Improvement in properties of cotton fabric through synthesized nano-chitosan application

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In this paper, the study on synthesis, characterization and application of nano-chitosan on cotton fabric has been reported. The nano-chitosan treated fabrics are then tested for appearance, tensile, absorbency, stiffness, dyeing behaviour, wrinkle recovery and antibacterial properties. Low molecular weight chitosans are prepared by nitrous acid hydrolysis method; the molecular weights are determined viscometrically. Nano-chitosans are synthesized by ionic gelation of pentasodium triplyophosphate and chitosan, and then characterized by particle size determination. The fabric samples are pretreated with normal and nano-chitosan solutions by pad-dry-cure technique. The surface morphology of treated cotton fabric has been studied by SEM analysis. The treated fabrics have also been dyed and their whiteness, yellowness and brightness indices are evaluated. It is found that the particle size and polydispersity of chitosan in solution are affected by the variation in molecular weight. The dye uptake and wash fastness of nano-chitosan treated fabrics are found to be improved. An enhanced antibacterial property is observed with the reduction of nano-chitosan particles and when coupled with nano silver colloid.

Keywords: Antibacterial property, Chitosan, Cotton, Dyeing behaviour, Nano-chitosan, Wrinkle recovery

1 Introduction

Various wet processing operations of textiles from initial preparatory processes to final finished clothes are now focused for green technology. Several conventional non-ecofriendly chemicals are being replaced by natural based products that are safe to environment and health during manufacturing and usage. Applications of enzymes in preparatory and in bio-polishing, natural dyes for coloration, biopolymers and their derivatives in fibre production and finishing processes, etc are some of them. One such biopolymer of great interest in recent years is chitosan, derived from alkaline deacetylation of chitin.1

The precursor chitin is a nitrogen containing polysaccharide, which is second most abundant biopolymer after cellulose; distributed in the shells of crustaceans such as crabs, shrimps and lobsters as well as in the exoskeleton of marine zoo-plankton, including coral, jellyfish and squid pens. It is totally ecofriendly and renewable.2,3

Chemically, chitosan is a linear (1-4) linked 2- amino-2-deoxy-β- d- glucan (i.e. β- d-glucosamine) having the structure very much close to that of cellulose except the hydroxyl group in C (2) of cellulose is being replaced by amino group in chitosan. Indeed, it is a copolymer of N-acetyl-glucosamine and glucosamine units. Being a primary aliphatic amine, chitosan can be protonated by various acids.1,2,4

By virtue of several valuable inherent properties such as antibacterial, antifungal, antiviral, antacid, non-toxic, total biodegradable, biocompatible with animal and plant tissues as well as film formation, fibre formation and hydrogel formation properties, chitosan has prospective applications in many fields such as biomedical, waste water treatment, cosmetics, dentifrices, food, agriculture, pulp & paper, and textile industries.5-7

In textiles, the application potential of chitosan is reviewed comprehensively.8,9 Investigations have shown that it can also be used as a dye fixing agent, for shade and naps coverage, to improve the fastness of dyed fabrics, as a binder in pigment printing, as a thickener in printing. By virtue of its bacteria impeding property, chitosan can prevent garments to develop bad odour.4,10,14 An improved wrinkle recovery of cotton fabric is reported on finishing cotton with citric acid solution in presence of chitosan with minimum loss in tensile strength due to citric
acid treatment\textsuperscript{15}. It is found that complete inhibition of \textit{Escherichia coli} and Hay bacillus bacteria is possible by treatment of cotton with 0.5gpL chitosan concentration\textsuperscript{16}. Tiwari and Gharia\textsuperscript{17} attempted to use chitosan as a thickener in printing paste. Performance of the prints with respect to $K/S$, wash fastness, crock fastness and hand are observed to be unsatisfactory. Our earlier investigations\textsuperscript{18} have shown improved dyeability towards direct dyes of Chitosan pretreated cotton fabric and the degree of improvement was found to be a function of molecular weight and concentration of chitosan. The fastness to washing of direct dyes on chitosan pretreated fabric, however, was only slightly improved especially for the low molecular weight chitosan applications. Chitosan treated cotton fabric also showed a substantial dyeability towards acid dyes. The appearance and handle of the treated fabric, however, was severely affected. The wrinkle recovery property was found to be reduced. The loss in inherent qualities of cotton fibres due to chitosan may be attributed to the rigid film deposition of it, mostly confined to surface of fibre only.

