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Properties of Cotton Fabric Modified with a Chitosan Quaternary Ammonium Salt Nanoparticle

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Abstract
In this study, a novel fibre-reactive nanoparticle was synthesised in three steps. First a water-soluble chitosan derivative, N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (short for HTCC), was prepared by reacting chitosan with 2,3-epoxypropyltrimethylammonium chloride. Second the HTCC was further modified by reacting it with N-(hydroxymethyl)-acrylamide to prepare a fibre-reactive chitosan derivative, O-methyl acrylamide quaternary ammonium salt of chitosan (short for NMA-HTCC), which can form covalent bonds with cellulose fibre under alkaline conditions. Thirdly NMA-HTCC nanoparticles were prepared by the ionotropic gelation reaction method. The particle size and TEM researches indicated that the globular NMA-HTCC nanoparticle with a size distribution of 15–50 nm was successfully prepared and presented good dispersity and stability. Then the NMA-HTCC nanoparticle was used for the textile finishing of cotton fabric. The modified cotton fabric demonstrated excellent durable wrinkle-resistance and antibacterial activity against Staphylococcus aureus and Escherichia coli, even after 50 repeated launderings. Moreover the shrinkage-resistance of the modified cotton fabric was distinctly improved, and the contact angle was slightly larger, while the whiteness and mechanical properties had not changed in an obvious way.

Key words: *fibre-reactive quaternary ammonium salt of chitosan, nanoparticle, cotton fabric, antibacterial activity, wrinkle-resistance, laundering durability.*

Introduction

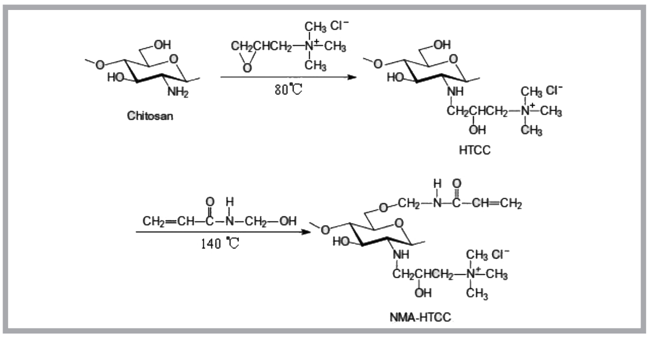
Cotton, one of the most important natural textiles, is widely used in clothing fields due to its excellent characteristics including regeneration, bio-degradation, softness, affinity to skin, and hygroscopicity, but there are some shortcomings such as being easy to wrinkle, mildew and deform, and hence the use of functional finishing agents on cotton fabric is becoming a popular and promising method to meet the demands of the commercial cotton textile market [1-3].

Chitosan has been widely used in many fields such as the textile industry, daily environmental protection, biological medicine, and so on, due to its biocompatibility, degradability, non-antigenicity, adsorption, and so forth [4]. However, chitosan cannot be dissolved in water and organic solvent, only in acid solution, which greatly limits its application. Thus it is necessary to improve the solubility of chitosan by chemical modification. As one of the important modification methods of chitosan, alkylation modification has been widely researched and applied [5-7]. Moreover another major drawback of chitosan as a textile functional finish is its lack of strong bonding with textile fibres. As a result, the textile activities of chitosan treated fabric decrease with repeated launderings.

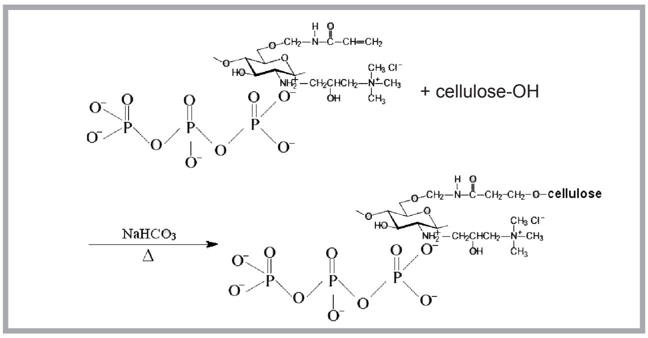
In this research, we report a new water-soluble chitosan derivative with a fibre-reactive group,which can be covalently bonded to textile fibres having nucleophilic groups. A water-soluble chitosan derivative, HTCC, was first prepared by reacting chitosan with glycidyltrimethylammonium chloride, then the HTCC was further modified by reacting it with N-(hydroxymethyl)-acrylamide to prepare a fibre-reactive chitosan derivative, O-acrylamidomethyl-HTCC (NMA–HTCC), which could directly crosslink react with cellulose fibres to form a strong combination between NMA-HTCC and fibres [3, 8-10].

