CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF NANO-CHITOSAN DISPERSIONS AND THEIR APPLICATION ON COTTON FABRIC

3.1 INTRODUCTION

Preliminary experiments reported in chapter 2 shown that some of properties of the cotton fabric improved on application of chitosan on it. The dyeability of cotton fabric towards direct dyes was enhanced significantly due to chitosan pretreatment and the degree of improvement was found to be a function of molecular weight and concentration of chitosan. The fastness to washing of direct dye on chitosan pretreated fabric, however, was only slightly improved especially for the low molecular weight chitosan applications. But the post-dyeing chitosan treatment, in general, has improved the washing fastness of direct dyed cotton fabric. The moisture related properties were in tolerable limits. Chitosan treatment was found to impart resistance to microbial attack. The appearance and handle of the treated fabric, however, was severely affected and lost its natural 'cotton feel'. The wrinkle recovery property was found to be deteriorated. The very large molecular size and consequently high viscosity of chitosan restricts its penetration into the fibre and fabric structure and leads to only the surface deposition. The surface deposition of this high polymer affects the feel and appearance of the treated textiles. This may also leads to maximum accumulation of dye on surface thereby reducing the all round fastness properties especially washing, rubbing and light fastness. 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 low concentration. Penetration of chitosan solution can be improved by lowering the viscosity of its solution, which can be obtained by lowering the concentration and/or by reducing its particle size. Reduction in concentration of chitosan, however, decreases its effectiveness. An alternative way of improving its effectiveness is to drop down its particle size towards nano level. Reduction

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in particle size decreases viscosity, offers greater surface area and hence enhances the effectiveness of chitosan. This is the basic of 'nano technology'.

The concept of 'nanotechnology' lies in the fact that the properties of substances dramatically change when their size is scaled down to nanometer range. The first use of this concepts (but predating use of that name) was in "There's Plenty of Room at the Bottom," a talk given by a Nobel laureate physicist Richard P. Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. The word nanotechnology, however, was used for the first time in 1974 by Prof. Norio Taniguchi of Tokyo Science University while explaining the Silicon machined down to the small particle-smaller than one micron. In 1986, K Eric Drexler wrote "Engines of Creation" and also introduced the term Nanotechnology. In general, "Nanotechnology is the engineering and fabrication of objects with size less than 100 nm. Below 100 nm the properties like melting point, hardness, catalytic activity and magnetic properties vary with size, otherwise these properties in other material are considered to be constant" or "Nanotechnology is concerned with developing the tools for characterizing and manipulating materials on nanoscale (1-100 nm) and exploiting these tools for the development of new products and processes" or "Nanotechnology is defined as the understanding, manipulation, and control of matter at the nanoscale (1-100 nm) , such that the physical, chemical, and biological properties of materials (individual atoms, molecules, and bulk matter) can be engineered, synthesized, or altered to develop the next generations of improved materials, devices, structures, and systems" [1-4]. A nanometer is one billionth of a meter, roughly the width of three or four atoms. The average human hair is about 25,000 nanometers wide. The magnitude of nano-size can be visualized on scale shown in Figure 3.1.

Nanotechnology basically deals with the individually arranging atoms or molecules in desired places to obtain a hybrid product with desired and diverse properties [5]. Fabrication of nano matrices can, broadly, be done by two approaches:

- **Top down approach:** The top-down approach involves the fabrication of components from larger materials

- **Bottom up approach:** An approach to building things by combining smaller components, as opposed to carving them out of larger ones (top down)

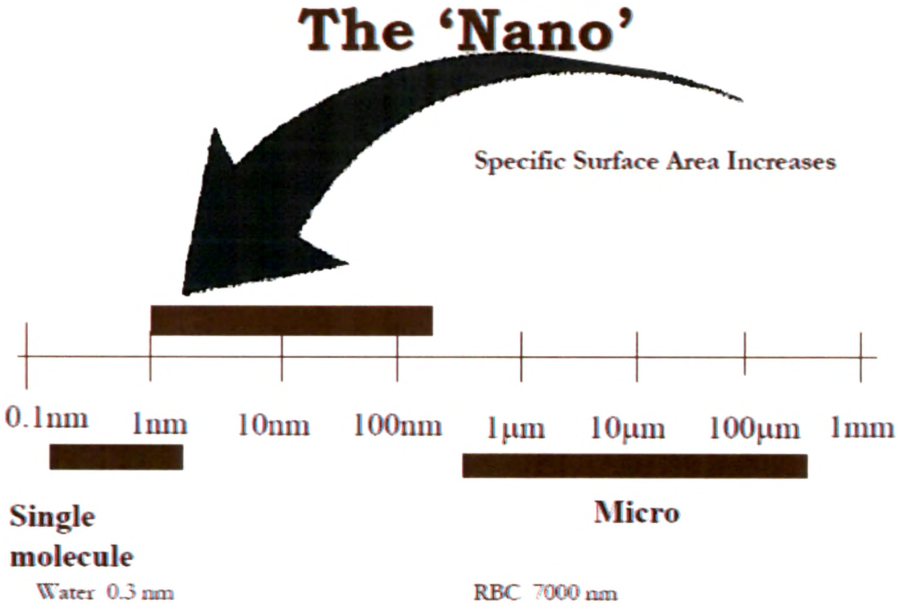


Figure 3.1 Nano size on scale

Nature follows the 'bottom up approach' rather than the 'top down approach' usually followed by humans to produce materials. The shapes are 'grown' rather than cut. All the living being can trace their origin to a single cell. Reduction in particle size to nanoscale can lead to changes in properties related to specific surface area, reactivity, quantum effects, strength, electrical characteristics, optical properties, magnetic behavior etc. As the particle size decreases, greater proportion of atoms are found at the surface compared to those in the 'body' [1, 5].

Nature has already developed polymeric nanoparticles with an elegant approach that combines chemistry and physics to create super-repellent hydrophobic surfaces. Lotus leaves are unusually water repellent and keep themselves spotless. The reason for this phenomenon is understood as the presence of nano sized bead like waxy structures on the surface of lotus leaf, which prevent water from wetting it. This phenomenon of water repellency has in lotus leaves has actually inspired development of water repellant nano-finish, which while conferring the water repellency to textile substrates allows the textile material to retain its natural handle and feel [6-8]. It has been demonstrated in recent years that the nanotechnology can be applied to textiles to enhance various properties, especially in functional coatings, such as fabric softness, durability and breathability, water repellency, fire retardency, antimicrobial properties, anticrease properties, U.V. protection, self cleaning properties and like in fibre, yarn and fabrics [2,6,7,9]. Undyable polypropylene fiber can be made dyeable by dispersing nanoclay, modified with quaternary ammonium salts, into polypropylene melt before spinning. After fiber formation the infused quaternary ammonium groups act as efficient dye sites [10]. A combined effect of wrinkle free and stain repellency can be obtained by treating fabric with 10nm tiny particles with both polar and non polar moieties imparting extremely low free surface energy. These nanoparticles cross link with cellulose to give the desired amount of wrinkle resistance. Such hybrid nanoparticles when incorporated with highly fluorinated silanes impart stain repellency. Nanotechnology can also be made applicable in the production of smart textiles. Application of carbon nano tubes can give rise to textile materials that have thermal and electrical conductivity sensible to touch and feel. Garments of such fabric can understand any abnormality in heart beat and then send a signal to family doctor or spouse [6, 11, 12]. The inorganic UV blockers are preferable to organic blockers as they are non-toxic and chemically stable under exposure to both high temperature and UV. Usually certain semiconductor oxides such as TiO_2, SiO_2, ZnO and Al_2O_3 are used as UV blockers. Rayleigh's scattering is dependent upon the wavelength where the scattering is inversely proportional to the wavelength to the fourth power. This theory predicts that in order to scatter UV radiation between 200 to 400 nm, the optimum particle size will be between 20 to 40 nm. UV blocking treatment for cotton fabric is given by using sol-gel method. A thin layer of titanium dioxide is formed on the surface of the treated fabric which provides excellent UV protection fast to washing [6, 13]. Nanosized silver, TiO2 and ZnO exhibit antimicrobial properties. Nanosilver is very reactive to protein when contacting with bacteria and fungus; it will adversely affect the cellular metabolism and inhibit the cell growth. Fabrics treated with nano TiO2 can provide effective protection against bacteria and discoloration of stain due to the photo catalysis effect of this agent. Nano ZnO provides effective photo catalytic properties once it is illuminated by light and it is employed to impart antibacterial properties to textiles [14-18].

Chitosan is a biopolymer that has received much attention and has been extensively studied for micro- and nanoparticles preparation. It is possible, for a given molecular size chitosan, to reduce the particle size to nano level by 'bottom-up' approach as a result of a self assembling or cross linking processes in which the molecules arrange themselves in to ordered nano scale structure either by physical or covalent inter- or intramolecular interactions. One of the trends in synthesis process is to pursue a nano scale emulsion, through which finishes can be applied to textile material in a more thorough, even and precise manner. Finishes can be emulsified into nano -micelles, made into nano-sols or wrapped in nano-capsules that can adhere to textile substrates more evenly. One popular method of nano fabrication of chitosan is gel ionization technique by reaction with polyanions such as sodium tripolyphosphate (TPP) [19-21]. The potential applications of nano chitosan are well demonstrated in medical field particularly as controlled drug delivery systems [22, 23]. However, their applications in textiles are not yet clearly investigated. The practical applications of such nano chitosan to textiles at shop floor level demands the consideration of establishment of suitable technology for the productions of nano chitosan dispersions, characterization and the stability of standing baths. Therefore an attempt, in the present chapter, is made to set a simple methodology to produce nano chitosan by ionotropic gelation with sodium tripolyphosphate (TPP). The samples were characterized by particle size analysis and their polydispersity indices (pdi). Effect of various parameters such as molecular weight & concentration of chitosan, concentrations of TPP on particle size were determined. Attempts were made to correlate the viscosity behaviour with particle size of chitosan.

The synthesized nano-chitosan was applied to cotton fabric and then various properties of the treated fabric like appearance, absorbency, stiffness, dyeing behaviour, wrinkle recovery, resistance to microbial attack etc were examined. The fabric samples were pretreated with normal and nano chitosan solutions by pad-dry cure technique. The surface morphology of the nano chitosan treated cotton fabric was examined by SEM analysis.

3.2 MATERIAL AND METHODS

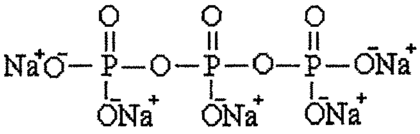
3.2.1 Fabric

The same fabric as specified in chapter 2, section 2.2.1 was used.

3.2.2 Dyes and chemicals

The details of various chemicals employed in present research investigation are given in Table 3.1.

