

Preparation and Characterization of Functionalized Chitosan Derivatives from Prawn Waste for Cellulose Fibre Modification to Enhance Textile Properties

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Abstract

The purpose of this research was to develop water soluble textile modifiers based on biopolymer having improved textile properties including tensile strength, moisture absorption, wash resistance, dye-ability and colour fastness properties. Two fibre reactive chitosan derivatives such as N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (HTAChC) and N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (NMA-HTAChC) were synthesized from chitosan through dispersion of chitosan with glycidyltrimethylammonium chloride (GTMAC) in aqueous medium and dissolution of HTAChC in aqueous N-methylolacrylamide (NMA) solution in presence of NH₄Cl and 4-methoxyphenol, respectively. The physicochemical properties of prepared derivatives were studied and the degree of quaternization (DQ) of HTAChC was 0.94, double bond content of the NMA-HTAChC was 0.926 mmol/g and moisture content of HTAChC and NMA-HTAChC were 22.06% and 18.78%, respectively. The FTIR spectra of HTAChC showed prominent peak at 1480 cm⁻¹ (C-H bending), 1650 cm⁻¹ (C=O group) and that of NMA-HTAChC showed the peaks at 1670 cm⁻¹ (C=O stretch) and 1545 cm⁻¹ (N-H bending) which confirms the synthesized derivatives. The prepared derivatives were further used for modification of cotton and jute fibres. Graft yield percent of HTAChC and NMA-HTAChC on cellulose fibre surfaces were 10.69% and 14.74% for jute and 14.56% and 18.86% for cotton, respectively. Grafting was investigated by FTIR, SEM, TGA, DTA and DTG analyses. The surface of modified fibre was investigated by SEM and the surface was smoother than unmodified fibre. The modified fibre showed decreased thermal stability, improved moisture absorption, wash resistances and tensile strength compared to unmodified fibres. It was also observed that textile modifying properties of NMA-HTAChC is better than HTAChC due to higher fibre affinity of NMA-HTAChC to cellulose fibres. Dyeing of modified and unmodified cotton and jute fibres with reactive and direct dyes revealed that dye exhaustions were increased up to 10% due to modification.

Keywords: Bio-waste; Biocompatibility; Biopolymer; Pathogenic; N-Methylolacrylamide

Introduction

The prawn processing industry has been rapidly growing in all the coastal countries. In these industries, prawns are processed to headless or peeled or both, while head and shell portions are considered as wastes. Therefore, a huge amount of bio-waste is generated throughout the world and it is estimated about 6-8 million tons annually [1]. It's a serious environmental concern to dispose such an enormous amount of waste. Although these wastes are biodegradable in nature but produce obnoxious smell, attract pathogenic insects and thus create an unhygienic atmosphere.

This problem can be solved by immediate recycling of the prawn shell generated and extraction of commercially valuable products to be further used in other applications [2]. We know that crustaceans shell contains 15-40% chitin, 25-40% proteins and 30-50% minerals [3]. Among them chitin is considered the second most abundant natural biopolymer after cellulose. Chemically chitin is poly-β-(1-4)-N-acetyl-D-glucosamine, whereas chitosan, a deacetylated form of chitin, is poly-β-(1-4)-D-glucosamine. As a natural bio-material, chitosan has versatile properties such as nontoxicity, biocompatibility, biological activity and biodegradability [4,5] that widen its applications in many fields such as drug delivery [6,7], waste water treatment [8,9], cosmetics [10,11], C industry [12-15], textile etc. But in all these cases, chitosan is only applicable for acidic condition due to its poor solubility in neutral and basic medium. So, it is necessary to enhance the solubility of chitosan in water over a wide range of pH.

The solubility of chitosan can be improved by introducing

hydrophilic groups on chitosan backbone such as carboxymethyl, dihydroxyethyl, sulfate, phosphate, hydroxyalkylamino, or by grafting a water soluble polymer [16-18] and quaternization of amine group of chitosan [19]. Among these, due to permanent positive charge on nitrogen atom, the quaternary chitosan derivatives show higher affinity for cellulose fibre surface and H-bonding potential, which can improve the tensile strength of the modified cellulose fibres [20]. Hence, it is assumed epoxide of glycidyltrimethylammonium chloride (GTMAC) reacts with the primary amino groups of chitosan following a nucleophilic addition pathway to synthesize quaternary derivative N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (HTAChC). Again, HTAChC is treated with N-Methylolacrylamide (NMA) to obtain N-methylolacrylamide-N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (NMA-HTAChC) for higher functionality with excellent textile finishing properties, because NMA

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has two reactive groups, a N-methylol group and a double bond conjugated with a carbonyl group.

The demands of natural cellulose jute and cotton fibres in apparel industry is increasing day by day throughout the world due to several unique properties such as biodegradability, agricultural renewability, softness, moisture absorbency, comfort ability in wear etc. Beside these, cellulose fibres possess some inherent limitations such as high dimensional stability, shrinkage, susceptibility towards sunlight (UV), microbial degradation, lower dye uptake etc. which limit the direct use of these fibres in textile. To minimize the unfavorable properties and to achieve the quality textile fibre, surface modification is necessary. Many workers have modified the cellulose fibres with numerous chemicals prior to dyeing and achieved better results in many cases [21]. But the environmental issue was not considered because the modifiers were synthetic, toxic in nature, non-biodegradable as well as non-hygienic for human health. An ideal textile modifier needs to be safe, nontoxic, environmental friendly and durable to wash, so textile researchers prefer to apply eco-friendly modifiers on cellulose fibres.

This paper deals with the preparation of water soluble quaternary ammonium chitosan derivatives such as HTAChC and NMA-HTAChC from prawn shell waste and modifications of cellulose jute and cotton fibres with these prepared bio-materials to functionalize the fibre backbone which in turn will enhance the dyeability. Considering chemical characteristics and modification properties, these derivatives would play significant role in textile areas mainly as a modifier for cellulose fibres instead of petroleum based chemical modifier and at the same time would help to manage the environmental pollutions around the prawn processing industrial areas.

Experimental Section

Materials

Prawn shell was collected from Mongla (near Sundarban forest), Khulna, Bangladesh that are waste of prawn processing area. Cotton fibre was collected from Keya spinning mill, Dhaka, Bangladesh. *Corchorus olitorius* (Tossa Jute) variety of jute fibre was collected from Rajshahi Jute Mill, Bangladesh. Potassium iodide, iodine, absolute alcohol, sodium meta-bi-sulphite, sodium chloride, etc. were purchased from Merck (Germany), while 2-mercaptoethanol, ammonium chloride, glycidyltrimethylammonium chloride (GTMAC), N-methylolacrylamide (NMA), silver nitrate, Triton X-100 were brought from Sigma (USA). All the reagents used were of analytical grade.