So far nanotechnologies have been applied in textile fields to provide good antimicrobial activity, self-cleaning activity, UV-resistance, infrared activity, antistatic properties, anti-aging properties, and so on [2, 11-13]. For example, amino functional silver nanoparticles were prepared and grafted on oxidized silk fabric to obtain a silk fabric with excellent antimicrobial properties and laundering durability. Nanochitosan treated wool fabric possessed better antimicrobial activity and shrink-proofing properties even after washing 20 times [14-16]. Like those ordinary nano-materials, at a nano-scale, the nanoparticles of NMA-HTCC are expected to have characteristics such as small size, great specific surface area, high surface activity, and so on. NMA-HTCC has been applied to improve the dyeing behaviors and antibacterial activity of textiles [3, 17], but the applications of NMA-HTCC nanoparticles has been seldom reported in textile fields.

NMA-HTCC nanoparticles were prepared by ionotropic gelation reaction in this paper. NMA-HTCC nanoparticles were directly crosslink reacted with cellulose fibres to form a strong combination, and thus it could be used in the functional finishing of cotton fabric directly. When applied to cotton fabric modification, the effects of NMA-HTCC nanoparticles on the antibacterial activity, wrinkle-resistance and laundering durability of cotton fabric were researched.



Equation 1.



Equation 3.

Experimental

Materials

Chitosan with a deacetylation degree of 92.6% and molecular weight of 2×10^4 was supplied by Nantong Xingcheng Biological Industrial Co. Ltd. (Jiangsu, P.R. China), and 2,3-epoxypropyltrimethyl ammonium chloride, N-(hydroxymethyl)-acrylamide, 4-Methoxyphenol and ammonia chloride were provided by Yancheng Chunyu chemical Co. Ltd. (Jiangsu, P. R. China). All chemical reagents, including isopropyl alcohol, sodium bicarbonate, sodium tripolyphosphate (STTP), citric acid (CA), Tween-80 (as a dispersant), ethanol and acetone, used for the following investigations were of analytical grade. Deionized water was used throughout the work.

Preparation of NMA-HTCC

5 g of chitosan, 25 g of 2,3-epoxy propyl trimethyl ammonium chloride and 250 ml of isopropyl alcohol were put into a 4-mouth flask. The solutions were reacted at 80 °C for 12 h in a water bath, washed by ethanol and acetone after cooling, then filtrated and dried. The yellow product obtained was HTCC. After that the HTCC, N-Methylol acrylamide, 4-Methoxyphenol and NH_4Cl were put into the flask and stirred evenly until dissolution. The solutions were reacted at 140 °C for 10 min in an oil bath. Ethylalcohol and acetone were put into the reaction solutions and stirred to precipitate the product [8, 18]. The product was washed in a mixture of ethylalcohol-acetone and dried. Finally the white product obtained was NMA-HTCC. The reaction equation was as ***Equation 1***.

Preparation of NMA-HTCC nanoparticle

A NMA-HTCC nanoparticle disperse system was prepared by the ionization gelation method. 5 g of NMA-HTCC was dissolved in 100 ml of aqueous solution containing 7 g of CA and 0.5 g of Tween-80 in deionized water, and then STTP was dropped into the above solution to prepare NMA-HTCC nanoparticles at 40 °C while stirring [2, 13, 19].

