

Cotton Fibre Functionalization With Prepared Carboxymethyl Chitosan From Prawn Shell Waste: An Eco-Friendly Approach

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Abstract

Chitosan and its derivatives such as carboxymethyl chitosan (CMCh) are safe, biocompatible and eco-friendly substance for human usages. CMCh was prepared from chitosan (89% degree of deacetylation) by carboxymethylation reaction which was confirmed by FTIR spectroscopy. Obtained CMCh had an average degree of substitution was 1.20 determined by titrimetric analysis. Moisture content and ash content of Ch and CMCh were 10%, 9% and 2.33%, 14.39% respectively which affect cellulosic fibre properties. Functionalization of cotton with chitosan and CMCh introduces amino (1610 cm^{-1}) and carboxyl groups (1737 cm^{-1}) on the cellulose chain of the cotton fibre surface, causes the increment of reactive sites on the fibre backbone. The modified fibres were characterized by FTIR, SEM and thermal behaviours were also investigated by TGA, DTA and DTG. The unmodified and modified cellulosic fibres were dyed with two reactive dyes to compare the dyeability. Among them, modified fibre showed 10-15% higher dye exhaustion and better fastness properties than that of unmodified fibre.

Keywords – Cotton, chitosan, carboxymethyl chitosan, functionalization.

Introduction

The outermost shell of crustacean's like shrimps, lobsters, etc. is discarded as waste during their processing. Fortunately, this shell contains a potential component called chitin which is a polysaccharide and found abundantly in nature after cellulose. As chitin is an intractable polymer it is insoluble in most organic solvents

which limit its end uses in various sectors. So structurally modified chitin has been developed is named chitosan, (1 \rightarrow 4) linked 2-amino-2-deoxy- β -D-glucan (i.e. β -D-glucosamine) which is only soluble in dilute acetic acid medium. Chitosan has drawn researcher's interest due to its renewability and some unique properties like biodegradability, biocompatibility, bioactivity, etc [1,2]. But to overcome the solubility problem as well as to promote usability, a completely water-soluble chitosan derivative carboxymethyl chitosan (CMCh) has been developed which is safe for consumer's health and also for the environment. That's why, CMCh has been widely used for various smart applications like drug delivery system, blood anticoagulant, wound dressings, industrial effluent treatment, wash-off dyes absorption, water purification and so on [3-5].

Cotton, a naturally occurring renewable cellulosic fibre, is the most used fibre in textiles as well as other products. Although this fibre has several drawbacks, such as large hydrodynamic volume, creases badly, attacked by mildew, lower dye absorption capacity, poor colour fastness, etc. in the usage of textile fibres [2]. Cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$)_n builds up negative charges on its surface when immersed in water, resulting in an inverse effect on exhaustion of anionic dyes such as reactive dye.

The present investigation has been undertaken to minimize the undesirable properties of cotton fibre by using prepared CMCh from prawn shell wastes as an eco-friendly modifier with ensuring proper prawn shell waste management.



Experimental

Materials

Cotton fibres were collected from local market of Rajshahi and prawn shell was collected from prawn processing area of Bagerhat, Khulna, Bangladesh. The chemicals were used in this experiment were procured of analytical grade.

Fibre preparation

Cotton fibres were treated with 0.2% Na₂CO₃ solution at 75°C for 30 min in the fibre to liquor ratio of 1:50 [6,7]. Then the fibres were thoroughly washed with distilled water until the neutralization and then dried at 105°C.

Preparation of chitin and chitosan

According to Alam et al., 2008, extraction of chitin was followed by three successive chemical treatments i.e. deproteinization, demineralization and decolourisation of prawn shell waste [8-10]. The extracted chitin was treated with 40% aqueous NaOH solution in presence of ethanol with a solid to liquor ratio of 1:30 at 80°C for 4h for deacetylation (**Fig. 1**). After washing and drying the obtained product was chitosan.