Deacetylation of chitin to chitosan from prawn shell waste

The collected prawn shell was first washed with water and dried at 105°C for 72 h, then the size was reduced to 40-60 mesh using hammer mill. The ground prawn shell was treated with 1 N HCl and 1 N NaOH

maintaining shell to extractant ratio of 1:16 (w/v) at 105°C for 4 h for demineralization and deproteinization [22]. The process was carried out second and third time for pure chitin extraction [2,22]. The conversion of chitin to chitosan was achieved by the treatment of chitin with 40% NaOH (w/v) at 105°C for 3 h to remove the acetyl groups with a solid to solvent ratio of 1:20 (w/w). After this process solid separated from the alkali layer were extensively washed with distilled water to neutral and dried in a vacuum oven at 50°C for 24 h. The process was repeated out second and third time for pure chitosan extraction [2,23]. The reaction of chitin into chitosan is given below (Figure 1).

Preparation of HTAChC

Chitosan (1 g) was dispersed in 20 mL of distilled water maintaining at 85°C by a hot plate with magnetic stirrer. As chitosan was completely dispersed, GTMAC was added three times with constant stirring at a 2 h interval. After a total 10 h reaction, the clear and yellowish reaction solution was poured in 200 mL cold acetone while stirring and kept in the refrigerator overnight. The next day, acetone was decanted and the remaining gel-like product was dissolved in 100 mL methanol. The solution was precipitated in a 250 mL acetone and ethanol (4:1) mixture. The filtrated crude HTAChC was purified by washing with hot ethanol using a soxhlet extractor for 24 h. The final product was collected and dried at 60°C overnight. The obtained product was HTAChC. The reaction of chitosan and GTMAC to obtain HTAChC is shown in Figure 2.

Preparation of NMA-HTAChC

Acrylamidomethylation of HTAChC is carried out by dissolving HTAChC to an aqueous NMA solution in presence of NH_4Cl . The HTAChC (1 g) was dissolved in 5 mL of 48 wt. % aqueous NMA solution with a small amount of 4-methoxyphenol (0.2% w/v) which was added as a polymerization inhibitor at room temperature. To the solution, NH_4Cl (0.5 g) was added and dissolved to maintain the acidic medium for acrylamidomethylation reaction. The reaction solution was reacted at 140°C for 8-20 min using an oil bath. After reaction, 15 mL of methanol was added to the reaction solution and it was stirred for 10 min. The product was precipitated in 100 mL acetone and kept overnight for decant. The decanted product obtained is crude NMA-HTAChC. Crude NMA-HTAChC was washed thoroughly with a mixture of acetone and ethanol (1:1) for several times and finally with ether. The white reaction product was dried at 40°C under vacuum for 2 days. The synthesis reaction of NMA-HTAChC is shown in Figure 3.

Preparation of jute fibre

Jute fibre (30 cm) was taken from middle portion for the present investigations. The raw jute fibre was scoured with a mixture of 6.50 g detergent and 3.50 g soda in one litre water at 75°C for 30 min in a beaker in the ratio of 1: 50 (w/w) [24]. This scoured jute fibre was bleached with a 5 g/L sodium chlorite solution of pH 4 at 85-90°C, for

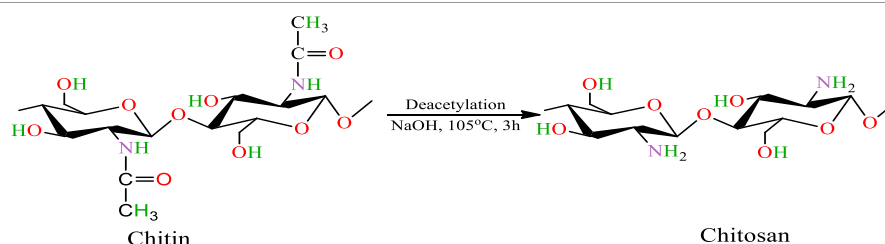


Figure 1: Deacetylation of chitin to chitosan.

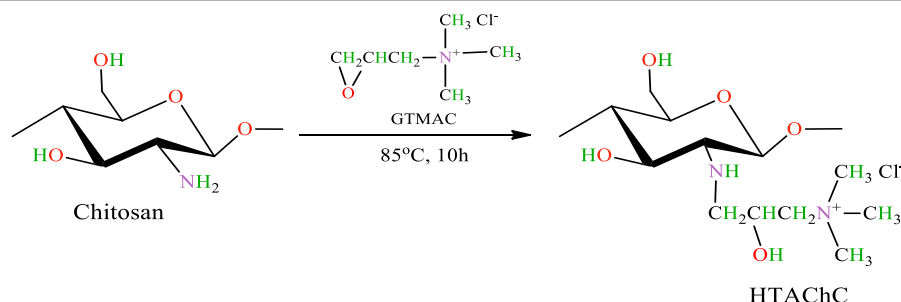


Figure 2: Synthesis of HTAChC.

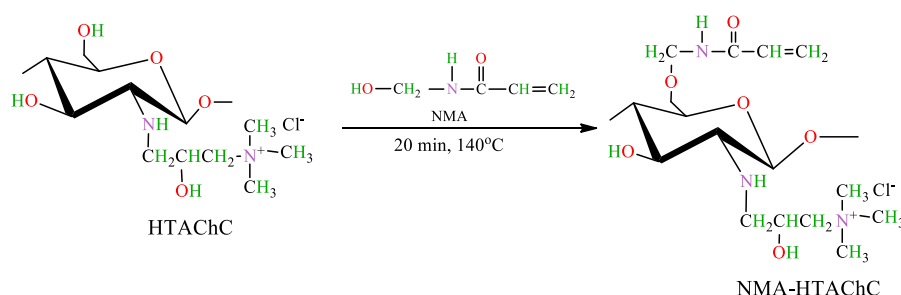


Figure 3: Synthesis of NMA-HTAChC.

90 min, in a fibre-liquor ratio of 1:50 [25]. The fibres were then washed thoroughly with distilled water and dried in the open air. After that the fibres were dried in an oven at 60°C.

Preparation of cotton fibre

At first, the cotton fibres were washed with 0.2% Na_2CO_3 solution at 75°C for 30 min in a beaker in the fibre to liquor ratio of 1:50. The fibres were then washed thoroughly with distilled water and dried in the open air. After that the fibres were dried in an oven at 60°C and then stored in a desiccator [24,26].