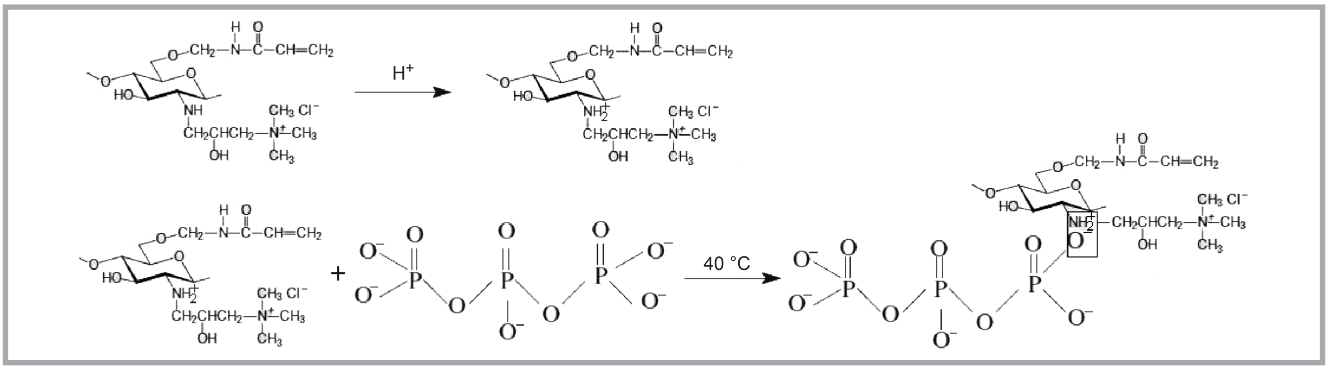
In disperse system above, CA was used as the dispersion medium of nanoparticles. Tween-80 was the dispersant, which was also used as the penetrating agent in the cotton treatment process. The reaction equation was as ***Equation 2*** [2].

Treatment process of cotton fabric/fibre with NMA-HTCC nanoparticle

The NMA-HTCC nanoparticle has a fibre reactive group with a side double bond, which can directly crosslink with cotton fibre under alkaline conditions; thus sodium bicarbonate was used as the catalyst in this experiment. Cotton fabric/fibre was immersed in the NMA-HTCC nanoparticle treatment solution with a liquor ratio of 1:50, NMA-HTCC nanoparticle concentration of 8 g/l, and $NaHCO_3$ mass fraction of 6%. The treatment process was as follows: Cotton fabric/fibre → treated in NMA-HTCC nanoparticle treatment solution at 60 °C for 1 h → pre-baked at 80 °C for 5 min → baked at 160 °C for 3 min → washed with deionized water → dried at 80 °C. The reaction equation was as ***Equation 3***.

Treatment process of cotton fabric with chitosan and HTCC

Because of the lack of chemical crosslinking between chitosan (or HTCC) and cotton fibre and the limited water-solubility of chitosan, the reaction between chitosan (or HTCC) and cotton fibre had to be undertaken under acidic conditions, with CA used as the catalyst and solvent, which could not only catalyse the crosslinking reaction but also make the chitosan dissolve. Chitosan (or HTCC) solution was prepared with a bath solution ratio of 1:50, a chitosan (or HTCC) concentration of 8 g/l and CA mass fraction of 6%. The treatment process was as follows: cotton fabric → treated in chitosan (or HTCC) solution at 60 °C for 1 h →



Equation 2.

pre-baked at 80 °C for 5 min → baked at 160 °C for 3 min → washed with deionized water→ dried at 80 °C.

Treatment process of cotton fabric with NMA-HTCC

NMA-HTCC has a fibre reactive group with a side double bond, which can directly crosslink with cotton fibre under alkaline conditions. Sodium bicarbonate was used as the catalyst in this experiment, which could not only catalyse the cross-linking reaction but also facilitate effective permeation of NMA-HTCC to fibres by reducing the hydrolysis of NMA-HTCC and promoting the swelling of cotton fibres. NMA-HTCC solution was prepared at a bath solution ratio of 1:50 under alkaline conditions, at an NMA-HTCC concentration of 8 g/l and $NaHCO_3$ mass fraction of 6%. The treatment process was as follows: cotton fabric → treated in NMA-HTCC solution at 60 °C for 1 h → pre-baked at 80 °C for 5 min → baked at 160 °C for 3 min → washed with deionized water → dried at 80 °C.

Fourier transform infrared (FT-IR) spectroscopy

A Nicolet 5700 FT-IR spectrophotometer was used to observe infrared spectra with the traditional transmission technique of KBr pellets. The round pellets were prepared with a standard device under a pressure of 30 MPa. IR spectra were recorded at 4 cm^{-1} resolution, and 64 scans were taken for each sample. The measurements were performed at 20 °C and a relative humidity of 65%.