Table 3.1 Specifications of various chemicals

Sr no	Name and Supplier	Specifications
1.	Pentasodium tripolyphosphate (TPP) (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical  $Na^{+}O^{-}-\overset{O}{\overset{\Vert}{\underset{O^{-}Na^{+}}{\underset{\vert}{P}}}}-O-\overset{O}{\overset{\Vert}{\underset{O^{-}Na^{+}}{\underset{\vert}{P}}}}-O-\overset{O}{\overset{\Vert}{\underset{O^{-}Na^{+}}{\underset{\vert}{P}}}}-O^{-}Na^{+}$ - Mol wt 367.86
2.	Silver sulphate (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical $AgSO_4$ - Mol wt 311.8
3.	Sodium borohydride (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical Chemical formula: $NaBH_4$ - Mol wt 37.83
4.	Trisodium citrate (Qualikem Fine Chemicals Pvt Ltd, Vadodara, Gujarat)	Grade: Analytical $Na_3C_6H_5O_7$ - Mol wt 258

Dyes namely C.I.Direct Red 81, C.I.Direct Blue 71, C.I. Acid Blue 158, Chitosan (CHT) and chemicals namely Chitosan (CHT), DMDHEU, acetic acid (CH_3COOH), sodium nitrite ($NaNO_2$), sodium acetate (anhydrous) (CH_3COONa), sodium hydroxide ($NaOH$), sodium carbonate (Na_2CO_3), sodium sulphate (Na_2SO_4) etc used were same as specified in chapter 2, section 2.2.1. Double distilled water was employed for all synthesis and analytical purposes.

3.2.3 Synthesis of low molecular weight chitosan

Low molecular weight chitosans were synthesized using same method described in chapter 2, section 2.2.4. Different grades of low molecular chitosan so prepared are listed in Table 3.3.

3.2.4 Synthesis of nano-chitosan and its characterization

Chitosan (CHT) stock solution (10 g/L) was prepared by dissolving CHT (1g) in 100 ml of acetic acid (10 g/L) solution and then filtered through filter fabric (mesh 128). Required amount of this solution (e.g. 10 ml) was taken in glass beaker, mixed with water (65 ml) and kept stirring on magnetic stirrer at about 400 rpm. TPP solution (5 g/L, 3ml) together with water (22 ml) was added drop wise to above stirring solution to give an opalescent nano chitosan dispersion corresponding to chitosan concentration 1 g/L. The sample was allowed to stand overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. The prepared nano-chitosan was nomenclatured as CHTN.

The particle size and size distribution of the chitosan were analyzed on the particle size analyzer (Zetasizer Nano ZS90, Malvern Instruments Ltd, UK). The test was performed at Chemical Engineering Department, Sardar Vallabhbhai National Institute of Technology, Surat.

3.2.5 Preparation of nano silver (Ag) colloid

Nano silver colloid was prepared using the method as discussed elsewhere [24]. In brief, a 100 ml solution of $1x10^{-3}$ M $AgSO_4$, kept in the specially designed reaction chamber, was slowly reduced by drop-wise addition of very dilute chilled solution (temperature ~2 ^0C) of sodium borohydride in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously. When the colour of the solution turned to light yellow, 5 ml of 1 % trisodium citrate were added drop by drop with vigorous stirring.

3.2.6 Determination of viscosity

The viscosity and molecular weight of chitosan were determined as discussed in chapter 2, section 2.2.10.

3.2.7 Treatment of cotton fabric with nano-chitosan

Nano chitosan dispersion was applied onto fabric on a padding mangle (Model - PM0060388, R. B. Electronics & Engineering Pvt Ltd, Mumbai) with wet pick-up of

70% (Mangle Pressure: 20 psi, Speed: 3 m/min) by two dip- two nip method. After drying the fabric was cured in oven at 150 ^{0}C for 4 min. The sample was then washed in the following sequence: Hot wash (Twice) [85 ^{0}C/20 min] → Alkali wash [Soda ash 1 g/L, MLR 1:50] → Hot wash → cold wash →Dry

3.2.8 Dyeing with direct dyes

Dyeing with direct dyes and the evaluation of colour depth (K/S) and fastness properties were done as described in chapter 2, section 2.2.7.

3.2.9 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.

3.2.10 Determination of indices and stiffness of fabric

Determination of appearance indices and stiffness of fabric samples were done as described in chapter 2, sections 2.2.15 and 2.2.16 respectively.

3.2.11 Determination of tenacity

The tenacity and elongation of treated and untreated cotton fibres were measured on Stelometer described in chapter 2, section 2.2.9.

4.2.12 Determination of absorbency and crease recovery angle of fabric

Determination of absorbency and crease recovery angles of fabric samples were done as described in chapter 2, sections 2.2.17 and 2.2.18 respectively.

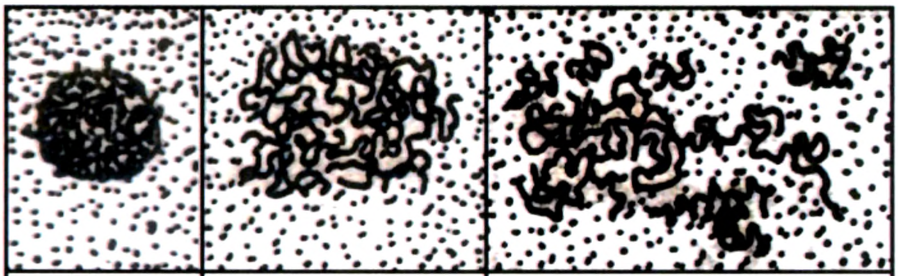
3.2.13 Soil burial test

The soil burial test fabric samples was carried out using the same method as described in chapter 2, section 2.2.19.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis and characterization nano chitosan

Chitosan has fairly long linear structure with rigid conformation. These long molecules in solid state are, mostly, in the form of tightly folded random coils. Individual molecular coils are also not discrete and separate but are interpenetrating and entangled with each other. In solution, the solvent gradually diffuse into the polymer aggregates resulting into the swelling of the polymer. As swelling continues, the segments of the polymer are solvated and loosened out. The loosened polymer molecule then diffuses slowly out of the polymer phase and disperses in solvent phase, forming the solution. Since the molecules in a solid polymer remains entangled with neighbouring ones, polymer molecules during dissolution diffuse out as bunches of entangled molecules. Even when 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 with the 'bound' solvent in the empty space between the unfolded segments. Such polymer coils along with 'bound', known as 'hydrodynamic' sphere or ellipsoid and the apparent volume is referred to as 'hydrodynamic volume'[25-27]. The overall dissolution process of chitosan acidic aqueous medium is schematically shown in Figure 3.2 and Figure 3.3.



Solid polymer just added to solvent	Swollen polymer in solvent	Solvated polymer molecules diffusing out of the swollen mass

Figure 3.2 Dissolution of chitosan in acetic acid/water solvent

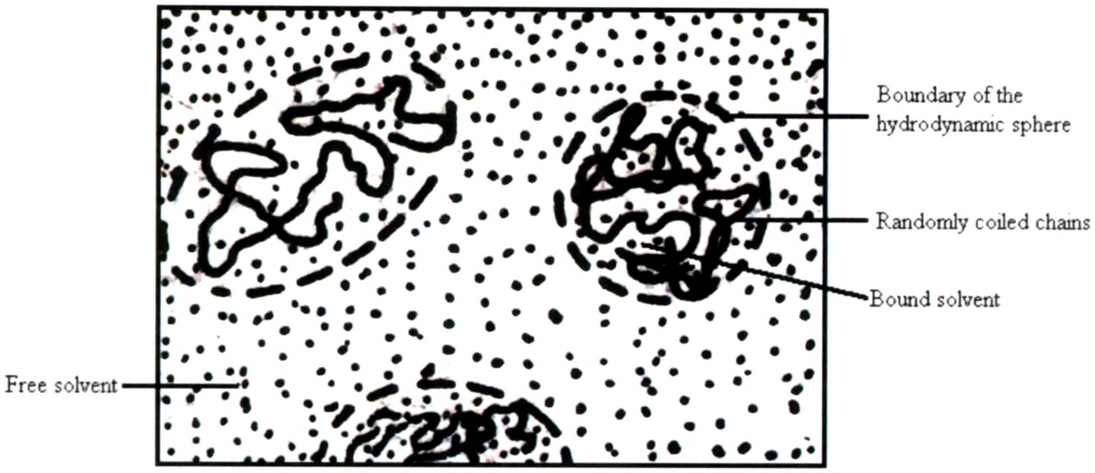


Figure 3.3 Hydrodynamic spheres of chitosan molecules in solution

The characteristic size of CHT hydrodynamic sphere, in our case, at 1 g/L concentration was determined to be 4014 nm. Such higher particle size offer higher viscosity to the solution confining the surface deposition of polymer film. The particle size of chitosan molecule can be scaled down by to nano level by 'bottom-up' approach as a result of a self assembling or cross linking processes [19]. To build materials by bottom-up approach, the first requirement is to have clusters of the material consisting of a few molecules. One such system of clusters of particles is the colloidal system. Colloids can be defined as: "a mixture with properties between those of a solution and fine suspension" [5]. Various method of synthesis of nano chitosan are described in literature [28, 29], which include precipitation or coagulation or desolvation method, covalent cross-linking, ionic cross-linking, emulsion droplet coalescence and reverse micellar method.

Drop wise addition of sodium sulfate into a solution of chitosan and polysorbate 80 (used as a stabilizer for the suspension) under both stirring and ultrasonication, desolvated chitosan in a particulate form. Although the investigators called the resulting suspensions micro spheres, the precipitated particles were at micro/nano interface (900±200 nm). Comparatively larger particle was attributed to their higher porosity observed by higher swelling ability [30, 31]. Dambies *et al.*[32] prepared chitosan particles using molybdate. It was observed a double layer structure corresponding to a very compact 100 μm thick external layer and an internal structure of small pores.

Emulsion-droplet coalescence method, introduced by [33], utilizes the principles of both emulsion cross-linking and precipitation. In this method, instead of cross-linking the stable droplets, precipitation is induced by allowing coalescence of chitosan droplets with sodium hydroxide droplets. A stable emulsion containing aqueous solution of chitosan along with the drug to be loaded is produced in liquid paraffin. Reverse micelles are thermodynamically stable liquid mixtures of water, oil, and surfactant. Microscopically, they are homogenous and isotropic structures consisting of aqueous-in-oil droplets separated by surfactant-rich films. Nano particles prepared by conventional emulsion polymerization methods are not only large (200 nm), but also possess a broad size range. Preparation of ultrafine polymeric nano particles with narrow size distribution could be achieved by using reverse micellar medium [34]. In this method, the surfactant is dissolved in an organic solvent to prepare reverse micelles. To this, aqueous solutions of chitosan and drug are added gradually with constant vortexing to avoid any turbidity. The aqueous phase is regulated in such a way as to keep the entire mixture in an optically transparent microemulsion phase. Additional amount of water may be added to obtain nano particles of large sizes. To this transparent solution, a cross-linking agent is added with constant stirring overnight. The self-assembly of chemically modified chitosan into nano particles can be employed through the fractional conjugation of polyethylene glycol, PEG, via an amide linkage and subsequent self-aggregation at basic pH [35-37]. Gong et al [38] reported a facile nonaqueous electrochemical approach to synthesizing different singlecrystal chitosan nanostructures on a stainless steel substrate, without using a template, catalyst, or surfactant. Chitosan was dispersed in propylene carbonate (PC) under mild ultrasonication and $LiClO_4$ was used as the supporting electrolyte during the electrochemical process.

