Citric Acid Used as a Crosslinking Agent for the Grafting of Chitosan onto Woolen Fabric

S. M. Gawish, S. M. Abo El-Ola, A. M. Ramadan, A. A. Abou El-Kheir

National Research Centre, Textile Research Division, Tahrir Street, Dokki, Cairo, Egypt

Received 1 February 2010; accepted 27 September 2010
DOI 10.1002/app.33873
Published online 15 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Modification of woolen fabrics was done by the grafting of low-molecular-weight deacetylated chitosan in the presence of citric acid as a crosslinking agent with the pad–dry cure method at different conditions (times and temperatures). The add-on of chitosan and the optimum conditions were determined. The improved properties of modified wool by chitosan were evaluated with the urea bisulfite solubility test, crease recovery angle, yellowness index, and scanning electron microscopy. The dyeing properties of modified wool fabrics were studied with acid and reactive dyes. The biocidal activities of the modified and unmodified wool samples were evaluated and compared against some species of microorganisms, including *Escherichia coli* (Gram negative), *Staphylococcus aureus* (Gram positive), *Candida albicans*, and *Aspergillus flavus*. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3345–3353, 2012

Key words: biofibers; crosslinking; curing of polymers; esterification; mechanical properties

INTRODUCTION

Textile fabrics, especially those made from natural fibers; provide an excellent environment for microorganisms to grow because of their large surface area and their ability to retain moisture. A number of chemicals have been used to impart antimicrobial activity to textile materials.

Chitosan has received great attention by researchers in the textiles field and specifically in wool chemistry, as it is a natural and ecofriendly environmental product, which replaces the synthetic cationic polyelectrolytes, which are used in the conventional Hercosett process for the partial removal of wool scales.

Chitosan possess excellent properties, such as nontoxicity, biodegradability, and antimicrobial activity, which attract industrial scientists in different fields to a great extent. Chitosan, known as poly(1,4)-2-amino-2-deoxy-β-D-glucose (Scheme 1), is a derivative of chitin and is obtained by the deacetylation of chitin by alkaline treatment. The presence of amino groups in C_2 of chitosan confers to its polycationic nature. The concentration, molecular weight,[1,2] and degree of deacetylation (DD)[3,4] of chitosan are the main factors that affect the antibacterial behavior of chitosan and the solubility in acidic solution and afford antimicrobial activity against a variety of bacteria and fungi.

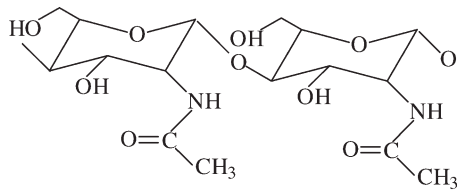
Correspondence to: S. M. Gawish (samihagawish@yahoo.com).

Journal of Applied Polymer Science, Vol. 123, 3345–3353 (2012)

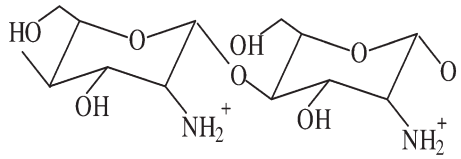
A literature review revealed that a great number of studies have used chitosan for the improvement of the wool finishing.[5–11] Poly(carboxylic acid)s, such as citric acid (CA) and 1,2,3,4-tetrabutane carboxylic acid, have been used as crosslinking agents and have at least two carboxyl groups that can react with active groups located in chitosan, such as amino (—NH_2) or hydroxyl (—OH) groups.[12] Also, diamines, polyamines, diols, polyols, and polyoxides are suitable crosslinking agents. Chitosan has been extensively investigated as a wool finishing agent. Studies have been done on its effectiveness for shrink resistance,[1] improvement of dyeing, and color fastness.[1]

Glutaraldehyde (2. 5 mL/L) was applied as a crosslinking agent for chitosan and wool, which was dipped overnight in the solution.[12]

Filipowaska et al.[13] adopted a new environmentally friendly method, which was developed to increase the felting resistance of wool. It is based on an enzymatic treatment that replaced the conventional chlorination pretreatment method. Wool washing was done followed by a protease enzyme treatment with 2% Perizim Lan at pH 8.5. The final wool treatment to shrink-proof the wool was effected with a solution of chitosan in acetic acid (AA) and glutaraldehyde as a crosslinking agent with the pad–dry–cure method. Drying was affected at 90°C for 40 s, and thermofixation was at 130°C for 20 s. The deposition of chitosan on wool fiber attained 2–2.5%. There was an improvement in the filtration properties with nonionic detergent at 40–60°C. Shrink-proofing properties were evaluated several times after dyeing with reactive dye; in



Chitin



Chitosan

Scheme 1 Chemical structure of chitin and chitosan.

addition, the tensile strength and elongation properties were determined.