Grafting of cellulose fibres with HTAChC and NMA-HTAChC

Required amount of HTAChC or NMA-HTAChC was dissolved in distilled water. Then the washed fibre sample was dipped into the liquor with maintaining fibre to liquor ratio of 1:50 at 70-75°C and allowed to stand for 1h. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2% of liquor) was added to the liquor as catalyst along with Triton X-100 (0.1% of liquor) as a penetrating agent and sodium lauryl sulfate (0.1% of liquor) as softening agent. The treated fibres were washed in distilled water to remove unfixed HTAChC or NMA-HTAChC. The fibre was dried at 60°C to a constant weight. The grafting reaction of cellulose with HTAChC and NMA-HTAChC are shown in Figure 4.

Exhaust dyeing of modified jute and cotton fibres

Dyeing was carried out using 0.3% reactive dye (on the weight of fibre) in a dyeing machine (DYSIN, Taiwan, China) at 65°C for 1.5 h using a plastic stoppered conical flasks. The exhaustion of dye was determined colorimetrically (Type-S104, No- 221, Spectrophotometer, WPA Linton Cambridge, UK) by using the following equation:

Where, D_0 and D_e are the initial and exhausted dye bath concentration, respectively.

Characterization of Prepared Chitosan and Its Derivatives

Determination of degree of deacetylation of chitosan

The degree of deacetylation (DD) of chitosan was determined by the potentiometric titration method. 0.5 g of chitosan was dissolved in 25 mL of 0.1 M standard aqueous HCl solution and calculated amount of KCl was added to adjust the ionic strength. The titrant was a solution of 0.05 M NaOH. pH of the solution during titration was measured using pH meter under continuous stirring [27]. The standard NaOH was then added stepwise and the conductivity of the solution were recorded by a Professional Benchtop Conductivity Meter (BC-3020, Singapore) and a curve with two inflection points is observed in Figure 5. The difference between the volumes of these two inflection points corresponded to the acid consumption for the salification of amine groups of chitosan and permitted the determination of degree of acetylation, through the following Equation:

$$\text{DDA}\% = (V_2 - V_1) \times M_b / W$$

Where, V_1 are the base volumes referred to first inflection points in mL, V_2 are the base volumes referred to second inflection points in mL, M_b is the base molarity in g/mol, and W is the original weight of the polymer in gram.

Determination of degree of quaternization of HTAChC

The degree of quaternization (DQ) of GTMAC on chitosan was measured by conductometric titration of Cl^- with aqueous silver nitrate (AgNO_3) solution [28]. Dried HTAChC (0.1 g) was dissolved in 100 mL of distilled water and conductometrically titrated with aqueous 0.017 N AgNO_3 aqueous solution. Conductivity of the solution was observed with a Professional Benchtop Conductivity Meter (BC-3020, Singapore). A curve with one inflection point was obtained by plotting

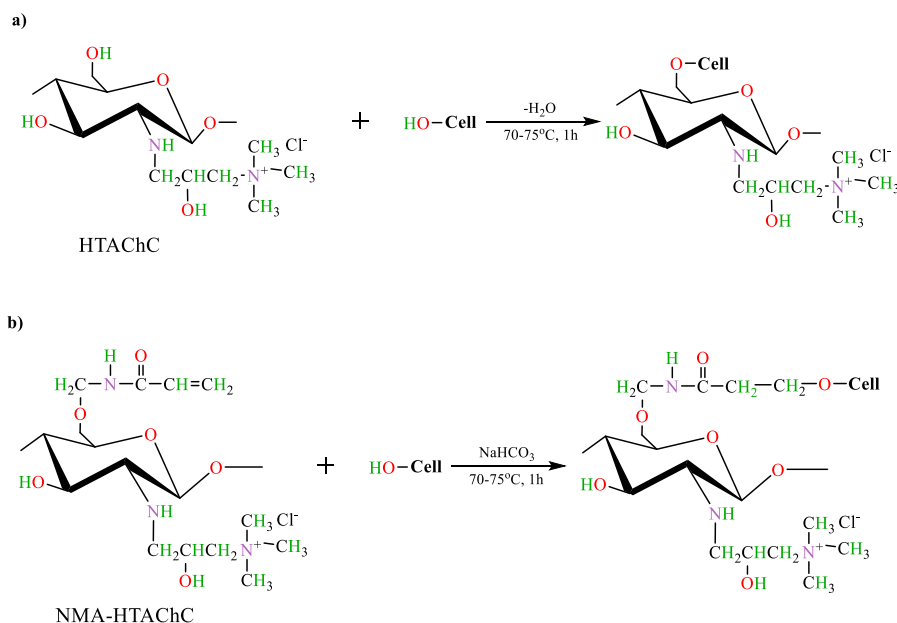


Figure 4: Grafting of cellulose on a) HTAChC and b) NMA-HTAChC.

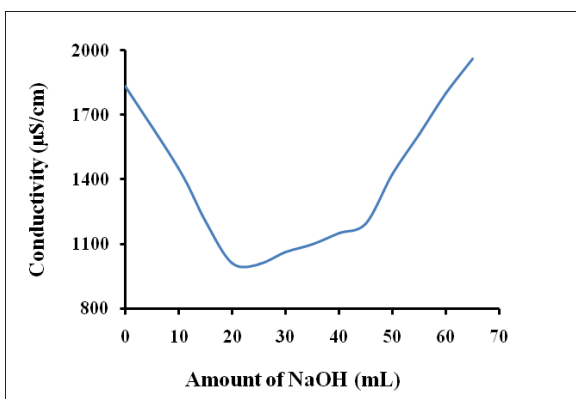


Figure 5: Conductometric titration curve of chitosan.

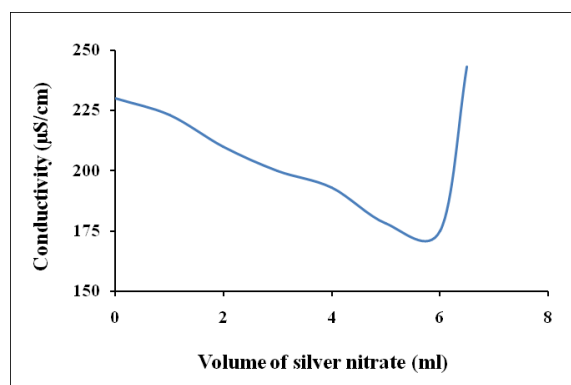


Figure 6: Conductometric titration curve for determination of DQ of HTAChC.

conductivity against the volume of silver nitrate (AgNO_3) which is shown in Figure 6. The amount of AgNO_3 used at the inflection point equals to the amount of Cl^- ions present on the HTAChC. The DQ of HTAChC can be calculated by the following equation:

$$\text{DQ} = \frac{M \times N_{\text{Cl}}}{m_{\text{dry}}}$$

Where, M is the molecular weight (g/mol) of glucosamine repeat unit, N_{Cl} is the number of moles of Cl^- ions in the samples and m_{dry} is the mass of dried sample in grams.