Chitosan, by virtue of primary amino groups, under goes Schiff's base formation with aldehydes and ionic interactions with anionic compounds [39]. With the former property, chemically cross linked leading to a quite stable matrix of nano chitosan are obtained. Dialdehydes such as glutaraldehyde, salicylaldehyde etc are broadly used for cross linking the molecule in covalent formulations [19, 29, 40]. In the latter, chitosan hydrogels can be obtained by ionic gelation, where nano particles are formed by means of electrostatic interactions with polyanions such as pentasodium tripolyphosphate (TPP), ethylene diamine tetra acetic acid (EDTA) etc. [23, 28, 41-43]. Owing to faster ionic reactions between chitosan and TPP, non toxic nature of these components [19] and ease of operation, the gel ionization technique for the synthesis of nano chitosan particles was adopted. From the physicochemical stand point, the interaction of chitosan with TPP is accepted to be mediated by the intramolecular crosslinking of tripolyphosphoric ($P_3O_{10}{}^{5-}$) ionic species, product of the dissociation of TPP in aqueous solution, with $-NH_3$ groups in chitosan. The intramolecular cross linking in chitosan molecule by gel ionization is schematically illustrated in Figure 3.4 and in Figure 3.5.

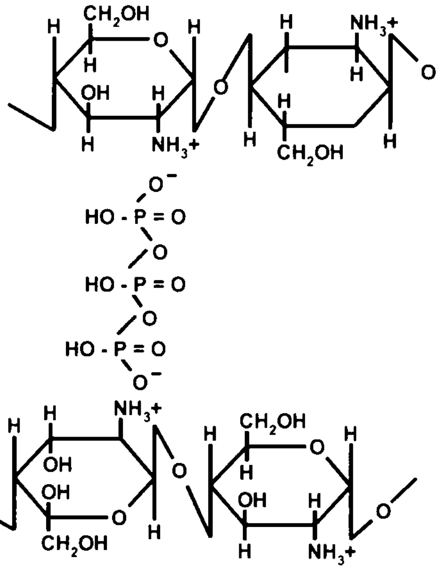
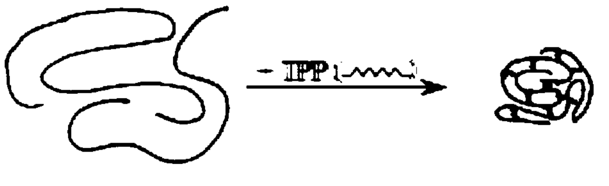


Figure 3.4 Chitosan-TPP complex formed as a result of ionic gelation



Chitosan- swollen molecule

Chitosan-TPP nano matrix

Figure 3.5 Schematic presentation of ionic gelation of chitosan with TPP

Stabilization of nano chitosan dispersion can be explained on the principle of Coulombic or electrostatic repulsion. Particles in a colloid, due to smaller size, are often pushed around by the molecular collisions of the surrounding media, an effect called Brownian motion. The Brownian motion is a rather random, causing the particles to collide with each other frequently and aggregate to form larger particles, which settle down due to their weight. A prerequisite to utilization of colloids for nanotechnology is that they remain colloidally stable, i.e. they remain in suspension and resist settling down. This stability of a colloid can be achieved by means of electrostatic stabilization due to polycationic nature of chitosan in acidic medium and/or involving the creation of an electrical double layer arising from ions adsorbed on the surface of the particle and associated counter ions that surround the particle. Thus, if the electric potential associated with the double layer is sufficiently high, the Coulombic repulsion between the particles will prevent their agglomeration (Figure 3.6) [44]. The diffused solvent in nano gel exerts pressure on polymeric chain of loop, known as osmotic pressure. The osmotic pressure and intramolecular ionic repulsion tend to swell or enlarge the particle while the elastic contribution and the degree of cross linking act to shrink the gel. Thus from thermodynamics point of view, the stability or equilibrium of nano gel is attained when the forces responsible for swelling are balanced with the forces offering shrinkage [19].

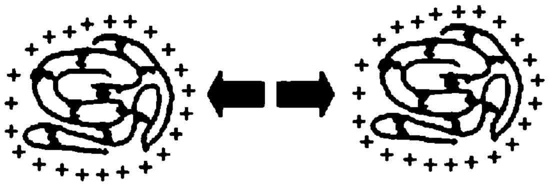


Figure 3.6 Stability of nanoparticles due to electrostatic repulsion between the same ionic charges

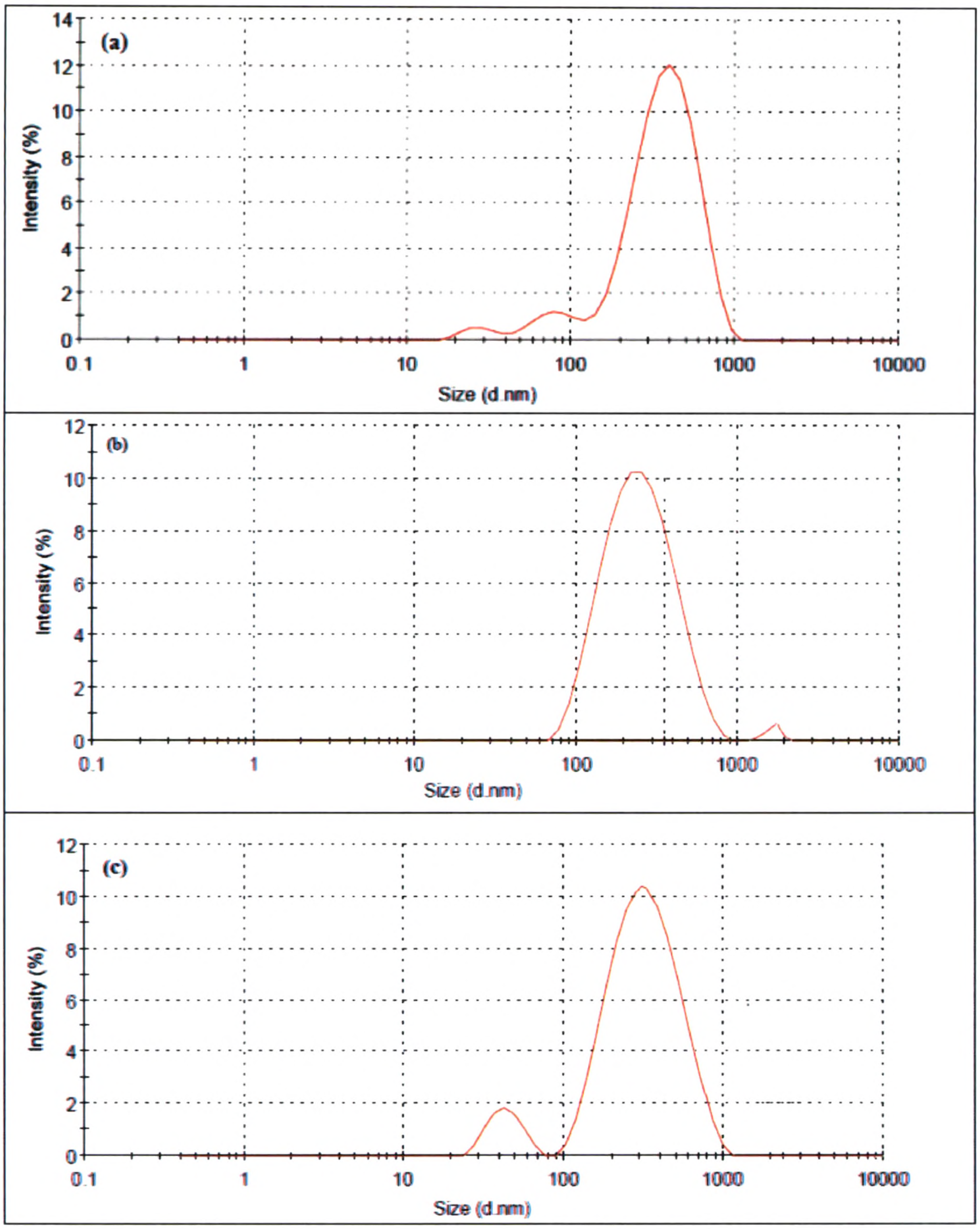
A simple experimental set up designed for the synthesis of nano chitosan sols is shown in Figure 3.7. Chitosan solution was taken in a glass beaker and subjected to rapid stirring on a magnetic stirrer at ambient temperature (30 °C). TPP solution was then added drop wise from the separation funnel and continued stirring for 3 h, stored overnight and filtered through sintered glass filter of porosity grade G3 and preserved in refrigerator. Amount of various ingredients taken for the synthesis of 100 ml of nano chitosan dispersion corresponding to 1 g/L concentration is enumerated in Table 3.2. The particle size distribution of above nanochitosan dispersions derived from varying molecular weight chitosans is shown in Figure 3.8 and their particle size is given in Table 3.3.

Table 3.2 Synthesis of CHTN

Ingredients	**Quantity, ml**
CHT (10 g/L)	10
Water	65
TPP (5 g/L)	3
Water	22
Total:	**100**

Conc of chitosan 1g/L, CHT:TPP=100:15, pH 4.3

Figure 3.7 Experimental set up for the preparation of nano chitosan by ionic gelation method


(a)
Intensity (%)
14
12
10
8
6
4
2
0
0.1
1
10
100
1000
10000
Size (d.nm)
(b)
Intensity (%)
12
10
8
6
4
2
0
0.1
1
10
100
1000
10000
Size (d.nm)
(c)
Intensity (%)
12
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8
6
4
2
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Size (d.nm)

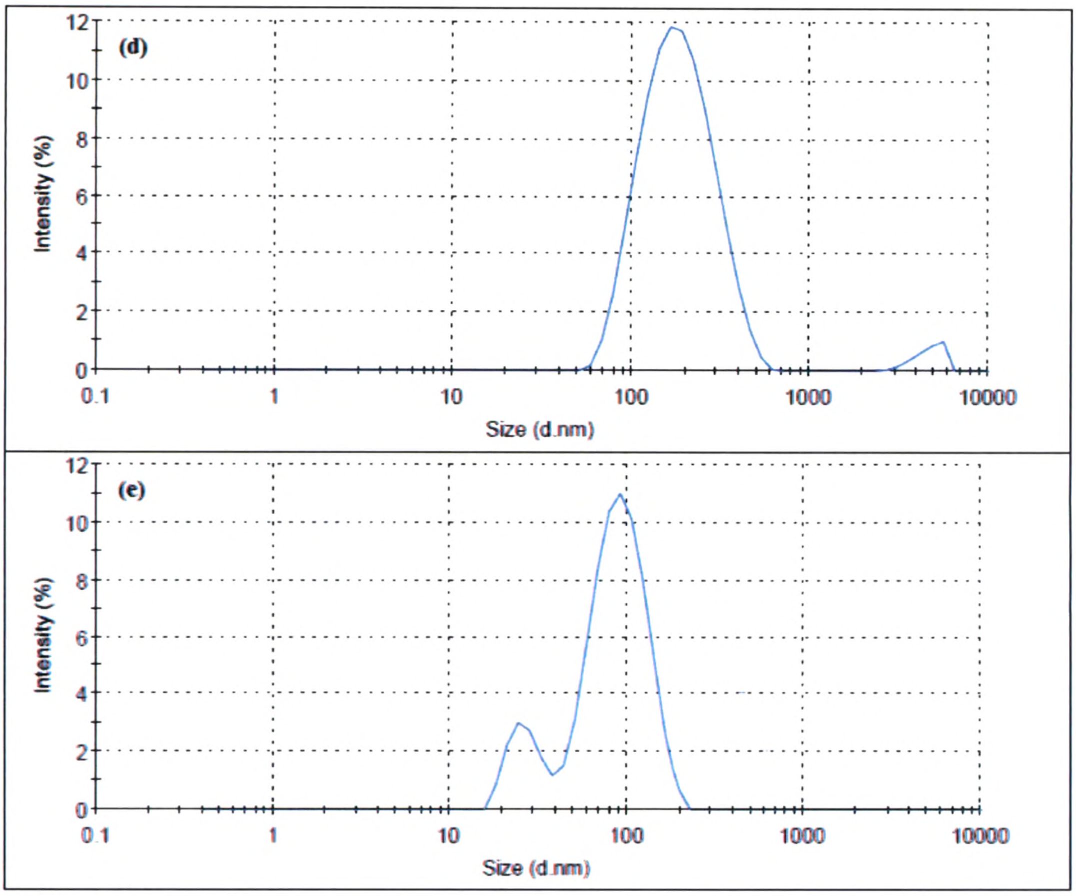


Figure 3.8 Size distribution of nano chitosan by intensity: (a) CHTN (319.4 nm) (b) CHT-D2N (271.6 nm) (c) CHT-D3N (231.1 nm) (d) CHT-D4N (195.2 nm) and (e) CHT-D5N (110.74 nm)