Today’s need, however, is to improve above properties without altering the inherent natural qualities of cotton. It is possible by achieving the maximum penetration of polymer particles into fibre structure and increasing its effectiveness at lowest possible concentration. Penetration of chitosan solution can be improved by lowering the viscosity of its solution, which is obtained by lowering the concentration and/or by reducing the particle size. Reduction in concentration of normal chitosan in solution, however, may reduce its effectiveness and larger chain does not permit its entry into the yarn/cellulose structure. The only possible way is to reduce the particle size, which, in addition to decrease in viscosity, offers greater surface area and hence increase the effectiveness of chitosan. This is the basis of today’s most popular technology ‘nano technology concept’.

The potential applications of nano-chitosan are well demonstrated in medical field particularly in controlled drug delivery systems\textsuperscript{19-21}. However, their applications in textiles are not yet well investigated. The practical application of such nano-chitosan to textiles at shop floor level demands suitable technology for the production of nano-chitosan dispersions, characterization and the analysis of stability of standing baths.

Therefore, in the present work, an attempt has been made to set a simple methodology to produce nano-chitosan by ionotropic gelation with pentasodium tripolyphosphate. Chitosans of different molecular weights are obtained by controlled depolymerisation of parent chitosan using nitrous acid hydrolysis and these products are subsequently used for the synthesis of nano-chitosan. The study reported here is the final results of many basic experiments after getting the confirmation of reproducibility. A representative concentration of 1gpL is, therefore, only reported and discussed here to make it as brief as possible and to avoid presenting less important data. The effect of particle size on various properties of nano-chitosan treated cotton fabric, such as appearance, stiffness, absorbency, dyeing behaviour and wrinkle recovery, is discussed. Scanning electron microphotographs of nano-chitosan treated cotton fabric are also analysed.

2 Materials and Methods

2.1 Materials

100% cotton fabric (count 40s × 40s, EPI 142, PPI 72 and GSM 125), ready for dyeing stage, was procured from local process house.

Direct dyes, namely C.I.Direct Red 81 and C.I.Direct Blue 71, were obtained from M/s Colourtex Industries Ltd, Gujarat State, India. Chitosan (CHT1), having degree of deacetylation (DAC) 90% and viscosity 22cPs, was obtained from M/s Mahtani Chitosan Pvt. Ltd., Gujarat State, India. Dimethylol dihydroxy ethylene urea (DMDHEU) was obtained from local process house and other chemicals such as sodium tripolyphosphate (TPP), acetic acid, sodium nitrite, sodium acetate (anhydrus) and sodium hydroxide were of analytical grade.

2.2 Synthesis and Characterization of Nano-chitosan

Different molecular weight grades chitosans were first obtained by depolymerization of CHT1 by nitrous acid hydrolysis method, which were employed for the preparation of nano-chitosan dispersions as described elsewhere\textsuperscript{22}. In general, chitosan was dissolved in acetic acid solution and optimized quantity of TPP was added drop wise with rapid stirring (about 400 rpm) to obtain an opalescent solution. The sample was allowed to stand overnight, filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was termed as CHT1N. The synthesized nano-chitosan was applied to cotton fabric within 24 hours since the stability of nano-chitosan gets adversely affected with time as discussed earlier\textsuperscript{22}. The specifications of different grades of chitosan and nano-chitosan are given in Table 1. The particle size and size distribution of the chitosan were analyzed on
2.3 Treatment of Fabric with Nano-chitosan

Nano-chitosan dispersion (1gpL) was applied onto fabric on a padding mangle with wet pick-up of 70% by two dip- two nip method. After drying the fabric was cured in oven at 150 °C for 4 min. The sample was then washed in the following sequence: rinse → alkali wash (soda ash 1 gpL, MLR 1:50) → hot wash (twice) (85 °C / 20min) → cold wash → dry.