Results and Discussion

Degree of deacetylation of chitosan

The content of free amino groups in the polysaccharide can be determined by degree of deacetylation (DD) which differentiates between chitin and chitosan. This deacetylation process involves the substitution of acetyl groups from the molecular chain of chitin with complete amino group ($-\text{NH}_2$) and the end use of chitosan depends

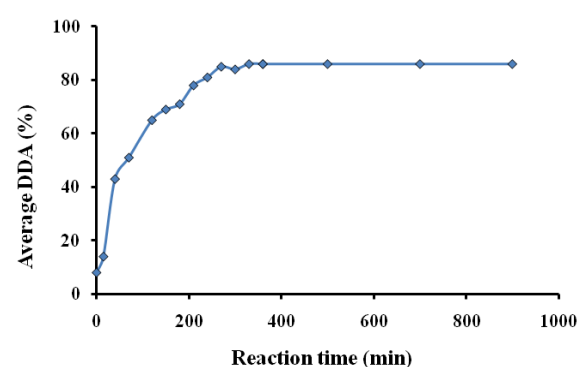


Figure 7: Effect of time on deacetylation percent.

mainly on this high degree chemically reactive amino groups. Since the degree of deacetylation depends mainly on the method of purification and reaction conditions [29], it is therefore essential to determine its degree of deacetylation prior to its end usages. From Figure 7, it is

seen that the degree of deacetylation (DDA) value of chitin was 85% at temperature 80°C, 50% alkaline solution, solid to liquor ratio of 1:50 (w/v) for 4 h refluxing in presence of ethanol.

Moisture content

Moisture content of chitosan, HTAChC and NMA-HTAChC were 10.3%, 22.4% and 18.7% respectively. Moisture absorption capacity of HTAChC is much higher than chitosan because of its high affinity to moisture due to the presence of quaternary amino group and secondary alcoholic group. Moisture absorption capacity of NMA-HTAChC is also higher than chitosan but slightly lower than HTAChC because primary hydroxyl group of chitosan backbone of HTAChC is occupied by NMA in NMA-HTAChC. Moisture content of prepared compounds is shown graphically in Figure 8.

In the present investigation it is observed from Figure 8 that HTAChC and NMA-HTAChC modified fibre showed higher moisture content compared to unmodified fibres. Because HTAChC and NMA-HTAChC provide more hydrophilic group on cellulose fibre backbone which in turn increases the moisture content of modified jute and cotton fibres.

Tensile strength of cellulose fibres

As shown in Figure 9, HTAChC and NMA-HTAChC modified cellulose fibre has more breaking strength than unmodified cellulose fibres. These are due to the modification of cellulose fibres with HTAChC and NMA-HTAChC which cause reduction of crystallinity of cellulose fibre. The improvement in fibre strength of modified cellulose fibre may be attributed to the penetration of modifier particles in fibre pores and crosslinking to the adjacent fibre molecules. It is also clear that NMA-HTAChC has higher fibre strength improving properties compare to HTAChC which is due to better crosslinking activity with cellulose fibre than HTAChC.

Wash resistance of modified jute and cotton fibres

From Table 1, it is seen that, when the modified fibres were washed with distilled water and detergent solution at room temperature there was minor change in weight loss (loss in grafting) whereas when it was washed with distilled water and detergent solution at 40°C and 60°C temperature there were occurred a considerable decreases in weight loss.

This was due to the fact that when fibres were washed at room temperature, only some extra deposition of compounds on fibre surfaces was removed. In case of high washing temperature, loosely bonded substances and impurities deposited on the fibre surface were removed finally resulting some weight loss and decreased the grafting percentage. Loss in grafting percentage in case of NMA-HTAChC modified jute and cotton fibres were comparatively greater than that of HTAChC modified jute and cotton fibres. This is due to the higher solubility of NMA-HTAChC modifiers in water and detergent solution. Also, loss in grafting is slightly higher in case of detergent wash compare to distilled water wash due to the more surface activity of detergent solution.

Washing condition

- Fibre: Liquor=1:50; Time: 30 min.
- Detergent conc.: 0.5% (w/v).

FTIR Spectroscopy

FTIR spectroscopy of the chitosan, HTAChC and NMA-HTAChC shows the evidence of the conversion of chitosan to HTAChC and NMA-HTAChC. Chitin and chitosan can be differentiated by FTIR peak analysis. Chitin shows two strong absorption peaks at 1660 cm^{-1} and 1557 cm^{-1} for C=O stretching and the N-H bending of the secondary amide respectively. In the case of chitosan, peak at 1600 cm^{-1} indicates that most of the secondary amide has been changed to primary amine by the alkaline deacetylation (Figure 10b).

In Figure 10c, two absorption peaks at 1480 cm^{-1} and 1650 cm^{-1} corresponding to the C-H bending of trimethylammonium group and C=O stretch of the secondary amide, respectively in the spectra of HTAChC. It can be mentioned that the H atom of primary amine is successfully replaced by $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ group [30] and Degree of quaternization (DQ) of HTAChC obtained was 0.94 (Table 2).

The IR spectra of the NMA-HTAChC, as shown in Figure 10d, it can be observed that the peaks at 1670 cm^{-1} and 1545 cm^{-1} corresponding to the C=O stretch and N-H bending of the secondary amide in the acrylamidomethyl group, respectively. The double bond content of prepared NMA-HTAChC was calculated as 0.926 (mmol/g NMA-HTAChC).