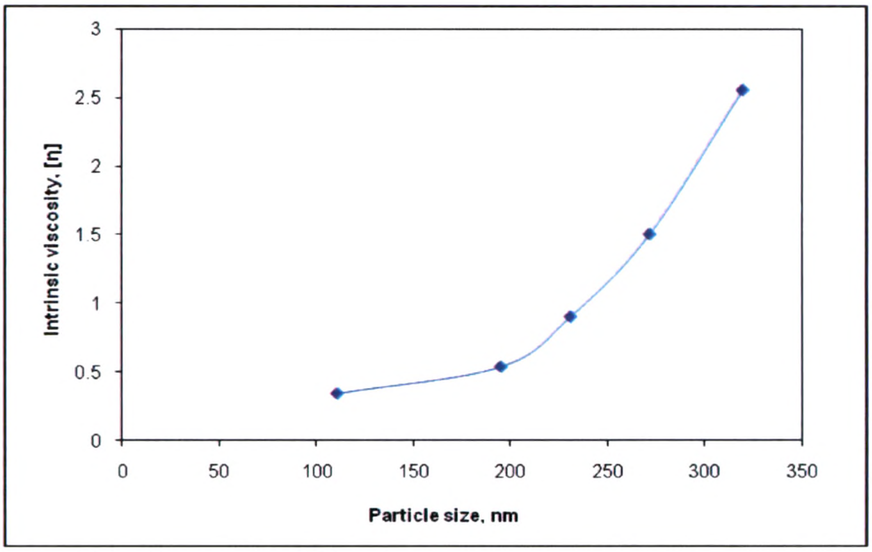
Table 3.3 Effect of molecular weight on particle size

Parent chitosan			**Synthesized nano chitosan**		
Sample code	**Intrinsic viscosity, [η]**	**Molecular weight, Mv**	**Sample code**	**Particle size, nm**	**Poly dispersity index (pdi)**
CHT	2.55	135,839	CHTN	319.4	0.422
CHT-D2	1.5	71,676	CHT-D2N	271.6	0.564
CHT-D3	0.9	38,733	CHT-D3N	231.1	0.466
CHT-D4	0.535	20,698	CHT-D4N	195.2	0.278
CHT-D5	0.34	11,986	CHT-D5N	110.74	0.467

Conc of chitosan 1g/L, CHT: TPP= 1:0.15

3.3.2 Effect of molecular weight of chitosan on particle size

Molecular weight of chitosan is an important property that determines the chain length and hence the hydrodynamic volume and therefore its influence on particle size of nano chitosan is expected. Various grades of low molecular weight chitosan can be produced by controlled depolymerization of high molecular weight one (namely CHT) by nitrous acid method as discussed in chapter 2. Very high molecular weight chitosans namely CHT-MC (Mol wt 654,127) and CHT-D1 (Mol wt 285, 231) were not chosen for the synthesis of nano particle due to their larger size. Chitosan (CHT) and its low molecular weight derivatives were employed for the synthesis nano chitosans in the present study.



Conc of chitosan 1g/L, CHT: TPP= 1:0.15

Figure 3.9 Particle size of chitosan as a function of intrinsic viscosity

The influence of molecular weight of chitosan on particle size is shown in Table 3.3 and the graphical correlation between intrinsic viscosity, a function of molecular weight, and particle size of nano chitosan is demonstrated in Figure 3.9. These data illustrate that, under a given condition of concentrations of CHT and TPP, with decrease in molecular weight, the particle size also decreased progressively and obeys a curvilinear relation. The tendency to form 'loop' is expected to be more favoured in larger chitosan chains than in shorter ones and can be expected to accommodate greater amount of solvent to produce higher hydrodynamic volume [25, 45] and hence packed into relatively larger gelled nanoparticles and vise-versa. The large amount of bound solvent in nano gel derived high molecular weight chitosan exerts higher osmotic pressure and the intramolecular ionic repulsion in acidic pH also contribute to larger size [19]. This relation of particle size with molecular weight in a definite condition of parameters may be useful for the preparation of nano chitosan of desired particle size. The regularity in particle size is determined by polydispersity index (pdi). Higher pdi value indicates the distribution in larger band width, multi population and varying degree of size. Almost similar levels of pdi value were observed (Table 3.3). A little deviation in values may be attributed to the molecular weight distribution of parent chitosan and depolymerization conditions.

3.3.3 Effect of concentration of chitosan on particle size

The effectiveness of nano chitosan on properties of treated cotton fabric is determined by its concentration in application bath. The concentration of chitosan in the formulation can be varied by two methods. Firstly, by the direct preparation method in which the dispersions of nano chitosan from CHT of different concentrations such as 0.25, 0.50, 1.0 g/L etc are prepared separately and secondly, by dilution method, where in a higher concentration nano chitosan dispersion (2 g/L) is prepared first and then diluted to desired concentration with rapid stirring (Table 3.4). The effects of these two methods and hence the concentration of starting material such as CHT for direct method and CHTN for dilution method respectively on particle size are presented in Figure 3.10 and in Table 3.5.

It was observed from above results that at higher concentration, in both the cases; the particle size of nano chitosan (CHTN) was comparatively larger and is progressively reduced with the lowering of concentration, nevertheless the molecular weight was same. The larger size of nano particles at higher concentration may be due to the aggregation of polymer molecules as a result of overlapping and also to the intermolecular cross linking through TPP bridging. On the other hand, as the concentration is lowered, the distribution of polymeric particle becomes more discrete and the intramolecular cross linkages in polymer molecule due to TPP bridging are likely to be favoured for lower particle size.

These results manifest that the poly dispersity indices (pdi) of directly prepared samples was comparatively lower and independent while for dilution method the values were higher and appeared to be dependent on the starting material. The particle size distribution curves, as illustrated in Figure 3.10, were broader for higher concentration samples and became narrow for lower concentration samples. Further, these bands were comparatively narrow for directly prepared samples indicating the uniform size distribution and are close agreement with their lower pdi values.

Table 3.4 Preparation of nano chitosan dispersions of varying concentrations

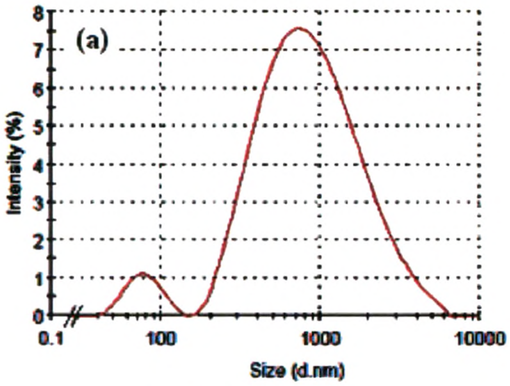
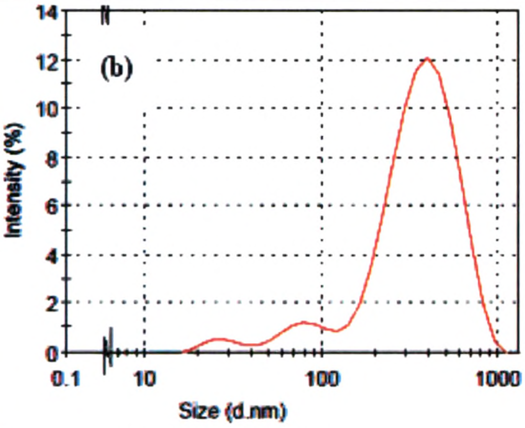
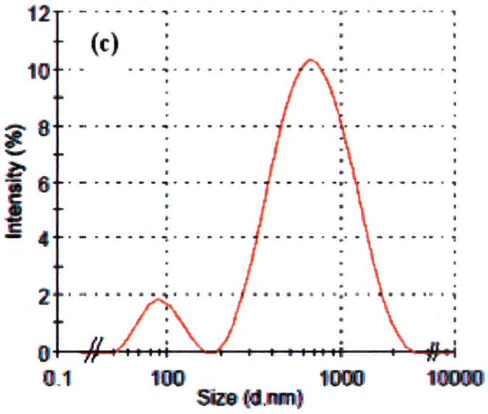
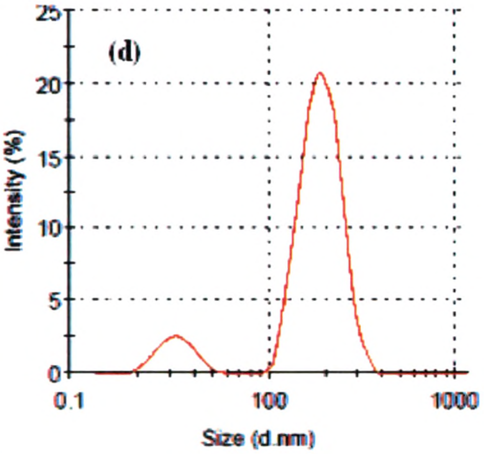
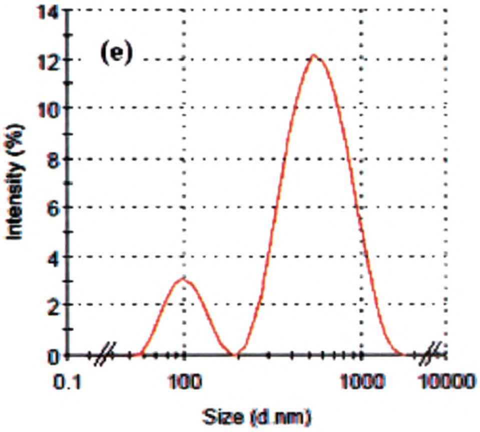
Method	**Ingredients**		**Quantity of ingredients (ml) for the preparation concentration grades, g/L:**				
			0.25	**0.50**	**1.00**	**1.50**	**2.00**
Direct method	Solution A	CHT (10 g/L)	2.5	5	10	15	20
		Water	72.5	70	65	60	55
	Solution B	TPP (5 g/L)	0.75	1.5	3.0	4.5	6
		Water	24.75	23.5	22	20.5	19
	Total (Solution A+B)		**100**	**100**	**100**	**100**	**100**
Dilution method	CHTN (2g/L)		12.5	25	50	75	100
	Water		87.5	75	50	25	-
	Total		**100**	**100**	**100**	**100**	**100**

