Utilization of chitosan citrate as crease-resistant and antimicrobial finishing agent for cotton fabric

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Chitosan citrate has been evaluated as non-formaldehyde durable press finish to produce wrinkle-resistance and antimicrobial properties for cotton fabrics. The carboxylic groups in the chitosan citrate structure were used as active sites for its fixation onto cotton fabrics. The fixation of the chitosan citrate on the cotton fabric was done by the padding of chitosan citrate solution onto cotton fabrics followed by dry-cure process. The factors affecting the fixation processes were systematically studied. The antimicrobial activity and the performance properties of the treated fabrics, including tensile strength, wrinkle recovery, wash fastness and whiteness index, were evaluated. The finished fabric shows adequate wrinkle resistance, sufficient whiteness, high tensile strength and more reduction rate of bacteria as compared to untreated cotton fabric.

Keywords: Antibacterial finishing agent, Chitosan, Chitosan citrate, Cotton, Crease resistance

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1 Introduction

Chitosan, a polymer having \( \beta \)-1,4-linked glucosamine residues, is usually obtained through deacetylation of chitin with concentrated sodium hydroxide solution. Chitosan has several properties, such as biocompatibility, non-toxicity and ability to improve wound healing, and therefore, it is evaluated in a number of medical applications such as drug delivery systems\textsuperscript{1,6}, wound dressing\textsuperscript{7,8} and as a hypocholesterolemic agents\textsuperscript{1}.

The application of chitosan as antimicrobial finishing agent for textiles has been studied\textsuperscript{9-12}. However, the use of chitosan as a finishing agent is limited to the after treatment of fabrics owing to its weak binding.

Polycarboxylic acids have been used successfully in durable press finishing of cotton fabrics in order to realize a smooth drying appearance without ironing after laundering\textsuperscript{13}. One of the possible ways to introduce carboxylic groups on the cellulose substrate is to treat it with polycarboxylic acid, such as citric acid and butanetetracarbxylic acid (BTCA), by a cross-linking reaction as a wrinkle resistance treatment\textsuperscript{14}.

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The cross-linking reaction of polycarboxylic acids with the cellulose substrate produces carboxylic residues that do not esterify with cellulose\textsuperscript{15}. The esterification reaction between carboxylic acid and cellulose molecule occurs at elevated temperatures in the presence of catalysts. Strong mineral acids, such as sulphuric acid, are not feasible because of severe fabric damage. While such phosphorus containing catalysts are effective in cross-linking cotton through an esterification reaction, their commercial application as catalyst in textile processing is limited because of other environmental concerns\textsuperscript{16}. The disadvantage of catalysts led to search for the fixation of chitosan on cellulose fabrics without using any artificial chemical.

The aim of this work was to use water-soluble chitosan citrate as finishing agent for cotton fabrics. The fixation of chitosan citrate on cotton was done by the padding of cotton fabrics onto chitosan citrate solution followed by high temperature curing. The antimicrobial activity and performance properties, including tensile strength, wrinkle recovery, wash fastness and whiteness index, of the treated fabrics were also evaluated.

2 Materials and Methods

2.1 Materials

Chitosan having 72% degree of deacetylation was obtained from Aldrich Chemical Co. Ltd. Mill
scoured, bleached and mercerized cotton fabric (plain weave and 169 g/m²), supplied by Misr Spinning and Weaving Co., Mehalla El-Kubra, Egypt, was used after purification by scouring for 2 h at boil using aqueous solution of 1% sodium hydroxide. The fabric was then thoroughly washed and air dried at room temperature. All the other chemicals used were of reagent grade.

2.2 Methods

2.2.1 Fixation of Chitosan on Cotton Fabric

Fabrics (5 cm × 5 cm) were padded in an aqueous solution of dissolved chitosan citrate (1 – 5 %) to give a wet pick up of 90 %. The treated fabrics were dried at 90°C for 1 min. The same procedure was used for the treatment of cotton fabrics with chitosan dissolved in 1% acetic acid solution. Curing of both chitosan treated and chitosan citrate treated fabrics was done by the pad-dry-cure processing method. The padded fabrics were dried and cured for different durations and temperatures at their original dimensions in an oven served with mechanical circulated air. The cured fabrics were washed with hot water followed by cold water and then dried.

2.2.2 Wash Fastness

Fastness to washing of the fixed chitosan on the cotton fabric was evaluated by washing the treated fabrics with 1% aqueous acetic acid solution at boiling temperature for 1 h followed by washing with tap water and drying.