Transmission electron microscope (TEM) analysis

A drop of sample solution was placed onto a 300-mesh copper grid coated with carbon. Approximately 2 min after deposition, the grid was dabbed with filter paper to remove surface water and was air-dried. The microstructure of the NMA-HTCC nanoparticle was observed using a Tecnai G20 transmission electron microscope at an accelerating voltage of 220 kV.

Scanning electron microscopic (SEM) analysis

The surface morphology of the cotton fibre was observed by means of a Quanta200 scanning electron microscope. The cotton fibre was gold sputtered and given electronic conductivity under a vacuum prior to observation. The measurements were performed at 20 °C and a relative humidity of 65%.

Antibacterial activity test of cotton fabric

AATCC 100-2012 ‘Assessment of Antibacterial Finishes on Textile Materials’ was referenced to evaluate antibacterial properties of the cotton fabrics before and after treatment. The shake flask method was adopted and the bacteria reduction rate calculated. *Staphylococcus aureus* (*S. aureus* /ATCC6538) and *Escherichia coli* (*E. coli* /ATCC8099), gram-positive and gram-negative bacteria commonly found on the human body, were chosen as the bacteria tested.

Wrinkle-resistance test of cotton fabric

The dry wrinkle-recovery angles of the cotton fabrics before and after being treated with the NMA-HTCC nanoparticle were evaluated using a YG541A wrinkle-recovery tester according to AATCC 66-2008 ‘Wrinkle recovery of woven fabrics: recovery angle’. The results were obtained by averaging 10 warp and 10 weft samples, respectively. The laundering durability of the cotton fabric treated against repeated launderings was evaluated according to AATCC 124-2010 ‘Smoothness appearance of fabrics after repeated home laundering’.

Results and analysis

Characterisation of NMA-HTCC nanoparticle

An HPPS Laser Particle Size Analyser was used to test the size of the NMA-HTCC nanoparticle. The results in ***Figure 1*** show that the average particle size of NMA-HTCC nanoparticles was 34.9, which were mainly distributed in the range of 15 to 50 nm. The TEM photograph in ***Figure 2*** indicates that the globular NMA-HTCC nanoparticle was successfully prepared and presented good dispersity and stability.

In order to further characterise the generation of the NMA-HTCC nanoparticle, FTIR was used to characterise and analyse its chemical structure. Compared with ***Figure 3.a***, there is a new absorption peak at 1540 cm^{-1} in ***Figure 3.b***, which illustrates that the group of $-PO_3^-$