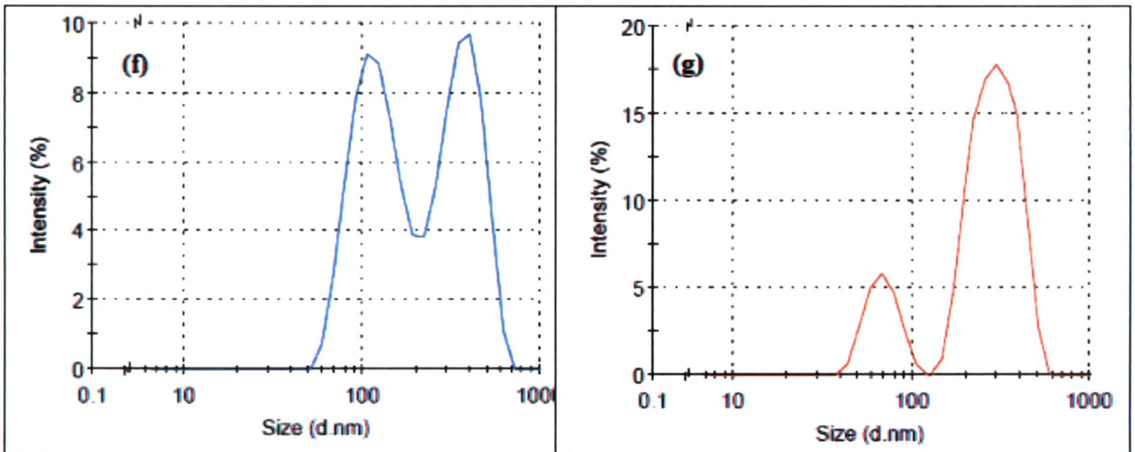
Stock solutions: CHT (10g/L) was prepared in acetic acid (10 g/L) solution, TPP (5 g/L); CHT:TPP=100:15

Table 3.5 Effect of preparation method and concentration of chitosan on particle size

Direct preparation method (Starting material: CHT, 10 g/L)				**Dilution method (Starting material: CHTN, 2 g/L)**			
CHT, g/L	**Particle size, nm**	**Poly dispersity index (pdi)**	**pH**	**CHTN, g/L**	**Particle size, nm**	**Poly dispersity index (pdi)**	**pH**
0.25	304	0.550	4.4	0.25	347.3	0.42	4.4
0.50	313.5	0.465	4.4	0.50	354.9	0.42	4.4
1.00	319.4	0.42	4.3	1.00	468.1	0.464	4.3
1.50	408.73	0.44	4.3	1.50	516.43	0.471	4.3
2.00	534.2	0.515	4.2	-	-	-	-

CHT1: TPP = 1:0.15

 Direct method: 2g/L (534.2nm)	
 Direct method: 1g/L (319.4nm)	 Dilution method: 1g/L (468.1 nm)
 Direct method: 0.5g/L (313.5nm)	 Dilution method: 0.5g/L (354.9 nm)



Direct method: 0.25g/L (304 nm)

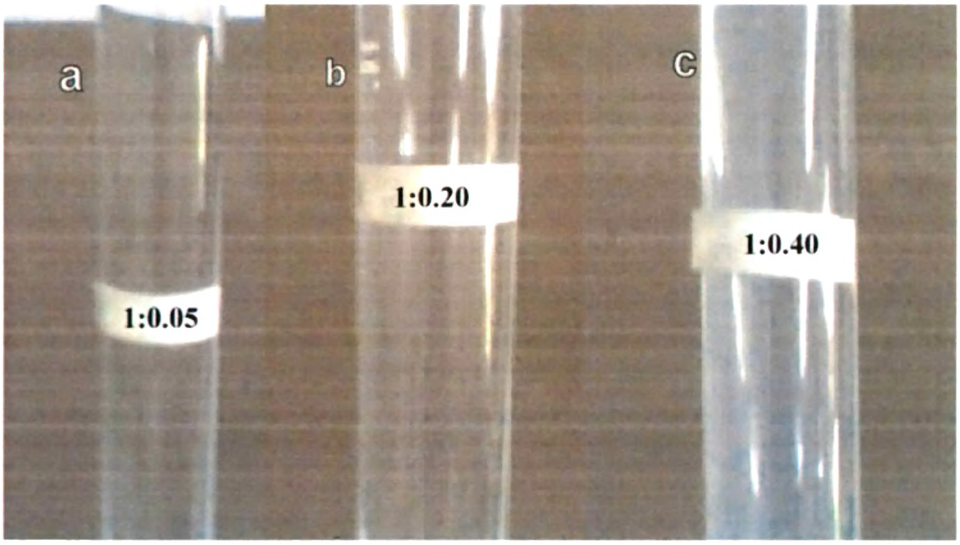
Dilution method: 0.25g/L (347.3 nm)

Figure 3.10 Particle size distribution of nano chitosan as a function of preparation methods

3.3.4 Effect of TPP concentration on particle size

In ionic gelation reaction, TPP a major ingredient for cross linking has a pronounced effect on the properties of CHTN dispersion. Therefore, the optimal amount of TPP concentration with respect to CHT1 concentration in formulation was investigated in detail. It was observed that with increase in the concentration of TPP the appearance of the system changed from clear viscous liquid to opalescent fluid and then precipitated (Figure 3.11). The effect of TPP concentration on the particle size is illustrated in Table 3.6 and in Figure 3.12.

At concentration of TPP below 0.05 g, very few phosphate ions were present to produce effective ionic linkages with chitosan amino groups; hence, the solution was clear. As the concentration of TPP was increased gradually, the solution became opalescent indicating the formation of nano chitosan. It was revealed from the same figure that with increase in concentration of TPP, the particle size of CHT-TPP nanomatrix decreased, reached to minimum at TPP concentration of about 0.15 to 0.25 g and then increased. Concentration of TPP above 0.30 g resulted precipitation. The precipitation at excessively higher concentration of TPP may be attributed to the aggregation of chitosan molecules due to excessive cross linking through TPP bridging. Similar trend in terms of viscosity was noticed when the relative viscosity was plotted against TPP concentration, Figure 3.13.



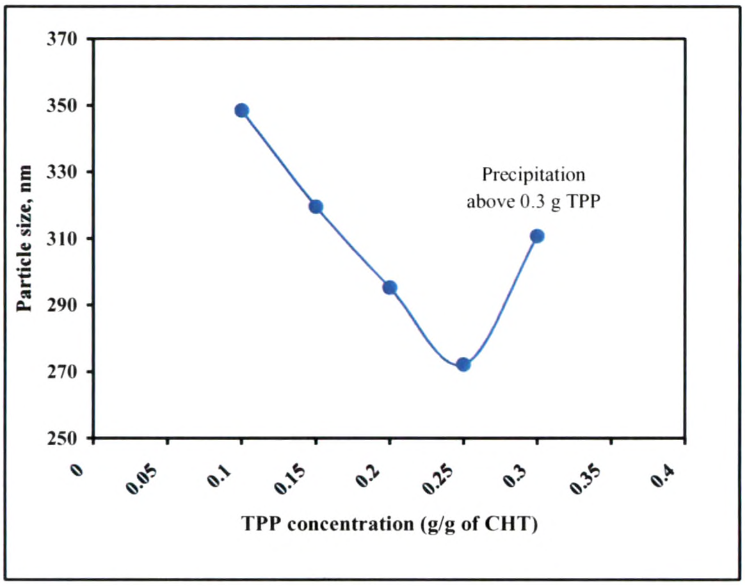
Conc of chitosan 1g/L

Figure 3.11 Effect of TPP concentration on appearance CHTN dispersion

Table 3.6 Effect of TPP concentration on particle size of nano chitosan

CHT:TPP	Ingredients, ml				Viscosity		Particle size, nm
	CHT	TPP	Water	Total volume	Flow time (T), sec	Relative viscosity (η_{rel})	
1:00	10	-	90	100	51.85	3.328	4014
1:0.05	10	1	89	100	46.86	3.010	-
1:0.10	10	2	88	100	39.04	2.507	348.3
1:0.15	10	3	87	100	32.25	2.071	319.4
1:0.20	10	4	86	100	27.16	1.745	295.1
1:0.25	10	5	85	100	23.12	1.485	272.06
1:0.30	10	6	84	100	30.13	1.935	310.6
1:0.35	10	7	83	100	16.91	1.086	ppt
1:0.40	10	8	82	100	16.28	1.045	ppt

Stock solutions: CHT (10 g/L) prepared in acetic acid solution 10 g/L, TPP (5 g/L);
Conc of nano-chitosan 1g/L, T_0 (Water) 15.57 sec, Temp 30 ^{0}C



Conc of chitosan 1g/L, Size of CHT molecular sphere in absence of TPP was 4014 nm

Figure 3.12 Effect of TPP concentration on particle size of CHTN

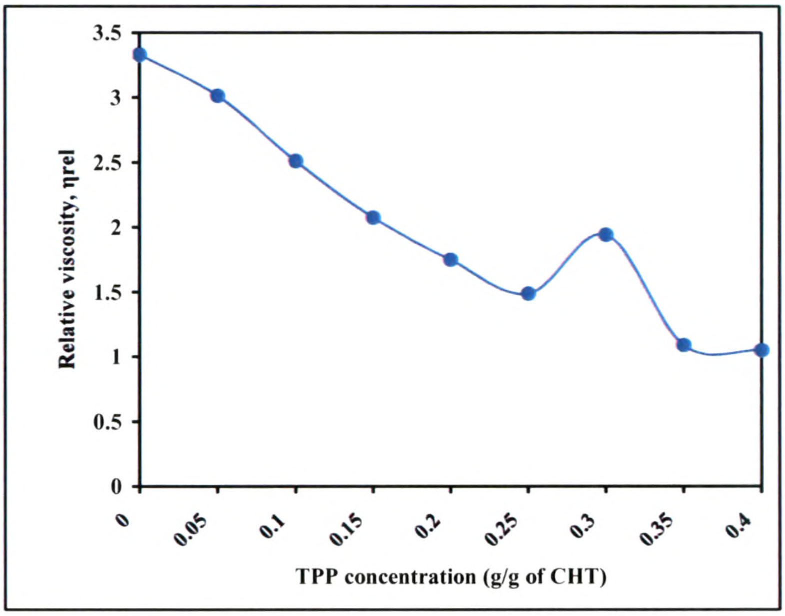


Figure 3.13 Relative viscosity of CHTN dispersion as a function of TPP concentration

3.3.5 Viscosity behaviour of nano chitosan dispersion

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 the chain length and hence the molecular weight [26]. A correlation of molecular weight of chitosan with the particle size of respective synthesized nano chitosan is elucidated in section 3.3.2. The particle size of nano chitosan is also expected to influence the viscosity behaviour of its dispersion, which is presented in Table 3.7. The extent to which a parent chitosan scales down to nano level at a given concentration of CHT and TPP was also examined by comparing the relative viscosity of nano chitosan dispersion with that of respective parent chitosan solution as demonstrated in same table and graphically in Figure 3.14.

