CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF VARYING MOLECULAR WEIGHT CHITOSANS AND THEIR APPLICATION ON COTTON FABRIC

2.1 INTRODUCTION

Chitosan is polycationic biopolymer that exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non toxic, total biodegradable as well as film formation, fiber formation, hydrogel formation etc properties. These unique properties of chitosan make it suitable for a number of textile applications. The application of chitosan in textiles can be categorized into two main domains namely in the production of fibres and in textile wet processing that includes dyeing and finishing.

The linear structure of chitosan is mainly responsible for the fibre forming property. Chitosan fibres are produced by wet spinning method. In earlier approach (1980), Chitosan was dissolved in acetic acid to give a solution of 3% w/v and then extruded through the spinneret into a caustic coagulation bath (0.5%) to obtain a regenerated fibre. The fibre strength, however, was very poor (2.2 gpd). To obtain the good fibre out of chitosan a homogeneous solution with maximum polymer to solvent ratio is required apart from non gelling tendency. Several attempts by making suitable modifications in spin dope composition and coagulation bath are reviewed in literature [1]. Spin dope composition can be modified by using urea along with acetic acid or formic acid. Extrusion of chitosan dope into a coagulating bath containing sodium acetate, sodium hydroxide, sodium dodecyl sulphate or methanol in aqueous medium was found to improve the fibre strength by reaching the tenacity to 3.8 g/d.

Chitosan fibres find use in the production of textiles having antimicrobial, antithrombogenic, haemostatic, deodorizing, moisture controlling, and non allergenic properties which are intern used as bandages for wound- dressing, as sutures, as perfume releasing fabrics, carriers to for active drugs and artificial limbs [1-3]. Hemostatic activity

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of chitosan is high when used as a high molecular weight solid. Therefore, this has been explored as a modulator of wound healing. It has been found that chitosan has the ability to form coagulum on contact with erythrocytes, defibrinated blood and washed red blood cells and therefore the bandages for wound dressing were found to be effective in regenerating skin tissue of wound area. Recently, chitosan has been proposed to serve as a non protein matrix for three dimensional tissue growths. Chitosan provides the biological primer for cell tissue proliferation. The glucosaminoglycan constitutes the wound tissue play an important role in giving structure and strength to newly formed collagen in the granulating tissue of the healing wound. Chitosan provides amino sugars which in turn can be made available to the fibroblasts that proliferate under the action of interleukin-1 for incorporation into hyaluronate and glycoaminoglycans, thus guiding ordered deposition of collagen leading to wound healing [4-6].Introduction of carboxymethyl groups on to chitosan fibres imparts typical gelling property that can absorb large quantity of fluid. These fibres were found to be more effective the normal chitosan fibres as a wound dressing material. By holding water inside the fibre structure, such wound dressings can limit the lateral spreading of wound exudates, reduce wound maceration, and generally improve the quality of healing process [7]. Chitosan fibres can be converted back to chitin fibres by acetylation reaction with acetic anhydride. These fibres find application as surgical suture, which has enough strength for clinical uses. The suture is digestible in the tissues by lysozyme and chitinase [2]. A composite material of chitin/chitosan and cellulose are produced by mixing powder chitin/chitosan with viscose pulp and then wet spun, known as crabyon (Omikenshi). These fibers have high moisture keeping property than cellulosic fibres and have dyeability towards direct and reactive dyes. These fibres are used as textile materials for under wears, socks, etc as these keep skin from drying. At the same time, these give velvet touch and no irritation to skin .Therefore; clothes made up of these fibres are excellent for babies and old aged people, who have weak and sensitive skin [8]. Similar type of fibre exhibiting deodorant property was produced by a Kokai Tokkyo Koh (Japan), which is useful for clothing, beddings, interior materials, medical care materials, curtains and carpets [9].

Applications of chitosan in textile processing domain are widely known. Over last few years, the usage of chlorine containing bleaching compounds has become limited due to the formation of highly toxic chlorinated organic byproducts (AOX). Therefore chorine free bleaching agents like peracetic acid have gained attention as an alternative ecofriendly bleaching agent [10]. Hashem et al. [11] used chitosan-Mo and chitosan-Co complexes for the activation of peracetic acid and were able to obtain satisfactory results at low temperature of 70 °C. Replacement of hydrogen peroxide with other oxidizing agents, namely ammonium persulphate and potassium bromate was not successful. In contrast, the perborate did succeed but with lower but with lower efficiency when compared with hydrogen peroxide.

Cotton and other cellulosic fibres, conventionally, are dyed with direct, reactive, vat, reactive, azoic etc dyes, which are anionic in nature. Cotton also acquires negative surface charge when immersed in dye baths of above dyes leading to repelling action to them. To dissipate this -ve surface charge and to facilitate the dyeing, large amount of electrolytes such as common salt or Glauber's salt are added into the dye bath. These electrolytes and unexhausted dyes add to the pollution load when discharged through effluents. Thus attempts have been made to adopt salt free and alkali free dyeing by cationization of cotton by treatment with glycidyl trimethyl ammonium chloride, *N, N*-dimethyl azetidinium chloride, *N*-methylol acrylamide, chloropropionyl chloride etc. However, the question of ecological aspects arises here too [12]. Pretreatment of chitosan, due to its polycationic nature, has found to improve the direct dye uptake significantly and also reduce the salt consumption [6, 13]. Bandyopadhyay et al. [14] examined the effect of chitosan treatment on reactive dyeing of cotton. They reported decrease in salt requirement by 50% to produce a comparable shade to that of untreated fabric. The chitosan-treated fabric also showed improvement in fixation of reactive dyes. This result was explained by the increased exhaustion of negatively charged reactive dyes to the cotton, whose negative potential at the fiber surface was suppressed by the cationic chitosan treatment. Consequently, when alkali was added to the dye bath, a substantial quantity of dye was available for the reaction with cotton. It was also suggested that the amino groups of chitosan reacted with the reactive group in the dye and the fixation was further improved. The chitosan-treated fabric showed comparable color fastness properties to the untreated fabric. Lim and Hudson [15] used fibre reactive chitosan derivative containing quaternary ammonium group *O*-acrylamidomethyl-*N*-[(2-hydroxy

3-trimethylammonium) propyl] chitosan chloride (NMA-HTCC) for the treatment of cotton. They reported higher colour yield by cotton fabric when dyed with direct and reactive dyes without using salt. Kavitha et al. [16] studied the effect of chitosan treatment on natural dyeing of cotton namely turmeric. They reported increased tensile strength, flexural rigidity and shear strength. Cotton yarn coated with chitosan was found to be darker compared to uncoated yarn while dyeing for the same shade percentage. They reported the dyed yarn coated exhibited excellent activity against bacteria.

Often cotton fibres show small lightly colored or white spots due to presence of immature cotton fibers known as neps. Metha and Combs [17] evaluated nep coverage in the direct dyeing of cotton by the pretreatment of cotton with chitosan. The chitosan pretreatment was done by exhaust method. The reported by addition of sodium sulfate (Na_2SO_4) during the exhaust process improved the absorption of chitosan on cotton and fully covered the neps. The neps coverage was only partial when chitosan treatment was done in absence of salt. Further, the pretreatment was more effective for neps coverage in direct dyeing than reactive dyeing of cotton. Rippon [18] postulated that the affinity of chitosan to cotton would be by Van der Waals' forces due to the similar structures of chitosan and cotton. Another possibility mentioned for the binding chitosan to cellulose was cross linking by formation of Schiff base between cellulose's reducing end (−CHO) and the amino group of chitosan. In addition to the two possible bindings suggested by the authors, hydrogen bonding should also play an important role. Houshyar and Amirshahi [19] observed that the chitosan pretreatment increases the exhaustion of reactive dyes and the maximum dye up take was achieved by the fabric on which chitosan was applied by pad-dry cure method.

Though the literature does not explore the possible use of chitosan as pigment print thickener, it appears to be a good candidate, especially with the recent worldwide growth in the popularity of textile pigment printing [20-22]. They showed the prints of satisfactory colour fastness to rubbing, washing and light, however, the major problems were the poor colour value and undesired stiffness of the printed fabric. Tiwari and Gharia [23] attempted to use chitosan as a thickener in printing paste using various organic acids such as acetic, formic and oxalic acid respectively. They observed the chitosan unsuitable for print paste due very low viscosity and produce a high solid paste.

The rheology of pastes was reported to be pseudoplastic. Performance of the prints with respect to K/S, wash fastness, crock fastness and hand were observed to be unsatisfactory. Yuen et al.[24] studied the possibility of chitosan in preparing the pretreatment print paste for textile ink-jet printing. They employed a two bath method for the pretreatment of fabric with chitosan paste. The fabric was first treated with acidic chitosan solution by pad-dry cure (170 ^{0}C) method and then, in second stage, with alkaline bath containing sodium bicarbonate and urea. The two bath treated fabric was reported to give better colour yield when compared with chitosan treated and alginate treated fabrics.

Cotton fabric has a tendency for wrinkling when it is subject to severe bending, which is attributed to the presence of free hydroxyl groups in the fibre molecules. The creasing problem is minimized by cross linking these free hydroxyl groups on adjacent molecules in the fibre using a suitable cross linking agent such as *N*-methylol compounds (UF, DMDHEU etc resins). However, these finishing agents suffer from one serious drawback of release of toxic free formaldehyde [25, 26]. As an alternative, on formaldehyde cross linking agents such as citric acid, butane tetra carboxylic acids (BTCA) etc are recommended. Among these, BTCA is most effective cross linking agent; but the cost is very high. Citric acid, although cheaper, is less effective and has drawback of yellowing problem due to the formation of unsaturated polycarboxylic acid (due to dehydration of citric acid). To counteract this yellowness, additives such as hydroxyethyl amines, borates or polyethylene glycols to citric acid bath are recommended. However, the process is still less effective [27]. The crease recovery power of citric acid can be improved satisfactorily by the incorporation of chitosan in presence of sodium hypophosphite monohydrate to the citric acid bath as reported by Waly and Okeil [28]. Here, the esterification reaction not only occurs between citric acid and cellulose but also between citric acid and hydroxyl groups of chitosan and the free carboxylic groups can also react with amino groups of chitosan by salt linkages. Tahlawy [29] studied the effect of chitosan in the finishing of cotton with citric acid in presence of sodium hypophosphite catalyst. He reported a recovery of losses (due to citric acid treatment) in dye uptake and tensile strength, and improved wrinkle recovery by the addition of chitosan in citric acid bath. The whiteness index, however, was deteriorated.

Authors proposed citric acid reacts with amino and hydroxyl groups of chitosan and hydroxyl groups and cotton through to form ester crosslinking or an inter-ionic attraction. Similar works were reported by several workers [30-32]. It is well known that the amino groups of chitosan readily react with aldehyde groups to form Schiff's base. This property of chitosan was employed by Bhattacharyya et al. [33] to scavenge free formaldehyde released from DMDHEU-finished cotton fabrics. They reported that the use of chitosan as an additive in DMDHEU finishing after dyeing was more effective in reduction of formaldehyde release as compared to the fabric which is chitosan-pretreated, dyed, and then DMDHEU-finished. The authors indicated that this result might be due to the blocking of the amino groups of chitosan by dye molecules on subsequent dyeing in the case of chitosan-pretreated cotton, and as a result, reduced reactions between chitosan and formaldehyde.

A major route towards the development of flame retardant cotton textiles has been the introduction of flame retardant materials containing nitrogen (N) and phosphorus (P) within the molecular structure of cellulose. Resin finishing with organophosphorus compounds such as THPC, THPC-APO, *N*- methylol dimethyl phosphonopropionamide seem to be most prevailing and reliable methods, but such treatments cause drop in tensile strength and skin irritation due to the liberation of formaldehyde [34]. Treatment of cellulosic based textiles with sodium stannate/phosphate to impart flame retardency is becoming one of the most interesting areas of research due to its non toxic, high durability, economically favourable, white colour and aesthetic properties [35]. Tahlawy et al.[36] incorporated chitosan in the phosphorylation bath as a nitrogen source. They reported that incorporation of 1% chitosan could reduce sodium stannate concentration to the one third of the amount that is used in the conventional process and hence the harsh feel of stannate was reduced. Thermogravimetric analysis of the treated fabric showed an increase in the residual percent of the fabric and decrease in both thermal degradation onset point (TDOP) and maximum degradation rate points as a function of stannate concentration. Increasing diammonium hydrogen phosphate from 2 to 10% in the finishing bath showed an increase in residue at 500 ^{0}C to 39.24%.

Chitosan and its derivatives exhibit good to excellent antibacterial and antifungal properties. The degree of deacetylation (DAC), molecular weight and concentration of chitosan influence the antimicrobial activity [1]. Seong et al. [37] reported chito-oligosaccharide (DP 3 and 10) found to exhibit good antimicrobial activity and durability to washing without the need of crosslinking agent. The polycationic nature of chitosan is mainly responsible the inhibition of bacterial and fungal growth. Fang et al. [38] reported that the chitosan inhibited growth of *Aspergillus niger* and induced considerable leakage of UV-absorbing and proteinaceous materials from it at pH 4.8 which was not induced at pH 7.6. Similarly, Tsai and Su [39] observed the chitosan-induced leakage of glucose and lactate dehydrogenase from *E. coli* cells and suggested that the death of cells resulted from the interaction between chitosan and the *E. coli* cell. The maximum antimicrobial activity exhibited by chitosan at acidic pH is also reported by other workers [40, 41]. The early work indicated that the antimicrobial effect was potent against a range of microbes, but the finishing was not durable. To improve durability, chitosan has been crosslinked to cotton using chemicals such as dimethylol dihydroxy ethylene urea (DMDHEU), 1,2,3,4-butane tetra carboxylic acid, citric acid or glutaric dialdehyde [30, 42]. These chemicals, some of which are used in durable press finishing of cotton, crosslink chitosan to cotton through hydroxyl groups. Ye et al.[43, 44] synthesized nanoscale core-shell particles of poly (n-butyl acrylate) core and chitosan shells and applied them to cotton fabric in a pad-dry -cure process. The antibacterial activity was maintained at over 90% reduction levels after 50 washes.

Chitosan has several beneficial applications in wool processing. One of the undesired properties of wool fibers is felting, which is the process of progressive entanglement of fibers under mechanical action in the presence of water i.e. directional frictional effect. The felting shrinkage results from the interlocking and hooking of contingent fibers due to the scales on the wool fibers [45, 46]. The scaly structure and the covalently bound fatty acids and the high amount of disulphide bridges make the outer wool surface (cuticle) highly hydrophobic and hence the diffusion of hydrophilic dyes and chemicals at and into the fibres is thus hindered [42]. Treatment of wool with chitosan has been found to reduce the felting problem. The bio-adhesive and cationic nature of chitosan enables it to form a strongly adhered film on individual fibres and prevent their entanglements [20]. Julià et al. [47] reported the peroxide pretreatment (alkaline or acidic) or oxidative plasma treatment could create new anionic groups such as sulphonate and carboxylate which can improve the wettability of wool fibre and hence the binding power of chitosan. In another study of Julià's research group [48], they examined the effect of chitosan MW on the shrink-resistance of H_2O_2 pretreated (at pH 9.0) wool fabrics. The higher the molecular weight was, the greater the shrink resistance. However, such degradative treatments lead to considerable weight loss and damage to the fibre. Treatment of wool with a surfactant containing anionic groups can lead to higher pick up of chitosan causing no damage to the fibre. A combination of controlled enzymatic treatment followed by chitosan treatment can also give satisfactory antifelting effect. Further, these treatments have also shown increased shrink resistance and dyeability of wool towards reactive dyes [49]. Erpa et al. [50] reported the enhanced shrink resistance when air plasma treated wool is treated with chitosan. Jeong et al. [51] investigated the effect of chitosan treatment on changes in mechanical properties of wool due to pressure decatizing. They reported that the chitosan treatment increased the bending rigidity of fabric. The shear rigidity was also found to be increased but the tensile properties and frictional coefficient decreased. Okeil and Hakeim [52] conducted an experiment to give a pretreatment of chitosan to wool fabric to increase metal binding during the mordanting process with copper sulphate. The pretreated mordanted wool samples were successfully printed with natural dye, lawsone. Radetic et al. [53] investigated the possibility of improving the sorption of acid dyes from waste water using non woven material based on recycled wool. The woolen material was treated with low temperature air plasma and chitosan. These treatments were found to introduce new favourable functional groups and increased the active surface area. They reported the remarkably improved sorption properties of recycled wool for acid dyes for chitosan and plasma + chitosan treatment. Park et al.[54] investigated the antimicrobial and deodorant activities of chitosan treated wool fabric showed the chitosan of DAC above 70% good antibacterial and deodorant activity regardless of the molecular weight of chitosan.

Among synthetic fibres, polyester exhibits excellent properties such as elastic recovery, dimensional stability and blending compatibility with other fibres. However, polyester suffers from one serious drawback of hydrophobicity and consequently the static charge built-up problem. This static electricity is mostly responsible for dust/dirt attraction, sticking of clothes to human skin and uncomfortable feel, overlapping of fabric on roller at plaiter end of stenter during heat setting process, malfunctioning of electric devices, sparks and ignition of its materials etc. To dissipate static charges, the fibre surface is coated with an antistatic agent, which is mostly synthetic hydrophilic resins, by simple pad-dry cure method. However, the effect is not durable [25]. An ecofriendly and durable antistatic finish can be obtained by the treatment of polyester with chitosan. Chitosan has the advantage that it shows high moisture regain even in low relative humidity and does not swell much in water. The finish is more stable on polyester that has under gone a caustic reduction treatment. Eom [55] treated polyester with chitosan in presence of malonic acid as a crosslinking agent between amino groups of chitosan and hydroxyl groups of polyester. Halim et al. [56] reported improved water uptake capacity of polyester and polyester/cotton blended fabrics by chitosan and monochlorotriazinyl -β-cyclodextrin treatments. They reported increased electrical conductivity and antistatic properties of finished fabrics.

In order to understand various properties of chitosan, different molecular weight chitosan derivatives were synthesized and applied on cotton. The present chapter deals with the synthesis and characterization of chitosans of varying molecular weights, synthesized by hydrolytic degradation of high molecular weight chitosan using nitrous acid and subsequent applications of these chitosans to cotton fabrics. The molecular weights of chitosans were determined viscometrically using Ubbelohde capillary viscometer and Mark-Houwink equation. The viscosity behaviour of the synthesized chitosans was studied in presence and absence of electrolyte. The characterization of varying molecular weight chitosans was performed by FTIR analysis. The degree of deacetylation (DAC) was verified by ^{1}HNMR spectrum and elemental analysis.

The effects of applications of chitosan on dyeing and finishing properties of cotton were analyzed. Chitosans of varying molecular weights and concentrations were applied to cotton fabric by conventional pad-dry cure method. The surface morphology of treated fabric was examined under scanning electron microscope (SEM). Effect of such treatments on physical properties like appearance (in terms of whiteness, yellowness and brightness), stiffness, tenacity and water absorbency was evaluated. The chitosan was applied before and after dyeing of cotton, with direct dye and its effect on dyeing properties was examined. The effect of chitosan pre- treatment on the dyeability towards acid dyes was also investigated. This biopolymer was used as a finishing agent with an intension to incorporate crease resistant property to cotton. The effect was compared with the commercially available wrinkle resistant agents and also examined its compatibility with them. The effect of different molecular weight chitosan treatment on antimicrobial properties was also evaluated using soil burial test as recommended by AATCC Test Method 30-2004.The work was further extended to the application of chitosan to cotton fabric by pad-dry-alkali treatment process.

2.2. MATERIALS AND METHODS

2.2.1 Fabric

100% cotton fabric (warp and weft count 40s, ends/in 142, picks/in 72 and fabric density: 125 g/m^2), at ready for dyeing stage, was procured from Mafatlal Industries Ltd, Nadiad, Gujarat State. All preparatory processes such as desizing, scouring, bleaching, mercerization etc were given in factory itself.