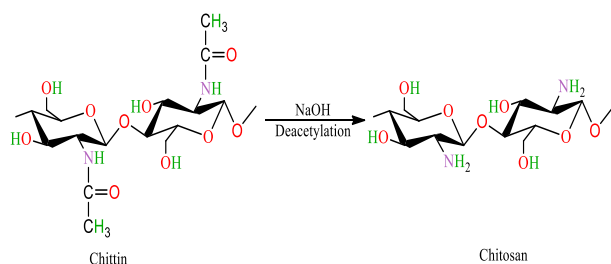


Fig. 1. Preparation of chitosan from chitin.

Preparation of CMCh

CMCh was prepared according to the procedure of carboxymethyl cellulose preparation [11]. The required amount of pure chitosan was dispersed in iso-propanol using a magnetic stirrer at room temperature for 20 min. Then concentrated NaOH solution (40%) was added to the suspension and which was further followed by a solution of monochloroacetic acid/isopropanol (1:1 w/w) and preceded for 7h. After neutralization, filtration and ethanol washing the dried product was CMCh.

Cotton Fibre Modification

The bleached cotton fibres were taken into an aqueous solution of CMCh (20% of fibre weight) at 65°C

for 1h in a water bath maintaining fibre to liquor ratio 1:20 [12] where Triton X-100 (0.1% of liquor) was as a wetting agent and sodium lauryl sulfate (0.1% of liquor) as a softening agent. In case of chitosan modification, an acetic acid medium was used maintaining pH, 3.5-4.

Dyeing of cotton fibre with reactive dyes

The dyeing process was carried out at 80°C for 120 min in a benchtop dyeing machine (DYSIN, Taiwan, China) where fibre to liquor ratio was maintained at 1:50 using 0.5% dye (on the weight of fibre). The dye exhaustion was calculated by the following equation [13]:

$$\text{Exhaustion of dye, \%} = \frac{(D_0 - D_e) \times 100}{D_0}$$

Where D_0 is the initial dye concentration and D_e is the exhausted dye concentration of the bath.

Characterizations

Molecular weight of chitosan

Molecular weight of chitosan and prepared CMCh was determined by Ostwald viscometer using “Mark-Houwink-Sakurada” equation [14,15]:

$$[\eta] = K(Mw)^a$$

Where K and a are constant for a given solute-solvent system and temperature [8]. The values of K and a are 1.8×10^{-3} and 0.93 respectively.

Degree of deacetylation of chitosan

The degree of deacetylation of chitosan was determined from FTIR spectra of chitosan which depends on the base-line of the IR spectra [16]. Following equation was used to calculate the DD value.

$$\text{DD \%} = 118.883 - [40.1647 \times (A_{1655} / A_{3450})]$$

where A_{1655} is the absorbance of the amide band at 1655 cm⁻¹ and A_{3450} is the absorbance of the -OH band at 3450 cm⁻¹. The factor 40.1647 denotes the value of the ratio of A_{1655}/A_{3450} for fully N-acetylated chitosan. The number 118.883 was proposed to be related to the baseline.

Degree of substitution of CMCh

The degree of substitution (DS) of CMCh was determined by titration method [1] according to Guo et al., 2005 where the degree of substitution can be calculated as follows:

$$DS = \frac{161 \times A}{M_{CMCh} - 58 \times A}; A = V_{NaOH} \times C_{NaOH}$$

Where V_{NaOH} and C_{NaOH} are the volume and molarity of aqueous NaOH, respectively, M_{CMCh} is the mass of CMCh, 161 and 58 are the respective molecular weights of glucosamine (chitosan skeleton unit) and a carboxymethyl group.

Infrared spectroscopy

FTIR spectra of chitin, chitosan, CMCh, unmodified and modified cotton fibres were recorded with KBr pellets on Shimadzu IR-8900 spectrophotometer (Shimadzu, Kyoto, Japan).