2.2.3 Antibacterial Test

This test was carried out using the Shake-Flask method in accordance with the method approved by the Association of Antibacterial Treatments of Textile, Japan, and was limited to the Staphylococcus aureus micro-organism. In short, the number of living micro-organisms were counted after stirring the micro-organism suspension in an Erlenmeyer flask [1(2×10⁸)/ cm³ of micro-organism]. The test solution was then shaken for 1 h with 320 rpm speed at 25°C after the addition of 1 g textile sample. The decrease in the number of living micro-organism was estimated from the number of living micro-organism present in the medium containing sample according to the following equation:

Reduction (%) = [(X₁ – X₂) / X₁] × 100

where X₁ is the number of living micro-organism before shaking; and X₂, the number of living micro-organism after shaking.

2.2.4 IR Study

Infrared spectra were recorded on a Nicole 5DX system FT-IR spectrophotometer. Cut sample (2mg) was mixed with 198 mg of potassium bromide and pellet was prepared. Scanning was carried out from 3750 cm⁻¹ to 650 cm⁻¹ at slow speed.

2.2.5 Thermal Stability

The thermal stability of membrane was investigated by using a Perkin-Elmer thermobalance with professional computer, TGA standard software and a printer plotter. A few milligrams of the different samples were automatically weighed with the thermobalance (TGA 7). The heating rate was taken as 10°C/min and the nitrogen flow rate was 50 ml/min.

2.2.6 Whiteness Testing

Whiteness testing was done on ICS type spectrophotometer (TEXICON Limited, England).

2.2.7 Tensile Strength

Tensile strength (warp + weft) was determined by the strip method according to ASTM procedure D2256-66T.

3 Results and Discussion

In the previous study, chitosan citrate was prepared by mixing chitosan powder with citric acid and its characterization was investigated. In this study, the carboxylic groups remaining on the chitosan citrate act as fixation sites for chitosan on the cotton fabrics. The reaction mechanism is shown in Scheme 1.

In the cross-linking reaction of citric acid with chitosan, chitosan citrate is produced with carboxylic residue which is not esterified with chitosan [Eq (1)]. The carboxylic groups remaining on the chitosan citrate act as fixation sites at high temperature for chitosan on the cellulose fabric [Eq. (2)].

Fig. 1 shows the effect of the curing temperature on the amount of chitosan (expressed by nitrogen per cent) fixed on the cotton fabric. The nitrogen per cent was calculated before and after washing of the fabric treated with 1% aqueous acetic acid solution for 1 h at 90°C. It is observed that the amount of chitosan increases with the increase in curing temperature. The curing of fabric at temperature higher than 180°C produces appreciable yellowing because this treatment temperature is similar to the temperature needed for the esterification reaction between citric
and cotton. The increased nitrogen per cent may be attributed to the increased reaction between chitosan citrate and cellulosic cotton fabric.

Fig. 2 shows the effect of curing time on the amount of chitosan fixed on the cotton fabrics. The samples were padded in 2% chitosan citrate solution with 90% pick up, dried at 90°C for 1 min and cured at 175°C for different duration. Fig. 2 shows that the curing time appears to have a significant influence on the amount of nitrogen per cent. The latter increases by increasing the curing time before and after washing with acetic acid solution at 90°C for 1 h. The samples treated with chitosan citrate solution at 175°C curing temperature for >90 s curing time show yellowing and, therefore, 90 s seems to be the suitable curing time.

Table 1 shows the performance of cotton fabric treated with 1-3% chitosan citrate solution. It is observed that the concentration of chitosan citrate and curing temperature are the two most influential factors in determining the wrinkle resistance and tensile strength of the treated fabrics. An increase in chitosan citrate concentration as well as curing temperature has the most significant effect on the improvement in wrinkle resistance of the finished fabric and loss in fabric tensile strength. The data also indicate that the curing temperature has the highest impact on the fabric whiteness. The whiteness of the washed treated fabrics is substantially lower than that of the untreated control. The fabric whiteness is found to be the highest for the samples treated with 1% chitosan citrate solution at 160°C for 90 s.