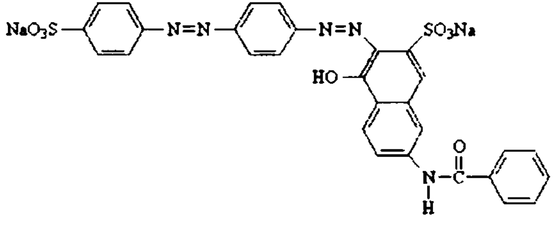
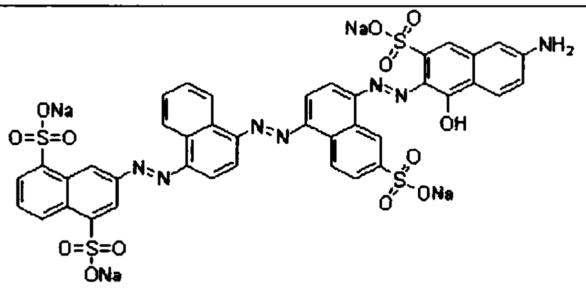
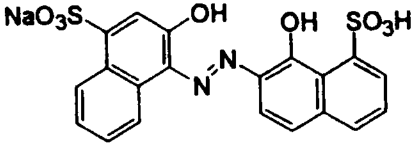
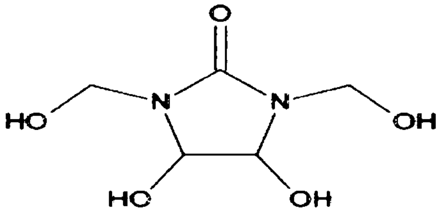
2.2.2 Dyes and chemicals

The details of various dyes and chemicals employed in present research investigation are given in Table 2.1. Other chemicals like acetic acid (CH_3COOH), sodium acetate (CH_3COONa), acetone (CH_3COCH_3), methyl alcohol(CH_3OH), sodium iodide (NaI), sodium hydroxide (NaOH), soda ash/sodium carbonate (Na_2CO_3), sodium sulphate (Na_2SO_4), sodium nitrite ($NaNO_2$), magnessium chloride ($MgCl_2$) etc used were of analytical grade obtained Qualikem Fine Chemicals Pvt Ltd, Vadodara. Anionic detergent (Ezee) was obtained from Godrej India Ltd. Double distilled water was employed for all synthesis and analytical purposes.

2.2.3 Purification of chitosan

Chitosan (1g) was dissolved in acetic acid solution (1.5 ml/L) using magnetic stirrer. The solution was filtered through filter fabric (mesh 128) to remove insoluble impurities. The filtrate was neutralized with sodium hydroxide solution to precipitate out the chitosan. The recovered chitosan was washed repeatedly with distilled water till neutral pH and then filtered. The precipitate was dewatered by treatment with methanol, filtered and washed with acetone 3-4 times and then oven dried at 60 ^{0}C and stored in refrigerator.

Table 2.1 Specifications of various dyes and chemicals

Sr no	Name and Supplier	Specifications
1.	C.I.Direct Red 81 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt. 675.6
2.	C.I.Direct Blue 71 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 1029.9
3.	C.I. Acid Blue 158 Colourtex Industries Ltd, Gujarat State, India.	 • Mol wt 495.45
6.	Chitosan • CHT MC (Marine Chemicals, Cochin, Kerala) • CHT (Mahtani Chitosan Pvt. Ltd., Veraval, Gujarat)	DAC 89.03%; Molecular weight 654,127; Viscosity 180 cPs, DAC 90%; Molecular weight 135,839; Viscosity 22 cPs.
7.	DMDHEU Mafatlal Industries Ltd, Nadiad, Gujarat State	Grade: Commercial, Active content: 40%, Chemical Formula: 

2.2.4 Synthesis of low molecular weight chitosan

Chitosans of different molecular weights were prepared by nitrous acid depolymerization method. A 2 % solution of chitosan in acetic acid (15 ml/L) and sodium acetate (10 g/L) was prepared. Predissolved dilute solution required amount of sodium nitrite was then added gradually to chitosan solution and stirred for two hrs at 30°C to get desired viscosity level. The depolymerized chitosan was then precipitated out by caustic solution and washed to neutral pH with distilled water and then filtered. The precipitate was dewatered by treatment with methanol, filtered and washed with acetone 3-4 times and then oven dried at 60 ^{0}C and stored in refrigerator.Different grades of low molecular chitosan so prepared are listed in Table 2.8.

2.2.5 Fabric treatment with chitosan

Separate solutions of different molecular weight chitosan derivatives were made in solution containing acetic acid 15ml/L and sodium acetate 10 g/L and applied to fabric on a laboratory padding mangle (Model -PM0060388, R. B. Electronics & Engineering Pvt Ltd, Mumbai) with wet pick-up of 70% by two dip- two nip method (Mangle Pressure: 20 psi, Speed: 3 m/min). After drying the fabric samples were cured in oven at 150 ^{0}C for 4 min. The samples were then washed in the following sequence:

Hot wash (Twice) [85 ^{0}C /20mins] → Alkali wash [Soda ash 1 g/L, MLR 1:50] → Hot wash → cold wash →Dry.

2.2.6 Application of chitosan by pad-dry-alkali process

Cotton fabric was soaked for 30 minutes in chitosan solution prepared with solution containing acetic acid 15ml/L and sodium acetate 10 g/L. The fabric was then passed through a laboratory padding mangle (Model-PM0060388, R. B. Electronics & Engineering Pvt Ltd, Mumbai) with wet pick-up of 70% by two dip- two nip method (mangle pressure 20 psi, speed 3 m/min) and air dried. The sample was then dipped in sodium hydroxide solution (1 g/L) for 15 minutes, washed thoroughly until neutral pH, dried and hot pressed.

2.2.7 Dyeing with direct dyes

The cotton fabric was dyed with direct dye (1% o.w.m.) in presence of Glauber's salt (20% o.w.m.) and soda ash (5% o.w.m.) at pH 10.9 and temperature 90 ^{0}C for 60 minutes on water bath. The material- to- liquor ratio was maintained at 1:40. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed.

The dyed samples were evaluated for colour strength in terms of K/S values on computer colour matching system namely Spectroscan 5100A (Premier Colorscan, Mumbai, Maharastra, India) using Kubelka-Munk equation (2.1). The readings were taken for the average of four scans.

$$K/S=\frac{(1-R)^2}{2R} \tag{2.1}$$

Where, K is absorption coefficient, S is scattering coefficient and R is reflectance.

The washing fastness of dyed samples was evaluated according to ISO1. The test was carried out in Launder-o-meter (R.B. Electronics, Vapi, Gujarat). The dyed specimen (10 X 4 cm), sandwiched between undyed cuttings of same material, was treated with detergent solution containing: detergent (Ezee detergent, Godrej) 0.5 % w/v at 40 ^{0}C for 30 minutes. The material- to- liquor ratio was maintained at 1:40. The sample was taken out, rinsed, air dried and hot pressed. The fastness ratings were assessed using SDC grey scale for change in colour (ISO 105A02, 1993: BS EN 20105 A02, 1995).

The rubbing fastness of dyed samples was determined according to AATCC test method 8-2005.The dyed test specimen was placed on the base of the crockmeter (Paramount crockmeter) along the warp. Rubbing was carried out, to and fro, along a straight line 10 cm long, 10 times and for 10 sec with rubbing finger (under 900g wt) clamped with dry white cotton cloth. Staining was assessed by comparing with grey scale for assessing staining (ISO 105A03, 1993: BS EN 20105 A03, 1995).

2.2.8 Dyeing with acid dye

The fabric sample was dyed with acid dye (2% o.w.m.) at 90 ^{0}C for 60 minutes from a dye bath containing acetic acid (1 ml/L) at pH 3.8. The dyed sample was then rinsed with cold water, air dried and hot pressed. The dye up take was evaluated in terms of K/S values using equation 2.1.

2.2.9 Determination of tenacity

The tenacity and elongation of treated and untreated cotton fibres were measured on Stelometer (SITRA, Coimbatore, India). The breaking load (kg) and elongation at break were obtained directly from scale. The samples were then collected and weighed. The tenacity (average of 5 readings) was calculated using following formula.

$$\text{Tenacity (g/tex)} = \frac{\text{Breaking Load (kgs)} \times 1.5 \times 10}{\text{Sample Weight (mg)}} \qquad \textbf{(2.2)}$$

Sample Length = 1.5 cm

2.2.10 Determination of viscosity

The molecular weight and viscosity behaviour of chitosan was determined using Ubbelohde capillary viscometer (No 1A) at 30 ^{0}C having flow time for distilled water, T_0=15.57 seconds. Chitosan solutions of different concentrations in 0.25M acetic acid and 0.25M sodium acetate were prepared. During preparation, all the solutions were magnetically stirred for 1 hour to ensure proper dissolution of chitosan and were filtered using Whatman filter paper no 4. The flow time of chitosan solutions at different concentrations and of the solvent was recorded in triplicate and the average value was calculated. The intrinsic viscosity $[\eta]$ was calculated graphically by extrapolating the curve of reduced viscosity Vs concentration to zero concentration. The molecular weight was then calculated by using Mark-Houwink equation (2.5) [57].

2.2.11 FTIR analysis

FTIR of chitosan samples were taken on a Thermo Nicolet iS10 Smart ITR spectrophotometer (Thermo Fisher Scientific, USA), equipped with an OMNIC-Software, a DTGS detector, and a Ge-on-KBr beamsplitter (4000–500 cm^{-1}). The FT-IR ATR spectra (32 scans, 4 cm^{-1} resolution) were recorded using a single reflection horizontal ATR accessory with a spherical ZnSe crystal fixed at an incident angle of 45°. A sample with a 2-mm diameter was measured.

2.2.12 ^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra of chitosan in D2O were obtained by using a Bruker Avance 400 spectrometer (USA), at a resonance frequency of 400 MHz using Topspin1.3 software. The ^{1}H-NMR spectra were performed at a temperature of 25 °C. Test was performed at Dept. of Chemistry, S.P. University, Vallabh Vidyanagar, Gujarat.

2.2.13 Elemental analysis

The carbon, hydrogen and nitrogen content of chitosan samples were estimated by using CHN/S/O analyzer Perkin Elmer, Series II, 2400. Test was performed at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat.

2.2.14 Scanning electron microscopy

Treated and untreated fabric samples were fixed on carbon coated aluminium sheets and then were observed under scanning electron microscope (Model JSM5610LV, version 1.0. Joel, Japan) in vacuum. Test was performed at Dept of Metallurgy, Feculty of Tech and Engg, Vadodara, Gujarat.

2.2.15 Evaluation of indices

The samples were evaluated on Spectroscan 5100A (Premier Colorscan, Mumbai, India) for whiteness index (WI) (10 deg/D65/Hunterlab), yellowness index (YI) (2 deg/C/ASTM D 1925), brightness index (BI) (2 deg/C/TAPPI 452/ISO 2470). The readings were taken for the average of four scans.

2.2.16 Evaluation of stiffness of fabric

Stiffness of the fabric sample (27 X 200 mm) in terms of bending length was measured as per standard ASTM D 1388-996 (Prolific stiffness tester, Prolific Engineers, Noida, UP, India). The readings were taken for the average of four measurements.

2.2.17 Evaluation of absorbency of fabric

Absorbency of treated and untreated cotton fabrics were evaluated by drop penetration method as per AATCC test method 79-2000. The fabric was mounted on embroidery ring and a drop of water was placed on it using burette. The time required for complete absorption of water drop was measured using stop watch. The absorbency was recorded for the average of nine readings.

2.2.18 Determination of crease recovery angle of fabric

Crease recovery angles were measured as per AATCC test method 66- 2003. The test specimen (26 X 52 mm) was folded (26 X 26 mm) and loaded under 500 g weight for 5 minutes to create a folded angle (crease). The specimen was then suspended in crease recovery tester (SASMIRA, Mumbai, India) for 5 minutes for a controlled recovery and then the recovery angle was examined. The total of crease recovery angle (CRA) measured for warp way and weft directions was considered. The average of two readings was recorded.

2.2.19 Soil burial test

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004. The standard soil for the burial test was prepared by mixing Garden soil 50 parts, cow dung 20 parts and water 30 parts and allowed to ferment for one month. The compost soil was covered with polythene paper to prevent the evaporation of moisture.

The treated and untreated cotton fabrics (15 X 4 cm) were incubated in the compost soil bed at 30±2°C for a stipulated period of five days. The specimen were then washed with water and dried in air and tested for strength measurement (tenacity) on stelometer (SITRA, Coimbatore, India) using equation 2.2.

2.3. RESULTS AND DISCUSSION

Two different grades of chitosan namely CHT and CHT-MC having viscosities 22 and 180 cPs respectively and almost similar degree of deacetylation (DAC) values (90%) were employed for the present investigation. The purified samples were analysed for

FTIR spectroscopy and ^1H NMR spectroscopy for structural characterization. The DAC values were verified from ^1H NMR spectra and CHN analysis. Molecular weights were determined viscometrically.

2.3.1 FTIR spectroscopy

The structural characterization of CHT and CHT-MC was done by FTIR spectra analysis, which is presented in Figure 2.1 and Figure 2.2. The spectra of these two samples were found to be almost similar indicating that both the samples possessing same structural features. In the spectra, the region above 1500 cm^{-1} wavenumber is commonly known as 'functional group region' to identify functional groups such as primary amine, alcohols, methylene groups etc. Another region which is below 1500 cm^{-1} wavenumber known as 'finger print region' referred to characterize the saccharide backbone [58].

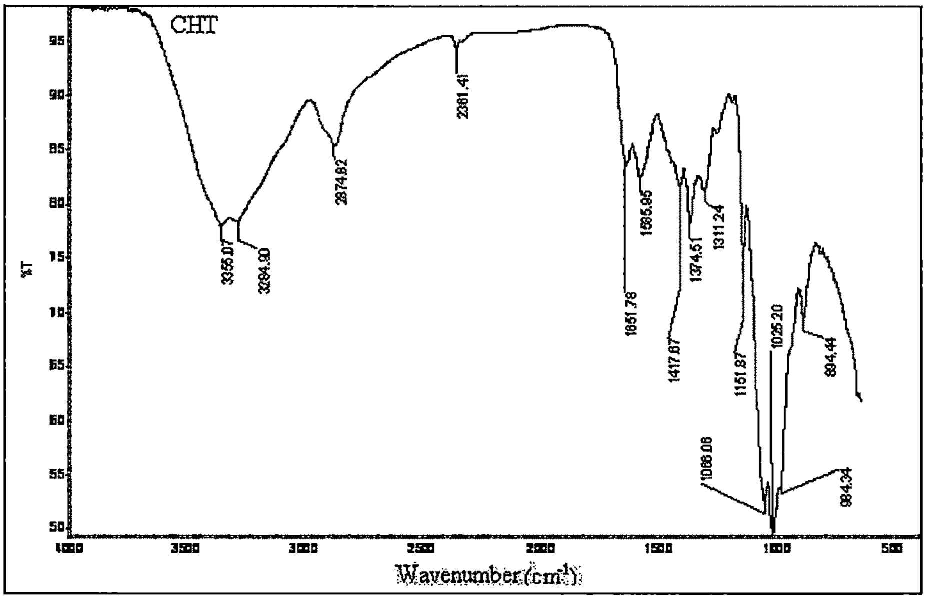


Figure 2.1 FTIR spectrum of CHT

A broad band observed at wavenumber around 3355 cm^{-1} is mainly attributed to O-H, NH and NH_2 stretch [59-61] and the absorption peak in region 2864 to 2874 cm^{-1} is due to the C-H symmetrical and unsymmetrical stretch. The absorption band at 1651 cm^{-1} is assigned to C=O (carbonyl) stretching of secondary (amide I) amide group, which is characteristic of *N*-acetyl group and the medium peak at 1585 cm^{-1} is due to bending vibrations of N-H of amide II bond (*N*-acetyl residue) and the primary amine[59, 60]. The corresponding peaks of CHT-MC in Figure 2.2 are 1650 and 1572 cm^{-1} respectively. Another medium absorption peak at 1374 to 1376 cm^{-1} characterizes the N-H of amide III bonds [60]. Absorption peaks at wave numbers 1151, 1066, 984 and 895 cm^{-1} are assigned to secondary hydroxyl groups (-CH-OH) due to C-O bending in cyclic alcohols or saccharide structure [59-61]. A strong absorption peak at 1025 cm^{-1} is due to 1° hydroxyl group, characteristic peak of $-CH_2OH$ in primary alcohols, arised from C-H bending [60]. Also, various bending vibrations of C-O at different peaks like 894 and 1151 cm^{-1} in fingerprint region characterize the saccharide structure.

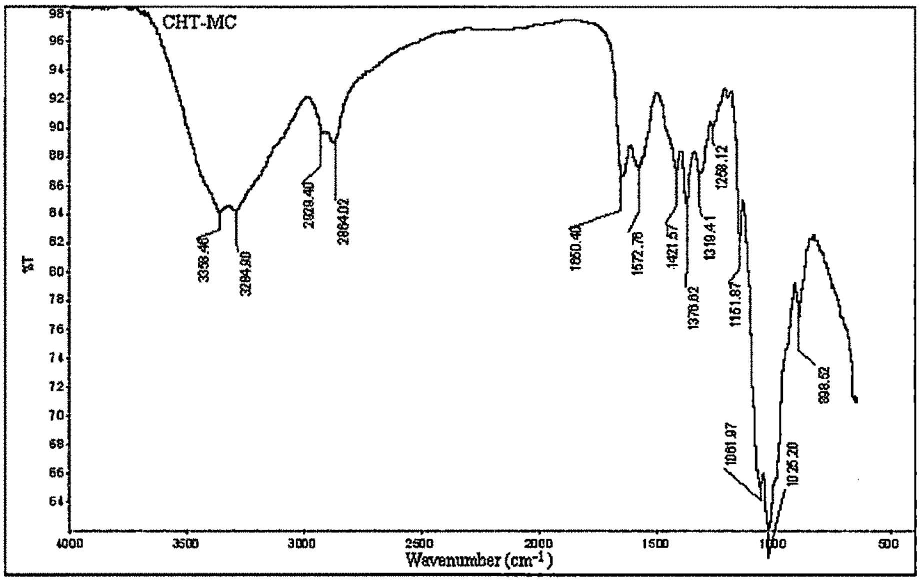


Figure 2.2 FTIR spectrum of CHT-MC

2.3.2 ^{1}H-NMR Spectroscopy

The ^{1}H-NMR spectra have been extensively used in quantitative determination of degree of deacetylation (DAC, %), degree of quaternization (DQ, %), degree of substitution (DS, %) etc properties of chitosan due to its reliability and is shown to cause no degradation of polymer [62-64]. It can be observed from the spectrum of CHT (Figure 2.3) that the signal (chemical shift, δ) at 3.114 ppm corresponds to the hydrogen bonded to the carbon atom C2 of the glucosamine ring and the integral (I_{H2}) is 3.66. The peak at δ=1.964 ppm corresponds to acetyl group (i.e. H of methyl group of acetamido moiety) with intensity (I_{NAc}) 1.01. While the signals between 3.30 and 4.00 ppm correspond to the hydrogen atoms bonded to carbons C3, C4, C5 and C6 of the glucopyranose units. The signal for anomeric protons H1 (the anomeric protons of the D-glucosamine units) and H1' (the anomeric protons of the *N*-acetyl D- glucosamine units) respectively are traced at peaks δ= 4.67 and 5.423 ppm respectively having the intensities (I_{H1}) 1.03 and ($I_{H1'}$) 0.73 respectively.

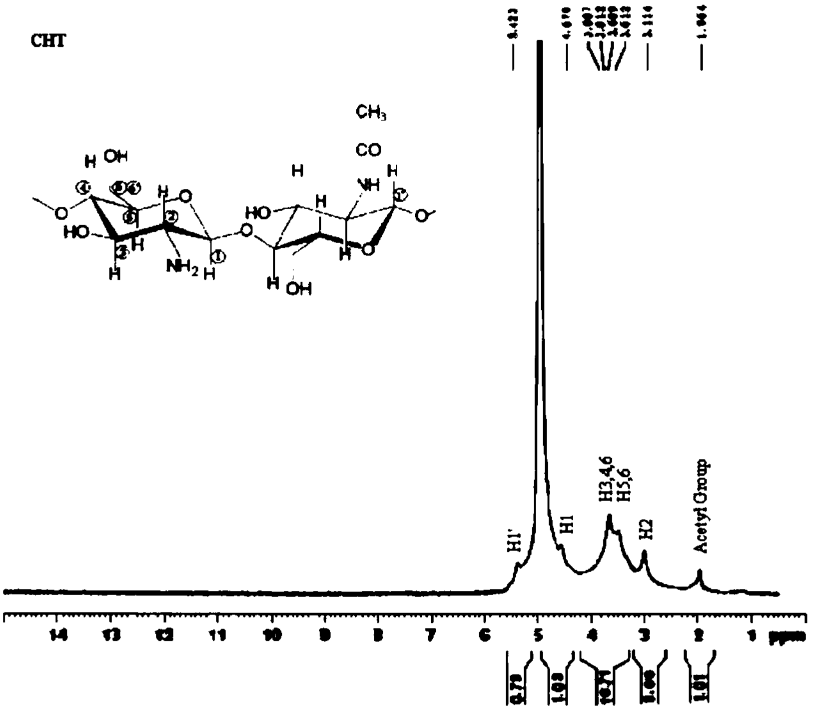


Figure 2.3 ^{1}H NMR spectrum of CHT

From the signal integrals of ^{1}H-NMR spectrum, the degree of deacetylation (DAC, %) can be evaluated by using following equation (2.3).

$$\mathrm{DAC}\ (\%) = \left(1 - \frac{1/3\ (\textit{Signal}\ \text{int}\ \textit{ensity due to acetyl group}, I_{NAc})}{(\textit{Signal}\ \text{int}\ \textit{ensity due to H of C2}, I_{H2})}\right) \times 100 \qquad \mathbf{(2.3)}$$

I_{NAc} = δ at 1.964 ppm = 1.01

I_{H2} = δ at 3.114 ppm = 3.66

$$\text{DAC} = \left(1 - \frac{1/3\,(1.01)}{(3.66)}\right) \times 100 = 90.80\ \%$$

2.3.3 Elemental analysis

Elemental analysis for carbon, nitrogen, oxygen, hydrogen etc of chitosan and its derivatives can be a useful tool for the determination of parameters like degree of deacetylation (DAC value) [65, 66]. The DAC value of chitosan can be calculated from the equation (2.4)

$$\frac{C1}{N1} \times (1 - D) + \frac{C2}{N2} \times D = \frac{C3}{N3} \qquad \textbf{(2.4)}$$

Where, D is degree of acetylation. C1/N1 is calculated from the formula of glucosamine residue, C2/N2 from the *N*-Acetyl Glucosamine residue and C3/N3 is found value of sample by elemental analysis.