Thermal analysis

Thermal analysis of fibre samples was performed using a Seiko-Exstar-6000, TG/DTA-6300 (Seiko Instruments Inc. Japan). The tests were conducted between 25°C and 600°C under an inert atmosphere (argon). The heating rate and the air flow rate were 10°C/min and 200 ml/min, respectively.

Scanning electron microscopy

Scanning electron microscopy (SEM) of fibre samples was performed using a scanning electron microscope (FEI Quanta Inspect, Model: S50, Netherlands) to observe the microstructure and the surface morphology of the treated as well as untreated fibres. The fibre surface was coated with a thin film of carbon to render them conductive.

Results and discussions

Molecular weight and degree of substitutions

Molecular weight and DS of chitosan and CMCh are very significant functions on which their physicochemical, biological, rheological and solubility properties as well as end uses depend [17-20]. The obtained molecular weight values were 139 KDa and 162 KDa, and whereas DS values were 89% and 1.20 of chitosan and CMCh respectively.

Moisture and ash content

The obtained moisture content was 10% and 9% for chitosan and CMCh respectively. The prepared CMCh was showed higher moisture content than that of chitosan due to containing hydrophilic carboxylic group. For the similar reason, the ash content of prepared CMCh was

high (14.39%), as the carboxylic group remains in Na-carboxylate form. Whereas the recorded ash content of prepared chitosan was 2.33%.

Infrared spectroscopy analysis

The characteristic FTIR spectra of prepared chitin, chitosan, CMCh, bleached and modified cotton fibres are shown in **Fig. 2(a-f)**. The add-on percentages of chitosan and CMCh on cotton fibre were approximately 12% and 17% respectively. The peak at 1659 cm^{-1} gradually decreased due to the replacement of $-\text{CONH}_2$ groups of chitin with a primary amine. At the same time, the peak at 1600 cm^{-1} was increased in the chitosan spectrum which confirms the successful deacetylation of chitin to chitosan. Again, the appearance of peaks at 1737 cm^{-1} , corresponding to carboxylic groups and 1420 cm^{-1} for $-\text{CH}_2$ bending is the evidence of carboxymethylation of chitosan. From **Fig. 2(d-f)**, FTIR spectra of unmodified and modified cotton are more or less similar, except the characteristics peaks of amine (1610 cm^{-1}) and carboxylic groups (1730 cm^{-1}) were appeared on the backbone of cotton which confirms the attachment of chitosan and CMCh respectively.

Thermal analysis

Thermal behaviour of bleached, chitosan and CMCh treated cotton fibres were studied by TGA, DTG and DTA thermograms and is shown in **Fig. 3**. From the thermogram (TGA) of both unmodified and modified cotton fibres, we see that total moisture was evaporated at a temperature range 85 to 120°C, then sharp weight loss was found at 200 to 270°C due to thermal degradation of cellulosic cotton fibres and finally, the weight loss was reached to a fixed value with the increase of temperature up to 580°C due to the residual char production. Based on initial decomposition temperature (T_i), the unmodified and modified cotton fibres were showed thermal stability as follows: Ch modified (275°C) > unmodified (260°C) > CMCh modified (220°C). Thus chemical modification affects the thermal stability of cotton fibre which in turn confirms the attachment of Ch and CMCh on the fibre backbone.