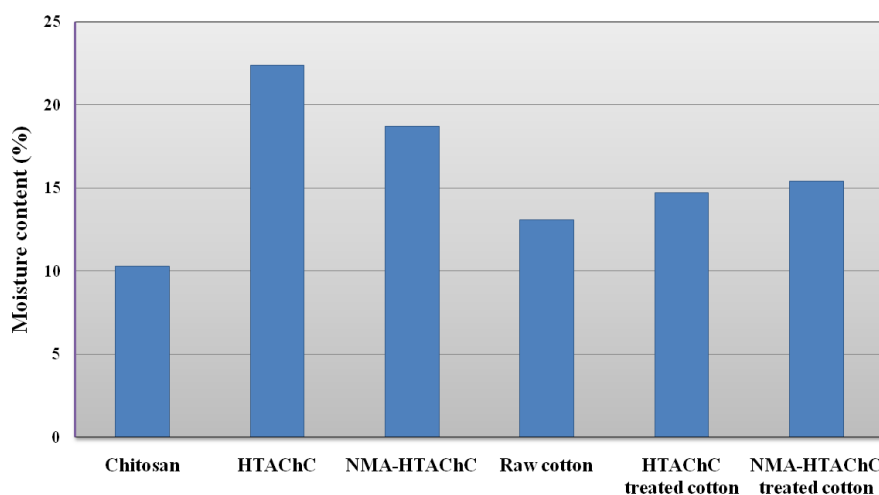
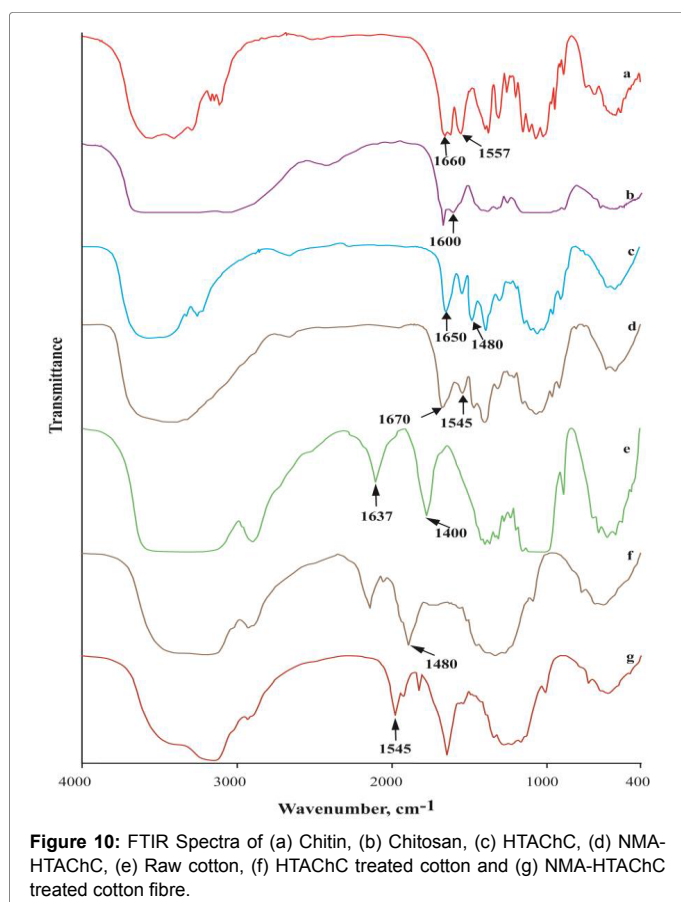
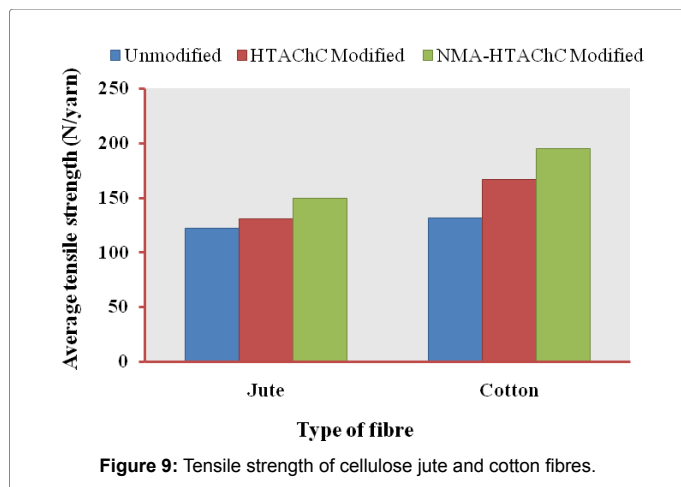


Figure 8: Moisture content of chitosan, HTAChC, NMA-HTAChC, raw cotton, HTAChC treated cotton and NMA-HTAChC treated cotton.



The FTIR spectra of unmodified, HTAChC modified and NMA-HTAChC modified cotton fibres are mostly similar as the adsorption peaks were obtained in the spectra of entire sample except the new additional peak in the modified cotton fibres. The FTIR spectra of modified cellulose fibres show a new peak at 1480 cm^{-1} for HTAChC and 1545 cm^{-1} for NMA-HTAChC which are the evidence of grafting of HTAChC or NMA-HTAChC on cellulose cotton and jute fibre.

Scanning Electron Microscopy Analysis

Surface morphology of unmodified and HTAChC and NMA-HTAChC modified cellulose fibres were studied by scanning electron

Types of modified fibres	Wash temp. °C	Weight loss, %			
		Distilled water		Detergent solution	
		Jute	Cotton	Jute	Cotton
HTAChC	Room	1.23	1.12	1.48	1.31
	40	1.92	1.84	2.06	1.89
	60	2.31	2.24	2.43	2.98
NMA-HTAChC	Room	1.32	1.26	1.73	1.6
	40	2.14	2.09	2.27	2.22
	60	2.83	2.67	3.48	3.19

Table 1: Resistance of modified cellulose fibres to wash with distilled water and detergent solution at different temperatures.

Name of compound	Wave numbers (cm ⁻¹)	Assignment
Chitin	3443	OH hydroxyl group
	3261	NH group-stretching vibration.
	2961, 2933, 2891, 1380	Symmetric or asymmetric CH ₂ stretching vibration
	1660	C=O in amide group (amide I band)
	1557	Vibration of N-H of amide I band
	1314	Vibrations of OH, CH in the ring
	1205, 1261	C-O group.
	1157, 1116, 1074	-C-O-C- in glycosidic linkage
	952, 896, 702	CH ₂ COH group
	561	OH out of plane bending
Chitosan	3251	Vibration of N-H of amide II band
	1600	N-H bending of the primary amine
	1382	-CH ₂ bonding
	1068	-C-O-C- in glycosidic linkage
HTAChC	587	OH out of plane bending
	3400	Increased number -OH hydroxyl group
	1650	C=O group
	1595	N-H bending
NMA-HTAChC	1480	C-H bending of trimethylammonium group
	1670	C=O stretch
	1590	N-H bending
	1545	N-H bending of the secondary amide in the acrylamidomethyl group

Table 2: Assignment of major absorption bands of raw chitin, chitosan and chitosan derivatives.

micrographs (Figure 11). The SEM micrograph shows the fractured surfaces of the untreated cellulose fibres and the smoother surfaces of HTAChC and NMA-HTAChC modified cellulose fibres. The SEM of unmodified cellulose fibres shows the presence of large amounts of micro pores on its surface while few pores are visible on HTAChC and NMA-HTAChC modified cellulose fibre which indicates the incorporation of HTAChC and NMA-HTAChC on cellulose chain of cotton and jute fibres surface.