Fastness to washing of the fixed chitosan on the cotton fabrics was evaluated by washing the treated fabrics with 1% aqueous acetic acid solution at boiling temperature for 1 h. In Fig. 3, the amount of residual chitosan on the treated fabrics after each washing test is plotted against the washing cycles. Fixation of chitosan citrate on cotton fabrics using the pad–dry–cure process was carried out using different

![Scheme 1—Reaction mechanism](image)

![Fig. 1—Effect of curing temperature on fixation of chitosan citrate](image)

![Fig. 2—Effect of curing time on fixation of chitosan citrate](image)
techniques: (i) padding in chitosan dissolved in 1% acetic acid solution, (ii) pretreatment of cotton fabric by padding in 6% citric acid solution, drying at 90°C for 3 min and then padding in chitosan dissolved in 1% acetic acid solution, (iii) padding in chitosan citrate solution, and (iv) padding in chitosan dissolved in 3% citric acid solution. The above chitosan−padded fabrics were dried at 90°C for 3 min then cured at 175°C for 90 s. The cured fabrics were then washed with 1% boiling acetic acid solution for 1 h and dried to remove unfixated chitosan. Fig. 3 indicates that before washing test, the initial amount of chitosan on the fabric treated with chitosan only is higher than the amount on the fabrics treated with chitosan citrate. But it is found to be inverse after washing test. This finding indicates that the free carboxylic acids in the chitosan citrate may act on effective fixation site for chitosan on cotton fabrics. Fig. 3 also shows that the amount of chitosan fixed on the fabric crosslinked with citric acid, chitosan padded and cured is approximately twice as much as that for the fabric treated with chitosan only, even if the treated fabric is washed in acetic acid for 5 cycles.

As described above, it can concluded that cross-linking reaction with chitosan and carboxylic acid, cotton padding, and final curing would be necessary to obtain fixation of chitosan on the cotton fabric. Here, it can be said that the fixation of chitosan on the cotton fabrics may be achieved in one step process, i.e. padding of the mixture of citric acid and chitosan followed by curing for the cross-linking reaction. It is evident from Fig. 3 that the amount of chitosan fixed on the cotton fabric treated in one step is approximately equivalent to the amount fixed using chitosan citrate.

FT-IR and TGA measurements were carried out to confirm the cross-linking reaction of chitosan citrate onto cellulose cotton fabric. Fig. 4 shows the FT-IR spectra of untreated cotton fabric (curve a) and chitosan citrate treated cotton fabric (curve b). IR spectra shows absorption of ester band (curve b) at 1745 cm−1 which can be attributed to the formation of carbonyl bond resulting in the reaction between hydroxyl and amino groups. On the other hand, the spectrum of untreated cotton fabric does not show this band. Several research workers have reached the similar conclusion through IR spectroscopic analysis that the polycarboxylic acids esterify cotton cellulose during a curing process. The thermogravimetric analyses (TGA) of the cotton fabric, chitosan citrate...
Chitosan citrate and cotton fabric treated with chitosan citrate, cured at 175°C for 90 s and washed with acetic acid solution at 90°C for 1 h were carried out. The results (not shown here) show that the thermal degradation of citric acid takes place at 252°C and that the thermogram curve of the chitosan citrate reveals two thermal degradation steps at 250°C and 325°C, where the thermogram curve of the chitosan citrate treated fabric reveals three thermal degradation steps at 114, 328 and 488°C.

It is well known that chitosan inhibits the growth of many bacteria including gram-negative and gram-positive. Recently, chitosan oligomer has received much attention because of higher antimicrobial activity and water solubility compared to chitosan of higher molecular weight.

Fig. 5 shows the effect of chitosan and chitosan citrate concentration on the antimicrobial activity of treated fabrics (expressed by reduction rate per cent of bacteria). It evident that the chitosan citrate is the most effective, exhibiting 98% of reduction rate at 1.5% chitosan concentration. Fig. 6 shows the durability of the antimicrobial activity during repeated laundering. After ten laundering cycle, the reduction rate of bacteria reaches 75% for the fabric treated with chitosan citrate. The reduction rate of the fabric treated with chitosan only is 58%. These results clearly show that the chitosan citrate can be used as antimicrobial finishing agent for cotton fabrics.

4 Conclusions

The chitosan citrate shows satisfactory results with regard to crease resistance and antimicrobial finishing for cotton fabrics. The results show that the concentration of chitosan citrate and curing temperature are the two most influential factors in determining the wrinkle resistance and tensile strength of the treated fabrics. The finished fabric shows adequate wrinkle resistance, sufficient whiteness, high tensile strength and more reduction rate of bacteria as compared to the untreated cotton fabric. The fabric treated with chitosan citrate shows high antimicrobial property with good repeated launderings as compared to that of the fabric treated with chitosan only.

References