chitosan modified fibres showed different dye exhaustion amount. Seventy percent exhaustion would mean that 70% of the total amount of dye has been attached to the fibre and 30% is still in solution. The treatment of the fibre with chitosan and N-octyl chitosan increased the number of dye sites in the cellulose macromolecules of cotton fibres. As a result, the modified fibre absorbed more dye than the unmodified sample as well as increased the exhaustion percentage of dye in the modified fibre. The dyebath exhaustion is shown in the higher bar diagram in Figure 7, where chitosan and N-octyl chitosan-modified fibre samples have higher bars than the unmodified cotton fibre. Chitosan and N-octyl chitosan-modified fibres exhibit had considerably better colour absorption. This could be due to the attachment of chitosan to the cotton fibre backbone, which helps to increase the functionality and the measure of reactivity. N-octyl chitosan-modified cotton fibre exhibits comparatively lower dye absorption because some amino (NH_2) groups bond with octyl groups to form the chitosan derivative.

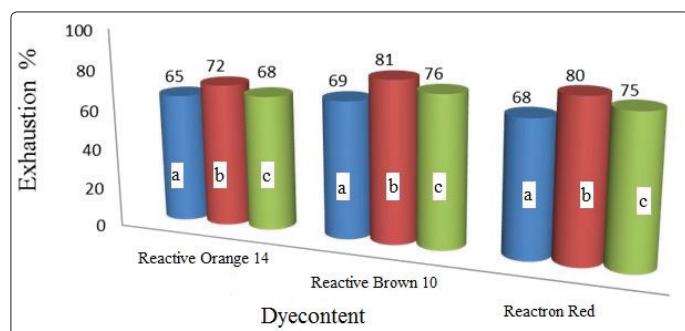


Figure 7: Effect of dye absorption on dyeing of a) unmodified, b) chitosan modified and c) N-octyl chitosan modified cotton fibres

Table 3: Effect of various dye absorption on dyeing of washed and modified cotton fibres

Name of dye	Dye exhaustion %		
	Washed fibre	Chitosan modified fibre	N-octyl modified fibre
Reactive Orange 14	65±0.51	72±0.42	68±0.35
Reactive Brown 10	69±0.97	81±1	80±1.02
Reactron Red	68±0.58	80±0.13	75±0.24

Table 4: Colour of unmodified and modified dyed fibres according to gray scale rating

Name of dyes	Washed fibre	Ch modified fibre	NOCh modified fibre
Reactive Orange 14	Orange 3	Bright Orange 5	Deep Orange 4-5
Reactive Brown 10	Light Brown 2-3	Deep Brown 4-5	Brown 4
Reactron Red	Fade Red 2	Deep Red 4-5	Red 3-4

Colour Fastness on Exposure to Sunlight

The light fastness of both the unmodified and modified fibres dyed with reactive dyes (Reactive orange 14, Reactive brown 10 and Reactron red) was assessed by Gray scale. The change in colour of dyed fibre occurs within 50-150 h exposure and then no or slight change occurs on further increase of exposure time. This is probably, due to the mechanism of the light action produced day by day on the fibre. It was also observed that chitosan and N-Octyl chitosan modified dyed fibres gave better colorfastness than unmodified dyed fibres when they were exposed to sunlight in air. It can be explained that after treatment, the OH groups on cellulosic fibre are blocked by hydrogen bonding reaction with chitosan and N-Octyl chitosan. As a result, the atmospheric oxygen cannot oxidize the fibre. So, the change in colour or fading does not occur or slightly occurs [31].

Colour Fastness to Washing

The colorfastness and change in colour of unmodified and modified fibres dyed with three reactive dyes (Reactive orange 14, Reactive brown 10 and Reactron red) was examined at 30, 50, 70, and 90°C. It was observed that modified dyed fibres showed better colour fastness to detergent solution than that of unmodified fibres. The wash fastness depends upon the physical and chemical properties

of the fibre and their forces of interaction and their interaction with detergent solution. From the structural feature it is assumed that the number and strength of covalent bonds between dye and modified fibre molecules are more than that of unmodified. This variation of covalent bonds may be the cause of showing better colorfastness of modified dyed fibres on washing with detergent solution.