The empirical formula of chitosan can be written as $(C_6H_{11}NO_4)_{1\text{-}D}\ (C_8H_{13}NO_5)_D$, from which the CHN values and C/N values can be determined as follows.

Glucosamine	C1 (%)	H1 (%)	N1 (%)	C1/N1
	44.72	6.83	8.70	5.14
N- Acetyl glucosamine	C2 (%)	H2 (%)	N2 (%)	C2/N2
	47.29	6.40	6.89	6.86

C3/N3 value is determined from elemental analysis of chitosan samples as follows.

Sample	C3 (%)	H3 (%)	N3 (%)	C3/N3
CHT	35.52	6.75	6.67	5.325
CHT-MC	35.40	6.80	6.68	5.30

Theoretical values calculated from empirical formula of chitosan (DAC 90%): C45.04%, H 6.78%, N 8.47% and C/N 5.32

Calculations:

Determination of DAC of CHT

Substituting respective C/N values in equation (2.4), the value of degree of acetylation (D) and from which the DAC value can be calculated.

$$\frac{C1}{N1}\times(1-D)+\frac{C2}{N2}\times D=\frac{C3}{N3}$$

$$5.14\,(1-D)+6.86\times D=5.325$$

D = 0.1076 or 10.76%

DAC of CHT = 100-10.76 = 89.24 %.

Similarly, the DAC value for CHT-MC was obtained as 90.7 %. The DAC values obtained from various analytical methods such as ^{1}HNMR spectroscopy and elemental (CHN) analysis were in close agreement with the data provided by the supplier as summarized in Table 2.2. Therefore for a common DAC value of 90% was taken for all the calculations whenever required hereafter.

Table 2.2 Degree of deacetylation of parent chitosan samples

Sample code	**Degree of deacetylation, %**		
	Manufacturers' data	**^{1}HNMR method**	**Elemental analysis method**
CHT	90	90.8	89.24
CHT-MC	89.03	-	90.7

2.3.4 Studies on determination of viscosity average molecular weight of chitosan

The viscosity of polymer solution, at the molecular level, is a direct measure of the hydrodynamic volume of the polymer molecules which in turn is governed by the molecular size or chain length and hence the molecular weight [67, 68].Therefore the viscosity, measured by capillary viscometer, is widely employed to determine the average molecular weight of a polymer by using the famous Mark-Houwink equation (2.5).

$$[\eta]=k\,[M_V]^{\alpha} \qquad \textbf{(2.5)}$$

Where M_V is the viscosity average molecular weight of polymer, α and k are constants (α = 0.83 and k = 1.4×10^{-4} for 0.25M acetic acid and 0.25M sodium acetate solvent system) [57] and [η] is the limiting viscosity number or intrinsic viscosity and can be determined from the Huggins equation (2.6) [68].

$$[\eta] = \lim_{C \to 0} (\eta - \eta_s)/\eta_s C \tag{2.6}$$

Where η is the viscosity of solution and η_s is the viscosity of solvent and C is the concentration. As indicated in equation (2.6), when $(\eta - \eta_s)/\eta_s C$ i.e. reduced viscosity (η_{red}) is plotted against concentration (C), the intercept to Y-axis corresponds to intrinsic viscosity [η].

In general, the viscosity average molecular weight (Mv) of chitosan was determined using Ubbelohde capillary viscometer by measuring the flow time (T) of chitosan solutions at varying concentrations (C) through the determination of reduced viscosity and intrinsic viscosity as shown in Table 2.3 using equations 2.7, 2.8 and 2.9 and Figure 2.4, and using Mark-Houwink equation (2.5). The calculated molecular weights of CHT and CHT-MC are shown in Table 2.8.

Relative viscosity: $$\eta_{rel} = \frac{T}{T_0} \tag{2.7}$$

Specific viscosity: $$\eta_{sp} = \eta_{rel} - 1 \tag{2.8}$$

Reduced viscosity: $$\eta_{red} = \frac{\eta_{sp}}{C} \tag{2.9}$$

Table 2.3 Viscometric analysis of chitosan solution

Conc (C) g/dL	**CHT-MC**				**CHT**			
	Flow time (T), Sec	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**
0.05	23.77	1.49	0.49	10.21	-	-	-	-
0.1	34.63	2.18	1.18	11.82	21.27	1.34	0.34	3.4
0.15	46.65	2.94	1.94	12.93	-	-	-	-
0.2	58.79	3.71	2.71	13.52	28.27	1.78	0.78	3.91
0.25	76.81	4.84	3.84	15.36	-	-	-	-
0.3	98.90	6.23	5.23	17.44	37.23	2.35	1.35	4.49
0.4	143.91	9.07	8.07	20.17	49.14	3.10	2.10	5.24
0.5	217.25	13.69	12.69	25.38	62.61	3.95	2.95	5.89
0.6	330.75	20.84	19.84	33.03	78.69	4.96	3.96	6.60
0.7	-	-	-	-	98.32	6.20	5.20	7.42
0.8	-	-	-	-	125.28	7.89	6.89	8.62
0.9	-	-	-	-	157.41	9.92	8.92	9.91
1.0	-	-	-	-	196.00	12.35	11.35	11.35

Solvent: Acetic acid 0.25M, sodium acetate 0.25M, T_0 15.87 sec

Calculations

The intrinsic viscosities$[\eta]$ of CHT and CHT-MC, from Figure 2.4, were determined to be 2.55 and 9.5 respectively.

Mark-Houwink equation, $[\eta] = k\,[M_V]^{\alpha}$ **(2.5)**

Where, $\alpha = 0.83$ and $k = 1.4 \times 10^{-4}$ for 0.25M acetic acid and 0.25M sodium acetate solvent system

(1) Molecular weight of CHT

Intrinsic viscosity, $[\eta] = 2.55$

$2.55 = 1.4 \times 10^{-4} M^{0.83}$

$M_V = 135{,}839$

(2) Molecular weight of CHT-MC

Intrinsic viscosity, $[\eta] = 9.4$

$9.4 = 1.4 \times 10^{-4} M^{0.83}$

$M_V = 654{,}127$

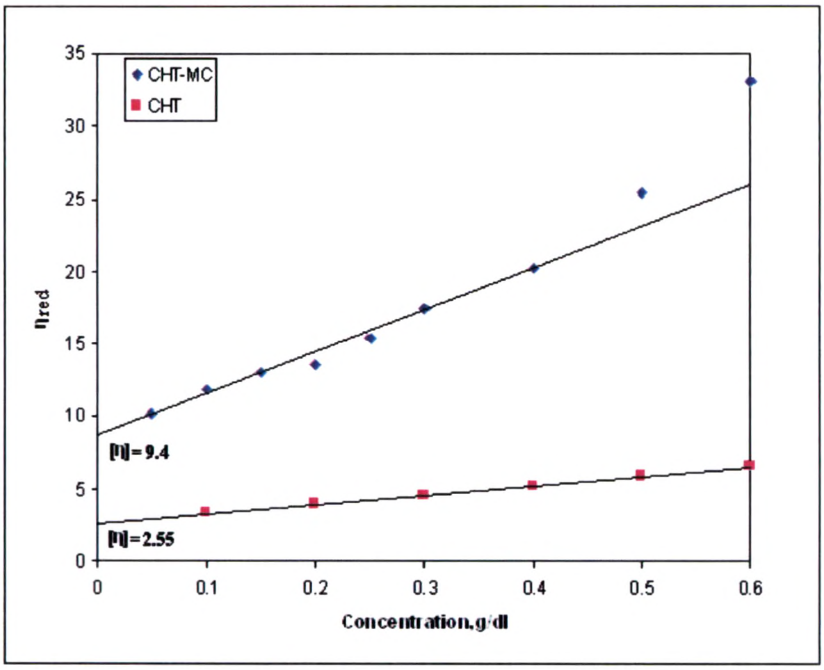


Figure 2.4 Intrinsic viscosity determination of chitosan

2.3.5 Depolymerization of chitosan for synthesizing low molecular weight chitosans

Chitosan is characterized mainly by two variables, namely, degree of deacetylation and the molecular weight. Degree of deacetylation determines the number of free amino groups present in the chitosan macromolecule, which in turn determines the functionality/reactivity, polarity and water solubility of the polymer. On the other hand, molecular weight determines the strength of its fiber/film and viscosity of its solution [2, 69]. The molecular weight of chitosan depend on the source of precursor chitin and deacetylation conditions (time, temperature, and concentration of NaOH), respectively. The molecular weight of most of native chitosan, obtained from deacetylation of crustacean chitin, may be of the order 10^5 to 10^6 [69], which may be very high for the textile applications as they produce highly viscous solutions. Consequently, for ease of applications, it is necessary to reduce the molecular weight to much lower value. Various methods controlled depolymerization have been proposed to obtain chitosan of desired molecular weights.

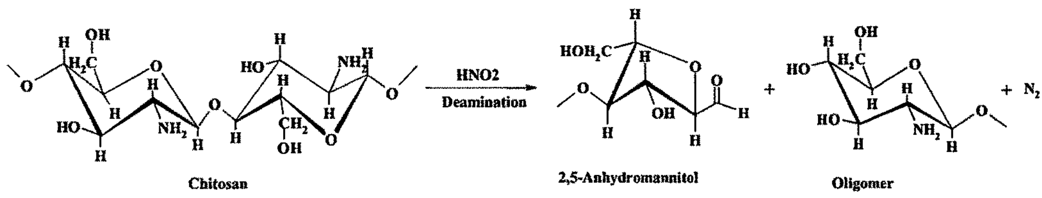
Chitosans of desired molecular weight can be obtained by controlled depolymerization by methods such as acid hydrolysis (HCl, H_2SO_4, HNO_2 etc) [28, 37, 70-72], free radicals (H_2O_2, $K_2S_2O_8$) [73], enzymatic [72, 74], radiations (UV, γ rays) [75, 76], ultrasound [77], microwave and thermal treatments [78]. In physical methods, Baxter et al. [77] studied the effect of ultrasonication on the degradation of chitosan. They found that intrinsic viscosity of samples decreased exponentially with increasing sonication time and rates of intrinsic viscosity decreased linearly with ultrasonic intensity. Choi et al. [76] investigated the depolymerization of chitosan using irradiation with different doses (2~200 kilograys) of gamma rays. Their results showed that viscosity of irradiated chitosan rapidly decreased with increasing irradiation dose.

Feng Tian et al.[73] reported the method for depolymerization of chitosan by hydrogen peroxide and their IR and ^{1}HNMR studies confirmed the depolymerization leading to breakage of 1-4 -β-D- glucoside bonds of chitosan. They proposed the attack of per hydroxyl radical (HO$^\cdot$), generated from the H_2O_2 decomposition, at amino group leading to hydrogen abstraction. The resulting unstable glucosamine radical in presence of water leads to rupture of adjacent glucosidic linkage. They also proposed that the depolymerization in crystalline region mainly takes place at the surface by peeling-off process while the amorphous region is depolymerized by penetrating pattern. Trzcinski [75] employed the combined degradation of chitosan using hydrogen peroxide and UV light for the enhanced degradation rate. Photochemical degradation by means of UV light also undergoes as a result of free radical reactions along the macromolecules. Kabal'nova et al.[79] employed the ozonation of chitosan in dilute acid solution and showed a remarkable decrease of molecular mass of polysaccharide in proportion to reaction time or amount of applied ozone. According to Demin et al. [80], the initial stage of the interaction of ozone with polysaccharide is its electrophilic attack on C(1)-H bond with the formation of labile hydrotrioxides, destruction of which results in depolymerization of polysaccharide

Enzymatic degradation of chitosan polymer is possible to get low molecular weight chitosan. Enzymatic process has the advantage of its specificity and the ease in the fractionation of product [81]. Lee et al.[74] used commercial bromelain for the partial depolymerization of chitosan. The enzymatic reactions were determined by the liberation of reducing sugar and the reduction in viscosity. They proposed/recommended 7% w/w enzyme treatment for 2h at pH 5 for the satisfactory results. Ilyina et al [82] reported chitinase and chitosanase as most effective enzymes, which are found in fungus, bacteria and plants, to hydrolyze chitosan. Other enzymes such as glucosanase, lipase, tannase and protease were found to have chitosanolitic activities, as reported by Yalpani and Pantaleone [81].

Nitrous acid method for the oxidative depolymerization of chitosan has been well documented [28, 37, 52, 83]. When chitosan solution is treated with nitrous acid, produced from acidic sodium nitrite it undergoes deamination reaction with subsequent cleavage of β- glycosidic linkages. Mao et al. [83] reported a large series of chitosans with desired molecular weights could be obtained by changing chitosan/NaNO2 molar ratio, chitosan initial concentration and reaction time. The molecular weight of the depolymerized chitosan was linear with chitosan/$NaNO_2$ ratio. The reproducibility of this method was fairly good. The overall stoichiometry of the reaction between chitosan and nitrous acid (HONO) is shown scheme 2.1. Nitrosating species originating from HONO attack the amino groups and subsequently cleave the β- glycosidic linkages to produce low molecular weight product and 2,5-anhydro-D-mannose is formed as the reducing end group of the cleaved polymer [28, 37, 52].

$$NaNO_2 + H^+ \longrightarrow HNO_2 + Na^+$$



Scheme 2.1 Depolymerization of chitosan by nitrous acid

On account of these advantages and its better control on the extent of depolymerization nitrous acid method was used to depolymerize chitosan in this study. Most of the low molecular weight chitosan derivatives namely CHT-D2, D3, D4 and D5 were derived from the starting material CHT whereas CHT-D1 was obtained from CHT-MC. During depolymerization process, parameters like chitosan concentration (2 % w/v), acetic acid (15 ml/L), sodium acetate (10 g/L), temperature (30 °C) and treatment time (2h) was kept constant and the concentration of sodium nitrite was varied as shown in Table 2.4. The viscosity measurements data, determined using equations 2.7, 2.8 and 2.9 of low molecular weight chitosan derivatives produced from depolymerization of CHT and CHT-MC are presented in Table 2.5, Table 2.6 and Table 2.7. The intrinsic viscosities of depolymerised chitosan were determined from the plots of reduced viscosity against concentration of chitosan as shown in Figure 2.5 and the molecular weights of chitosan derivatives produced from depolymerization of CHT and CHT-MC are summarized in Table 2.8.

Table 2.4 Syntheses of low molecular weight chitosan derivatives

Sample code	Parent chitosan	Sodium nitrite, %
CHT-D1	CHT-MC	0.10
CHT-D2	CHT	0.5
CHT-D3	CHT	1.25
CHT-D4	CHT	2
CHT-D5	CHT	3.1

Conc: CHT-MC 10 g/L and CHT 20 g/L, Treatment time 2h,
Sodium nitrite conc was taken on the percentage of parent chitosan, temp 30 °C

Table 2.5 Viscometric analysis of CHT-D1 and CHT-D2 solutions

Conc (C), g/dL	CHT-D1				CHT-D2			
	Flow time (T), Sec	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**
0.1	25.73	1.621	0.621	6.21	18.44	1.162	0.162	1.62
0.2	40.50	2.552	1.552	7.76	21.46	1.352	0.352	1.76
0.3	60.00	3.781	2.781	9.27	24.96	1.573	0.573	1.91
0.4	84.49	5.324	4.324	10.81	28.50	1.796	0.796	1.99
0.5	112.92	7.115	6.115	12.23	33.01	2.080	1.080	2.16
0.6	147.37	9.286	8.286	13.81	37.29	2.350	1.350	2.25
0.7	203.28	12.809	11.809	16.87	42.98	2.708	1.708	2.44
0.8	268.90	16.944	15.944	19.93	48.37	3.048	2.048	2.56
0.9	352.38	22.204	21.204	23.56	54.86	3.457	2.457	2.73
1.0	424.68	26.760	25.760	25.76	61.26	3.860	2.860	2.86

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

Table 2.6 Viscometric analysis of CHT-D3 and CHT-D4 solutions

Conc (C), g/dL	CHT-D3				CHT-D4			
	Flow time (T), Sec	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Specific viscosity (η_{sp})**	**Reduced viscosity (η_{red})**
0.1	17.37	1.095	0.095	0.95	16.74	1.055	0.055	0.55
0.2	19.08	1.202	0.202	1.01	17.65	1.112	0.112	0.56
0.3	21.15	1.342	0.342	1.11	18.57	1.170	0.170	0.57
0.4	22.98	1.448	0.448	1.12	19.62	1.236	0.236	0.59
0.5	25.03	1.577	0.577	1.15	20.73	1.307	0.307	0.61
0.6	27.30	1.720	0.720	1.20	21.77	1.372	0.372	0.62
0.7	29.67	1.869	0.869	1.24	22.98	1.448	0.448	0.64
0.8	32.25	2.032	1.032	1.29	24.12	1.520	0.520	0.65
0.9	35.29	2.224	1.224	1.36	25.25	1.5913	0.5913	0.66
1.0	37.93	3.391	2.391	1.39	26.67	1.681	0.681	0.68
1.2	-	-	-	-	28.86	1.818	0.818	0.68
1.6	-	-	-	-	36.17	2.216	1.216	0.76
2.0	-	-	-	-	41.90	2.640	1.640	0.82

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

Table 2.7 Viscometric analysis of CHT-D3 and CHT-D4 solutions

Conc (C), g/dL	CHT-D5			
	Flow time (T), Sec	**Relative viscosity,**	**Specific viscosity,**	**Reduced viscosity,**
0.1	16.43	1.035	0.035	0.35
0.2	17.02	1.072	0.072	0.36
0.3	17.63	1.111	0.111	0.37
0.4	18.30	1.153	0.153	0.38
0.5	18.96	1.195	0.195	0.39
0.6	19.70	1.241	0.241	0.40
0.7	20.44	1.288	0.288	0.41
0.8	21.20	1.336	0.336	0.42
0.9	22.00	1.385	0.385	0.43
1.0	22.87	1.441	0.441	0.44

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0= 15.87 sec

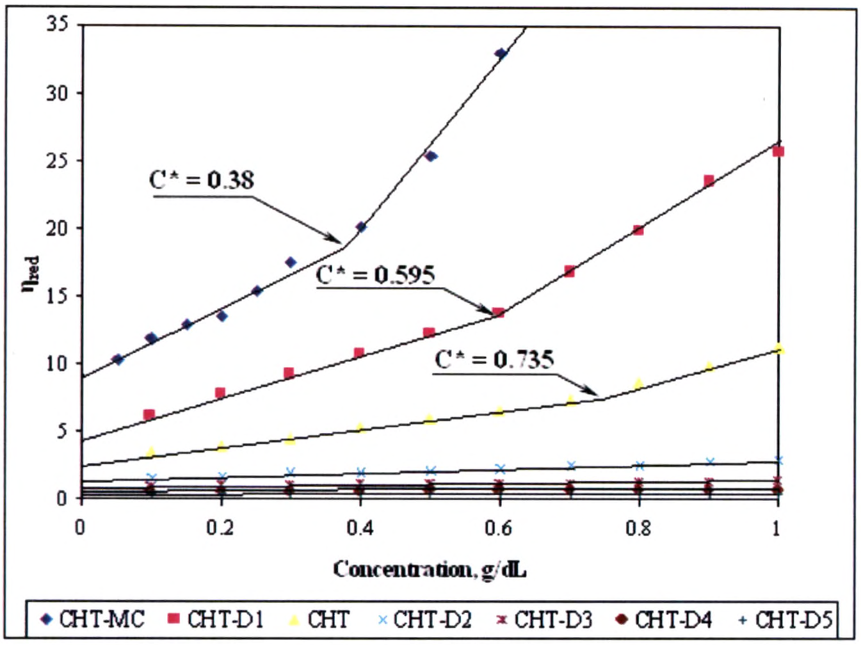


Figure 2.5 Intrinsic viscosities of different grades of chitosan solutions

Table 2.8 Intrinsic viscosity and viscosity average molecular weights of different grades of chitosan

Chitosan	**Intrinsic Viscosity [η]**	**Molecular Weight, Mv**	**Overlap concentration (C*), g/dL**
CHT-MC	9.40	654,127	0.38
CHT-D1	4.72	285,231	0.595
CHT	2.55	135,839	0.735
CHT-D2	1.50	71,676	-
CHT-D3	0.91	38,733	-
CHT-D4	0.535	20,698	-
CHT-D5	0.34	11,986	-

It is envisaged from Figure 2.6 and Figure 2.7 that the IR spectra of chitosan and depolymerised chitosan are almost similar which indicates that the process of depolymerisation caused no chemical change in the structure of the polymer except reduction in molecular weight which is evident from the change in viscosity as presented in Table 2.8 Similar observations are reported by A. Hebeish et al.[28] and Mao et al. [83].