2.4 Test Methods

**SEM Study**

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.

**Evaluation of Indices**

The samples were evaluated on Spectroscan 5100A (Make: Premier Colorscan) for whiteness index (10 deg / D65 / Hunterlab), yellowness index (2 deg / C / ASTM D 1925), brightness index (2 deg / C / TAPPI 452 / ISO 2470).

**Fabric Stiffness, Tenacity and Absorbency**

Stiffness in terms of bending length was measured as per standard ASTM D 1388-996. The tenacity and elongation-at-break of treated and untreated cotton fibres were measured on Stelometer (Make: Eureka Precision Instrument & Co., Coimbatore, India). The breaking load (kg) and elongation-at-break were obtained directly from scale. The samples were then collected and weighed. An average of 5 readings was calculated using following formula:

\[
\text{Tenacity (g/tex)} = \frac{\text{Breaking load (kg) } \times 1.5 \times 10}{\text{Sample weight (mg)}} 
\]

Sample length = 1.5 cm

Absorbency of treated and untreated cotton fabrics was evaluated as per AATCC test method 79-2000.

**Fabric Dyeing**

The fabric sample was immersed in dye bath maintained at material-to-liquor ratio of 1:40 and containing 1% direct dye, Glauber’s salt (20% owf) and soda ash (5% owf). The sample was run in the bath for 15 min at room temperature. Temperature was then raised to 90 °C and dyeing was continued for 60 min. The dyed sample was then rinsed with cold water 3 times, air dried and hot pressed.

In case of nano-chitosan pretreated material the dyeability was also checked after making the dye bath slightly acidic using 0.5 gpL acetic acid after completion of conventional dyeing process. Presence of acid protonate the amino group which enhances further absorption of dyes.

The dyed samples were evaluated for colour strength in terms of K/S values on Premier Colorscan (India) make computer colour matching system namely Spectroscan 5100A. The wash fastness of dyed samples was evaluated according to ISO 1.

**Crease Recovery Angle and Antimicrobial Activity**

Crease recovery angles were measured as per AATCC test method 66-2003. The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004. After the stipulated period the samples were removed, washed with water and dried in air. The samples were then tested for strength measurement on stelometer.

3 Results and Discussion

3.1 Synthesis and Characterization of Nano-chitosan

Chitosan has fairly long linear structure with rigid conformation. The characteristic size of CHT1 hydrodynamic sphere is found to be 4014 nm. Such a higher particle size offers higher viscosity to the solution. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by ‘bottom-up’ approach.

Chitosan, by virtue of polycationic nature, undergoes ionic gelation with polyanions such as pentasodium tripolyphosphate (TPP), ethylene diamine tetra acetic acid (EDTA), etc to form nano-particles. Such particles are stabilized by electrostatic hindrance due to coulombic repulsion between particles of same ionic charges. Owing to faster
ionic reactions between chitosan and TPP, non-toxic nature of these components and ease of operation, we adopted the gel ionization technique for the synthesis of nano-chitosan particles. The particle size distribution of CHT5N, having particle size 110.74nm, is given in Fig.1. Scaling down the particle size of large polymeric materials to nano level is a big challenge. It is clear from the present study that the molecular weight (Table 1) has a great role in controlling the particle size and by reducing the molecular weight we achieved about 110 nm particle size. It is clear from this investigation that the particle size can be reduced below 100 nm by experimenting with parent chitosan of low molecular weight (lower than 10,000). We believe that the study would act as a platform for further work of this kind and would serve basic information to the future researchers.