Thermal Analysis

The Thermo Gravimetric Analysis (TGA) describes the thermal behaviour of a sample. Figure 12 shows the thermal behavior of raw and modified jute and cotton fibres. From the thermograms, necessary thermal information of jute and cotton fibres is enlisted in Table 3. TGA thermogram shows that decomposition paths for unmodified and modified cellulose fibres have three stages of thermal degradation. There is a weight loss in first stage between $100\text{--}120^\circ\text{C}$, due to dehydration of cellulose. In second stage between 200°C and 270°C , rapid weight losses are observed for thermal degradation of the cellulose fibres. In third stage, residual char is formed through weight loss which reaches

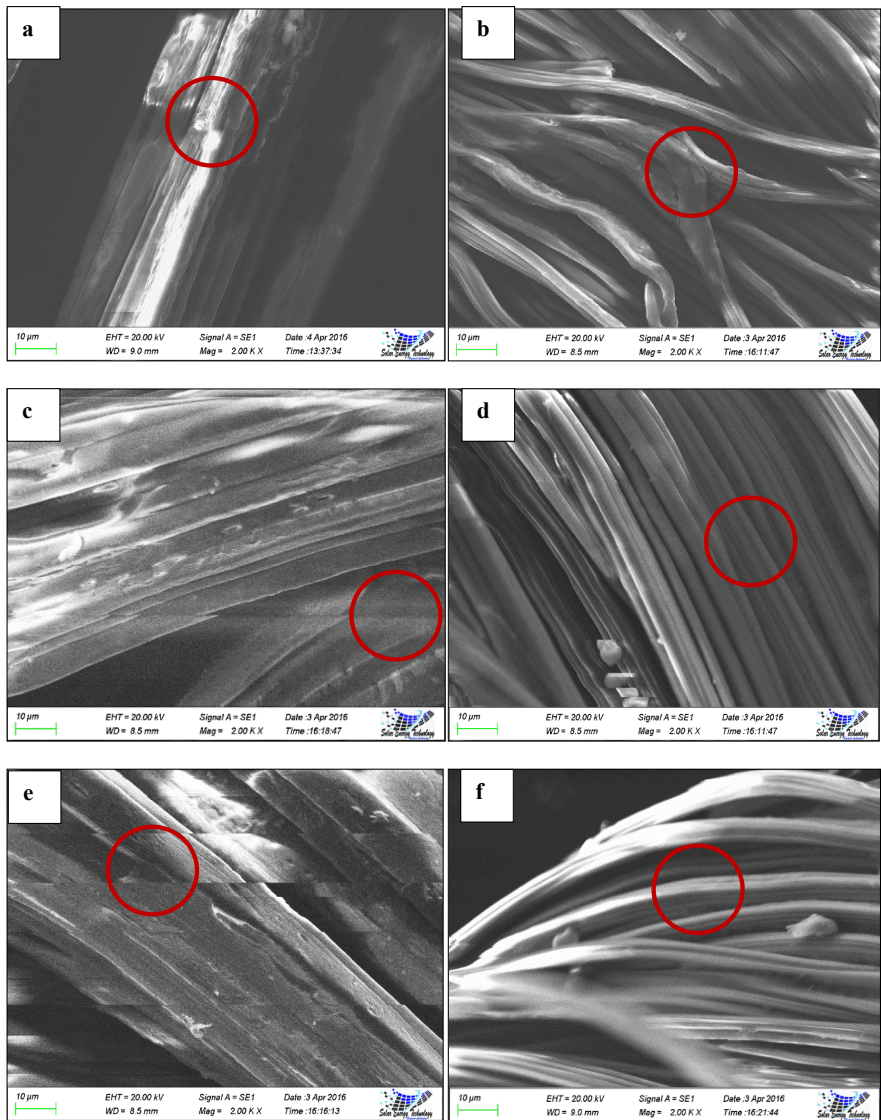


Figure 11: Scanning electron micrograph of cotton and jute fibres:(a) Unmodified jute, (b) Unmodified cotton, (c) HTAChC modified jute, (d) HTAChC modified cotton, (e) NMA- HTAChC modified jute and (f) NMA-HTAChC modified cotton fibres.

Samples	T _i	Char yield at 600°C,	DTG peak maxima temperature, °C	DTA maxima, °C	Nature of DTA peak	DTA peak range, °C
	°X	%				
Unmodified jute	250	5	415	430	Exothermic	420-440
HTAChC modified jute	230	12	340	452	Exothermic	425-465
NMA-HTAChC modified jute	200	6	445	470	Exothermic	445-475
Unmodified cotton	260	9.2	460	480	Exothermic	450-470
HTAChC modified cotton	245	19	460	470	Exothermic	420-520
NMA-HTAChC modified cotton	225	16	450	475	Exothermic	450-470

Table 3: Data calculated from TG, DTG and DTA thermograms of unmodified and modified cellulose jute and cotton fibres.

to be a fixed weight. On the basis of initial decomposition temperature (T_i), the thermal stability of unmodified and modified cellulose fibres shows the following order: unmodified >HTAChC modified >NMA-HTAChC modified.

From DTA curve, a large exothermic peak is observed, due to

oxidative decomposition of cellulose fibre samples, which involves the evolution of CO and CO₂, and formation of carbonaceous residue [31].