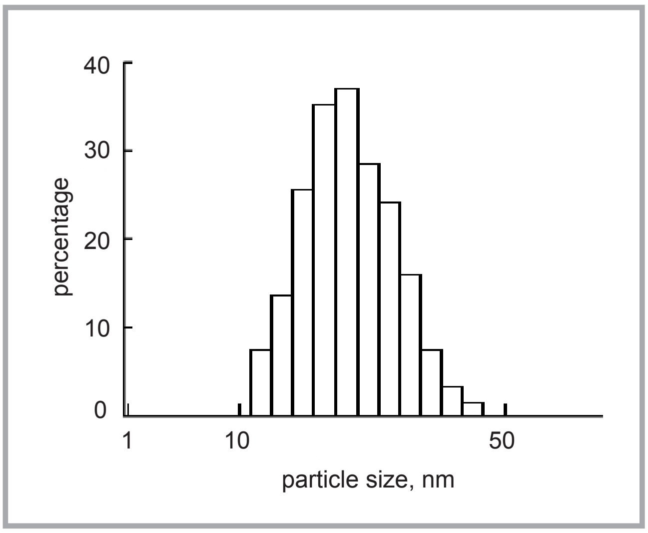


Figure 1. *Particle size distribution of NMA-HTCC nanoparticles.*

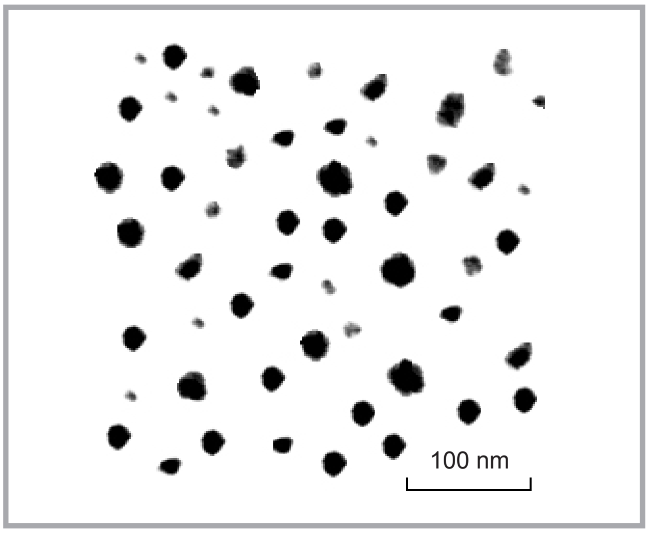


Figure 2. *TEM photograph of NMA-HTCC nanoparticle.*

in STTP was connected with that of –NH with NMA-HTCC macromolecular chains. In ***Figure 3(b)***, a series of new peaks appears in the range of 600 to 1000 cm^{-1} and 1060 to 1250 cm^{-1}, respectively, corresponding to the P-O bending and stretching of the $-PO_3^-$ group [2, 13]. All of these indicated that the NMA-HTCC nanoparticle was successfully generated.

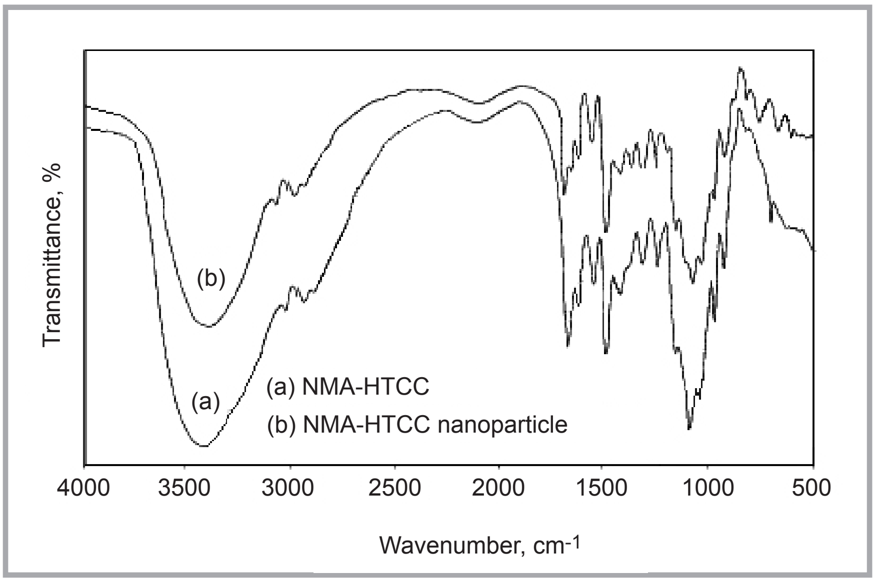


Figure 3. *FTIR spectroscopy of (a) NMA-HTCC and (b) NMA-HTCC nanoparticle.*

SEM analysis of cotton fibre before and after treatment with NMA-HTCC nanoparticle

SEM images of the untreated and NMA-HTCC nanoparticle treated cotton fibre are shown in ***Figure 4***. The images indicate obviously different morphology between the untreated and NMA-HTCC nanoparticle treated cotton fibre. The surface of the untreated cotton fibre is smooth in ***Figure 4.a***, while that of the cotton fibre treated with the NMA-HTCC nanoparticle in ***Figure 4.b*** is relatively rough, with some particles apparent. This could be attributed the absorption of NMA-HTCC nanoparticles on the cotton fibre through esterification or etherification reactions.