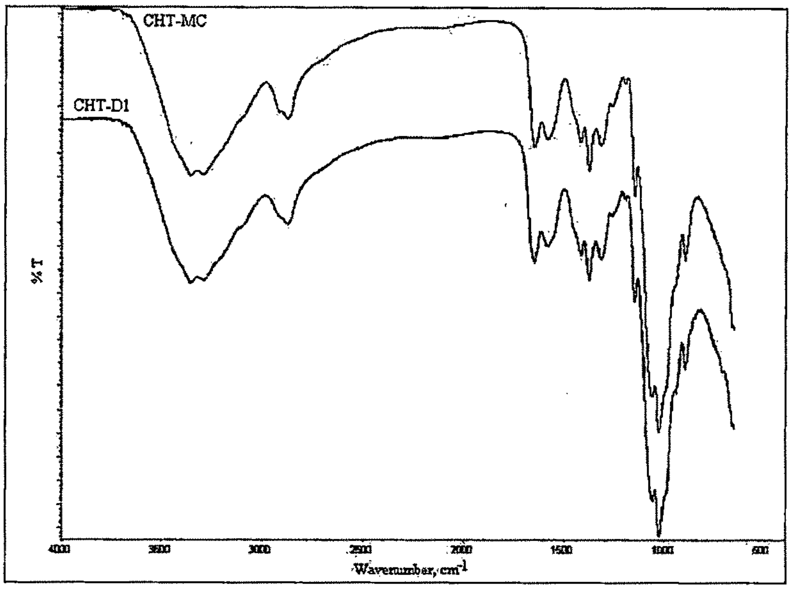


Figure 2.6 FTIR spectra of CHT-MC and its low molecular weight derivative

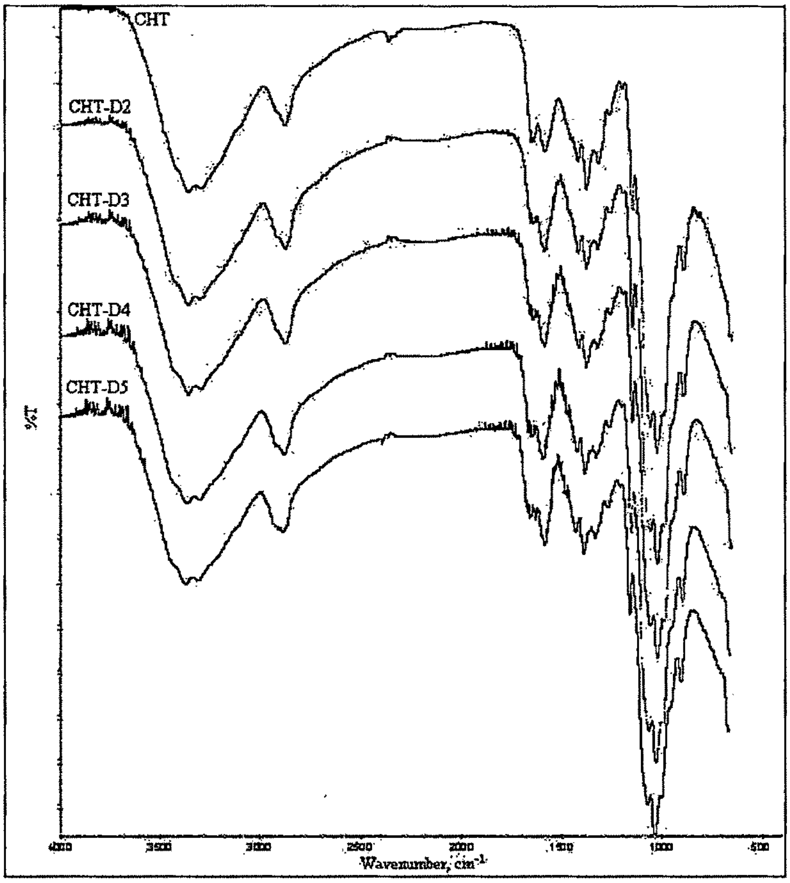
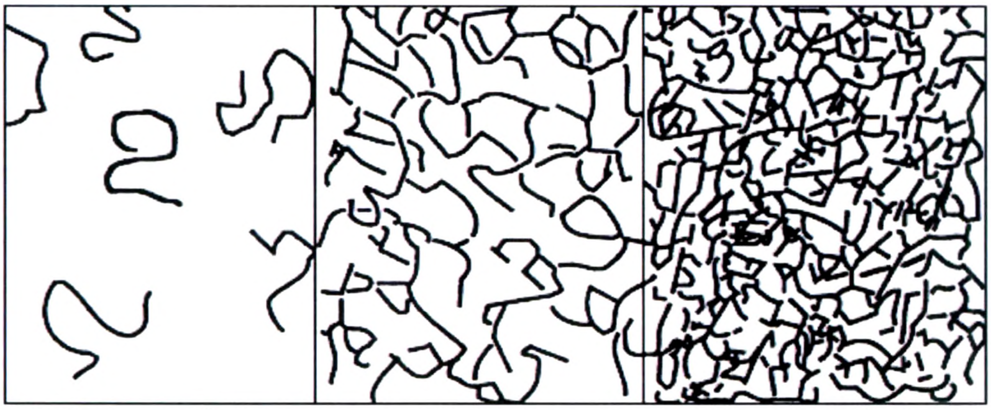


Figure 2.7 FTIR spectra of CHT and its low molecular weight derivatives

2.3.6 Effect of molecular weight and concentration on viscosity of chitosan solutions

It can be seen from Figure 2.5 that the curves of high molecular weight chitosan, namely CHT-MC, CHT and CHT-D1, do not strictly follow the linearity of the Huggins equation (2.6) in the selected range of concentration. These curves show the inflection at a certain critical concentration (C*) and then after the curves bend upwards. Further, the value of C* increases with decrease in molecular weight and ultimately the curves flatten for low molecular weight chitosan, used in this research work. This can be explained on the fact that, when chitosan or any other polymer is added into a solvent, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of polymer are solvated and loosened out. Since the molecules in a solid polymer are entangled with neighbouring ones, polymer molecules during dissolution diffuse out as bunches of entangled molecules. Even though all chain segments of a polymer molecule in solution are unfolded and fully solvated, the molecules does not assume the shape of an extended straight chain but present in a coil form. These coils or aggregates offer resistance for the mobility or flow of molecules and hence impart viscosity [67, 84]. When the molecular size and concentration are increased, as in this case, the extent of entanglement is increased as shown in Figure 2.8.



$c < C^*$ $c > C^*$ $c >> C^*$

Viscous solution ⇔ Viscoelastic gel

Figure 2.8 Aggregation of chitosan molecules as a function of molecular weight and concentration

In other word the critical concentration (C*) is, indeed, the 'overlap' concentration. Thus, when C>C* the intermolecular entanglements or aggregation predominate and precludes the overall molecular motion of polymers, while individual polymers molecules are statistically separated from other molecules at C<C*. Thus, the critical concentration (C*) is a measure of molecular size and conformation of a polymer, the higher the molecular weight and the more rigid conformation, the lower will be the C*. The results are in close agreement with earlier reports [85, 86]. Hence low molecular weight chitosans can be conveniently used for textile application and applied at reasonably higher concentrations.

2.3.7 Effect of storage time on viscosity of chitosan solution

Polymeric chemicals are generally applied to textiles by padding technique where it is required to prepare a standing bath. Thus the chemical remains in contact with water for a longer period. As biodegradability of chitosan is a well-known phenomenon the effect of storage time on the stability of its solution was studied in terms of change in solution viscosity. The molecular weight of CHT-MC is extremely high for textile applications and synthesis of various derivatives due its very high viscosity. Hence the chitosan having moderate viscosity and molecular weight, namely CHT, was chosen for most of studies hereafter. The stability behaviour of CHT solution in terms of viscosity behaviour and molecular weight determination as a function of storage time presented in Table 2.9 and Table 2.10 and Figure 2.9. The intrinsic viscosity of CHT solutions at different storage times was obtained from Figure 2.9. The molecular weights of CHT were determined by substituting intrinsic viscosities values in Mark-Houwink equation (2.5), which are presented in Table 2.11 and graphically in Figure 2.10.

Table 2.9 Effect of storage time on viscosity of CHT solution

Conc (C), g/dL	**Flow time (T, Sec) at storage time (h):**					
	0	**24**	**72**	**120**	**192**	**264**
0.1	21.27	20.39	19.92	19.77	-	-
0.2	28.27	26.69	25.23	24.69	24.25	23.65
0.3	37.23	35.02	31.79	31.20	-	-
0.4	49.14	44.40	40.16	38.28	36.95	35.29
0.5	62.61	56.81	50.45	46.98	-	-
0.6	78.69	70.03	60.95	56.53	53.58	50.05
0.7	98.32	86.14	74.45	68.64	-	-
0.8	125.28	105.49	91.14	81.38	74.02	69.83
0.9	157.41	128.8	108.97	96.43	-	-
1.0	196.00	155.2	130.13	114.58	100.14	91.57

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0*= 15.87 sec*

Table 2.10 Reduced viscosity of CHT solution as a function of storage time

Conc (C), g/dL	**Reduced Viscosity ($\eta_{red} = \eta_{Sp}/C$)at storage time (h):**					
	0	**24**	**72**	**120**	**192**	**264**
0.1	3.4	2.85	2.55	2.46	-	-
0.2	3.91	3.41	2.96	2.78	2.64	2.45
0.3	4.49	4.02	3.34	3.22	-	-
0.4	5.24	4.50	3.83	3.53	3.32	3.06
0.5	5.89	5.16	4.36	3.92	-	-
0.6	6.60	5.69	4.73	4.27	3.96	3.59
0.7	7.42	6.33	5.27	4.75	-	-
0.8	8.62	7.06	5.93	5.16	4.58	4.25
0.9	9.91	7.91	6.52	5.67	-	-
1.0	11.35	8.78	7.20	6.22	5.31	4.77

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25M, T_0*= 15.87 sec*

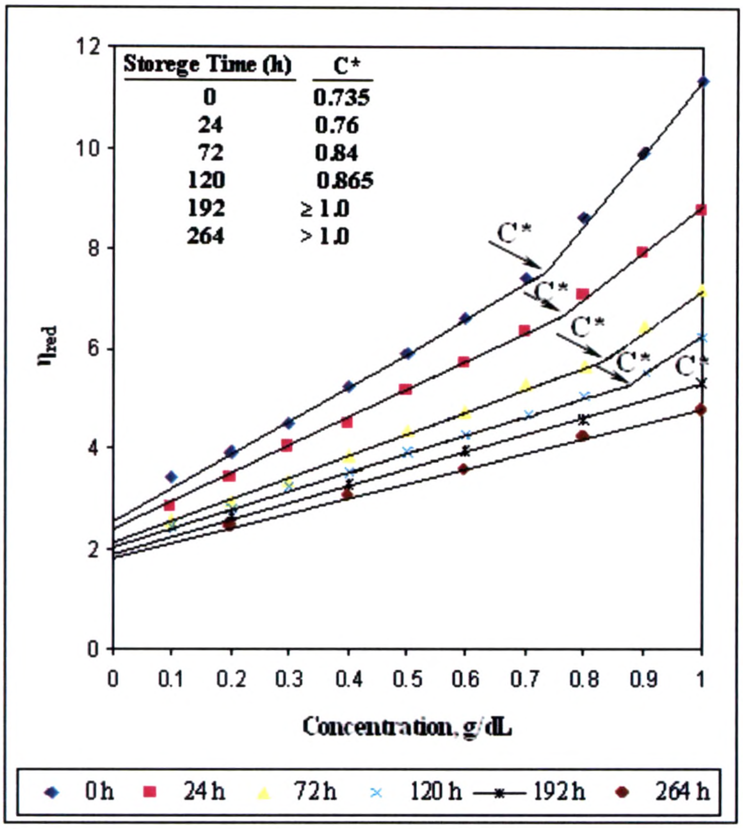


Figure 2.9 Viscosity of chitosan (CHT) solution as a function of storage time

Table 2.11 Effect of storage time on stability chitosan (CHT) solution

Storage time, h	Intrinsic viscosity [η]	Molecular weight (Mv)	Critical concentration (C*), g/dL
0	2.55	135,839	0.735
24	2.2	113,704	0.76
72	2.1	107,506	0.84
120	2.05	104,430	0.865
192	1.95	98,323	**≥ 1.0**
264	1.9	95,294	>1.0

Solvent: Acetic acid 0.25M, sodium acetate 0.25M, T_0*= 15.87 sec*

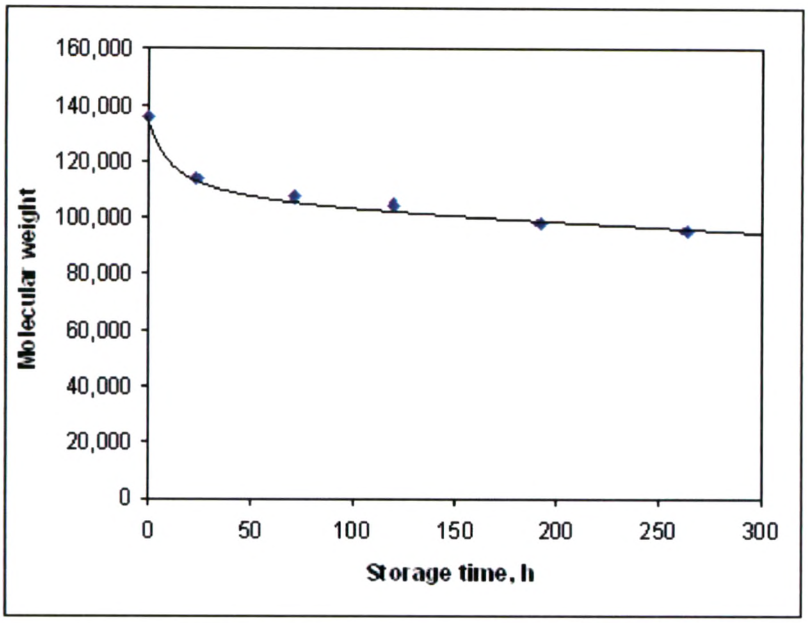


Figure 2.10 Effect of storage time of chitosan (CHT) solution on molecular weight

It is seen from Table 2.11, Figure 2.9 and Table 2.12 that the initial molecular weight and the concentration of polymer have the influence on the stability of the solution. The reduced viscosity curve is observed to be segmented with an overlap/ critical concentration (C*) at the point of inflection and then flattened as the storage time was increased i.e. the critical concentration shifted towards right. It is also observed from Figure 2.10 that the drop in viscosity in first 24 h was much faster and was more significant at higher concentration i.e. above C* as illustrated in Table 2.11. The loss in viscosity may be attributed to the biodegradation of chitosan molecules and/or hydrolysis of polymer molecules and slow detachment of polymer segments from the entanglements which are present above C*. Initially the large molecules, especially at higher concentration, occupy large "hydrodynamic" volume due to aggregation as result of intermolecular cross linkages, which leads to less mobility indicating higher viscosity. The hydrolytic degradation of the polymer leads to the production of smaller molecular entities which in turn causes a drop in hydrodynamic volume of the polymer molecules resulting in higher molecular mobility and as a result reduces the viscosity of the solution [57, 84, 86]. It shows that dilute chitosan solutions made from low molecular weight samples (e.g. CHT-D5) are more stable in terms of viscosity behaviour as illustrated in

Table 2.13, Figure 2.11 and Table 2.14. Hence lower molecular weight chitosan solutions particularly at low concentration may be preferred for textile applications as their standing baths have more consistent viscosity.

Table 2.12 Effect of initial concentration on stability of chitosan (CHT) solution

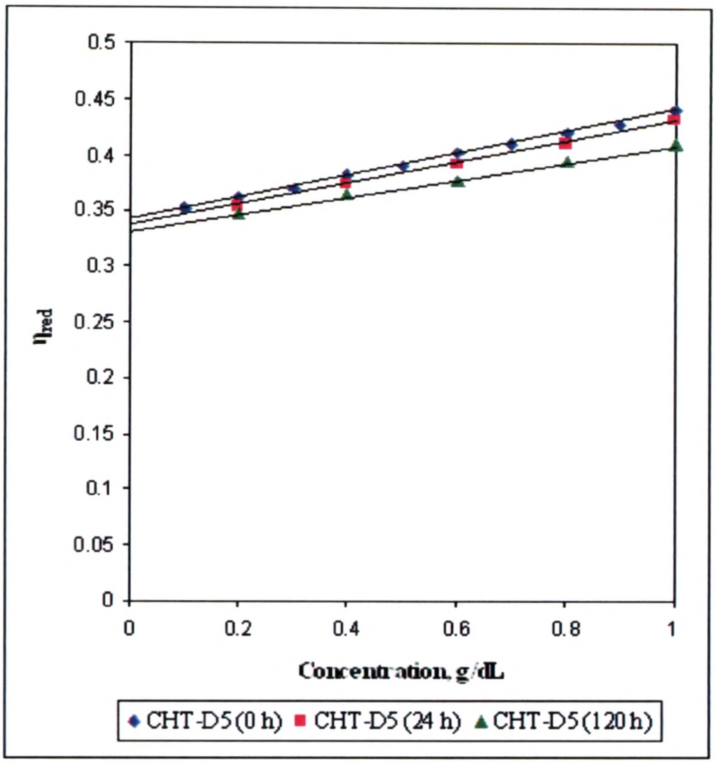
Storage time, h	**Change in viscosity (%) of CHT from initial solution at concentrations:**	
	0.2 g/dL	**1.0 g/dL**
0	100	100
24	87.22	77.36
72	75.70	63.43
120	71.10	54.80
192	67.52	46.78
264	62.66	42.03

Solvent: Acetic acid 0.25M, sodium acetate 0.25M, T_0*= 15.87 sec*

Table 2.13 Effect of storage time on viscosity of low molecular weight chitosan, CHT-D5 solution

Conc (C), g/dL	**Viscosity of CHT-D5 solution at storage time:**					
	0 h		**24 h**		**120 h**	
	Flow time (T), sec	**Reduced viscosity (η_{red})**	**Flow time (T), sec**	**Reduced viscosity (η_{red})**	**Flow time(T), sec**	**Reduced viscosity (η_{red})**
0.1	16.43	0.35	-	-	-	-
0.2	17.02	0.36	16.99	0.35	16.97	0.35
0.3	17.63	0.37	-	-	-	-
0.4	18.30	0.38	18.24	0.37	18.18	0.36
0.5	18.96	0.39	-	-	-	-
0.6	19.70	0.40	19.60	0.39	19.47	0.38
0.7	20.44	0.41	-	-	-	-
0.8	21.20	0.42	19.77	0.41	20.88	0.39
0.9	22.00	0.43	-	-	-	-
1.0	22.87	0.44	22.74	0.43	22.39	0.41

Solvent ingredients: Acetic acid 0.25M, sodium acetate 0.25; T_0 *15.87 sec*



CHT-D5: Mol wt 11,986

Figure 2.11 Viscosity of CHT-D5 solution as a function of storage time

Table 2.14 Effect of storage time on stability chitosan (CHT-D5) solution

Storage time, h	Intrinsic viscosity [η]	Molecular weight (Mv)
0	0.34	11,986
24	0.334	11733
120	0.33	11564

Solvent ingredients: acetic acid 0.25M, sodium acetate 0.25M, T_0 15.87 sec

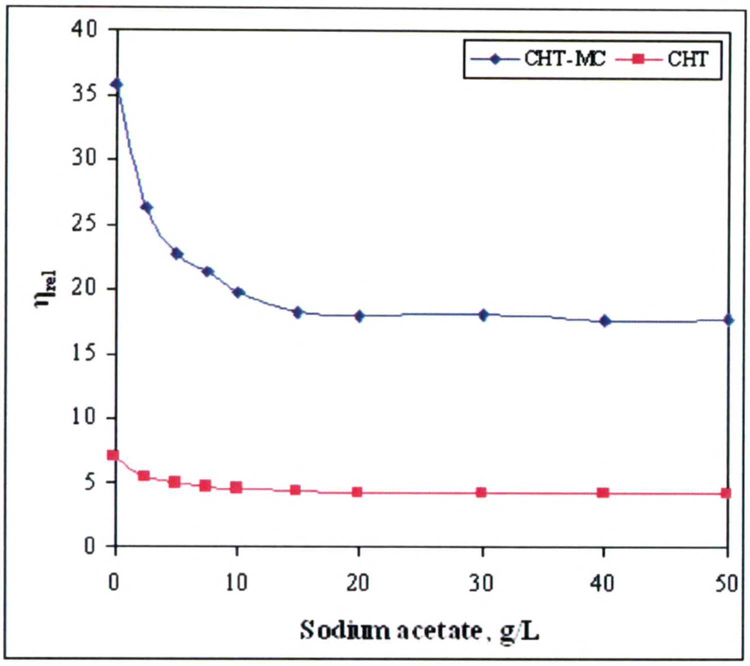
2.3.8 Effect of electrolyte on viscosity of chitosan solution

Chitosan, being a polycationic material having pKa value 6.3, requires acidic pH is for its dissolution [69]. The conformational arrangements of polyelectrolyte chains, mainly responsible for viscosity behaviour, are influenced by various factors such as pH, concentration of polyelectrolyte, molecular weight, nature of counter ion and added electrolyte etc [87-89]. Chitosan salts such as acetate, formate, lactate, citrate, chloride, and nitrate are soluble in water [69] while sulphate salt is insoluble [90, 91]. The effect of pH on chitosan chain conformational arrangements in aqueous medium can be understood due to the protonation of amino groups, which is responsible for the charge extension on the polyelectrolyte chains [87]. Polyanions such as sodium tripolyphosphate (TPP) lead to ionotropic gelation of chitosan, which is one of the fundamental principles of nano chitosan synthesis [92]. Velásquez et al [93] reported the effect of sodium chloride on the behaviour of two chitosan salts namely nitrate and chloride. The η_{red} values for chitosan nitrate were found to be markedly more affected than chitosan chloride by the increasing added ionic strength of the medium. According to them, nitrate counter ions cause a lesser stiffness than chloride counter ions, which has been attributed to higher screening due to bigger nitrate ions. The applications of chitosan the syntheses of various derivatives and in textiles, in this research, was mainly employed in acetic acid solution with sodium acetate as electrolyte. Therefore, the effect of sodium acetate concentrations on two different grades of chitosan namely, CHT-MC and CHT was studied as demonstrated in Table 2.15 and graphically in Figure 2.12.