Table 3.7 Viscosity of nano chitosan dispersion as a function of particle size

Parent chitosan solution				**Nano chitosan dispersion**				
Sample code	**Molecular weight (Mv)**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Sample code**	**Flow time (T), Sec**	**Relative viscosity (η_{rel})**	**Drop in viscosity on nano conversion, %**	**Particle size, nm**
CHT	135,839	51.81	3.33	CHTN	32.25	2.07	37.76	319.4
CHT-D2	71,676	28.57	1.84	CHT-D2N	22.80	1.46	20.26	271.6
CHT-D3	38,733	20.03	1.29	CHT-D3N	17.74	1.14	11.43	231.0
CHT-D4	20,698	17.77	1.14	CHT-D4N	16.38	1.05	7.76	195.2
CHT-D5	11,986	16.43	1.06	CHT-D5N	16.13	1.04	1.77	110.7

Conc of chitosan 1 g/L, CHT:TPP=1:0.15, T_0 (Water)= 15.57 sec, Temp 30 °C

It can be seen from Table 3.7 that the viscosity of CHTN dispersion decreased with reduction in particle size. However, the effect was more significant for larger particles than the smaller one. Obviously, the larger the particle size the higher will be the resistance offered for the flow of liquid and hence the higher will be the viscosity and vise versa. Comparatively slower fall in viscosity for small CHTN particles may be attributed to the low molecular weights of parent chitosan. It can be observed from Figure 3.14 that the percentage drop in viscosity from molecular (CHT) solution to corresponding nano chitosan (CHTN) dispersion follows a straight line. It means higher molecular weight chitosan scales down to nano size to greater extent than the lower molecular weight chitosan. This can be explained as follows; large size chitosan molecules in solution accommodate comparatively more amount of solvent and occupy large 'hydrodynamic' volume. These swollen molecules compress to greater extent by ionotropic intramolecular cross linking with TPP by displacing the solvent, as demonstrated in Figure 3.5. On the other hand, the extent of swelling of low molecular weight chitosan is comparatively less [27] and hence lesser will be its tendency to compress.

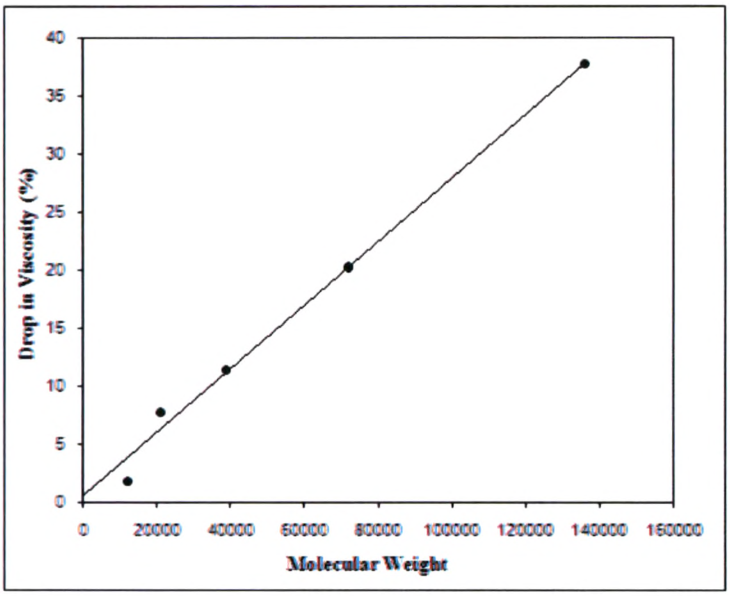


Figure 3.14 Drop in viscosity from parent to nano chitosan solution as a function of molecular weight

The biodegradability of chitosan is anticipated to be influenced by its particle size. Therefore the stability behaviour of standing baths of nano chitosan dispersion should be taken into consideration during its applications particularly to textile fabrics. The stability of nano chitosan dispersions for 24 hrs were analysed by viscosity measurements as shown in Table 3.8. It was observed that the change in viscosity of parent chitosan solution was governed by its molecular weight, which improved with decrease in weight. The stability behaviour of nano chitosan dispersion, on the other hand, was found to be different from that of parent chitosan solutions. The loss in viscosity of high molecular weight parent chitosan solution was somewhat higher than that of corresponding/respective synthesized nano chitosan dispersions. The integrity of nano chitosan i.e. small particle size was found to lose which were obtained from low molecular weight chitosans. The viscosity changes for most of the nano chitosan dispersions in 24 h storage were tolerable and can be safely employed for applications. Complete biodegradation of nano chitosan dispersion, in general, was resulted in 3-4 days showing the formation of white globules as shown in Figure 3.15. Such spontaneous disintegration takes place under very mild conditions. The viscosity of parent chitosan solution sustained for longer time after initial loss in viscosity, chapter 2. This suggests that chitosan-TPP nanogels behave as metastable system and must be used fresh or must be stored lyophilized and fresh aqueous solutions only prepared when required [19]. Viscosity analysis and visual observations, therefore, may be the useful tools for stability inspections.

Table 3.8 Stability of nano chitosan solution as a function of particle size

Parent chitosan solution					**Nano chitosan dispersion**				
Sample Code	**Mol Wt (Mv)**	**Relative viscosity(η_{rel})**		**Drop in viscosity (%) after 24 h**	**Sample Code**	**Particle size, nm**	**Relative viscosity (η_{rel})**		**Drop in viscosity (%) after 24 h**
		Initial	**After 24 h**				**Initial**	**After 24 h**	
CHT	135,839	3.33	2.98	10.27	CHTN	319.4	2.07	2.00	3.68
CHT-D2	71,676	1.84	1.76	4.1	CHT-D2N	271.6	1.46	1.45	1.05
CHT-D3	38,733	1.28	1.25	2.6	CHT-D3N	231.0	1.14	1.13	1.18
CHT-D4	20,698	1.10	1.08	2.15	CHT-D4N	195.2	1.05	1.01	3.6
CHT-D5	11,986	1.05	1.04	1.73	CHT-D5N	110.74	1.04	1.01	2.27

Conc of chitosan 1 g/L, CHT:TPP=1:0.15, T_0 (Water)= 15.57 sec, Temp 30 °C

Figure 3.15 Stability study: white globular residue formed by microbial attack on CHTN

3.3.6 Effect of nano chitosan treatment on cotton fabric

Chitosan and nano chitosan solutions were applied onto fabric by conventional pad-dry-cure technique. Having understood from chapter 2 that the progressive changes in performance in various properties of chitosan treatment at various concentrations, only a representative concentration of 1 g/L was chosen.

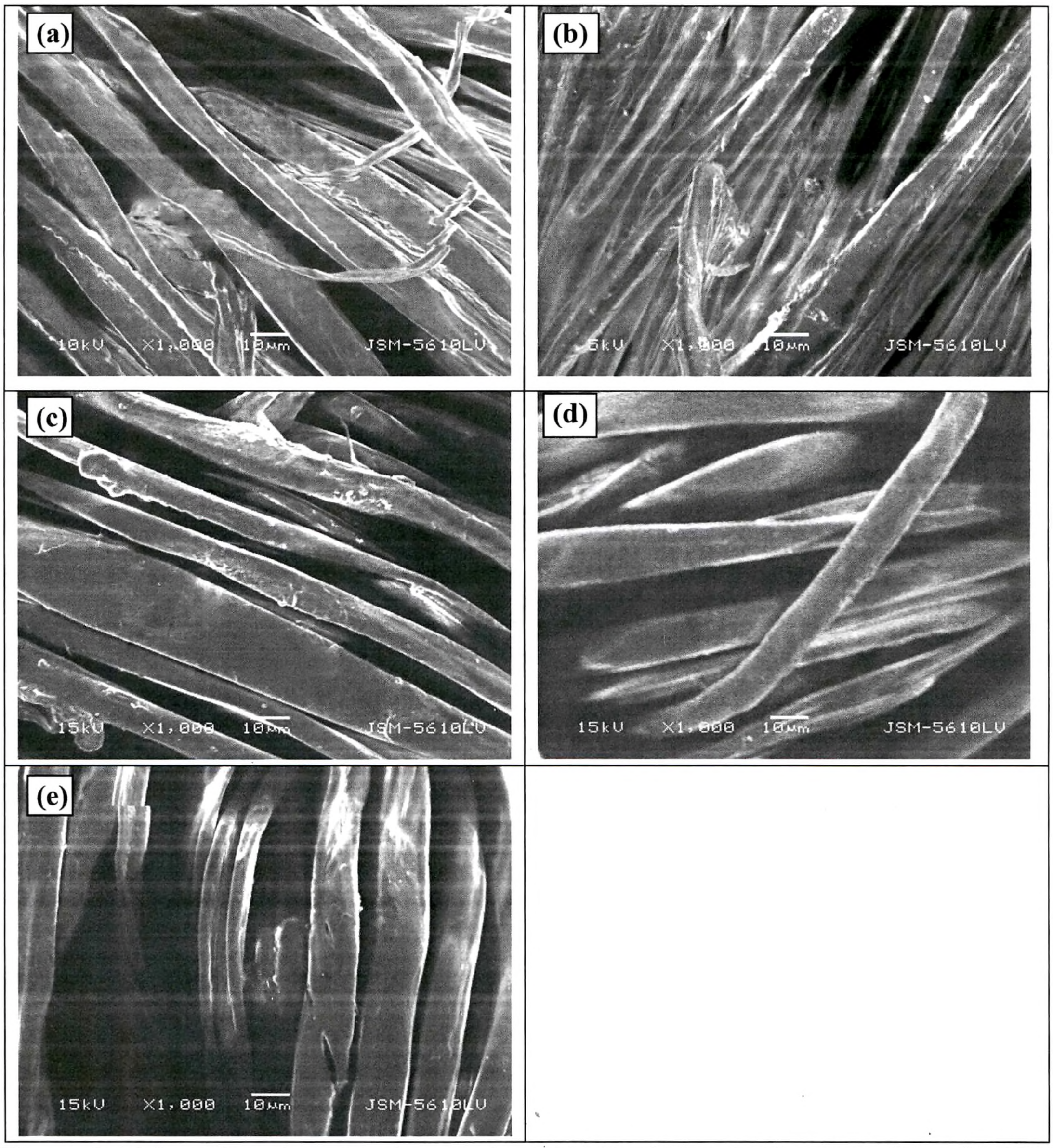


Figure 3.16 Scanning electron micrographs (x1000) of (a) control cotton fibre, (b) CHT treated fibres, (c) CHTN (319.4 nm) treated cotton fibres, (d) CHT-D4N (195.2 nm) treated cotton fibres and (e) CHT-D5N (110.7 nm) treated cotton fibres

The surface morphology of treated and untreated cotton was studied under scanning electron microscope, which is presented in Figure 3.16. Chitosan exhibits an inherent property of film formation, which is clearly seen as gloss on fibre surface as shown in figure SEM (b). Nano chitosan treated samples showed a different look in its microphotographs, which are presented in Figures 3.16(c, d and e).The appearance was non glossy and somewhat swollen. This effect became more significant when the particle size was reduced. It indicates a greater extent of penetration into the fibre structure rather than a surface deposition as film.