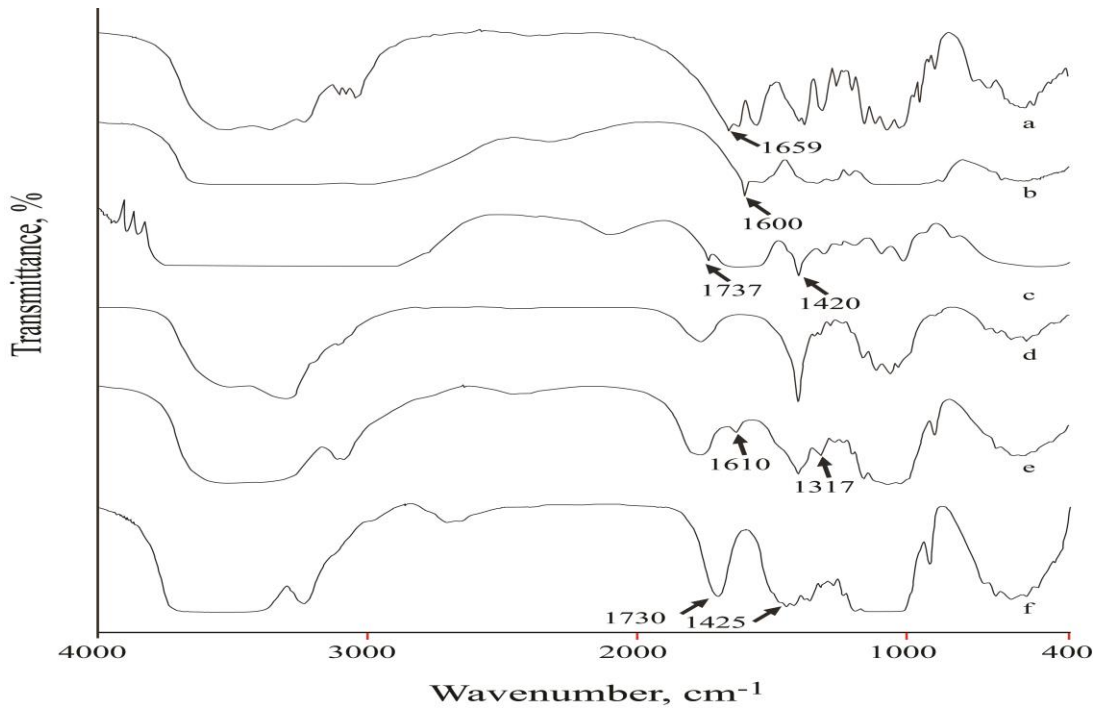


Fig. 2. FTIR spectra of (a) Chitin, (b) Chitosan, (c) CMCh, (d) Cotton, (e) Chitosan treated cotton and (f) CMCh treated cotton [21].