In the DTG, two exothermic peaks were observed at 310-350°C and 425-470°C, respectively. The second peak is deeper and sharp than that of the first peak which reveals that weight loss in second stage is higher

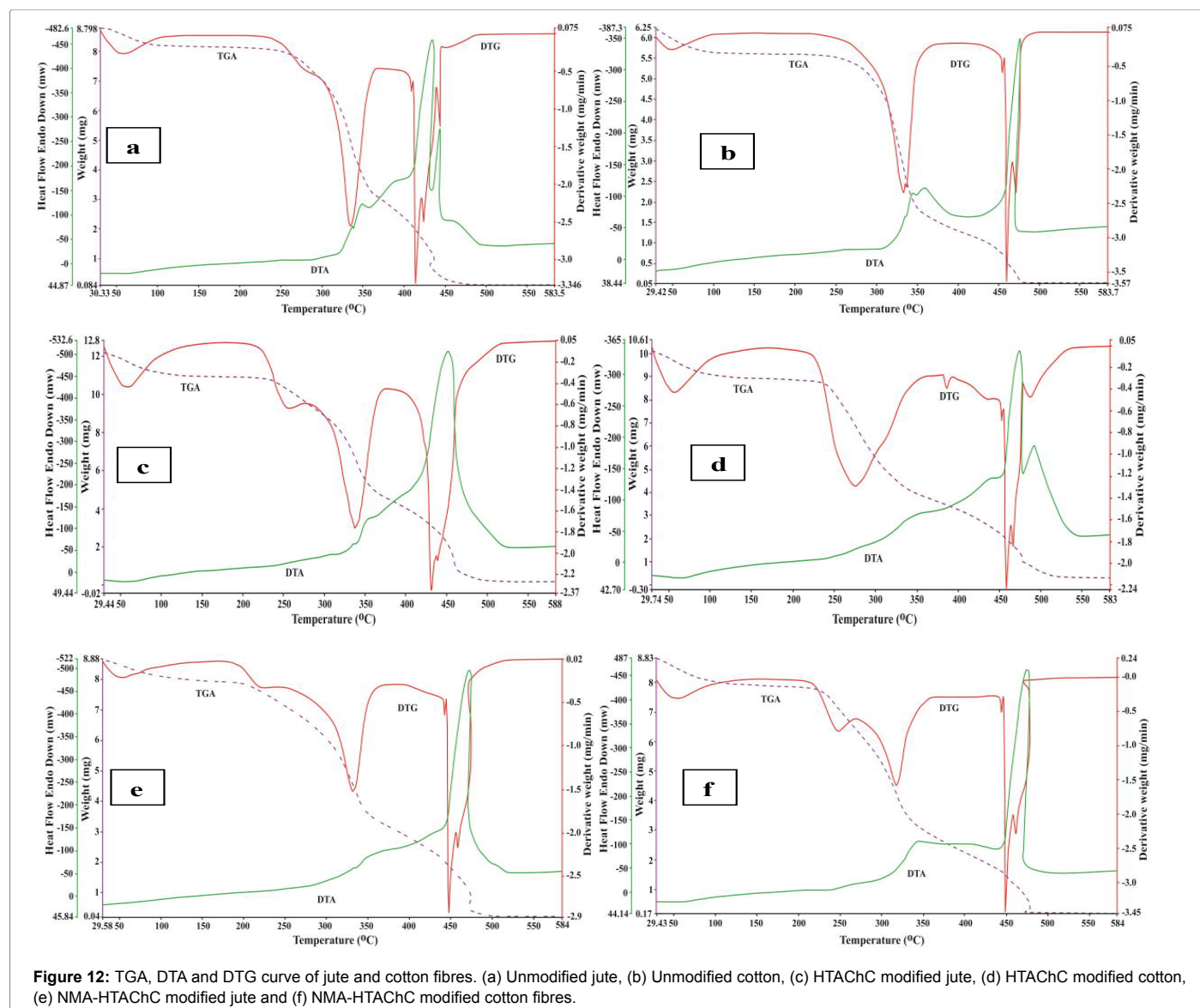


Figure 12: TGA, DTA and DTG curve of jute and cotton fibres. (a) Unmodified jute, (b) Unmodified cotton, (c) HTAChC modified jute, (d) HTAChC modified cotton, (e) NMA-HTAChC modified jute and (f) NMA-HTAChC modified cotton fibres.

Name of dye	Exhaustion, %					
	Jute fibre			Cotton fibre		
	Bleached	HTAChC modified	NMA-HTAChC modified	Bleached	HTAChC modified	NMA-HTAChC modified
Reactive Orange 14	41	47	50	53	57	64
Reactive Brown 10	45	53	59	47	56	60
Direct Orange 31	60	65	71	68	82	84
Direct Yellow 29	53	61	65	59	70	72

Table 4: Dye exhaustion for different dye in dyeing of cellulose fibre.

than first stage. The first stage is connected with depolymerization of cellulose fibre and the second one corresponds to the residual cross-linked degradation of fibre [32].

So, it can be said that the thermal stability of HTAChC and NMA-HTAChC modified fibres are decreased compared to that of unmodified fibres. This could be the result of the incorporation of comparatively lower thermally stable bio-polymer HTAChC and NMA-HTAChC with the cellulose fibres.

Effect of modification on dye exhaustion in dyeing

The unmodified and modified jute and cotton fibres were dyed with both reactive and direct dyes. It is observed from Table 4 that the dye exhaustion by the fibres is higher in case of HTAChC and NMA-HTAChC modified fibres compared to unmodified fibres. The treatment of the fibres with HTAChC and NMA-HTAChC enhanced the dye sites due to their attachment on the cellulose macromolecules

Name of Dye	Washed fibres	HTAChC Modified	NMA-HTAChC Modified
Reactive orange 14	Medium orange	Orange	Orange
Reactive brown 10	Light brown	Brown	Bright brown
Direct orange 31	Orange	Bright orange	Deep orange
Direct yellow 29	Yellow	Deep yellow	Deep yellow

Table 5: Colour of unmodified and modified cellulose fibres.

of cellulose fibres. As a result, the modified fibres absorbed more dye than the unmodified fibres sample.

HTAChC and NMA-HTAChC modified fibres exhibit considerably deep dye colour (Table 5). This could be due to attachment of HTAChC to the cellulose fibre backbone, which helps to increase the functionality as well as reactivity. NMA-HTAChC modified cellulose fibre exhibits comparatively higher dye absorption due to presence of secondary amino group and vinyl group in NMA-HTAChC.

Conclusion

Two water soluble functionalized chitosan derivatives (HTAChC and NMA-HTAChC) were successfully prepared from prawn shell waste via chitin and chitosan. Later prepared HTAChC and NMA-HTAChC were applied to cellulose fibres to evaluate their textile finishing properties. The incorporation of HTAChC and NMA-HTAChC on fibres backbone was confirmed by both FTIR and SEM analysis. The modified cellulose fibres showed improved tensile strength, moisture absorption, wash resistances and dyeability than that of unmodified fibres, whereas thermal stability decreases. The prepared HTAChC and NMA-HTAChC can be successfully used as textile modifier for the improved performance of jute and cotton fibres. The synthesis of HTAChC and NMA-HTAChC for value added environmentally friendly textile modifier and other applications will thus help to manage pollution from prawn shell waste in prawn processing zone.