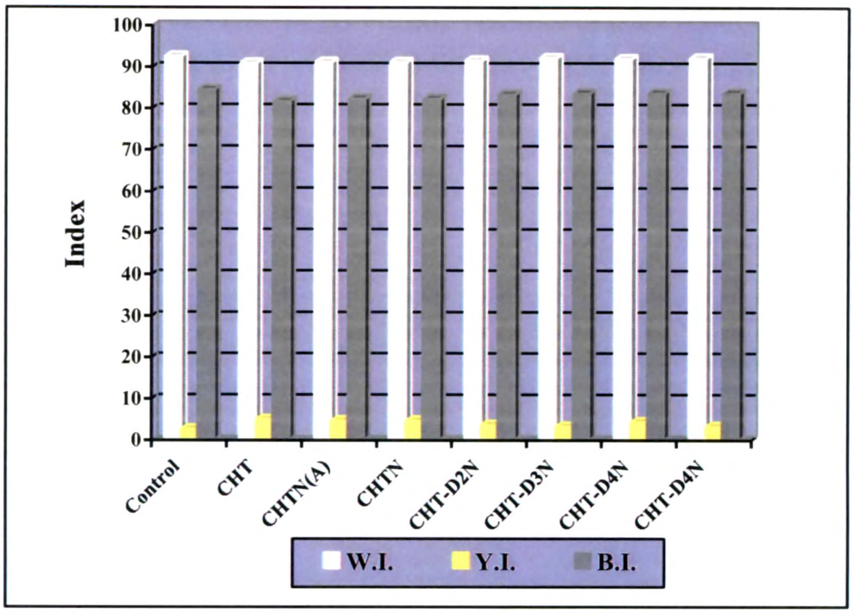
3.3.7 Effect of nano chitosan treatment on appearance and feel of cotton fabric

The appearance and the fabric feel are quite satisfactory. The results are illustrated in Table 3.9 and Figure 3.17. It was envisaged that the whiteness improved with reduction in particle size and reached 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 alter the whiteness to some extent. This film may also impart stiffness to the fibre, where as a nano chitosan shows a little influence, as can be observed in same table.

Table 3.9 Effect of particle size of nano chitosan on appearance and stiffness of cotton fabric

Sample code	Particle size, nm	Appearance			Bending Length, cm	
		W.I.	Y.I.	B.I.	Warp	Weft
Control	-	92.5	2.6	84.6	2.05	1.68
CHT	4014	90.9	4.9	81.8	2.44	1.70
CHTN(A)	468.1	91.1	4.6	82.4	2.29	1.71
CHTN	319.4	91.1	4.6	82.3	2.26	1.70
CHT-D2N	271.6	91.5	3.6	83.4	2.24	1.70
CHT-D3N	231.0	92.1	3.2	83.7	2.24	1.71
CHT-D4N	195.2	91.9	3.4	83.8	2.21	1.70
CHT-D5N	110.7	92.1	3.2	83.8	2.19	1.70

Conc of chitosan derivatives in pad liquor 1g/L, CHTN (A) was obtained from nano CHT (2 g/L) by dilution method



Conc of chitosan derivatives in pad liquor 1g/L, CHTN (A) was obtained from nano CHT (2 g/L) by dilution method

Figure 3.17 Effect of particle size of nano chitosan on appearance of treated cotton fabric

3.3.8 Effect of nano chitosan on tensile properties of cotton fabric

During wet processing operations textile fabric is subjected to various chemical and thermal treatments. These treatments affect various properties of the fabric. The effect of nano chitosan on tensile properties such as tenacity and elongation at break are presented in Table 3.10. It is observed that there is reasonable reduction in fibre strength of normal chitosan treated fabrics. This drop in strength seems to be arised from the acid hydrolysis and/or thermal treatments and not due to chitosan, which is obviously envisaged from the strength of the blank treated sample. While, normal chitosans of different molecular weights show somewhat higher strength than that of the blank treated sample, nevertheless lower than the untreated one. The elongation property was not altered much when compared to blank sample. The nano chitosan treatment on the other hand showed improvement in fibre strength which further increased with the reduction in particle size. The elongation property, however, was slightly affected with the scaling down of particle size. Normal chitosan mostly confines its film deposition on fibre surface only and thus contribute to very small extent in load bearing phenomenon rather may affect its symmetrical distribution of load. The improvement in fibre strength may be attributed to greater penetration of small particles and crosslink the adjacent fibre molecules by various forces between amino (-NH_2) and hydroxyl (-OH) groups of chitosan and hydroxyl (-OH) groups of cellulose molecules. The smaller the particle size, higher will be the surface area and hence the higher will be the cross links. The formation of *in-situ* three dimensional networks probably resists the adjacent fibre molecules to slip and lowers the elongation at break.

Table 3.10 Effect of nano chitosan treatment on tensile properties of cotton fabric

Parent chitosan treated fibres			**Nano chitosan treated fibre**		
Sample code	**Tenacity, g/tex**	**Elongation at break, %**	**Sample code**	**Tenacity, g/tex**	**Elongation at break, %**
Untreated cotton fabric	23.33	5.25	Untreated cotton fabric	23.33	5.25
Control	20.87	4.75	Control	20.87	4.75
CHT	20.48	4.75	CHTN-A	23.48	4.5
			CHTN	25.17	4
CHT-D2	21.01	4.5	CHT-D2N	25.62	4
CHT-D3	21.45	4.5	CHT-D3N	25.56	4
CHT-D4	22.19	4.25	CHT-D4N	25.71	3.75
CHT-D5	21.81	4.5	CHT-D5N	25.72	3.5

Conc of chitosan derivatives in pad liquor 1g/L, CHTN-A was obtained from nano CHT (2 g/L) by dilution method, Control: Blank treatment was given with acetic acid (10 g/L) by pad-dry cure method

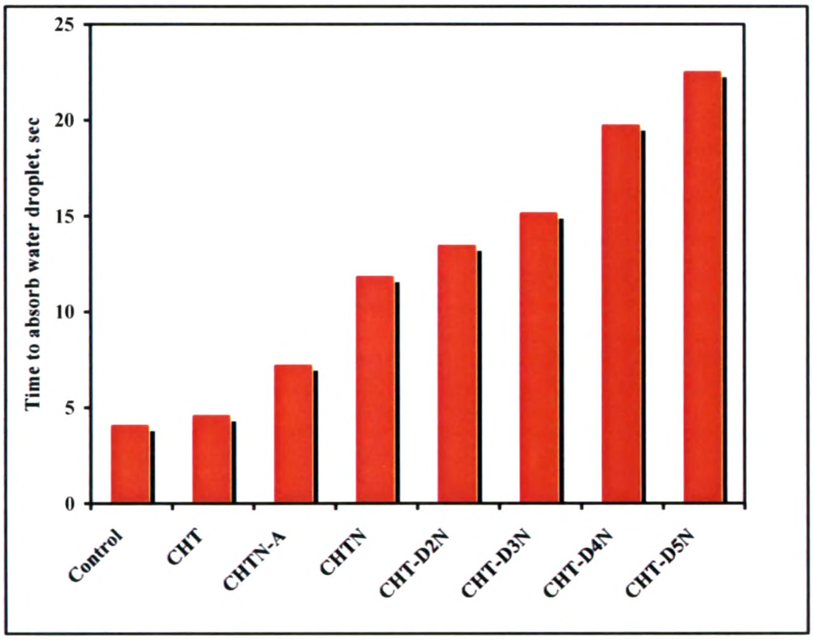
3.3.9 Effect of nano chitosan treatment on absorbency of cotton fabric

The absorbency, measured by drop penetration method, of nano chitosan treated cotton fabric was evaluated and shown in Table 3.11 and graphically in Figure 3.18. The absorbency was found to be 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, illustrated in Figure 3.16 (c, d and e), 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 since this rise in water drop penetration time is due to the initial resistance offered by nano chitosan particles and not due to any hydrophobic or water repellant hydrocarbon or silicone type films.

Table 3.11 Effect of particle size of nano chitosan on absorbency of treated cotton fabric

Sample code	**Particle size, nm**	**Absorbency, sec**						
		Readings						**Average**
Control	-	3.88	3.88	3.24	4.95	4.41	3.78	4.0
CHT	4014	4.28	3.95	4.62	5.12	4.46	4.81	4.5
CHTN-A	468.1	8.03	5.47	8.14	4.95	7.21	9.22	7.2
CHTN	319.4	10.98	11.52	11.92	12.36	9.81	14.15	11.8
CHT-D2N	271.6	13.45	13.68	12.69	15.08	13.36	12.26	13.4
CHT-D3N	231.0	14.81	15.12	16.71	12.61	17.43	13.86	15.1
CHT-D4N	195.2	20.36	19.52	22.81	18.08	23.01	14.36	19.7
CHT-D5N	110.74	22.51	18.71	26.08	22.32	21.42	23.78	22.5

Conc of chitosan derivative in pad liquor 1 g/L, CHTN-A was obtained from nano CHT (2 g/L) by dilution method



Conc of chitosan derivative in pad liquor 1 g/L, CHTN (A) was obtained from nano CHT (2 g/L) by dilution method

Figure 3.18 Effect of particle size of nano chitosan on absorbency of treated cotton fabric

3.3.10 Dyeing behaviour of nano chitosan treated cotton fabric

Chitosan pretreatment has shown improved dye uptake on cotton fibre both in presence and absence of electrolyte as discussed in chapter 2. However the dye was mostly confined to surface of fabric due to lack of penetration of parent chitosan. Fastness properties were also found to be deprecated. Thus, in this work, the effect of pretreatment of nano chitosan on direct dyeing of cotton was studied. In another approach, the dye bath was made slightly acidic with acetic acid (0.5 g/L) and treated for 15 minutes after the conventional dyeing was over (i.e. after the 60 minutes). The effects of chitosan and nano chitosan pretreatment on dye uptake are illustrated in Table 3.12 and graphically in Figures 3.19 and 3.20.