3.2 Effect of Nano-chitosan Application on Surface Morphology

The surface morphology of the treated and untreated cotton was studied under scanning electron microscope (Fig. 2). Chitosan exhibits an inherent property of film formation, which is clearly seen as

Fig. 1—Size distribution of nano-chitosan by intensity (CHT5N)

Fig. 2—Scanning electron microphotographs (×2700) of (a) cotton Fibre (control), (b) CHT1 treated fibres, (c) CHT1 treated and then prolong boiled cotton fibres, (d) CHT1N(ii) 319.4nm, treated cotton fibres, (e) CHT4N, 195.2nm, treated cotton fibres and (f) CHT5N, 110.74nm, treated cotton fibres
gloss on fibre surface as shown in Fig 2(b). 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 [Fig. 2(c)]. Nano-chitosan treated samples show all together different microphotograph [Figs 2(d) – (f)]. Nano-chitosan film is found to be more uniform.

3.3 Effect of Nano-chitosan on Fabric Appearance

The appeal of the fabric is manifested by its appearance and the feel. Effect of particle size of nano-chitosan on these properties of cotton fabric is illustrated in Table 2.

The appearance and the fabric feel are quite satisfactory. It is envisaged from Table 2 that the whiteness is improved with reduction in particle size and reaches well nearer to that of control sample. This may be attributed to the greater extent of penetration of nano-chitosan particles into fibre structure and allowing the cuticle for exposure. Deposition of normal chitosan, however, is confined to surface as a film, which alters the whiteness to some extent. This film may also impart stiffness to the fibre, whereas a nano-chitosan shows a little influence, as is observed in same table.

3.4 Effect of Nano-chitosan on Tensile Properties

The effect of nano-chitosan treatment on tensile properties of cotton fabrics is presented in Table 3.

There is a reduction in strength due to conventional chitosan application. Conventional chitosan mostly forms a film on the surface of the fabric and very less amount of it can enter in to the inter-fibre regions, thus cannot take part in load bearing phenomenon, rather affects symmetrical distribution of load. Nano-chitosan, on the other hand, because of its small size can easily enter into the inter-fibre region and to even inter-cellulosic chain regions, and work as a cross-link which bears the load to a great extent. The strength improvement is therefore clearly observed with the reduction in particle size. The elongation property is, however, decreased to some extent with the scaling down of particle size. The formation of \textit{in situ} three dimensional networks probably resists the adjacent fibre molecules to slip and lowers the elongation-at-break.

3.5 Effect of Nano-chitosan on Absorbency

The absorbency, measured by drop penetration method, of nano-chitosan treated cotton fabric is shown in Fig. 3. The results show that the absorbency is decreased with the reduction in particle size. This may be elucidated by the example of lotus leaf effect. Distribution of nano-chitosan particles as a thin layer over and beneath the surface, [Fig. 2 (d)-(f)], may roll out the water droplets. Nevertheless, the absorbency of nano-chitosan treated samples is still within the tolerable limits of conventional wet processing conditions.

3.6 Dyeing Behaviour of Nano-chitosan Treated Cotton Fabric

Since the structure of chitosan is very much similar to cellulose, it is anticipated that its treatment to cotton should influence the dyeing. Hence, the effect of pretreatment of nano-chitosan on direct dyeing of cotton has been studied. The effects of chitosan and nano-chitosan pretreatment on dye uptake are shown in Table 4. The dye uptake by treated cotton fabric, in conventional process, is increased progressively with reduction in particle size of CHTN. The results are superior to corresponding parent CHT treated materials. The dye uptake of CHTN treated samples is found to be significantly increased, resulting in almost complete exhaustion of dye bath, when acidification was followed. The increased dye uptake due to chitosan treatment may be attributed to the presence of primary amino groups of chitosan. These cations