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References

- Prashanth H, Tharanathan RN (2007) Chitin/chitosan: modifications and their unlimited application potential - An overview. Trends Food Sci Tech 18: 117-31.
- Roberts GAF (2008) Thirty years of progress in chitin and chitosan. Progress on chemistry and application of chitin and its derivatives 13: 7-15.
- Johnson EL, Peniston QP (1982) Utilization of shellfish waste for chitin and chitosan production. In Chemistry and Biochemistry of Marine Food Products. Martin RE, Flick GJ, Hebard CE, Ward DR editors. AVI Publishing: Westport.
- Dodane V, Vilivalam VD (1998) Pharmaceutical applications of chitosan. Pharm Sci Technol Today 1: 246-253.
- Xie W, Xu P, Liu Q (2001) Antioxidant activity of water-soluble chitosan derivatives. Bioorg Med Chem Letters 11: 1699-1701.
- Heller J, Chang AC, Rodd G, Grodsky GM (1990) Release of insulin from pH-sensitive poly (ortho esters). J Control Release 13: 295-302.
- Siegal RA, Firestone BA (1988) pH-dependent equilibrium swelling properties of hydrophobic polyelectrolyte copolymer gels. Macromolecules 21: 3254-3259.
- Northcot KA, Snape I, Scales PJ, Stevens GW (2005) Dewatering behaviour of water treatment sludges associated with contaminated site remediation in Antarctica. Chem Eng Sci 60: 6835-6843.
- Crini G (2005) Recent developments in polysaccharide-based materials used as adsorbents in waste water treatment. Prog Polym Sci 30: 38-70.
- Rinaudo M (2006) Chitin and chitosan: Properties and applications. Prog Polym Sci 31: 603-632.
- Sun LP, Du YM, Yang JH, Shi XW, Li J, et al. (2006) Conversion of crystal structure of the chitin to facilitate preparation of a 6-carboxychitin with moisture absorption retention abilities. Carbohydr Polym 66: 168-175.
- Beysseriat M, Decker EA, Mc Clements DJ (2006) Preliminary study of the influence of dietary fiber on the properties of oil-in-water emulsions passing through an in vitro human digestion model. Food Hydrocolloid 20: 800-809.
- Devlieghere F, Vermeulen A, Debevere J (2004) Chitosan: antimicrobial activity, interactions with food components and applicability as a coating on fruit and vegetables. Food Microbiol 21: 703-714.
- Ham-Pichavant F, Sebe G, Pardon P, Coma V (2005) Fat resistance properties of chitosan-based paper packaging for food application. Carbohydr Polym 61: 259-265.
- Suntornsuk W, Pochanavanich P, Suntornsuk L (2002) Fungal chitosan production on food processing by-products. Process Biochem 37: 727-729.
- Facin BR, Bruna M, Dilmar B, Belfiore LA, Paulino AT (2015) Immobilization and controlled release of beta-galactosidase from chitosan-grafted hydrogels. Food Chem 179: 44-51.
- Garcia-Valdez O, Ramirez-Wong DG, Saldivar-Guerra E, Luna-Barcenas G (2013) Grafting of chitosan with styrene and maleic anhydride via nitroxide-mediated radical polymerization in supercritical carbon dioxide. Macromol Chem Phys 214: 1396-1404.
- Yang Z, Degorce-Dumas JR, Yang H, Guibal E, Li AM, Cheng RS (2014) Flocculation of *Escherichia coli* using a quaternary ammonium salt grafted carboxymethyl chitosan flocculant. Environ Sci Technol 48: 6867-6873.
- Zhang WW, Xiao HN, Qian LY (2014) Beeswax-chitosan emulsion coated paper with enhanced water vapor barrier efficiency. Appl Surf Sci 300: 80-85.
- Kim YH, Choi HM, Yoon JH (1998) Synthesis of a quaternary ammonium derivative of chitosan and its application to a cotton antimicrobial finish. Text Res J 68: 428-434.
- Evans GE, Shore J, Stead CV (1984) Dyeing behaviour of cotton after pretreatment with reactive quaternary compounds. J Soc Dyers Colourists 100: 304-315.
- Alam R, Khan MA, Khan RA, Ghosal S, Mondal, MdlH (2008) Study on the physic-mechanical properties of photo-cured chitosan films with oligomer and acrylate monomer. J Polym Environ 16: 213-219.
- Islam M, Mondal MdlH, Hoque A (2015) Synthesis of chitosan derivative for an eco-friendly cotton fibre modifier with enhanced physico-chemical characteristics. In Cellulose and Cellulose Composites Mondal MdlH (ed), Nova Science Publishers, Inc., New York 81.
- Farouqui FI, Mondal Mdl H (1989) Scouring and bleaching of jute fibre in relation to its strength. Rajshahi University Studies, Bangladesh 17: 1-17.
- Mondal MdlH, Farouqui FI, Sheikh RK, Hoque MA (2007) Physico-chemical characteristics of jute fiber grafted with nitrile monomer. Cellul Chem Technol 41: 23-28.
- Singha AS, Thakur VK (2009) Synthesis and characterization of silane treated grewia optiva fibres. Intern J Polym Anal Charact 14: 301-321.
- Raymond L, Morin FG, Marchessault RH (1993) Degree of deacetylation of chitosan using conductometric titration and solid-state NMR. Carbohydr Res 246: 331-336.
- Lang GH, Wendel, Konard E (1990) Process for making quaternary chitosan derivatives for cosmetic agents. US Patent 4: 921- 949.
- Li J, Revol JF, Marchessault RH (1997) Effect of degree of deacetylation of chitin on properties of chitin crystallites. J Appl Polym Sci 65: 373-380.
- Lu YH, Cheng DH, Lu S, Huang F (2014) Preparation of quaternary ammonium salt of chitosan nanoparticles and their textile properties on Antheraea pernyi silk modification. Text Res J 84: 2115-2124.
- Muralidhara KS, Sreenivasan S (2010) Thermal degradation and burning behaviour of cellulose based and cellulose-silk blended upholstery fabrics. J Sci Ind Res 69: 879-885.
- Lopez FA, Merce ALR, Alguacil FJ, Lopez-Delgado A (2008) A kinetic study on the thermal behaviour of chitosan. J Therm Anal Cal 91: 633-639.