Table 2.15 Effect of sodium acetate concentration on viscosity of chitosan solutions

Sod. Acetate Concentration, g/L	**T_0, sec**	**CHT-MC solution**		**CHT solution**	
		Flow time (T), sec	**Relative viscosity (η_{rel})**	**Flow time (T), sec**	**Relative viscosity (η_{rel})**
0	15.58	557.8	35.8	110.68	7.1
2.5	15.60	409.2	26.2	82.79	5.3
5	15.63	354.47	22.7	77.91	5.0
7.5	15.68	332.71	21.2	73.52	4.7
10	15.71	310.35	19.8	71.32	4.5
15	15.78	285.63	18.1	67.92	4.3
20	15.82	282.72	17.9	67.61	4.3
30	15.85	284.75	17.9	67.60	4.3
40	16.23	286.70	17.7	67.81	4.2
50	16.37	289.63	17.6	68.03	4.2

Chitosan 5 g/L, acetic acid 15 g/L, flow time for water = 15.57 sec at 30 ^{0}*C,*
T_0 represents blank reading for solution containing acetic acid 15 g/L and sodium acetate



Chitosan 5 g/L, Acetic acid 15 g/L, Mol wt: CHT-MC 654,127; CHT 135,869

Figure 2.12 Relative viscosity of chitosan solution as a function of sodium acetate concentration

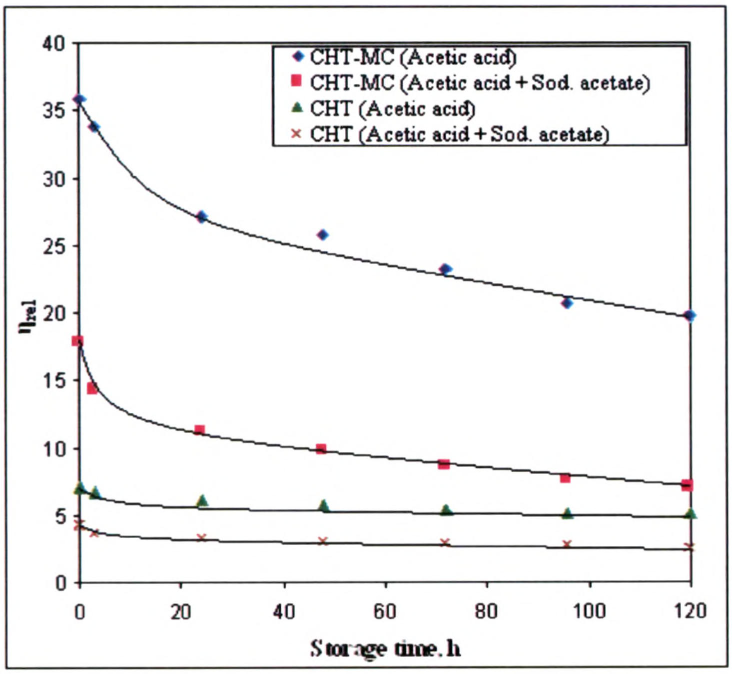
Sodium acetate was found to reduce the viscosity of chitosan solution (Figure 2.12). It was observed that with increase in concentration of sodium acetate, the viscosity of chitosan solution, for a selected concentration of 5 g/L, decreased up to certain concentration (~15g/L). No reduction in viscosity was noticed beyond this concentration. The effect of electrolyte was also observed to be more pronounced on high molecular weight chitosan, CHT-MC. With decrease in molecular weight of chitosan, the amount of sodium acetate required to attain the lower viscosity was decreased i.e. about 7.5 g/L of sodium acetate was required for CHT solution. The decrease in viscosity with increase in electrolyte concentration can be attributed to the shielding effect of counter ions [69]. Due to ion dipole forces; the acetate ions form a cascade negative charge over each chitosan molecule establishing repulsive forces between them. This offers low resistance to the flow or mobility of polymer molecules. As the number of amino groups content is large in high molecular weight chitosan, higher charge screening is effected due to added electrolytes resulting in to intensive lowering in viscosity of the solution [93]. The drop in viscosity of chitosan solution due to sodium acetate was found to be almost uniform during storage period as shown in Table 2.16 and graphically in Figure 2.13. The stability of chitosan solution, thus, is influenced by storage time and the presence of electrolyte. Thus almost a stable chitosan solution can be obtained by the judicious selection of low molecular weight chitosan and optimum concentration of electrolyte.

Table 2.16 Effect of sodium acetate on storage stability of chitosan solution

Storage time, h	CHT-MC				CHT			
	Flow time (T), Sec		Relative viscosity (η_{rel})		Flow time (T), Sec		Relative viscosity (η_{rel})	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0	557.8	282.7	35.80	17.87	110.7	67.6	7.11	4.27
3	526.3	227.3	33.78	14.37	104.0	59.5	6.68	3.76
24	422.7	178.6	27.13	11.29	96.1	53.8	6.17	3.40
48	402.1	155.2	25.81	9.81	89.0	48.5	5.71	3.07
72	362.5	137.5	23.27	8.69	84.0	46.1	5.39	2.91
96	321.4	121.1	20.63	7.65	80.2	43.8	5.15	2.77
120	307.5	112.3	19.74	7.10	78.5	41.2	5.04	2.60

Chitosan 5 g/L, (A) Solvent: Acetic acid 15 g/L, T_0 15.58 sec at 30 ^{0}C;

(B) Solvent: Acetic acid 15 g/L + Sodium acetate 20 g/L, T_0 15.82sec at 30 ^{0}C



Chitosan 5 g/L, Acetic acid 15 g/L, Sodium acetate 20 g/L

Figure 2.13 Effect of sodium acetate on storage stability of chitosan solution

2.3.9 Application of chitosan (CHT) derivatives on cotton fabric: Pad-Dry-Cure process

Chitosan can be applied to cotton fabric by exhaustion method or by padding method. The viscous nature of chitosan solution, however, restricts its application by exhaust method due the possibility of uneven sorption. The second method, which is prevalent in continuous dyeing or finishing processes of textiles, produces uniform effects and is most suitable for polymeric applications. Hence, the pad-dry cure method for the treatment of cotton fabric with different molecular weight chitosan derivatives (Table 2.8) was adopted. Since the treated fabric samples, in many cases, had to evaluate with optical instruments (CCMS), any changes in fabric construction due to above treatments could lead to variations in results. In order to minimize the error, fabric sample was padded with a solution containing acetic acid (15 ml/L) and sodium acetate (10 g/L), this sample was termed as 'control'.

Table 2.17 Effect of various treatments on fabric construction

Fabric Sample	Treatment	Ends/in (EPI)	Picks/in (PPI)
Untreated	-	142.0	72.0
Control	Blank treated*, (Pad-Dry cure)	149.1	76.4
CHT-MC	10 gpl (Pad-Dry cure)	149.4	75.9
CHT-D1	10 gpl (Pad-Dry cure)	148.6	76.1
CHT	10 gpl (Pad-Dry cure)	148.1	77.1
CHT-D2	10 gpl (Pad-Dry cure)	148.8	76.4
CHT-D3	10 gpl (Pad-Dry cure)	149.0	77.2
CHT-D4	10 gpl (Pad-Dry cure)	148.4	75.6
CHT-D5	10 gpl (Pad-Dry cure)	150.0	76.4

**Blank treatment: Acetic acid 15 ml/L, sodium acetate 10 g/L*

The fabric construction in terms of ends/in (EPI) and picks/in (PPI) (average of five readings) measured at different stages of treatment is presented in Table 2.17. It was observed that the fabric construction was not much affected due to such treatments and was very much close to the 'control' sample. Therefore the computer colour matching system was safely employed for the evaluation of appearance (indices) and colour (K/S values).

2.3.10 Surface morphology of chitosan treated fibres

Chitosan solutions (1 g/L) were applied on cotton fabric by conventional pad-dry cure technique and the surface morphology of the treated and untreated cotton was studied under scanning electron microscope, which is presented in Figure 2.14. Chitosan exhibits an inherent film formation property, which is clearly seen as gloss on fibre surface as shown in Figure 2.14 (b & c). Further the film deposition on fibre surface can be confirmed by prolong boiling of treated sample in distilled water so that the broken appearance of film can be viewed under SEM, as presented in Figure 2.14 (d). The molecular weight of the treated chitosan seems to play some role on the surface appearance in micrograph, the higher gloss of notices in higher molecular weight chitosan (CHT-MC) treated fibres. The micrograph of low molecular weight chitosan (CHT-D4) treated cotton fibres however looks somewhat different with slightly non glossy surface [Figure (e & f)] indicating the penetration of polymeric material in to the fibre structure. This may be attributed to the lower viscosity of low molecular weight chitosans that facilitates better penetration and high molecular weight chitosan having high viscosity confined to the surface depositions only.

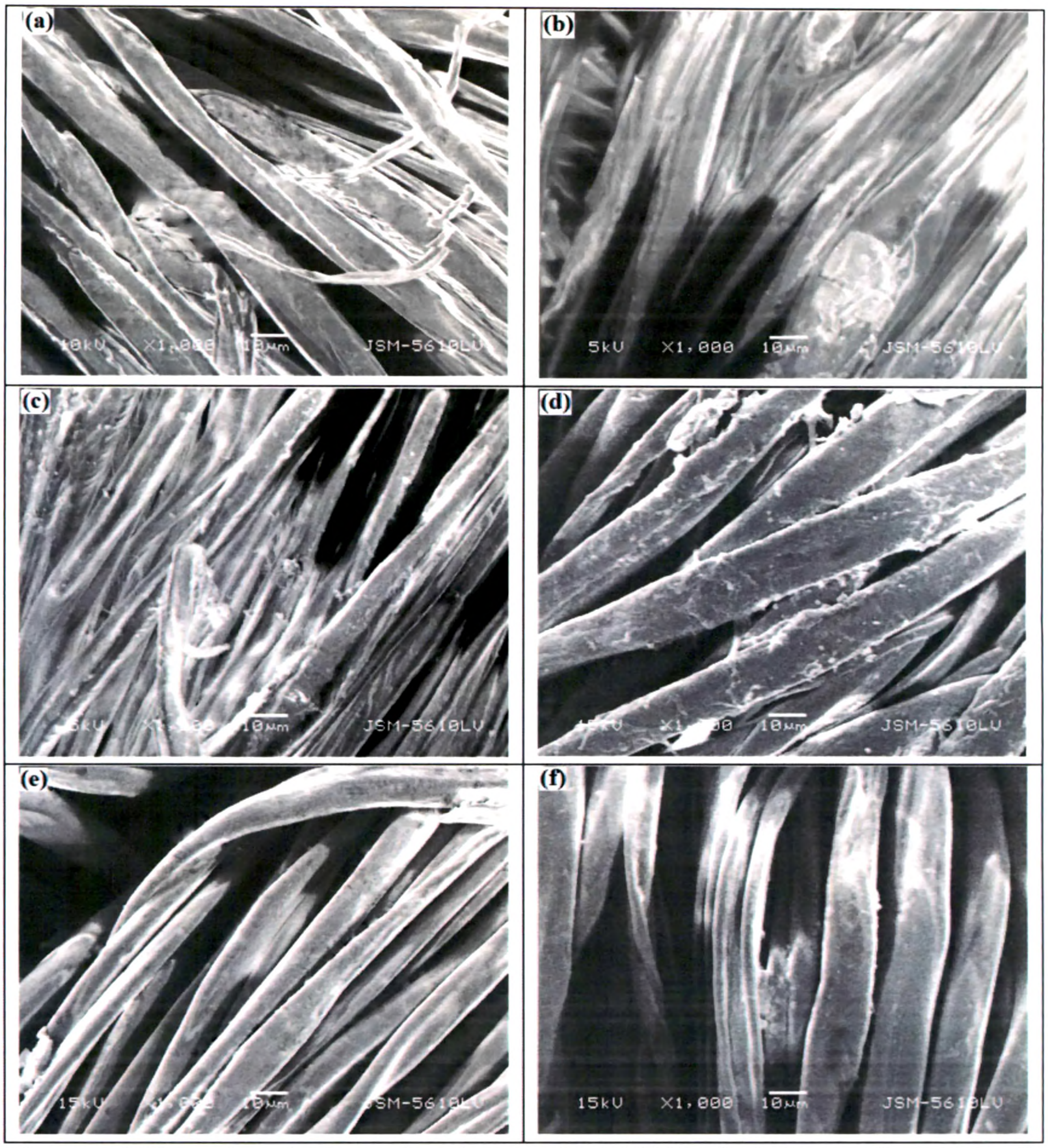


Figure 2.14 Scanning electron microphotographs (x1000) of (a) Cotton Fibre (control), (b) CHT-MC treated fibres, (c) CHT treated fibres (d) CHT treated and then prolong boiled cotton fibres, (e) CHT-D4 treated fibres and (f) CHT-D5 treated fibres

2.3.11 Effect of chitosan treatment on appearance and feel of cotton fabric

The appeal of the fabric is manifested by its appearance and the feel. Various factors such as colour and transparency of the polymeric film (chitosan), presence of functional groups, penetration level of chitosan in to fibre/fabric structure etc influence the appearance of treated cotton fabric. Level of deposition of polymer film on fibrous material is determined by the viscosity of its solution (padding liquor) which in turn is determined by its molecular weight and concentration in pad liquor [67, 68]. These two factors also influence the feel of the treated fabric. In order to understand the influence of chitosan treatment on cotton fabric, the appearance was evaluated in terms of whiteness index (W.I.), yellowness index (Y.I.) and brightness index (B.I.); and the feel in terms of stiffness (measured in bending length with the average of four readings) of different molecular weight chitosans at different concentrations. Results of these properties are presented in Tables 2.18 (A & B) & Tables 2.19(A & B) respectively and graphically in corresponding Figures 2.15, 2.16, 2.17 and 2.18.

Table 2.18A Appearance of chitosan treated cotton fabric as a function of molecular weight and concentration

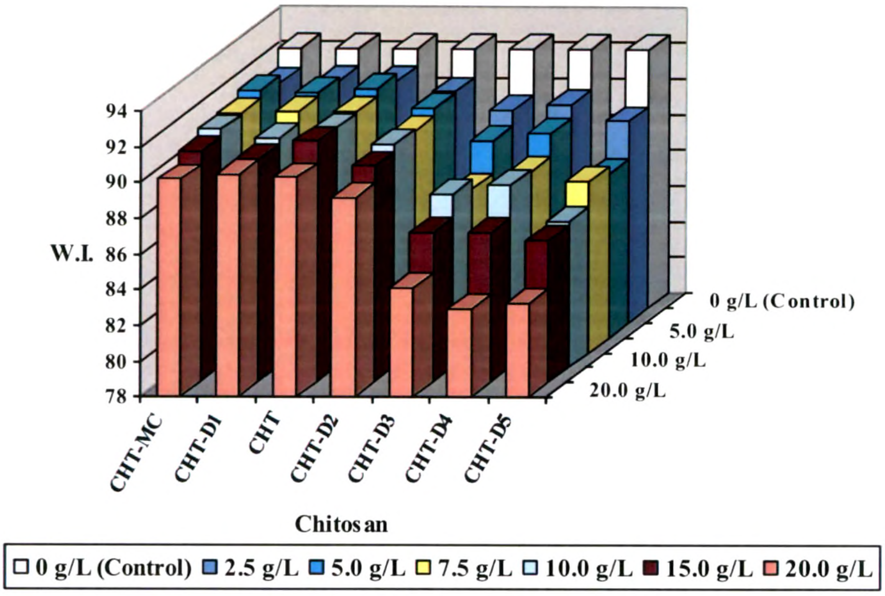
Conc, g/L	**CHT-MC (654,127)**			**CHT-D1 (285,231)**			**CHT (135,839)**			**CHT-D2 (71,676)**		
	WI	**YI**	**BI**	**WI**	**YI**	**BI**	**WI**	**YI**	**BI**	**WI**	**YI**	**BI**
2.5	91.4	3.6	82.4	91.5	3.7	82.3	91.5	3.3	81.6	90.9	3.6	81.4
5.0	91.8	3.6	83.2	91.7	3.6	82.6	91.9	3.4	81.4	90.8	3.6	81.6
7.5	91.4	4.7	82.2	91.5	4.3	81.8	91.5	4.3	80.6	90.4	4.0	82.9
10.0	91.3	4.4	81.9	90.8	4.3	81.6	91.4	4.7	80.6	90.5	4.3	82.6
15.0	90.9	4.9	81.3	90.5	4.8	80.5	91.5	4.5	79.8	90.1	4.7	82.3
20.0	90.2	5.4	79.8	90.5	5.6	80.1	90.3	5.4	77.9	89.2	5.8	79.9

Values in parentheses indicate the mol wt of chitosan,
Indices of control sample: WI= 92.5, YI= 2.6, BI= 84.6

Table 2.18B Appearance of chitosan treated cotton fabric as a function of molecular weight and concentration

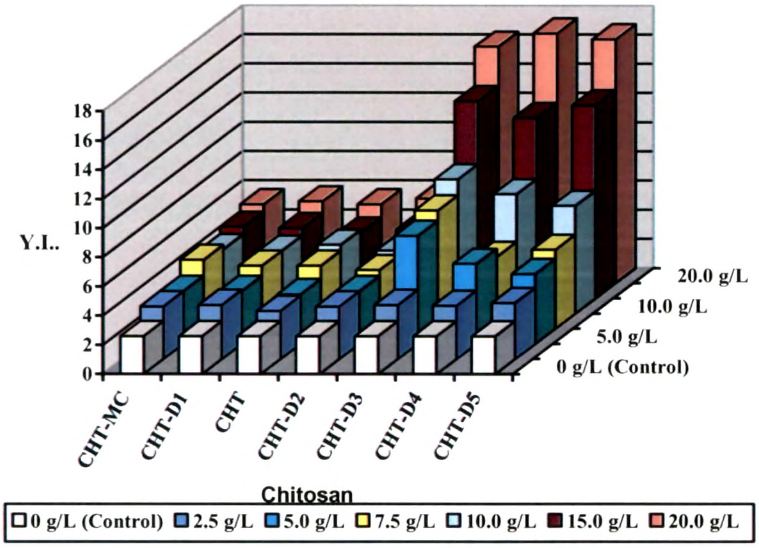
Conc, g/L	**CHT-D3 (38,733)**			**CHT-D4 (20,698)**			**CHT-D5 (11,986)**		
	WI	**YI**	**BI**	**WI**	**YI**	**BI**	**WI**	**YI**	**BI**
2.5	89.9	3.7	79.8	90.2	3.6	78.9	89.3	3.8	78.1
5.0	89.0	7.4	76.9	89.4	5.5	77.9	87.2	4.8	77.7
7.5	89.2	8.1	76.9	88.1	4.9	75.3	87.6	5.4	74.8
10.0	87.7	9.2	74.2	88.2	8.2	74.8	86.2	7.4	73.1
15.0	86.4	13.5	70.6	86.4	12.4	71.5	86.0	13.2	69.4
20.0	84.1	16.2	66.1	83.0	17.1	68.7	83.3	16.7	66.2