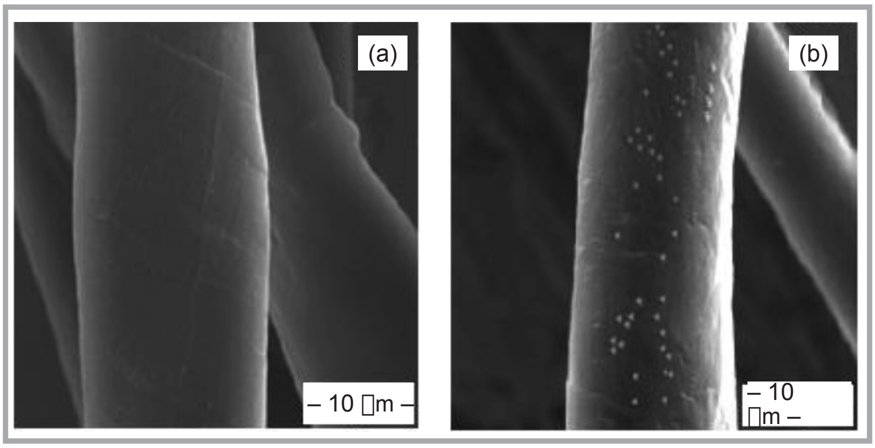


Figure 4. *SEM micrographs of (a) untreated fibre and (b) NMA-HTCC nanoparticle treated fibre (×3000).*

Antibacterial activity and washing durability of cotton fabric

Figure 5 shows the bacterial reduction of cotton fabrics treated with chitosan, HTCC, NMA-HTCC and NMA-HTCC nanoparticles for *S. aureus* and *E. coli*, respectively. It showed that the antibacterial activity of cotton fabric could be significantly improved after beibg treated by chitosan, HTCC, NMA-HTCC and NMA-HTCC nanoparticles with the same concentration. The antibacterial activity of cotton fabric treated with the NMA-HTCC nanoparticle was much better than those finished with chitosan, HTCC and NMA-HTCC. NMA-HTCC nanoparticle modified cotton fabrics were both achieved 100% bacterial reductions for *S. aureus* and *E. coli*.

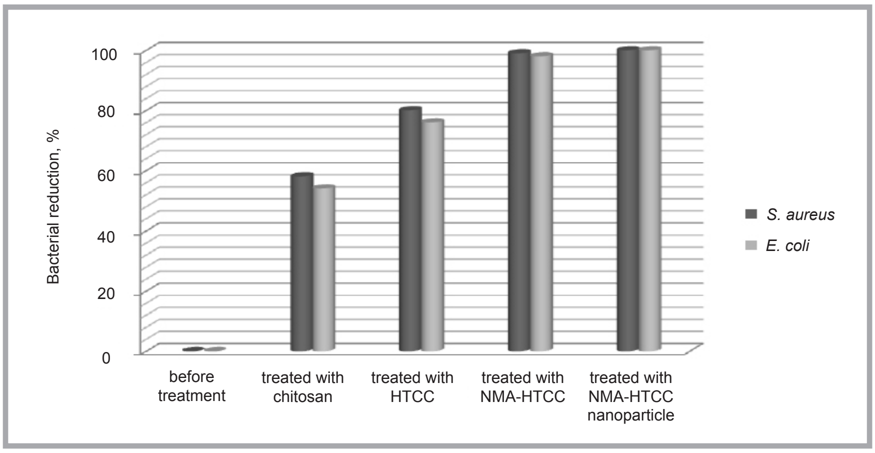


Figure 5. *Antibacterial activities of cotton fabrics treated with chitosan, HTCC, NMA-HTCC and NMA-HTCC nanoparticle.*

The NMA-HTCC nanoparticle is a kind of strong cationic polymer, and its quaternary ammonium ions can perform a flocculation effect with protein, peptidoglycan, teichoic acid, and lipopolysaccharide with negative charge on the surface of bacteria to destroy plasma membrane, disturb the normal physiological activity of bacteria, as well as restrict and destroy various physiological functions inside the bacteria [2, 13, 22, 23]. There were a large amount of NMA-HTCC nanoparticles on the cotton fabric after treatment, and the NMA-HTCC nanoparticles could contact with the bacterial cell wall and prevent the leakage of intracellular components. As a result, the contact area between the treated cotton fabric and bacteria increased, and more and more bacteria could be killed. Thus cotton fabric treated with the NMA-HTCC nanoparticle