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Particle size (nm)</th>
<th>Appearance</th>
<th>Bending length, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>92.5</td>
<td>2.05</td>
</tr>
<tr>
<td>CHT1</td>
<td>4014</td>
<td>90.9</td>
<td>2.44</td>
</tr>
<tr>
<td>CHT1N(i)</td>
<td>468.1</td>
<td>91.1</td>
<td>2.29</td>
</tr>
<tr>
<td>CHT1N(ii)</td>
<td>319.4</td>
<td>91.1</td>
<td>2.26</td>
</tr>
<tr>
<td>CHT2N</td>
<td>271.6</td>
<td>91.5</td>
<td>2.24</td>
</tr>
<tr>
<td>CHT3N</td>
<td>231.0</td>
<td>92.1</td>
<td>2.24</td>
</tr>
<tr>
<td>CHT4N</td>
<td>195.2</td>
<td>91.9</td>
<td>2.21</td>
</tr>
<tr>
<td>CHT5N</td>
<td>110.74</td>
<td>92.1</td>
<td>2.19</td>
</tr>
</tbody>
</table>

W.I.—Whiteness index, Y.I.—Yellowness index, B.I.—Brightness index.
dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye uptake may also been enhanced due to the dyeability of chitosan itself with direct dyes. The nano-chitosan due to increased surface area and hence higher accessibility for dye sites put much added value. The primary amino groups on chitosan get protonated (quaternized) in acidic medium having enhanced positive charge, thus form salt linkages with anionic (sulphonate) groups of residual dye in the bath. Secondly, the higher dye uptake value after acidification proves the presence of chitosan.

The wash fastness and rub fastness properties of direct dyed fabrics were also analyzed, which are presented in Table 5. The fastness to washing is improved with the reduction in particle size. This may be regarded to the formation of CHTN-dye complex in situ. The fastness to rubbing is also improved to some extent with the reduction in particle size.

3.7 Effect of Nano-chitosan on Crease Recovery

The proneness to creasing downgrades the aesthetic appeal of cotton cloth or garments. This problem of cotton fabric is conventionally overcome by the treatment with various cross-linking agents based on

<table>
<thead>
<tr>
<th>Parent chitosan</th>
<th>Nano-chitosan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample code</td>
<td>Tenacity g/tex</td>
</tr>
<tr>
<td>CHT1</td>
<td>20.48</td>
</tr>
<tr>
<td>CHT2</td>
<td>21.01</td>
</tr>
<tr>
<td>CHT3</td>
<td>21.45</td>
</tr>
<tr>
<td>CHT4</td>
<td>22.19</td>
</tr>
<tr>
<td>CHT5</td>
<td>21.81</td>
</tr>
</tbody>
</table>

Table 3—Effect of nano-chitosan on tensile properties of cotton fabric

[Control cotton fabric: Tenacity = 23.33 g/tex, Elongation-at-break=5.25%]

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Tenacity g/tex</th>
<th>Elongation-at-break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHT1</td>
<td>20.48</td>
<td>4.75</td>
</tr>
<tr>
<td>CHT2</td>
<td>21.01</td>
<td>4.5</td>
</tr>
<tr>
<td>CHT3</td>
<td>21.45</td>
<td>4.5</td>
</tr>
<tr>
<td>CHT4</td>
<td>22.19</td>
<td>4.25</td>
</tr>
<tr>
<td>CHT5</td>
<td>21.81</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 4—Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