The antibacterial and antifungal activities of wool have been described with chitosan and quaternary ammonium chitosan derivatives.[14] Chitosan is antimicrobial agent against a wide range of target organisms. The activity varies considerably with the type of chitosan, the target organism, and the environment in which it is applied. Generally, yeasts and modules are the most sensitive group, followed by Gram-positive bacteria, and then Gram-negative bacteria. There are several factors, both intrinsic and extrinsic, that affect the antimicrobial activity of chitosan. It has been demonstrated that low-molecular-weight chitosans have greater antimicrobial activity than native chitosan.[14] However, a degree of polymerization of at least seven is required; lower molecular weight fractions have little or no activity.[15,16] Highly deacetylated chitosans are more antibacterial than those with a higher proportion of acetylated amino groups because of increased solubility and higher charge density.[4]

Hsieh et al.[17] investigated the antimicrobial and physical properties of woolen fabrics cured with CA and chitosan. They cited that CA did not crosslink with the woolen fibers if they were not preoxidized by potassium permanganate and that, after oxidation, CA produced esterification with the hydroxyl groups of wool and chitosan and transamidation with the amino group of wool to form a crosslink. The authors concluded that the mechanical properties of wool were deteriorated after oxidation.

In this study, we were interested in increasing the weak binding character of chitosan to wool by covalently bonding it to wool through esterification and amide formation by poly(carboxylic acid) as a crosslinking agent and using the pad–cure method, which usually occurs near 160°C.[18,19,20] The optimum conditions (time, temperature, and concentration) for the thermofixation of chitosan were studied.

The add-on of chitosan onto wool in the presence of CA as a crosslinking agent was determined and compared to its absence. The modified wool fabric properties were examined with the urea bisulfite test, dry crease recovery angle (DCRA), yellowness index (YI), tensile strength, scanning electron microscopy (SEM), and dyeing properties with acid and reactive dyes. The modified chitosan wool fabric was resistant to bacteria compared to the control sample.

EXPERIMENTAL

Materials

Twill wool (100%) fabric weighing 276 g/m^2 was supplied by Misr Co. for Spinning and Weaving (Mehalla El-Kobra, Egypt).

Chemicals

The following chemicals were used. Extrapure anhydrous CA was supplied by Loba Chemie (Mumbai, India). Low-molecular-weight chitosan (150,000), with deacetylation at 85%, was supplied from Mallinckrodt., Inc. Nonyl phenol ethoxylate, a nonionic wetting agent, was supplied by ICI (England).

Dyestuff

The following dyes were used: C. I. Acid Red 1 from Ciba Co. Cairo (Egypt) and Reactive Red 24 from Isma Dye Co., Alex (Egypt).

Method

Low-molecular-weight, deacylated chitosans (different concentrations) were dissolved in CA of chosen concentrations or in 3% glacial AA and stirred with a magnetic stirrer until complete dissolution of chitosan to a clear solution.

The following treatment composition solutions were used: CA, 30–100 g/L; low-molecular-weight deacylated chitosan, 0.25–3 g/L; and nonyl phenol ethoxylate nonionic wetting agent, 2 g/L.

Wool fabric was dried at 105°C for 1 h in a desiccator over phosphorus pentoxide (P_2O_5) and then weighed (w_1 gm). The sample was then impregnated in the previous treatment solution and was padded to 100% wet pick-up. The treated wool fabrics were then fixed from their edges on a pin frame, dried at 90°C for 5 min, and cured successfully at 120–170°C for 1, 2, 3, and 5 min, respectively.

The cured wool sample was washed with warm water several times, oven-dried at 105°C for 1 h, and weighed (w_2; g). The percentage add-on onto wool was calculated as follows:

$$\%\text{Add} - \text{on} = [(w_2 - w_1)/w_1] \times 100$$

where w_1 and w_2 are the weights of the sample before and after treatment, respectively.

Analyses

YI

YI of wool fabrics was measured with a Hunter Laboratory 1229USP (N-J USA).