It is also evident that the wash fastness decreases with the increase of temperature. It seems that at higher temperature, dissolution of the dye particles from the fibre surface takes place and hence more dye is easily washed off the fibre. Noted that, the solubility of dye increases with the increasing of washing temperature.

Conclusions

Chitosan and its derivative, N-octyl chitosan were successfully prepared from abandoned prawn shell waste by chemical processes and examined by their characteristics. Both of the chitosans were used as biodegradable natural modifiers for the cellulosic fibres. Modifications were confirmed by FTIR spectra, TGA, DTA and DTG thermogram, SEM images and XRD patterns of the unmodified and modified cotton fibres. Chitosan and N-Octyl chitosan modified fibres showed improved textile properties with excellent colour depth and colourfastness properties to UV and wash fastness regarding conventional process. Thus chitosan and its prepared derivative from prawn shell waste would be a valuable chemical for the functionalization of other materials to produce value added products and they can easily be used as ecofriendly textile modifiers for improvement of cotton fibre quality as well as other textile performances.

Acknowledgement

The authors would like to acknowledge the Faculty of Engineering, Rajshahi University, Bangladesh for funding the Project Ref. No.: 1043/5/52/RU/Eng/2/18-19/83.

References

- Jocic D, Jovancic P, Petrovic Z, Bertan E, Navarro A, et al. (2002) The influence of surface modification on wool functional and dyeing properties. In Proceedings of the World Textile Conference 2nd Autex Conference, Textile engineering at the dawn of a new millennium: an exciting challenge, Bruges, Belgium 2002: 297-312.
- Gao Y, Cranston R (2008) Recent Advances in Antimicrobial Treatments of Textiles. Textile Research Journal 87: 60-72.
- Roberts G (1992) Chitin Chemistry. The Macmillan Press Ltd., Hong Kong.
- Muzzarelli RAA (1996) In the Polymeric Materials Encyclopedia, Salamone, JC (Ed.). CRC Press Inc., Boca Raton FL, USA 1996: 312-314.
- Hirano S (2003) Ullmanns Encyclopedia of Industrial Chemistry (Vol. 7). Wiley VCH, Weinheim, Germany 2003: 679.
- Oktem T (2003) Surface treatment of cotton fabric with chitosan. Coloration Technology 119: 241-246.
- Islam MM, Mondal MIH, Hoque MA (2015) Synthesis of Chitosan Derivative for an Eco-Friendly Cotton Fiber Modifier with Enhanced Physico-Chemical Characteristics. In Cellulose and Cellulose Composites: Modification, Characterization and Applications, Mondal MIH (Ed). Nova Science Publisher, New York 2015: 81-98.
- Singha AS, Thakur VK (2009) Synthesis and characterization of silane treated grevia optiva fibres. International Journal of