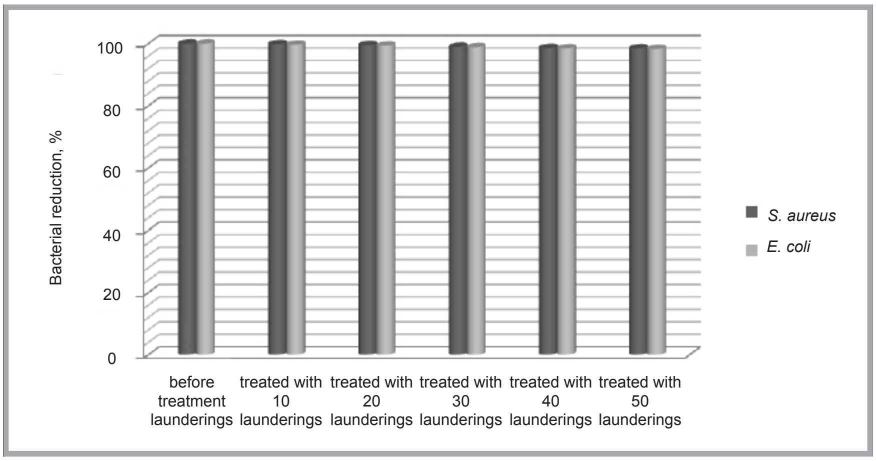


Figure 6. *Laundering durability of cotton fabrics treated with NMA-HTCC nanoparticles.*

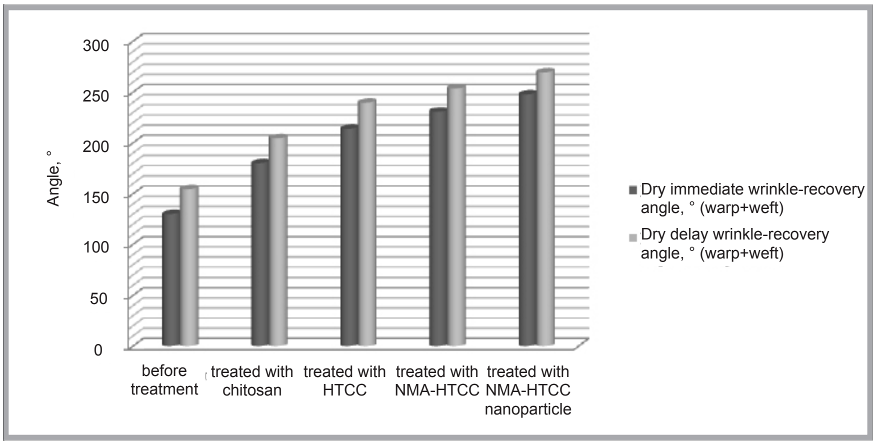


Figure 7. *Wrinkle-resistance of cotton fabric treated with chitosan, HTCC, NMA-HTCC and NMA-HTCC nanoparticles.*

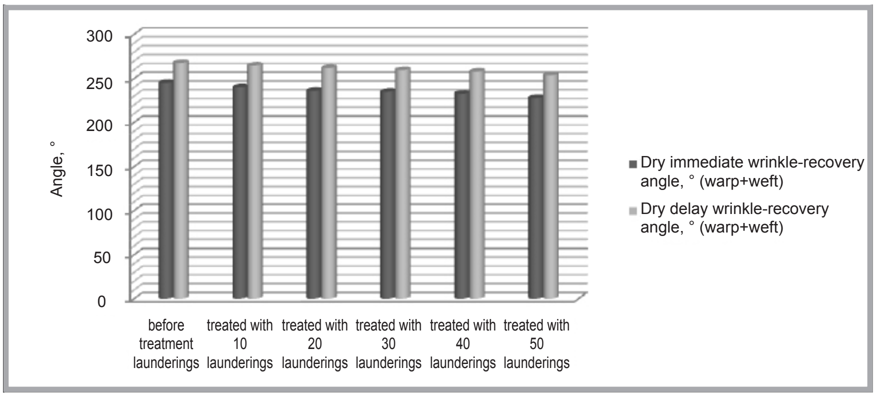


Figure 8. *Laundering durability of cotton fabrics treated with NMA-HTCC nanoparticles.*

had significantly improved antibacterial activity.

Figure 6 shows the bacterial reduction of cotton fabrics treated with NMA-HTCC nanoparticles for *S. aureus* and *E. coli* after 10, 20, 30, 40 and 50 launderings, respectively. The results showed that the bacterial reductions of the modified cotton fabric maintained 98.46% and 98.25% for *S. aureus* and *E. coli*, respectively, after 50 repeated launderings. The high laundering durability could be attributed to the strong cross-linking reaction between cotton fabric and NMA-HTCC nanoparticles. Hence it can be stated that the laundering durability of cotton fabric modified with the NMA-HTCC nanoparticle was excellent.