YI of wool fabrics was measured with an Ultra Scan PRO, Standards Box, S/n: USP 1229 (Hunter Laboratory). YI was determined with ASTM E 313:

$$\text{YI (E 313)} = 100[1 - (0.847Z/Y)] \quad (1)$$

where Y and Z are the first numerical scale offered to quantify color.

Washing test

Washing of the wool fabric was done [according to ISO 105-CO_2 (1989)] with 2 g/L nonionic surfactant of nonyl phenol exothylate at 50°C at a liquor ratio of 1 : 50 and shaken in the rotating cup of a launderometer for 45 min. The fabric was removed, rinsed well with warm water, and air-dried.

Urea bisulfite solubility test

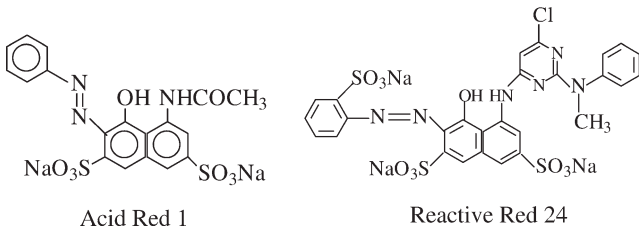
Accurately weighed wool samples[20] were immersed in a freshly prepared 50% urea solution containing 3% sodium bisulfite (adjusted at pH 7) in a stoppered conical flask. The mixture was maintained at 65 ± 5°C in a thermostated water bath for 1 h with occasional shaking. The contents of the bottles were then poured quickly into a coarse sintered glass filter (G1), and the liquid was removed by suction. The residue was washed and filtered three times with a 50% urea solution and six times with warm distilled water. It was then transferred quantitatively to a weighing flask and dried to a constant weight at 105°C. The weight loss was calculated on the basis of the dry wool weight.

DCRA measurement

DCRA for the modified wool was measured with an iron recovery apparatus (type FF-07Metrimpex, Hungary) for a 10-mm sample. Creasing angle was expressed as the sum of the crease recovery angle (CRA) in the warp and weft directions.

SEM

SEM for the untreated and treated wool fabrics was investigated with JEOL (JXA-840A, Tokyo, Japan) electron probe microanalysis. The dried samples were mounted on an aluminum device and sputter-coated with gold for SEM examination. A cathode sputter-coated with gold (S360 LEICA SEM apparatus) was used in this investigation with an accelerating voltage of 15 kV, a beam current of 300–500 pA, a pressure in the sample chamber < 10–5 mbar, image mode of a secondary electron image, and a magnification of 2000×.



Scheme 2 Chemical structure of Acid Red 1 and Reactive Red 24.

Mechanical properties

Tensile strength and elongation tests. The percentage tensile strength and elongation of the untreated and treated wool fabrics were measured with an Instron tensile apparatus (VEB Thuringer Industrie Werk Rauenstein). Textile tensile testing was performed according to ASTM D 3822.

Wool dyeing

Dyes. Bifunctional acid dyes (Acid Red 1 and Reactive Red 24) were used to dye the modified and control wool fabrics. The dye structural formulas are shown in Scheme 2.

Dyeing procedure. The dyeing bath was adjusted to 2% dye shade at 40°C (pH 4–5) for both acid and reactive dyes. Wool fabric was immersed in the dye solution. The temperature was raised gradually to 90°C over 30 min, and the dyeing process was continued at this constant temperature for 1 h.[21] The dyed fabric was washed with a nonionic surfactant at 50°C for 30 min, rinsed with warm water, and air-dried. The color strength (K/S, where K is the absorption coefficient and S is the scattering coefficient) was determined with a recording spectrophotometer (Hunter Laboratory, Ultra Scan Pro) according to the Kubelka–Munk equation:

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

where R is the decimal fraction of the reflectance of the dyed substrate and R_o is the decimal fraction of the reflectance of the undyed substrate.