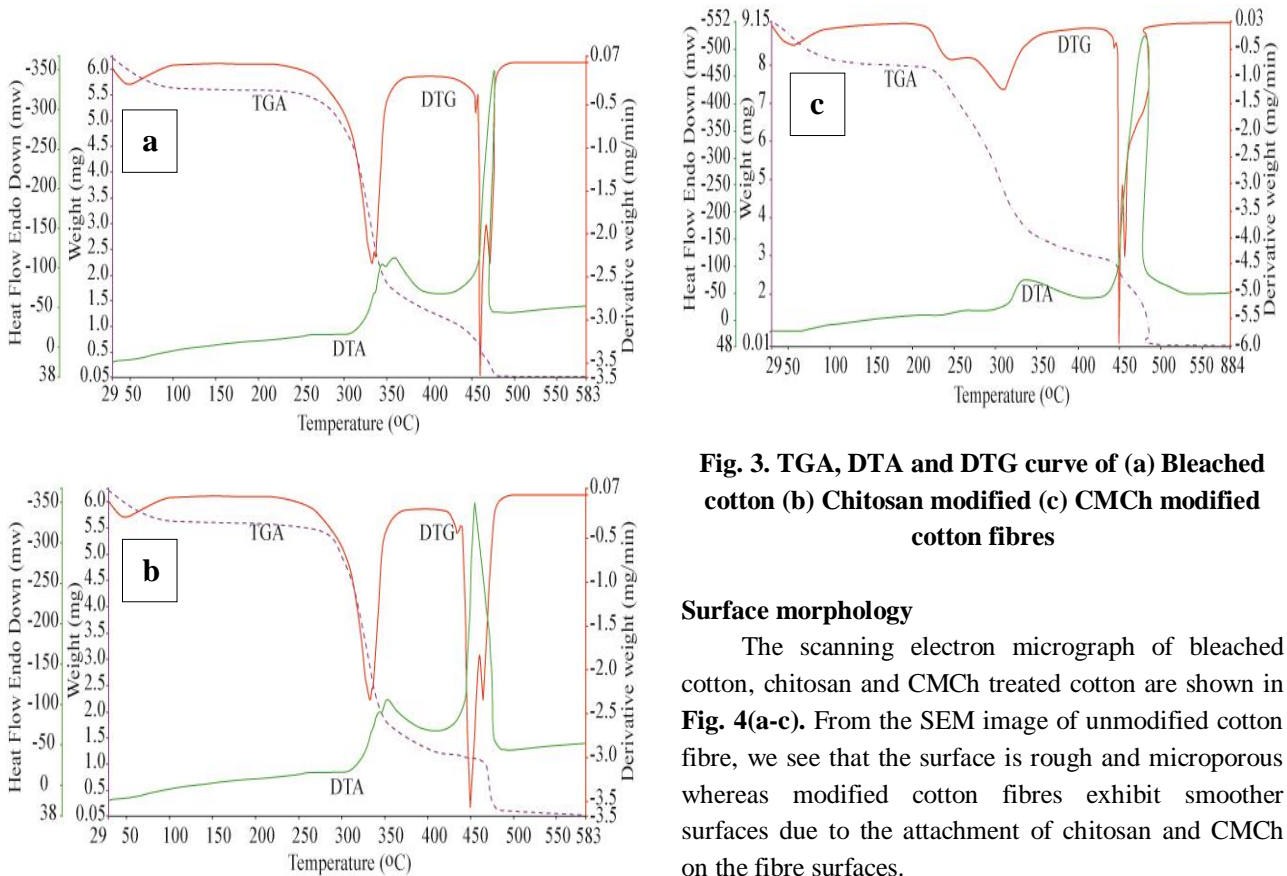


Fig. 3. TGA, DTA and DTG curve of (a) Bleached cotton (b) Chitosan modified (c) CMCh modified cotton fibres

Surface morphology

The scanning electron micrograph of bleached cotton, chitosan and CMCh treated cotton are shown in **Fig. 4(a-c)**. From the SEM image of unmodified cotton fibre, we see that the surface is rough and microporous whereas modified cotton fibres exhibit smoother surfaces due to the attachment of chitosan and CMCh on the fibre surfaces.