Wrinkle-resistance and washing durability of cotton fabric

Cotton fabric wrinkles up very easily, which has limited its application in textile fields. In this experiment, cotton fabrics were treated with chitosan, HTCC, NMA-HTCC and NMA-HTCC nanoparticles at the same concentration, respectively. The effect of the wrinkle-resistance is shown in ***Figure 7*** indicating that the recovery angles of the cotton fabrics were all improved after treatment with chitosan, HTCC, NMA-HTCC and NMA-HTCC nanoparticles, and wrinkle resistance activity of cotton fabric finished with the NMA-HTCC nanoparticle was much better than that finished with chitosan, HTCC and NMA-HTCC. The increase in the wrinkle-resistance of NMA-HTCC nanoparticle modified cotton fabrics is attributed to the cross-linking reactions that occurred between the NMA-HTCC nanoparticle and cotton fibre, with the cross-linking bonds between them limiting the movement of macromolecular chains in the amorphous field of the cotton fibre; thus the wrinkle-resistance was significantly improved.

The wrinkle resistance of cotton fabrics after 10, 20, 30, 40 & 50 consecutive launderings is shown in ***Figure 8***, indicating that the recovery angles of the cotton fabrics declined slowly after laundering. Therefore the cotton fabric treated with NMA-HTCC nanoparticles had a significantly improved and durable wrinkle-resistance, even after 50 consecutive launderings.

Other characteristics of the NMA-HTCC nanoparticle modified cotton fabric, including the shrinkage-resistance, contact angle, whiteness, and mechanical properties, were also tested. The results showed that the shrinkage rate was distinctly improved after treatment with the NMA-HTCC nanoparticle, because there are a number of micro-voids in cotton fibre and the NMA-HTCC nanoparticles could fill these, meanwhile the cross-linking bonds between the NMA-HTCC nanoparticle and cotton fibre limited the movement of macromolecular chains in the amorphous field of the cotton fibre, as a result of which the modified cotton fabric showed good anti-shrinkage properties. The contact angle of cotton fabric modified with the NMA-HTCC nanoparticle was slightly larger than that of untreated cotton fabric, as NMA-HTCC nanoparticles could fill the micro-voids of cotton fibre after treatment, which could make them smaller; thus the hydrophilicity of the cotton fabric was slightly reduced. Moreover changes in the breaking strength and whiteness of cotton fabrics before and after treatment were not very obvious, with a breaking strength retention rate of 98.2% and whiteness of 98.5%, which indicated that treatment with NMA-HTCC could not cause damage to the inner structure of the cotton fibre.

Conclusions

HTCC was first synthesised by reacting chitosan with 2,3-epoxypropyltrimethylammonium chloride, Secondly HTCC was further modified by reacting it with N-(hydroxymethyl)-acrylamide to prepare a fibre-reactive chitosan derivative, NMA–HTCC, which can form covalent bonds with cotton fibre under alkaline conditions. Thirdly NMA-HTCC nanoparticles were prepared by ionotropic gelation reaction and characterised through TEM and FTIR. Then the NMA-HTCC nanoparticle was used for the textile finishing of cotton fabric. The results showed that the globular NMA-HTCC nanoparticle with a size distribution of 15 – 50 nm was successfully prepared and presented good dispersity and stability. The antibacterial activity and wrinkle-resistance of cotton fabric treated with the NMA-HTCC nanoparticle were much better than those of cotton finished with chitosan, HTCC and NMA-HTCC. NMA-HTCC nanoparticle modified cotton fabric achieved 100% bacterial reduction for *S. aureus* and *E. coli*, and had significantly improved wrinkle-resistance. Because of the cross-linking reaction between cotton fabric and NMA-HTCC nanoparticles, NMA-HTCC nanoparticle modified cotton fabric demonstrated excellent durable antimicrobial activity and wrinkle-resistance, even after 50 repeated launderings. The shrinkage-resistance of NMA-HTCC nanoparticle modified cotton was distinctly improved, and the contact angle was slightly larger, while the breaking strength retention rate was 98.2% and the whiteness 98.5%.

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