Values in parentheses indicate the mol wt of chitosan,
Indices of control sample: WI= 92.5, YI= 2.6, BI= 84.6



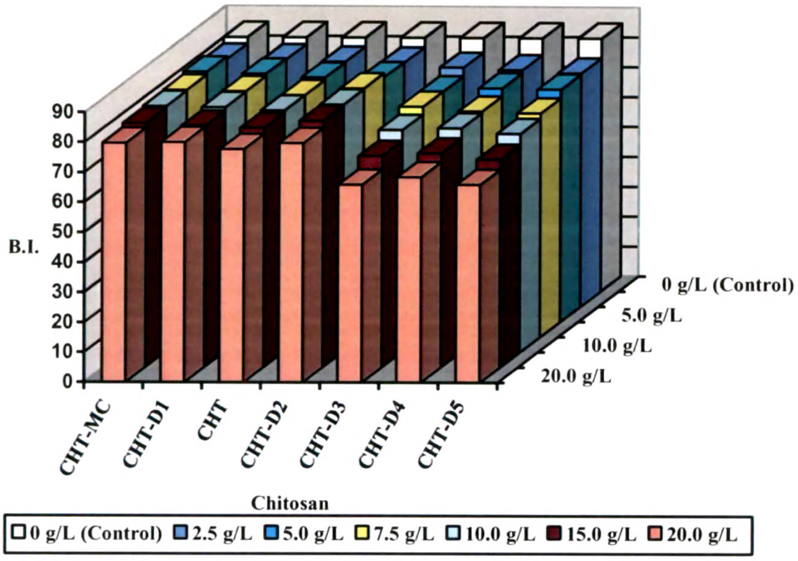
Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.15 Whiteness index (WI) of chitosan treated cotton fabric as a function of molecular weight and concentration



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.16 Yellowness index (YI) of chitosan treated cotton fabric as a function of molecular weight and concentration



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.17 Brightness index (BI) of chitosan treated cotton fabric as a function of molecular weight and concentration

The appearance of cotton fabric in terms of reduction in whiteness and brightness indices or rise in yellowness indices was influenced by normal chitosan as shown in Figure 2.15, Figure 2.16 and Figure 2.17. The whiteness and the brightness of parent chitosan i.e. CHT-MC and CHT treated fabrics were found to be satisfactory and were slightly decreased with increase in concentration of chitosan nevertheless they were in tolerable limits. The appearance of depolymerized chitosan treated fabrics, however, was found to be deteriorated more than that of parent chitosan treated fabrics. The whiteness and brightness depolymerized chitosan treated samples were decreased severely with decrease in molecular weight and increase in concentration. The loss in whiteness or discolouration in depolymerized chitosan treated fabric may be due the possible liberation of nitric oxide gas from $NaNO_2$ in acidic medium that gets adsorbed on various functional groups of chitosan imparting yellowness [94]. The higher extent of (increased) discolouration of treated fabric due depolymerized chitosan was thus governed by the amount of sodium nitrite used. It seems further that the excessive depolymerisation by sodium nitrite produces undesired impurities containing aldehyde end groups, which may react with free amino groups to form –N=C bond causing yellowness. The reduction in brightness of depolymerized chitosan treated fabric may be ascribed to the loss in gloss of fibre surface due to morphological changes occurred due to diffusion of oligomer into the fibre structure, which can be observed as matty surface as shown in scanning electron microphotographs in Figure 2.14(d & e).

Table 2.19A Stiffness of chitosan treated fabric as a function of molecular weight and concentration

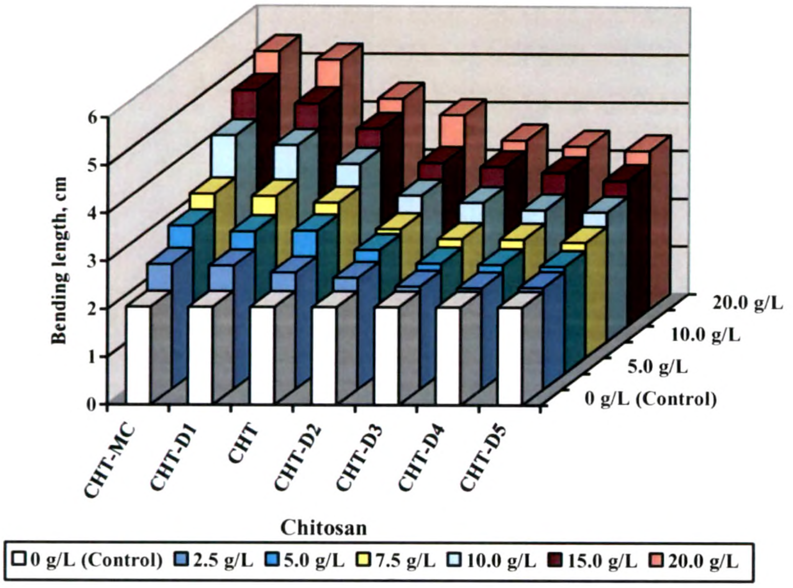
Conc, g/L	Bending length, cm							
	CHT-MC (654,127)		**CHT-D1 (285,231)**		**CHT (135,839)**		**CHT-D2 (71,676)**	
	Warp	**Weft**	**Warp**	**Weft**	**Warp**	**Weft**	**Warp**	**Weft**
2.5	2.61	1.76	2.58	1.72	2.44	1.70	2.33	1.85
5.0	3.08	2.10	2.96	2.10	2.98	2.05	2.58	1.85
7.5	3.41	2.55	3.37	2.40	3.23	2.25	2.68	2.01
10.0	4.29	3.03	4.09	2.89	3.70	2.74	3.05	2.19
15.0	4.90	3.23	4.63	3.11	4.10	3.00	3.39	2.21
20.0	5.38	3.53	5.21	3.38	4.40	3.33	4.06	2.88

Values in parentheses indicate the mol wt of chitosan,
Bending length of control sample: warp = 2.05 cm and weft = 1.68 cm

Table 2.19B Stiffness of chitosan treated fabric as a function of molecular weight and concentration

Conc, g/L	Bending length, cm					
	CHT-D3 (38,733)		**CHT-D4 (20,698)**		**CHT-D5 (11,986)**	
	Warp	**Weft**	**Warp**	**Weft**	**Warp**	**Weft**
2.5	2.15	1.70	2.12	1.69	2.13	1.70
5.0	2.30	1.71	2.27	1.68	2.24	1.70
7.5	2.48	1.86	2.47	1.76	2.41	1.73
10.0	2.90	2.00	2.75	1.94	2.71	1.88
15.0	3.31	2.38	3.19	2.21	3.03	1.96
20.0	3.53	2.68	3.41	2.43	3.32	2.11

Values in parentheses indicate the mol wt of chitosan,
Bending length of control sample: warp = 2.05 cm and weft = 1.68 cm



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.18 Stiffness of chitosan treated cotton fabric as a function of molecular weight and concentration

The handle of the fabric on chitosan treatment was adversely affected as seen from the rise in fabric stiffness with increase in concentration and the molecular weight of chitosan shown in Table 2.19A and Table 2.19B and Figure 2.18. The fabric stiffness and feel treated with low molecular weight chitosan namely CHT-D4 and CHT-D5 were found to be satisfactory and well in acceptable limits. The fabric surface was also found to be excessively harsh in case of high molecular weight chitosan and the inherent appeal of cotton or 'cotton feel' was almost lost. The rigid conformation of chitosan structure and due to the formation of large number of intra and intermolecular cross linkages due to amino and hydroxyl groups as shown in Figure 1.5 (Chapter 1), chitosan produces stiff films [95]. High viscosity solutions of large chitosan molecules confine the rigid film deposition onto fabric surface only thus imparting stiffness to fabric. The presence of chitosan films of high molecular weight chitosans (CHT-MC and CHT) can be clearly seen from Figure 2.14 (b & c). This property is undesired in pretreated fabrics but may be beneficial when applied during finishing process, which impart firmness and body to the fabric. Bhuvana et al.[96], in benefit to the uniform film formation of chitosan on fibre surface, have reported the low frictional values offering itself a better candidate as stiffening agent. The high viscosity solutions, however, cause difficulties during application in padding mangle.

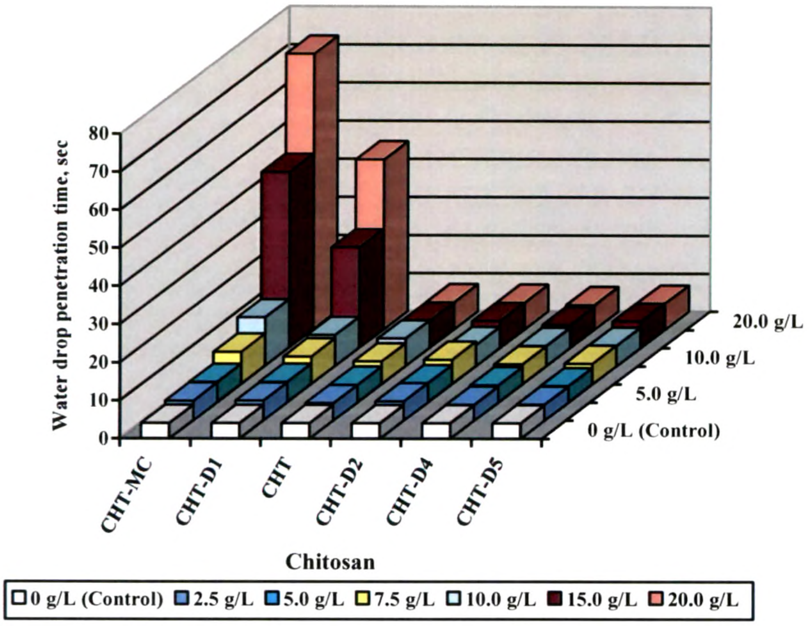
2.3.12 Effect of chitosan treatment on absorbency cotton fabric

Rapid and uniform absorbency for any pretreated fabric is indispensable for the better penetration of dyes and chemicals during the subsequent unit operations like dyeing, printing and finishing. Therefore the effect of chitosan applications on the absorbency was determined, which are shown in Table 2.20 and graphically in Figure 2.19. Absorbency, measured by drop penetration method, reported here are taken as the average of nine readings. The absorbency of chitosan treated fabric was found to be altered by the molecular weight and concentration of applied chitosan. The absorbency of high molecular chitosan (e.g. CHT-MC, CHT-D1 and CHT) treated fabric was high and progressively improved with lowering of molecular weight of chitosan. The absorbency was observed to be reduced with increase in concentration of chitosan. The concentration effect was more substantial in case of high molecular weight chitosan, where as this effect was meager in case of low molecular weight chitosan.

Table 2.20 Absorbency of chitosan treated cotton fabric as a function of molecular weight and concentration

Conc, g/L	**Water drop penetration time in seconds treated with:**					
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
2.5	5.1	5.2	4.5	5.0	4.2	4.2
5.0	5.3	5.3	4.6	5.0	4.5	4.3
7.5	8.4	7.2	5.9	6.4	5.3	5.4
10.0	12.7	8.1	7.2	5.5	5.3	5.4
15.0	46.0	26.3	7.1	7.0	6.0	7.0
20.0	72.3	44.6	7.2	7.1	6.5	6.9

Values in parentheses indicate the mol wt of chitosan, Absorbency of control sample: 4.02 sec



Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.19 Absorbency of chitosan treated cotton fabric as a function of molecular weight and concentration

The decreased absorbency in case of high molecular chitosan may be due to the formation of rigid film of chitosan over surface thus acting as a barrier for the penetration of water. The better absorbency conferred by low molecular weight chitosan treatment may be attributed to the capillary action of rough surface formed, which can be clearly visualized from scanning electron microphotographs in Figure 2.14 (d & e). The apparent drop in absorbency of cotton fabric due to chitosan pretreatment, however, is not expected to cause any hindrance on subsequent processing such as dyeing, printing or finishing. Since the poor absorbency of the fabric is due to rigid film formation on surface and not due to the introduction of hydrophobicity. Such chitosan films contain accessible sites such as -OH and -NH_2 nevertheless they are heavily crosslinked by hydrogen bonding.

2.3.13 Dyeing behaviour

Textiles made from cotton and other cellulose fibres are conventionally dyed with direct, reactive, azoic, vat, sulphur etc dyes. These dyes are characterized by certain inherent properties. Vat dye are known for excellent all round fastness properties but have limitations of high price and problems of poor dye bath stability due to susceptibility of leuco vat dye to oxidation. Reactive dyes from covalent linkages/bonding with fibre and confer good fastness to washing. Also, these dyes are available in wide spectrum of colour range. However, their tendencies to readily hydrolyze and moderate fastness to light are the major drawbacks. Azoics produce bright shades but they poor rubbing fastness properties. Sulphur dyes are very popular for black and blue colours and some fancy shades such as dull green or olive green, brown etc. The dyeings are fast to washing and light but fastness to bleaching is poor. Direct dyes are known for ease of application and for full colour range availability. These dyes possess strong affinity for cellulosic fibres and therefore, also known as substantive dyes. These dyes, however, suffer from poor fastness to washing and other agencies. Any modifications in fibre, dye bath additives, dyeing process and/or after treatments, direct dyes respond greatly in its behaviour [97, 98]. Under this background direct dyes were selected for studying the dyeing behaviour of chitosan treated cotton in the present research project.

Secondly, the structure of chitosan is very much analogous to cellulose (except that the –OH group in cellulose at C2 is being replaced by $-NH_2$ in chitosan), it is anticipated that its treatment should influence the cellulose dyeing in complimentary. In this work, therefore, the effect of pretreatment and after treatment of chitosan on direct dyeing of cotton and the washing fastness properties of these dyed samples was studied. Accordingly, two direct dyes namely C. I. Direct Red 81 (Mol wt 675.6) and C. I. Direct Blue 71 (Mol wt 1029.9) shown in Table 2.1 were selected. Attributing to the presence of cationic amino groups, the effect of chitosan pre- treatment on the dyeability towards acid dyes (C. I. Acid Blue 158, Table 2.1) was also investigated.

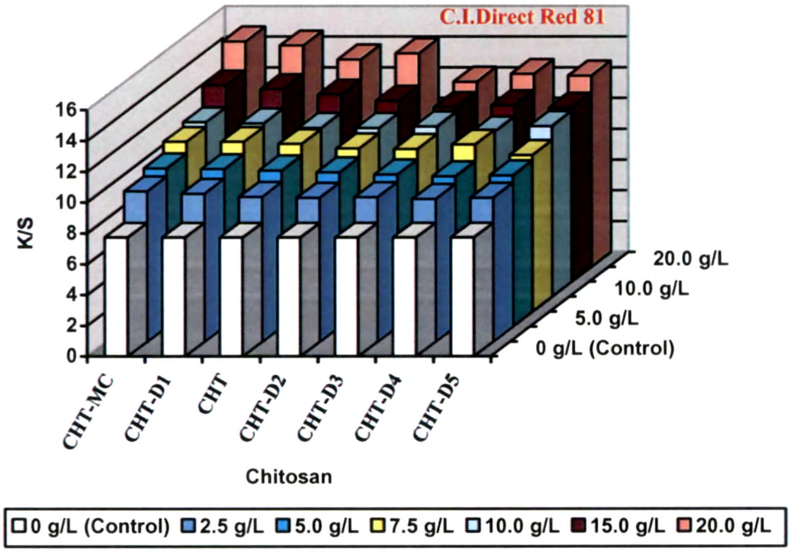
2.3.13.1 Effect of chitosan pretreatment on direct dyeing of cotton fabric

The chitosan, of varying degree of molecular weight, pretreated at different concentrations by pad-dry cure method was dyed with direct dyes mentioned above. The dye uptake, measured in terms of K/S, by these samples is presented in Table 2.21 and Table 2.22; and fastness properties in Table 2.24 and Table 2.25.

Table 2.21 C. I. Direct Red 81 uptake of chitosan treated cotton fabric as a function of molecular weight and concentration

Conc, g/L	**K/S values of C. I. Direct Red 81 dyed samples pretreated with:**						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
2.5	9.77 *[26]*	9.61 *[24]*	9.41 *[22]*	9.35 *[21]*	9.39 *[22]*	9.28 *[20]*	9.36 *[21]*
5.0	10.29 *[33]*	10.24 *[32]*	10.16 *[32]*	10.03 *[30]*	9.90 *[28]*	9.77 *[26]*	9.84 *[27]*
7.5	11.04 *[43]*	11.04 *[43]*	10.90 *[41]*	10.61 *[37]*	10.57 *[37]*	10.86 *[40]*	10.48 *[36]*
10.0	11.34 *[47]*	11.28 *[46]*	10.97 *[42]*	10.98 *[42]*	11.08 *[43]*	10.74 *[39]*	11.09 *[43]*
15.0	12.77 *[65]*	12.53 *[62]*	12.17 *[57]*	11.78 *[52]*	11.36 *[47]*	11.48 *[49]*	11.31 *[46]*
20.0	14.65 *[90]*	14.39 *[89]*	13.48 *[74]*	13.89 *[80]*	12.04 *[56]*	12.54 *[62]*	12.43 *[60]*

Values in parentheses indicate the mol wt of chitosan, Dye: 1% o.w.m.; K/S values of control sample is 7.73; Values in brackets indicate the per cent improvement in colour value compared to control sample



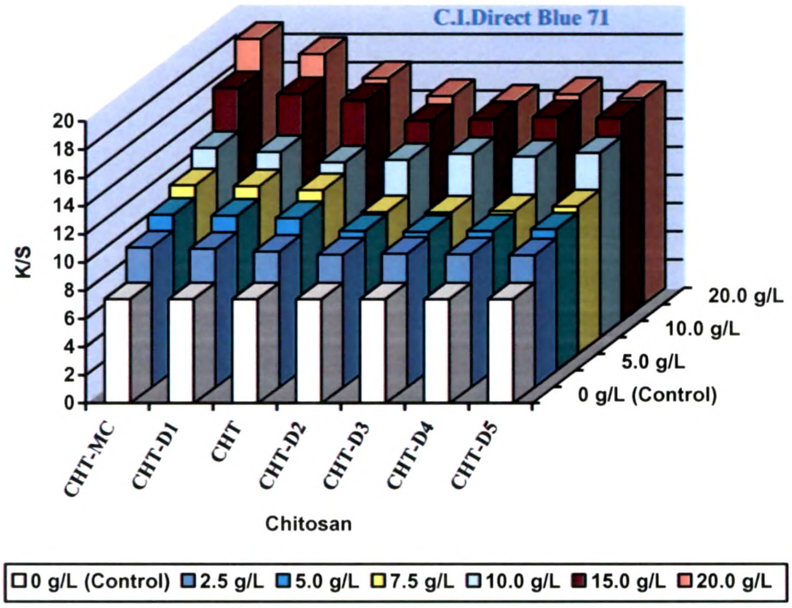
Dye: 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.20 C. I. Direct Red 81 uptake of chitosan treated cotton fabric as a function of molecular weight and concentration

Table 2.22 C. I. Direct Blue 71 uptake of chitosan treated cotton fabric as a function of molecular weight and concentration

Conc, g/L	K/S values of C.I. Direct Blue 71 dyed samples pretreated with:						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
2.5	9.89 *[33]*	9.81 *[32]*	9.60 *[30]*	9.39 *[27]*	9.46 *[28]*	9.41 *[27]*	9.34 *[26]*
5.0	11.04 *[49]*	10.98 *[48]*	10.81 *[46]*	9.90 *[33]*	9.82 *[33]*	9.88 *[33]*	10.01 *[35]*
7.5	11.96 *[61]*	11.90 *[61]*	11.60 *[57]*	10.05 *[36]*	10.02 *[35]*	10.12 *[37]*	10.45 *[41]*
10.0	13.44 *[81]*	13.16 *[78]*	12.42 *[68]*	12.58 *[70]*	13.03 *[76]*	12.82 *[73]*	13.08 *[77]*
15.0	16.50 *[123]*	16.09 *[117]*	15.64 *[111]*	14.18 *[91]*	14.32 *[93]*	14.47 *[95]*	14.39 *[94]*
20.0	18.83 *[154]*	17.76 *[140]*	16.05 *[117]*	14.79 *[99]*	14.40 *[94]*	14.92 *[101]*	14.63 *[97]*

Values in parentheses indicate the mol wt of chitosan, Dye: 1% o.w.m, K/S values of control sample is 7.41, Values in brackets indicate the per cent improvement in colour value compared to control sample



Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.21 C. I. Direct Blue 71 uptake of chitosan pretreated cotton fabric as a function of molecular weight and concentration

The dye uptake (K/S values) for C. I. Direct Red 81 and C. I. Direct Blue 71 by chitosan treated cotton fabric was improved substantially as observed from Table 2.21 and Table 2.22 (Figure 2.20 and Figure 2.21). The uptake was increased with the increase in the concentration of chitosan for a particular molecular weight grade and also the same was increased with increase in molecular weight for varying molecular weight chitosan treatment especially at higher concentration. The dye uptake of low molecular weight chitosan treated samples from CHT-D2 to CHT-D5 was almost remained unchanged for a particular concentration. The dyeing behaviour of chitosan treated fabric, however, was somewhat different for two dyes selected for the experiment. Blue dye showed high substantivity towards chitosan treated fabric than the red.