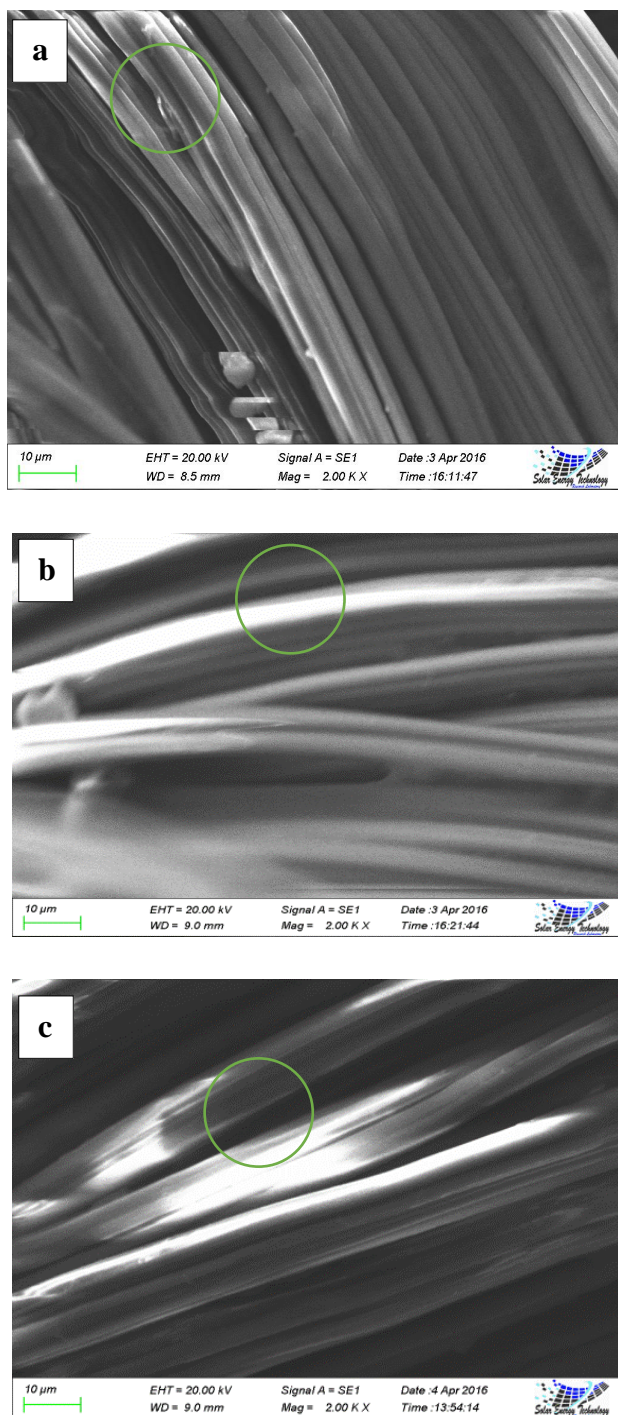


Fig. 4. SEM of (a) Unmodified, (b) Chitosan modified, (c) CMCh modified cotton fibres.

Dyebath exhaustion

The dyeing performance of modified and unmodified cotton fibres was studied with two reactive dyes i.e. reactive orange 14 and reactive brown 10. Their exhaustion behaviour is shown in **Fig. 5**. Among them, CMCh treated cotton fibres exhibit better dyeability as well as better colour. This could be due to a higher percentage of CMCh attachment to the cotton fibre backbone, which helps to increase the functionality and

the measure of reactivity toward reactive dye molecule [22, 23].

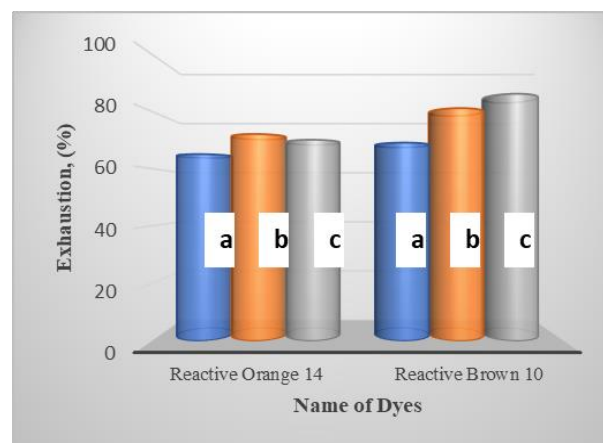


Fig. 5. Effect of dye absorption on dyeing of (a) Unmodified, (b) Ch modified and (c) CMCh modified cotton fibres [21].

Conclusion

This study has successfully demonstrated that textile performances specially dyeability of cotton fibre has been improved due to modification with prepared bio-based compounds i.e. chitosan and CMCh instead of petroleum-based modifier. Various instrumental techniques like FTIR, SEM, TGA were used for the confirmation of fibre modification. Modified cotton fibres showed noticeable dye attachment and colour fastness regarding the conventional process. Thus the production of chitosan and CMCh from prawn shell waste would be a valuable biomaterial for the functionalization of cellulosic fibres to enhance textile performances.

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Conflicts of interest

The authors declare there are no conflicts of interest.

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