<table>
<thead>
<tr>
<th>Sample code</th>
<th>K/S (Conventional dye bath)</th>
<th>K/S (Acidic dye bath)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHT1</td>
<td>9.0</td>
<td>6.9</td>
</tr>
<tr>
<td>CHT1N(i)</td>
<td>9.6 (24)</td>
<td>10.2 (62)</td>
</tr>
<tr>
<td>CHT1N(ii)</td>
<td>9.6 (24)</td>
<td>10.4 (64)</td>
</tr>
<tr>
<td>CHT2</td>
<td>9.0</td>
<td>7.0</td>
</tr>
<tr>
<td>CHT2N</td>
<td>9.8 (27)</td>
<td>10.5 (66)</td>
</tr>
<tr>
<td>CHT3</td>
<td>9.0</td>
<td>6.8</td>
</tr>
<tr>
<td>CHT3N</td>
<td>9.8 (27)</td>
<td>10.5 (66)</td>
</tr>
<tr>
<td>CHT4</td>
<td>9.0</td>
<td>6.7</td>
</tr>
<tr>
<td>CHT4N</td>
<td>9.8 (27)</td>
<td>10.5 (66)</td>
</tr>
<tr>
<td>CHT5</td>
<td>9.1</td>
<td>7.1</td>
</tr>
<tr>
<td>CHT5N</td>
<td>9.9 (29)</td>
<td>10.6 (67)</td>
</tr>
</tbody>
</table>

*Values in parentheses indicate per cent improvement in K/S as compared to corresponding control fabric sample.

C. I. Direct Red 81 — K/S values of controlled cotton fabric dyed in conventional dye bath is 7.7 and in acidic dye bath it is 6.3.
C. I. Direct Blue 71 — K/S values of controlled cotton fabric dyed in conventional dye bath is 6.1 and in acidic dye bath it is 4.9.
aminoplast resins, e.g. DMDHEU. The crease recovery property as a function of chitosan and nano-chitosan treatments has been compared against DMDHEU (Table 6). The crease recovery angle of cotton fabric is greatly reduced by the treatment of normal chitosan (CHT1). Treatment of cotton fabric with chitosan of lower particle size is found to improve the crease recovery of cotton fabric (Table 6). However yet it could not gain the rating of commercially used cross-linking agent DMDHEU. Conventional chitosan is believed to form a surface coating which lowers the possibility of cross-linking and therefore cannot contribute to the load sharing phenomenon. The improved wrinkle recovery property in case of nano-chitosan treatment may be attributed to the greater penetration into fabric structure. These polycationic nano-particles, due to better penetration, may bound the fibre molecules and resist creasing to some extent.

### 3.8 Effect of Nano-chitosan on Antibacterial Effect

Cotton fibres like other natural fibres provide favourable environment for the growth of microorganisms due to moisture and warmth. These organisms are mainly responsible for discolouration, development of rancid/bad odour, stains and strength loss of fabric as well as skin allergies and infection diseases to human body. The most popular ways of imparting antimicrobial resistance is to use nano-silver colloid. Chitosan, being polycationic material, binds to anionic surfaces of microbe cell wall and disrupt it leading to death of cell. Attributing to the antibacterial and metal particle retention properties of chitosan, the fabric was treated with chitosan and nano-chitosan and then with nano silver colloid. Nano-silver colloid of concentration 1·10^{-3} M /100 mL and average particle size 110nm was prepared as published elsewhere.

### 4 Conclusion

Ionotropic gelation with pentasodium tripolyphosphate is employed for the preparation of
nano-chitosan dispersion. From the stand point of application of nano-chitosan to cotton fabric, following conclusions can be drawn.

4.1 The appearance and handle of nano-chitosan treated cotton fabric is quite satisfactory.

4.2 Nano-chitosan treatment shows improvement in fibre strength that increases with the reduction in particle size. The elongation-to-break is slightly decreased with the scaling down of particle size.

4.3 Moisture related property such as absorbency is affected; nevertheless it is in acceptable limit of tolerance.

4.4 The dyeability of chitosan and nano-chitosan treated cotton a fabric towards direct dyes is improved significantly. The progress is sustained with reduction in particle size. The effect is further enhanced after acidification of dye bath. Fastness to washing is improved satisfactorily and fastness to rubbing slightly.

4.5 Wrinkle recovery property is slightly improved and use of suitable cross-linking agent is essential.

4.6 Nano-chitosan together with nano-silver treatment shows enhanced antibacterial activity.

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