Table 3.12 Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

Parent chitosan			**Nano chitosan**				
Sample Code	**K/S Conventional dye bath**		**Sample Code**	**K/S**			
	C. I. Direct Red 81	**C. I. Direct Blue 71**		**C. I. Direct Red 81**		**C. I. Direct Blue 71**	
				Conventional dye bath	**Acidic dye bath**	**Conventional dye bath**	**Acidic dye batt**
Control	7.71	6.08	Control	7.71	6.33	6.08	4.94
CHT	9.07 *(17.6)*	6.99 *(14.8)*	CHTN-A	9.62 *(24.7)*	10.24 *(61.8)*	7.26 *(19.4)*	8.05 *(63.1)*
			CHTN	9.6484 *(25.1)*	10.39 *(64.2)*	7.43 *(22.1)*	8.12 *(63.4)*
CHT-D2	9.02 *(17.0)*	7.02 *(15.4)*	CHT-D2N	9.81 *(27.1)*	10.49 *(65.8)*	7.47 *(22.8)*	8.24 *(66.9)*
CHT-D3	9.05 *(17.3)*	6.81 *(12.0)*	CHT-D3N	9.83 *(27.4)*	10.51 *(66.2)*	7.72 *(26.9)*	8.25 *(67.1)*
CHT-D4	9.07 *(17.6)*	6.68 *(9.8)*	CHT-D4N	9.82 *(27.3)*	10.50 *(66.0)*	7.79 *(28.2)*	8.28 *(67.7)*
CHT-D5	9.10 *(18.0)*	7.09 *(16.5)*	CHT-D5N	9.96 *(29.1)*	10.60 *(67.5)*	7.81 *(28.3)*	8.38 *(69.7)*

Conc of chitosan derivatives in pad bath 1 g/L, Values in parenthesis indicate percent improvement in K/S compared with the corresponding control fabric sample

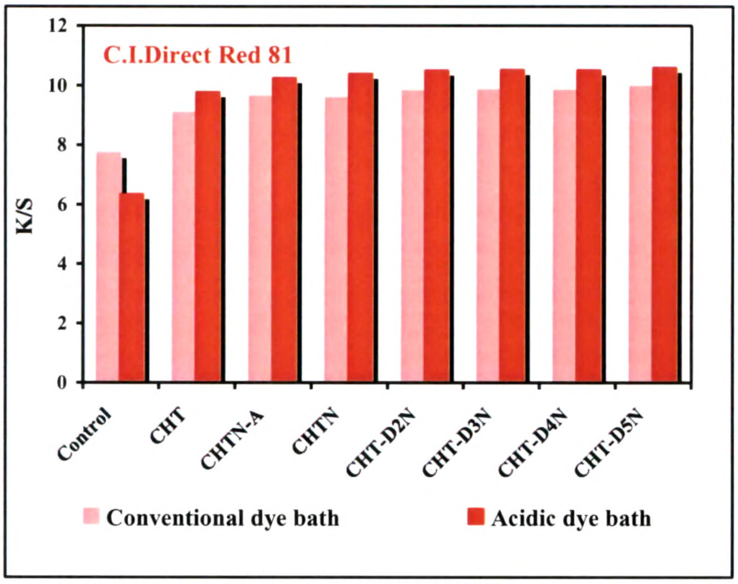


Figure 3.19 Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

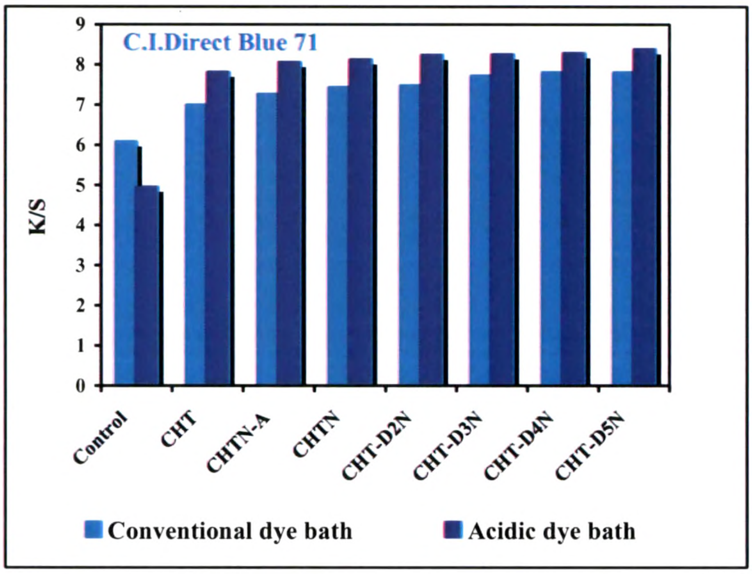


Figure 3.20 Effect of particle size of nano-chitosan on dye uptake of treated cotton fabric

Results revealed that the dye uptake by cotton fabric, in conventional process, increased marginally with normal chitosan treatment and further improved with the reduction in particle size of nano chitosan. On acidification, the dye up take was still increased compared to conventionally dyed samples. The increased dye uptake due to chitosan treatment may be attributed to the presence of primary amino groups on chitosan. These cat ions dissipate the negative surface charge on cotton and drives dye molecules to the fibre. Further, the dye up take 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 in acidic medium having enhanced positive charge can now form salt linkages with anionic (sulphonate) groups of residual dye present in the dye bath. This leads to almost complete exhaustion of dye bath.

The washing fastness and rubbing fastness properties of direct dyed fabrics were also analyzed, which are presented in Table 3.13. The fastness to washing was found to be improved with reduction in particle size. This may be regarded to the formation of CHTN-Dye complex in situ. The fastness to rubbing was also slightly improved with decrease in particle size. This property is mainly associated with the rubbing fastness of dyes chitosan molecules on cotton fibre.

Table 3.13 Effect of particle size on fastness properties of direct dyes

Sample code	**Particle size nm**	**C.I. Direct Red 81**		**C. I. Direct Blue 71**	
		Wash fastness	**Rub fastness**	**Wash fastness**	**Rub fastness**
Control	-	3	2-3	4	2-3
CHT	4014	3	2	4	2
CHTN(A)	468.1	3-4	2-3	4-5	2
CHTN	319.4	3-4	2-3	4-5	2-3
CHT-D2N	271.6	3-4	2-3	4-5	2-3
CHT-D3N	231.0	4	2-3	4-5	2-3
CHT-D4N	195.2	4	2-3	5	3
CHT-D5N	110.7	4-5	3	5	3

Dyeing process: Conventional

3.3.11 Effect of nano chitosan on crease recovery property of cotton fabric

It is shown in previous chapter that the chitosan treatment adversely affected the wrinkle recovery property of cotton fabric. The molecular size of polymer was the major reason for this drawback. Reduction of the particle size of chitosan has found to enhance various properties at minimal concentration and is expected the possibility to restore the aesthetics. The crease recovery property as a function of chitosan and nano chitosan treatments compared against commercial DMDHEU application and is presented in Table 3.14. The crease recovery angle of cotton fabric was greatly reduced by the treatment of normal chitosan (CHT). Treatment of cotton fabric with chitosan of lower particle size was found to improve the crease recovery property of cotton fabric. 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. However, a final touch up with conventional easy care finish is desired.

Table 3.14 Effect of particle size of chitosan on wrinkle recovery property of cotton fabric

Sample code	**Conc in pad bath, g/L**	**Particle size, nm**	**Crease recovery angle (CRA°)**		
			Warp	**Weft**	**Total**
Control	-	-	80	81	161
DMDHEU (40%)	20	-	85	95	180
	40	-	106	101	207
	60	-	112	113	215
CHT	1	4014	72	72	144
CHTN-A	1	468.1	79	79	158
CHTN	1	319.4	82	82	162
CHT-D2N	1	271.6	82	80	162
CHT-D3N	1	231.0	82	81	163
CHT-D4N	1	195.2	85	80	165
CHT-D5N	1	110.7	86	84	170

3.3.12 Effect of nano chitosan treatment on cotton fabric on its resistance against microorganism

Attributing to the polycationic nature, chitosan has shown resistance to microbial attack in soil burial test as discussed in chapter 2. The effect, however, was moderate and in order to improve the property the effect of particle size of nano chitosan was examined. The antibacterial property of nano chitosan can further be enhanced by loading it with other antibacterial agents such as silver nano particle. Silver nano particles are very effective antimicrobial and antifungal agents at lower concentrations and are much more effective than other metals such as mercury, copper, lead, chromium and tin. At lower concentration, silver nano particles directly damage the cell envelope by penetrating the cell and then silver binds to the DNA, this complex prevents the DNA replication by displacement of hydrogen bonds between adjacent nitrogen of purines and pyrimidines [46]. Nano silver dispersion is produced by reduction of silver sulphate with sodium borohydride in presence of trisodium citrate under inert atmosphere, scheme 3.1. Nano silver colloid of concentration $1X10^{-3}$ M / 100 ml and average particle size 110 nm was prepared as published elsewhere [24].

$$4Ag^{+2} + NaBH_4 + 2H_2O \rightarrow 4Ag + BH_4 + Na^+ + 4H^+ + O_2$$

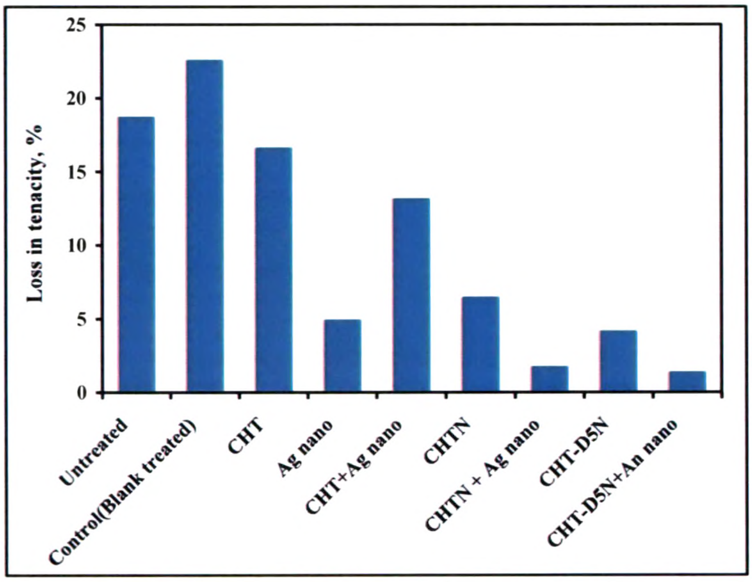
Scheme 3.1 Reduction of silver ions

Nevertheless it is extremely efficient antibacterial agent; its retention by the fibre for multiple washings is questioned. Attributing to the antibacterial and high metal particles retention properties of chitosan [47], the fabric was treated with chitosan (or nano chitosan) and then with nano silver colloid (two bath process). The resistance against bacterial attack of untreated and treated samples of cotton was determined by determining their loss in strength due to soil burial test. The results are presented in Table 3.15. It can be observed from these results that the chitosan can be employed as an efficient antibacterial agent. The effect is enhanced with the reduction in particle size of nano chitosan and coupling with nano silver.

Table 3.15 Effect of nano chitosan treatment on resistance towards microbial attack

Sample code	**Particle size, nm**	**Tenacity, g/tex**		***Drop in strength, %**
		Before soil burial	**After soil burial**	
Untreated cotton fabric		23.33	18.98	18.65
Control		20.87	18.08	22.5
CHT	4014	20.48	19.47	16.55
Ag nano	110	22.68	22.20	4.84
CHT+ --------- Ag nano		24.51	20.27	13.10
CHTN	319.4	25.17	21.84	6.39
CHTN + ---------- Ag nano		24.21	22.94	1.67
CHT-D5N	110.7	25.72	22.38	4.07
CHT5N + --------- Ag nano		25.67	23.03	1.29

Control: Blank treatment was given with acetic acid (10 g/L) by pad-dry cure method,
**Drop in strength was measured from untreated cotton fibre*



Conc of chitosan derivative 1 g/L

Figure 3.21 Effect of nano chitosan on resistance towards microbial attack

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