The enhanced dye uptake due to chitosan may be attributed to the cationic amino groups forming dye sites, which interact with direct dye through hydrogen bonding as well as ionic linkages. High molecular weight chitosan, due to highly viscous nature of their solutions, are confined mostly on the fibre surface resulting greater accumulation of dye on the surface. Also, the number of amino groups is increased with increase in molecular weight and with increase in concentration. It can be observed from the structures of C. I. Direct Red 81 and C. I. Direct Blue 71 (Table 2.1) that the molecular weight of blue dye is high and is characterized by greater degree of planarity due to conjugation system possessing high substantivity and moderate to good wet fastness properties. The structure also shows four anionic ($-SO_3^-$) groups that can form more strong linkages with amino groups. Attributing to these two features, C. I. Direct Blue 71 showed greater substantivity towards chitosan treated fabric.

A normal cotton fabric when entered in dye bath acquires negative surface charge and repels negatively charged dye anions. Conventionally, the negative charge is neutralized by the addition of electrolytes such as sodium chloride, sodium sulphate etc and facilitate approach of direct dyes, by their inherent affinity, towards fibre. The polycationic chitosan can also dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Such effects can be studied by comparing the dyeing results of chitosan treated samples conducted in electrolyte free dye bath with that in presence of electrolyte. The progressive decrease in importance of sodium sulphate taken as electrolyte with increase in chitosan concentration, as shown in Table 2.23 (Figure 2.22

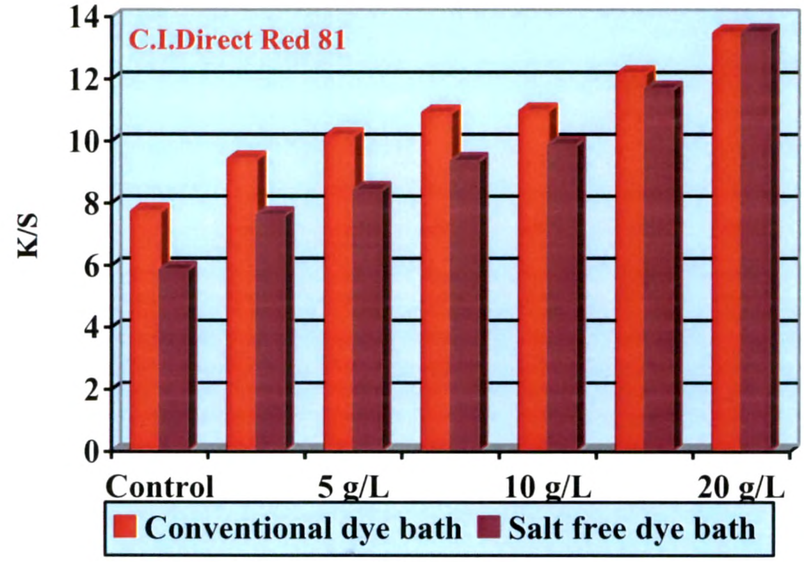
and Figure 2.23), clearly elucidates the role of chitosan in the improvement of dye uptake even at reduced electrolyte concentration.

Table 2.23 Effect of electrolyte (sodium sulphate) on dyeing of chitosan (CHT) treated cotton fabric

CHT, g/L	**K/S values**			
	C.I.Direct Red 81		**C.I. Direct Blue 71**	
	Conventional dye bath	**Salt free dye bath**	**Conventional dye bath**	**Salt free dye bath**
Control	7.73	5.86 *[-24]*	7.41	5.48 *[-26]*
2.5	9.41	7.62 *[-19]*	9.60	7.49 *[-22]*
5.0	10.16	8.43 *[-17]*	10.81	8.86 *[-18]*
7.5	10.90	9.37 *[-14]*	11.60	9.98 *[-14]*
10.0	10.97	9.89 *[-12]*	12.42	10.78 *[-13]*
15.0	12.17	11.68 *[-4]*	15.64	15.17 *[-3]*
20.0	13.48	13.51 *[+0.2]*	16.05	15.98 *[-0.4]*

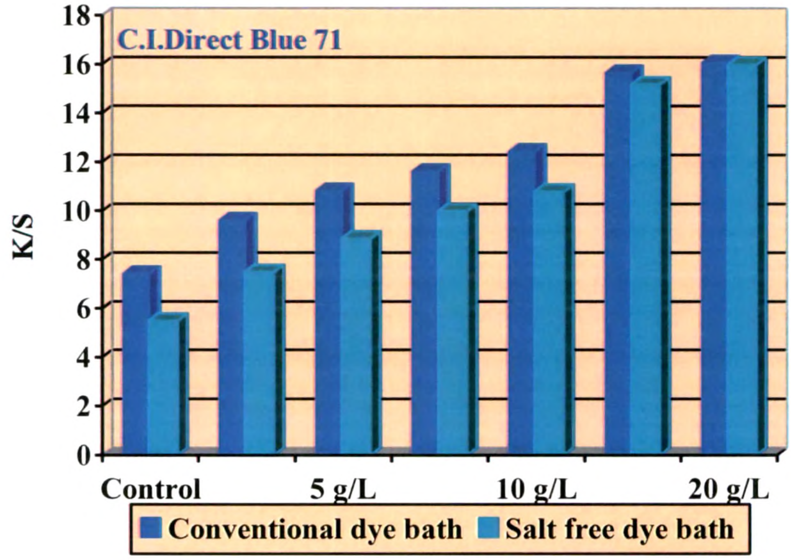
Dye 1% o.w.m, Values in brackets indicate % change in colour value form corresponding conventional dyed samples; -ve sign indicate decrease in colour depth

C. I. Direct Red 81 dye has shown poor washing fastness ratings which may be attributed to its low molecular weight and the poor substantivity due the lesser conjugation as can be seen from its structure (Table 2.1). The fastness of this dye on chitosan treated fabric, as observed from Table 2.24, is improved slightly with increase in concentration of chitosan, particularly in case of relatively low molecular weight chitosan treated samples. On the other hand a slight decline in ratings with increase in concentration of high molecular weight chitosan is noticed. This may be attributed to the preferential surface deposition of high molecular weight chitosan and hence the dye also that may be removed easily during washing. However, the effect of chitosan treatment on washing fastness of dyes having good washing fastness, i.e. C. I. Direct Blue, is only slightly altered, Table 2.25.



Dye 1% o.w.m.

Figure 2.22 Effect of electrolyte (sodium sulphate) on dyeing of chitosan (CHT) treated cotton fabric with C. I. Direct Red 81



Dye 1% o.w.m.

Figure 2.23 Effect of electrolyte (sodium sulphate) on dyeing of chitosan (CHT) treated cotton fabric with C.I. Direct Blue 71

Table 2.24 Effect of chitosan pretreatment on fastness properties of direct dye C.I.Direct Red 81

Conc, g/L	**Washing fastness ratings of C.I.Direct Red 81 dyed samples pretreated with:**						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
5.0	2-3	2-3	2-3	3	3	3	3
10.0	3	3	3	3	2-3	3-4	3-4
15.0	2-3	3	3-4	3-4	3-4	3-4	3-4
20.0	2	3	3	2-3	3-4	3-4	3-4
	Rubbing fastness ratings						
5.0	2	2	2	2	2-3	2-3	2-3
10.0	2	2	2	2	2-3	2-3	2-3
15.0	1-2	1-2	2	2	2	2	2
20.0	1-2	1-2	1-2	2	2	2	2

Values in parentheses indicate the mol wt of chitosan,
Dye 1% o.w.m., ratings of control samples: washing fastness 3 and rubbing fastness 2-3

Table 2.25 Effect of chitosan pretreatment on fastness properties of direct dye C.I. Direct Blue 71

Conc, g/L	**Washing Fastness Ratings of C.I.Direct Blue 71 dyed samples pretreated with:**						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
5.0	4-5	4	4-5	4-5	4	4-5	4-5
10.0	4	4-5	4-5	4	4-5	4-5	4
15.0	4	4-5	4-5	4	4-5	5	4-5
20.0	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Rubbing fastness ratings						
5.0	2	2	2	2	2-3	2-3	2-3
10.0	2	2	2	2	2-3	2-3	2-3
15.0	1-2	1-2	2	2	2	2	2
20.0	1-2	1-2	1-2	2	2	2	2

Values in parentheses indicate the mol wt of chitosan,
Dye: 1% o.w.m, ratings of control samples: washing fastness 4-5 and rubbing fastness 2-3

The rubbing fastness, as can be seen from the above tables, reduced with the increase in the molecular weight and concentration of chitosan in the treatment bath. This may be due to surface deposition of chitosan that can be easily rubbed off.

2.3.13.2 Effect of chitosan treatment on colour depth of direct dyed cotton fabric

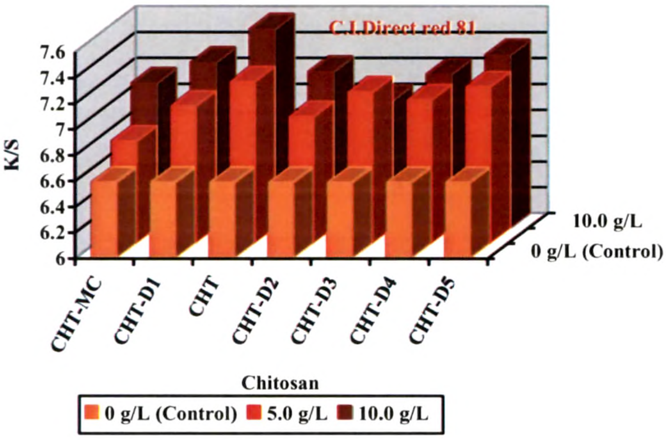
Chitosan, with due regards to its several inherent properties, can be employed as finishing agent and may be required to apply onto dyed fabrics. Chitosan, due presence of various functional groups, is believed to interact with the dyes present on fibre and alter their properties. In this study, cotton fabric was dyed separately with direct dyes namely C. I. Direct Red 81 and C. I. Direct Blue 71 of 1% shade by conventional dyeing method. The dyed fabric was then treated with chitosan solution by pad-dry cure method.

Table 2.26 Effect of chitosan treatment on colour depth and fastness of direct dyed cotton fabric

Sample	**Chitosan, g/L**	**C. I. Direct Red 81**			**C.I. Direct Blue 71**		
		K/S Values	**Washing Fastness**	**Rubbing Fastness**	**K/S Values**	**Washing Fastness**	**Rubbing Fastness**
Control	-	6.59	3	2-3	7.29	4-5	2-3
CHT-MC Treated	5	6.79 *[3.0]*	3	3	7.24 *[-0.7]*	4	3
	10	7.12 *[8.0]*	3-4	3	7.49 *[2.7]*	4-5	3
CHT-D1 Treated	5	7.06 *[7.1]*	3-4	3	7.19 *[-0.1]*	4-5	3
	10	7.28 *[10.5]*	3-4	3	7.33 *[0.6]*	4-5	3
CHT Treated	5	7.25 *[10.0]*	3-4	2-3	6.83 *[-6.3]*	4-5	3
	10	7.54 *[14.4]*	3-4	3	7.31 *[0.3]*	4	3
CHT-D2 Treated	5	6.98 *[5.9]*	3-4	2-3	6.75 *[-7.4]*	4-5	3
	10	7.21 *[9.4]*	3-4	3	7.02 *[-3.7]*	4-5	3
CHT-D3 Treated	5	7.17 *[8.8]*	3-4	2-3	6.59 *[-9.6]*	4-5	3
	10	6.99 *[6.1]*	4-5	2-3	6.62 *[-9.2]*	4-5	3
CHT-D4 Treated	5	7.11 *[7.9]*	4	2-3	6.64 *[-8.9]*	4-5	2-3
	10	7.19 *[9.1]*	4	2-3	6.81 *[-6.6]*	5	3
CHT-D5 Treated	5	7.21 *[9.4]*	4	2-3	6.71 *[-7.9]*	4-5	2-3
	10	7.34 *[11.4]*	4-5	2-3	6.74 *[-3.4]*	5	2-3

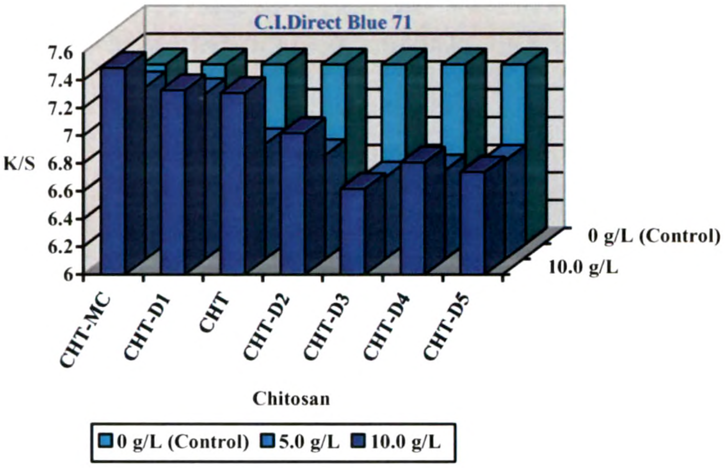
Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986,
Values in bracket indicate the per cent change in colour value compared to control sample

Table 2.26 (Figure 2.24 and Figure 2.25) shows that the colour value of C. I. Direct Red 81 improved whereas that of C.I. Direct Blue 71 decreased by the chitosan after treatment, nevertheless to very small extent. Any regular trend on the colour depth, however, is not noticed due to the molecular weight of treated chitosan. In all cases, the bloom is somewhat enhanced at higher concentration treatment. In case of red dyed samples, blooming is on higher side on high molecular weight chitosan treated samples whereas low molecular weight showed somewhat lesser but almost similar level of blooming. In blue dyed samples, the colour change was negligible when treated with high molecular weight chitosan and the loss in colour value was observed in low molecular weight chitosan treated samples. The apparent changes in shade may be attributed to the migration of dye from the fibre phase to the chitosan phase during padding and subsequently during drying operations due to the interaction of the anionic sulphonate group of dye with cationic groups of chitosan. The higher dye migration of C.I. Direct Red 81 may be attributed to its low molecular weight and poor washing fastness. The washing fastness of post dyeing chitosan derivative treatment was improved to some extent. This may be attributed to the complex formation between dye and the chitosan. Rubbing fastness, however, was not significantly altered.



Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.24 Effect of chitosan treatment on colour depth and fastness of direct dyed cotton fabric



Dye 1% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.25 Effect of chitosan treatment on colour depth and fastness of direct dyed cotton fabric

2.3.13.3 Effect of chitosan pretreatment on acid dyeing of cotton fabric

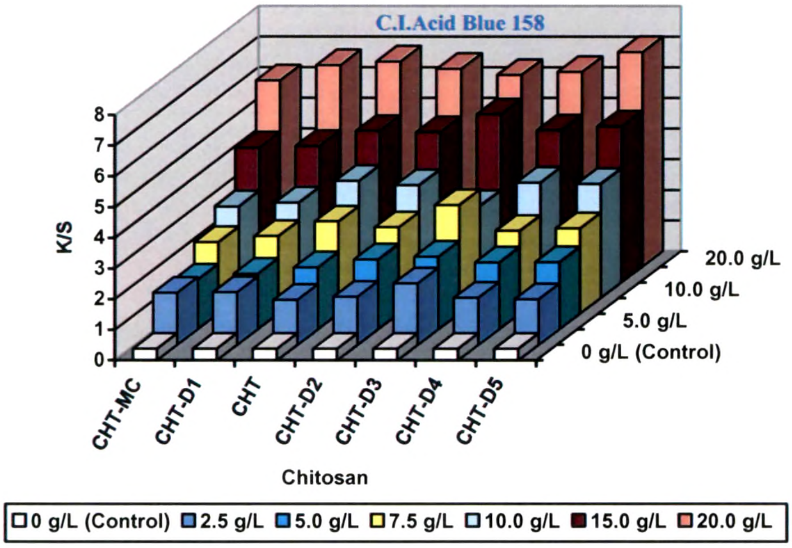
Chitosan possesses one amino group in its glucosamine unit, which forms positive charge in presence of acid. This positively charged amino group can form salt linkage with anions. To characterize the chitosan treated fabric, the work was extended further to investigate its dyeability towards acid dye (C.I. Acid Blue158), which is non dyeable towards normal cotton. The results are presented in Table 2.27 and graphically in Figure 2.26.

Table 2.27 Effect of chitosan treatment on acid dyeing

Conc, g/L	K/S values of C.I. Acid Blue 158 dyed samples pretreated with:						
	CHT-MC (654,127)	CHT-D1 (285,231)	CHT (135,839)	CHT-D2 (71,676)	CHT-D3 (38,733)	CHT-D4 (20,698)	CHT-D5 (11,986)
2.5	1.70	1.72	1.47	1.56	2.01	1.54	1.49
5.0	1.61	1.81	2.02	2.28	2.37	2.18	2.19
7.5	2.33	2.53	3.01	2.82	3.55	2.69	2.78
10.0	2.99	3.12	3.83	3.69	3.01	3.77	3.73
15.0	4.40	4.45	4.94	4.90	5.49	4.96	5.09
20.0	6.09	6.59	6.70	6.47	6.26	6.36	7.01

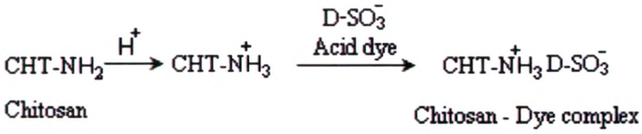
Dye 2% o.w.m, K/S values of control sample is 0.38; Values in parentheses indicate the mol wt of chitosan

It was revealed from these demonstrations that the chitosan derivatives treated cotton fabrics dyed substantially with acid blue158 as against only a tint on control and remained fast to hard soaping. A progressive increase in dye up take was observed with increase in concentration of respective chitosan. The dye uptake, however, was almost identical by the samples when treated with varying molecular weight chitosan at any particular concentration. This kind of dyeability can be purely attributed to the binding of acid dye to chitosan by salt linkages as shown in scheme 2.2. Thus, the dyeability toward acid dye can be taken as one of the characterization test for the retention of chitosan on cotton fabric and the progressive increase in dye uptake corresponds to the number of protonated amino groups of chitosan present on treated cotton fabric forming ionic linkage with stoichiometric amount of anionic acid dye.



Dye 2% o.w.m, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

Figure 2.26 Effect of chitosan pretreatment on acid dyeing



$$\underset{\text{Chitosan}}{\text{CHT-NH}_2} \xrightarrow{H^+} \text{CHT-}\overset{+}{\text{N}}\text{H}_3 \xrightarrow[\text{Acid dye}]{\text{D-SO}_3^-} \underset{\text{Chitosan - Dye complex}}{\text{CHT-}\overset{+}{\text{N}}\text{H}_3\,\text{D-SO}_3^-}$$

Scheme 2.2 Reaction of chitosan with acid dye

2.3.14 Effect of chitosan treatment on wrinkle recovery property of cotton fabric

The aesthetic appeal of cotton cloth or garments is severely affected due to its creasing tendency. Creasing in cotton fabrics occurs due to the bonding of free hydroxyl groups, present in the amorphous regions, through hydrogen bonds when pressed or folded. Thus the creasing behaviour of cotton may be directly associated with the ability of free hydroxyl groups in amorphous region to get bound to each other. The creasing problem can, therefore, be minimized by blocking or masking these hydroxyl groups by means of cross linking of hydroxyl groups of adjacent cellulose macromolecules. Crosslinking agent based on aminoplast resins, e.g. dimethylol dihydroxy ethylene urea (DMDHEU) are commercially employed easy care finishing of cotton, Figure 2.27 [25, 26]. The performance of DMDHEU and various grades of chitosan in terms of crease recovery angle in easy care finishing of cotton are illustrated in Table 2.28 and Table 2.29 respectively. DMDHEU was applied onto cotton fabric by pad-dry cureprocess using magnesium chloride as catalyst and acetic acid.