- Polymer Analysis and Characterization 14: 301-321.
9. Alam R, Khan MA, Khan RA, Ghosal S, Mondal MIH (2008) Study on the physico-mechanical properties of photo-cured chitosan films with oligomer and acrylate monomer. *Journal of Polymer and Environment* 16: 213-219.
 10. Cira L.A, Huerta S, Hall GM, Shirai K (2002) Pilot scale lactic acid fermentation of shrimp wastes for chitin recovery, *Process Biochemistry* 37: 1359-1366.
 11. Sini TK, Santhosh S, Mathew PT (2007) Study on the production of chitin and chitosan from shrimp shell by using *Bacillus subtilis* fermentation. *Carbohydrate. Research* 342: 2423-2429.
 12. Zhang C, Ping Q, Zhang H, Shen J (2003) Preparation of N-alkyl-O-sulfate chitosan derivatives and micellar solution of taxol. *Carbohydrate Polymer* 54: 137-141.
 13. Vinsova J, Vavrikova E (2008) Recent advances in drugs and prodrugs design of chitosan. *Current Pharmaceutical Design* 14: 1311-1326.
 14. Bobu E, Nicu R, Lupei M, Ciolacu FL, Desbrieres (2011) Synthesis and characterization of N-alkyl chitosan for paper making applications. *Cellulose Chemistry and Technology* 45: 619-625.
 15. Gerald L, Witucki A (1993) Silane Primer: Chemistry and application of alkoxy silanes. *Journal of Coatings Technology* 65: 57-60.
 16. Kasaai MR, Arul J, Charlet G (2000) Intrinsic Viscosity–Molecular Weight Relationship for Chitosan. *Journal of Polymer Science Part B Polymer Physics* 38: 2591-2598.
 17. Yeasmin MS, Mondal MIH (2015) Synthesis of highly substituted carboxymethyl cellulose depending on cellulose particle size. *International Journal of Biological Macromolecules* 80: 725-731.
 18. No HK, Lee SH, Park NY, Meyers SP (2003) Comparison of physicochemical, binding and antibacterial properties of chitosan prepared without and with deproteinization process. *Journal of Agricultural and Food Chemistry* 51: 7659-7663.
 19. Abbasipour M, Mirjalili M, Khajavi R, Majidi MM (2014) Coated Cotton Gauze with Ag/ZnO/chitosan Nanocomposite as a Modern Wound Dressing. *Journal of Engineered Fibers and Fabrics* 9: 124-130.
 20. Das S, Kothari VK (2012) Moisture Vapor Transmission Behavior of Cotton Fabrics. *Indian Journal of Fibre and Textile Research* 37: 151-156.
 21. Tam KY, Smith ER, Booth J, Compton RG, Brennan CM, et al. (1997) Kinetics and mechanism of dyeing processes: the dyeing of cotton fabrics with a procion blue dichlorotriazinyl reactive dye. *Journal of Colloid Interface Science* 186: 387-398.
 22. Giles HC (1974) *A laboratory course in dyeing* (3rd Edn. 1984.) Society of Dyers Colourist, Bradford, Yorksire, England 79: 54-58.
 23. Alimuniar, Zaubyddin, Brine CJ, Sanford PA, Zikakis JP (1992) An Economical technique for producing chitosan. In *Advances in Chitin and Chitosan*. Elsevier Appl Sci, Essex, UK 1992: 627.
 24. Brzeski MM, Hirano S, Tokura S (1982) Concept of Chitin/Chitosan isolation from Antarctic Krill (*Euphaeus superba*) shells on a technique scale, in proceedings of the Second International Conference on Chitin and Chitosan. Japan Soc. Chitin and Chitosan, Sapporo, Japan 1982: 15.
 25. Rout SK (2001) Physicochemical, Functional, and Spectroscopic analysis of crawfish chitin and chitosan as affected by process modification. *Journal of Carbohydrate Polymers* 16: 294-298.
 26. Tolaimate A, Desbrieres J, Rhazi M, Alagui A, Vincendon M, et al. (2000) On the influence of deacetylation process on the physicochemical characteristics of chitosan from squid chitin. *Journal of Polymer Research* 41: 2463-2469.
 27. Li Q, Dunn ET, Grandmaison EW, Goosen MFA (1992) Applications and properties of chitosan. *Journal of Bioactive and Compatible Polymer* 7: 370-397.
 28. Fernandez-Kim S (1991) Physicochemical and functional properties of crawfish chitosan as affected by different processing protocols. MS Thesis, Department of Food Science, Graduate faculty of the Louisiana state university and agricultural and mechanical college.
 29. No HK, Lee MY (1995) Isolation of Chitin from Crab Shell Waste. *Journal Korean Society of Food and Nutrition* 24: 105-113.
 30. Ojstrsek A, Doliska A, Fakin D (2008) Analysis of reactive dyestuffs and their hydrolysis by capillary electrophoresis. *Analytical Sciences* 24: 1581-1587.
 31. Lim SH, Hudson SM (2004) Application of a fiber-reactive chitosan derivative to cotton fabric as a zero-salt dyeing auxiliary. *Coloration Technology* 120: 108-113.

Copyright: ©2019 Md Ibrahim H Mondal, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.