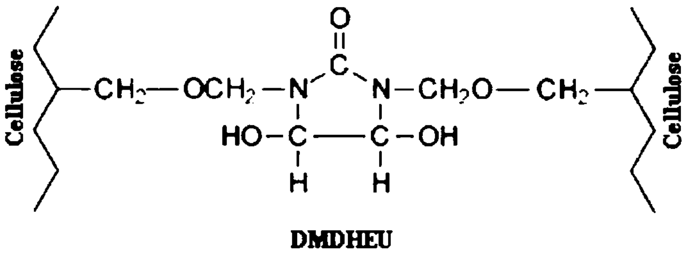


Figure 2.27 Crosslinking of cellulose macromolecules by DMDHEU

Compared to commercial cross linking agent DMDHEU treatment, Table 2.28; the wrinkle recovery of chitosan treated cotton fabrics was not satisfactory, Table 2.29. There was tremendous decline in CRA with increase in concentration of chitosan. However, there is slight improvement in wrinkle recovery by lowering the molecular weight especially for chitosan applications at low concentrations. The high molecular weight chitosan is believed to form a surface coating thus ignoring the possibility of cross linking. Therefore, stiff film formed may deform almost permanently when stressed. This may be the fundamental reason for low CRA values for any stiff finishes. In order to minimize the loss in resiliency, addition of commercial cross linking agents to the pad bath formulation is recommended, Table 2.30.

Table 2.28 Wrinkle recovery property of DMDHEU treated cotton fabric

DMDHEU, g/L	Crease Recovery Angle^{0}		
	Warp	**Weft**	**Total**
Control	80	81	161
20	85	95	180
40	106	101	207
60	112	113	215
80	114	112	226
100	119	123	233

Pad liquor: $MgCl_2$ 10 g/L, Acetic acid 15 ml/L; Curing temp/time 150 ^{0}C/4min

Table 2.29 Wrinkle recovery property of chitosan treated cotton fabric

Conc, g/L	Crease Recovery Angle^{0} of cotton fabrics pretreated with:						
	CHT-MC (654,127)	**CHT-D1 (285,231)**	**CHT (135,839)**	**CHT-D2 (71,676)**	**CHT-D3 (38,733)**	**CHT-D4 (20,698)**	**CHT-D5 (11,986)**
2.5	137	140	140	140	176	167	170
5.0	143	140	140	160	164	163	164
7.5	129	128	119	152	141	151	152
10.0	94	108	125	138	128	140	144
15.0	96	98	110	127	134	141	140
20.0	90	91	98	116	121	138	139

Values in parentheses indicate the mol wt of chitosan, CRA of control sample 161^{0}

Table 2.30 Wrinkle recovery property of chitosan and DMDHEU treated cotton fabric

DMDHEU concentration, g/L	Crease Recovery Angle^{0}		
	DMDHEU treated	**DMDHEU + CHT (10 g/L) treated**	**DMDHEU + CHT (20 g/L) treated**
20	180	153	134
40	207	163	139
60	215	177	158
80	226	191	170
100	233	198	179

Pad liquor: $MgCl_2$ 10 g/L, Acetic acid 15 ml/L; Curing temp/time 150 ^{0}C/4 min,
CRA of control sample is 161^{0}, CHT (10g/L) treated 125^{0}, CHT (20g/L) treated 98^{0}

2.3.15 Effect of chitosan treatment on resistance against microorganism of cotton fabric

Textile products made out of natural fibres provide favourable environment for the growth of microorganisms (algae, fungi, bacteria etc), due to moisture and warmth. These organisms are mainly responsible for discolouration, stains, strength loss etc of fabric and skin allergies, infection diseases etc to human body [42, 99-101]. The rancid smell is produced when bacteria that are present on the skin work on sweat and decompose it. The decomposition products that are responsible for odour are ammonia, methyl amine, hydrogen sulphide, low molecular weight fatty acids, urea etc [102-104]. Antimicrobial finishes can give rise to hygienic freshness and also can be used to fight against pathogenic and parasitic microorganism. Antimicrobial agents either inhibit the growth (-static) or kill (-cidal) the microorganism. Using number of chemicals such as organo-metallics, phenols, thiophenols, formaldehyde derivatives and several quaternary ammonium compounds, microbial growth can be inhibited. These, however, chemicals are non biodegradable and toxic. Some of the commercial antimicrobial textile products recently/currently marketed/available are: Biogaurd produced by Aegis Environments (formerly Dow Corning) is quaternary ammonium compound, namely, 3-trimethoxy silyl propyldimethyl octadecyl ammonium chloride, Reputex 20 (Arch Chemicals) is polyhexamethylene biguanide, Triclosan (2,4,4'-trichloron2'-hydroxydiphenyl ether) etc. Environmental issues of these products are still of concern [26, 99]. Cotton fabric with good antimicrobial activity is obtained by using chitosan, which is attributed to the amino groups that are present on chitosan macromolecule. Thus the degree of deacetylation, molecular weight and concentration of chitosan influence the antimicrobial activity [1]. The antimicrobial properties of chitosan and its derivatives are studied in present and subsequent chapters.

The composted soil bed composed of variety of microbes (e.g. bacteria and fungi) can be employed in soil burial test. The microbial attack of cellulolytic microflora in a composted soil bed is considered to be the most rigorous and practical means for the evaluation of anti deterioration treatments. The treated and untreated fabric strips are buried and exposed to the microbial attack (cellulolytic microflora) for a stipulated period. The change in fibre strength (tenacity) of the sample during incubation is taken as a measure of the effectiveness of the biocide compound [105]. The effect of different molecular weight grades of chitosan treatment on cotton fabric for resistance against microbial attack was studied. Similar study was conducted on chitosan treated dyed fabrics i.e. post dyeing chitosan treated.

Table 2.31 Effect chitosan treatment on resistance against microbial attack of cotton fabric (soil burial test)

Sample	Tenacity, g/tex		Drop in strength, %	Elongation at break, %	
	Before soil burial	**After soil burial**		**Before soil burial**	**After soil burial**
Untreated cotton fabric	23.33	18.98	18.65	5.25	3.50
Control	20.87	18.08	22.50	5.00	3.50
CHT-MC	22.02	19.38	11.98	5.00	3.50
CHT-D1	21.87	19.07	12.76	4.50	3.5
CHT	21.77	18.64	14.36	4.5	3.75
CHT-D2	21.87	18.83	13.90	4.5	3.75
CHT-D3	22.03	19.00	13.75	4.5	3.75
CHT-D4	21.88	18.75	14.31	4.5	3.5
CHT-D5	22.01	18.51	15.90	4.5	3.5

Conc of chitosan derivatives in pad liquor 10 g/L, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

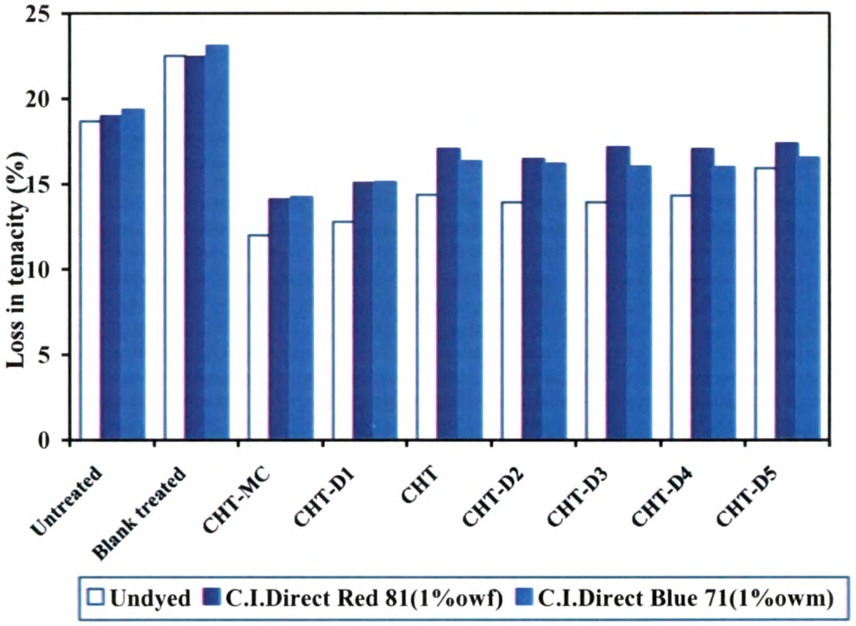
It was observed from Table 2.31 that the tenacity of cotton fibres decreased due hydrolytic degradation during blank treatment with acetic acid and curing at elevated temperature. The fibre strength was restored significantly by the treatment chitosan. The effect of molecular weight of chitosan on tensile properties of cotton fibre was found to be of almost identical level. The higher molecular weight chitosan, however, showed somewhat better strength fibre. This improvement may be attributed to the load bearing capacity of rigid film anchored over the fibre surface. The rigidity of high molecular weight chitosan and interaction of aldehyde end groups of anhydromannitol on depolymerized chitosan with cellulose may probably be the contributing factor in strength determination [37]. The undyed and dyed untreated cotton fabrics, as revealed from Table 2.31 and Table 2.32 (Figure 2.28), were more prone to microbial attack of cellulolytic microflora in a composted soil bed. The less loss in tenacity of fibre means better resistance against microbes. The blank treated samples, both undyed and dyed, showed maximum strength loss followed by untreated samples. Samples treated with chitosan were found to be more resistant to microbial attack as manifested by the lesser drop in strength. In case of undyed fabric, with increase in the molecular weight of chitosan, the strength loss was found to be progressively decreased. Further, the dyed fabrics treated with chitosan were slightly more susceptible for microbial attack in soil burial test. The elongation capacity of fibre was also found to be affected due to rotting; nevertheless the extent was almost of same level for all chosen grades of chitosan, Table 2.31.

Table 2.32 Effect chitosan treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

Sample	**C.I. Direct Blue 71**			**C. I. Direct Red 81**		
	Tenacity, g/tex		**Drop in strength, %**	**Tenacity, g/tex**		**Drop in strength, %**
	Before soil burial	**After soil burial**		**Before soil burial**	**After soil burial**	
Dyed Untreated	22.68	18.32	19.33	22.73	18.42	18.96
Dyed (Blank treated)	20.66	15.89	23.08	20.81	16.14	22.43
CHT-MC	21.86	18.75	14.23	21.72	18.66	14.09
CHT-D1	21.72	18.44	15.10	21.41	18.19	15.04
CHT	21.59	18.06	16.33	21.14	17.95	17.04
CHT-D2	21.69	18.18	16.18	21.20	17.71	16.46
CHT-D3	21.36	17.94	16.01	21.25	17.61	17.13
CHT-D4	21.54	18.10	15.97	21.04	17.46	17.02
CHT-D5	21.41	17.87	16.53	21.50	17.77	17.35

Dye 1%, o.w.m, Conc of chitosan derivatives in pad liquor 10g/L, Blank treatment was given with acetic acid 15 ml/L, sodium acetate 10 g/L by pad-dry cure method, Mol wt of chitosan grades: CHT-MC=654,127; CHT-D1=285,231; CHT=135,839; CHT-D2=71,676; CHT-D3=38,733; CHT-D4=20,698 and CHT-D5=11,986

The susceptibility of blank treated samples to microbial attack may be probably due to the acid hydrolytic degradation occurred during thermo curing. The mode of interaction between chitosan, its derivatives and the microorganism may be considered to be the combination of different mechanisms. Chitosan believed to form a rigid film over the fibre surface that share the load and also act as a protective layer against microbes during rotting. Increased losses in strength due to rotting in case of low molecular weight chitosans may be due to the greater permeability for microorganisms due to more opened surface as can be observed from SEM, Figure 2.14 (e & f).



Dye 1% o.w.m., Conc of chitosan derivatives in pad liquor 10 g/L, blank treatment was given with acetic acid 15 ml/L, sodium acetate 10 g/L by pad-dry cure method; Mol wt of chitosan grades: CHT -MC=654,127, CHT-D1=285,231, CHT=135,839, CHT-D2=71,676, CHT-D3=38,733, CHT-D4=20,698 and CHT- D5=11,986

Figure 2.28 Effect chitosan treatments on resistance against microbial attack of cotton fabric

Secondly, due to their polycationic nature, chitosan exhibit inherent antimicrobial properties. The cell wall of most of the microbes is a polysaccharide composed of lipopolysaccharide and/or peptidoglycan both having an ionic group due to the presence of phosphates, carboxylates, *N*-acetylmuramic acid etc that can interact with poly cations of CHT derivatives. This cell wall maintains the integrity of cellular components and shields the cell from the extracellular environments. Immediately beneath the cell wall is a semi- permeable membrane which encloses intracellular organelles and a myriad of enzymes and nucleic acid. The enzymes are responsible for the chemical reactions that take place within the cell, and the nucleic acids store all the genetic information of the organism. The survival or growth of microorganisms depends on the integrity of the cell and the concerted action and proper state of all these components. It is believed that the polycationic nature of chitosan initiates binding with the cell membrane by means of electrostatic attraction with negatively charged microbial cell membrane. Once bound to the cell surface, chitosan is thought to affect membrane permeability which results into the leakage of proteinaceous material and other intracellular constituents of the microbial cell causing death due to the loss of essential fluids [99, 106, 107]. Chitosan is also observed to bind DNA and inhibit mRNA and protein synthesis. Low molecular weight chitosan is more effective as it penetrates deeper into the cell of microorganisms [108, 109]. Due to chelation property, chitosan also binds trace of essential metal ions present in the intracellular fluid. Deficiency of such metal ions may inhibit production of toxins, enzymes and the microbial growth [110].

2.3.16 Pad-dry-alkali process

Application of chitosan by pad-dry cure process has faced certain challenges particularly of moisture related and drape. The treated fabrics acquired undesired stiffness and lost the inherent cotton feel and the absorbency was affected to some extent. In order to overcome such limitations, an attempt was made to modify the process. Chitosan is soluble in acidic medium and precipitates in alkaline and this principle was employed in pad-dry alkali method. This process is the combination of exhaust and padding method and thermal energy is conserved. Fabric was treated with acidic chitosan solution in presence of sodium acetate, as viscosity modifier, for thirty minutes and then passed through padding rollers. The treated fabric was air dried and soaked in sodium hydroxide solution for ten minutes so that chitosan particles can be deposited in situ of the fibre. The fabric was then washed thoroughly, dried and hot pressed. The surface morphology of the cotton fibres treated with chitosan by pad-dry-alkali process, as observed in SEM, is shown in Figure 2.29. The surface deposition of chitosan on fibre can be easily visualized from SEM of treated samples. A rough surface together with some discrete particles is the evidence of chitosan deposition on surface. Swelling of fibres to some extent is also seen when treated with low molecular weight chitosan.

Table 2.33A and Table 2.33B present various properties of CHT and CHT-D5 treated fabrics by pad-dry -alkali process.

Table 2.33A Properties of chitosan treated cotton fabric by pad-dry-alkali process

Properties	**Control**	**Pad - dry cure process, 2.5g/L**		**Pad - dry- alkali process, 2.5 g/L**	
		CHT Treated	**CHT-D5 Treated**	**CHT Treated**	**CHT-D5 Treated**
Whiteness Index,	*92.5*	91.5	89.3	92.5	92.4
Bending length, cm	*2.05*	2.44	2.13	2.08	2.06
Absorbency, sec	*4.02*	4.54	4.18	4.22	4.09
Dye up take, K/S					
C.I.Direct Red 81	*7.73*	9.41 [22]	9.36 [21]	9.47	9.51
C.I.Direct Blue 71	*7.41*	9.60 [30]	9.34 [26]	9.77	9.63
C.I. Acid Blue158	*0.38*	1.47	1.49	1.70	1.58
Washing fastness					
C.I.Direct Red 81	*3*	2-3	3	2-3	2-3
C.I.Direct Blue 71	*4-5*	4-5	4-5	3-4	3-4
CRA^0	161	140	170	138	126

Values in brackets indicate the change in colour value from control

Table 2.33B Properties of chitosan treated cotton fabric by pad-dry-alkali process

Properties	**Control**	**Pad - dry- cure process, 10 g/L**		**Pad - dry- alkali process, 10/L**	
		CHT Treated	**CHT-D5 Treated**	**CHT Treated**	**CHT-D5 Treated**
Whiteness Index,	92.5	91.4	86.2	92.3	92.3
Bending length, cm	2.05	3.70	2.71	2.32	2.26
Absorbency, sec	4.02	7.20	5.41	5.06	4.11
Dye up take, K/s					
C.I.Direct Red 81	*7.73*	10.97 [42]	11.09 [43]	11.43	11.21
C.I.Direct Blue 71	*7.41*	12.42 [68]	13.08 [77]	12.38	12.88
C.I. Acid Blue158	*0.38*	3.83	3.73	3.95	3.81
Washing fastness					
C.I.Direct Red 81	*3*	3	3-4	2-3	2-3
C.I.Direct Blue 71	*4-5*	4-5	4	3-4	3-4
CRA^0	161	125	144	128	134

Values in brackets indicate the change in colour value from control

The whiteness index was very much close to that of control. The stiffness was lower than that was observed with counterpart in pad-dry cure method. Absorbency and dyeing results were superior to curing method. This method, however, was not suitable for the treatment of post dyed fabrics due to heavy bleeding of dye. The fastness to washing of chitosan treated by pad-dry-alkali process and then dyed samples was unsatisfactory. Wrinkle recovery property was also affected severely.

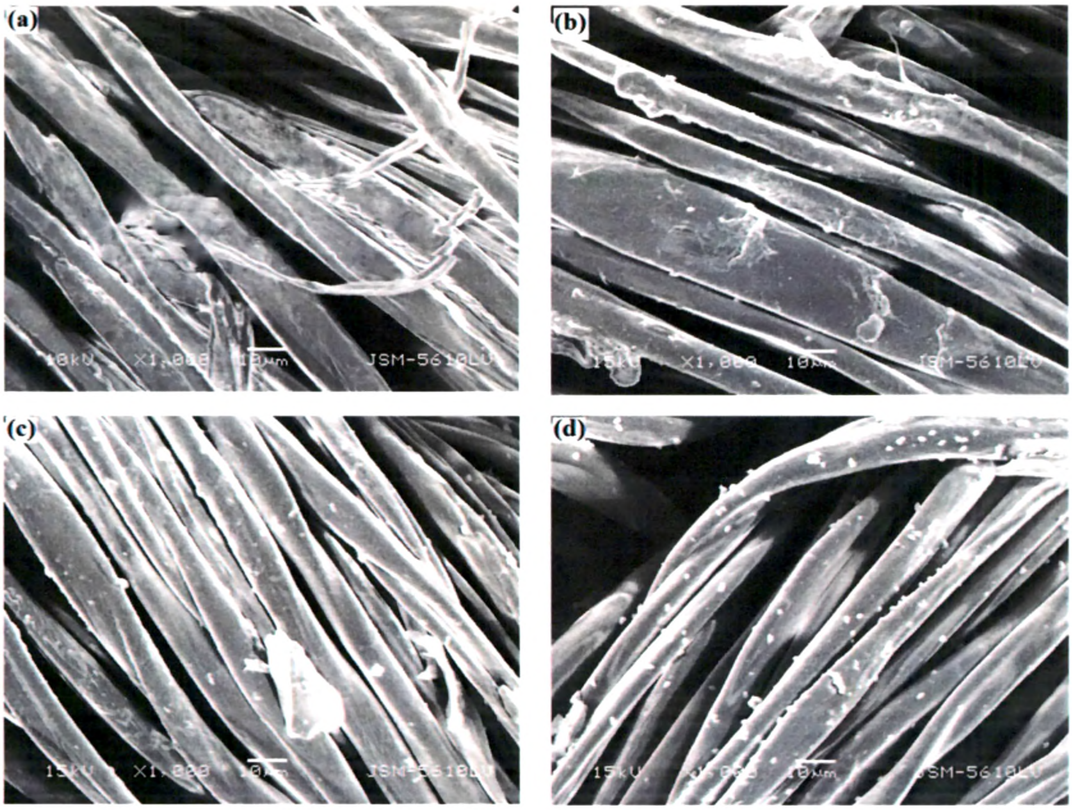


Figure 2.29 Scanning electron microphotographs chitosan treated samples by pad-dry-alkali method (x1000) (a) Cotton Fibre (control), (b) CHT-MC treated fibres, (c) CHT treated fibres and (d) CHT-D5 treated fibres

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