Antimicrobial activity

Antimicrobial activity was done by the diffusion disc method.[22–25] A fabric sample was placed in a

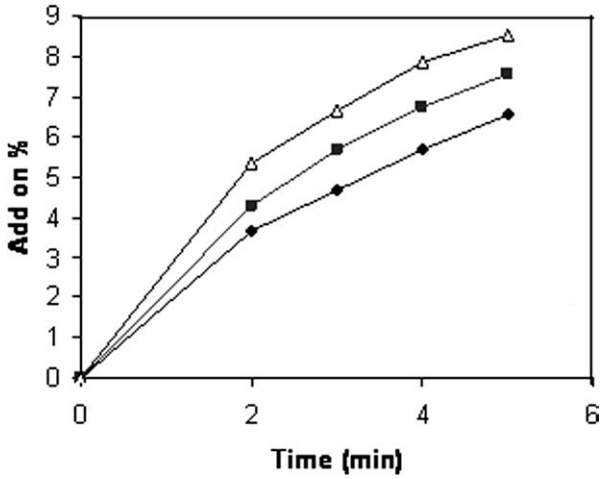


Figure 1 Effect of the curing time on the percentage add-on onto wool fabrics treated with 10% CA at different temperatures: (◆) 160, (■) 165, and (△) 170°C.

Petri dish containing solid bacterial medium (nutrient agar broth) or fungal medium (Doxs medium), which had been heavily seeded with the spore suspension of the tested organism. After inoculation, the sample was incubated at 37°C for 24–48 h. The diameter of the clear zone of inhibition surrounding the sample was taken as a measure of the fabric activity against the particular test organism.

RESULTS AND DISCUSSION

Treatment of wool fabric with chitosan

Effect of CA on the treated wool on add-on

The effect of 10% CA on wool modification with increasing add-ons of 6.5, 7.54, and 8.5% at 160, 165, and 170°C, respectively, for 5 min of curing time is shown in Figure 1.

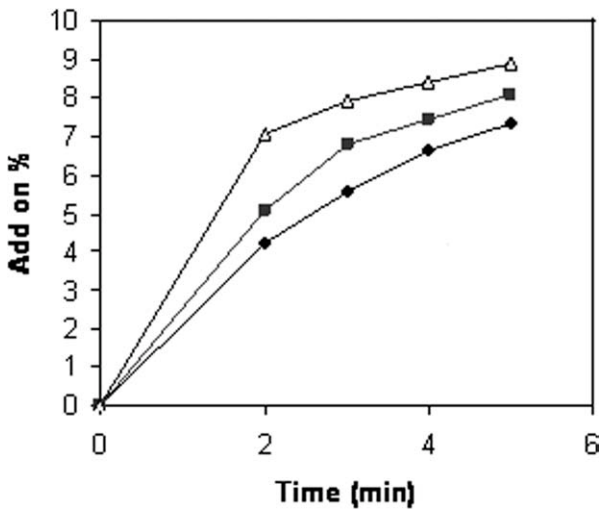


Figure 2 Effect of the curing time on the percentage add-on onto wool fabrics treated with 10% CA/6% SHP at different temperatures (◆) 160, (■) 165, and (△) 170°C.

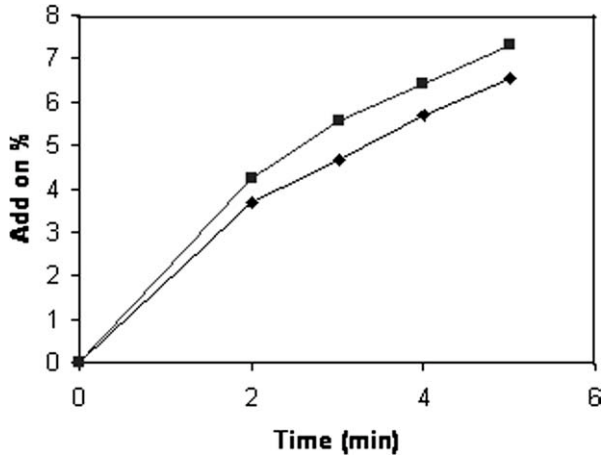


Figure 3 Effect of the curing time on the percentage add-on onto wool fabrics treated with (■) 10% CA/6% SHP and (◆) 10% CA.

Figure 2 demonstrates that the wool modified with a mixture of 10% CA and 6% SHP (sodium hypophosphite) gave percentage add-ons of 7.32, 8.09, and 8.89% at the listed temperatures and times.

The percentage adds-on slightly increased when SHP was added to the treatment bath (Figs. 3–5). These results may be attributed to the capability of SHP to accelerate the formation of a cyclic anhydride intermediate and the esterification between CA and wool.[10] From the previous data, we found that the highest add-on was detected when the curing temperature and time were 170°C and 5 min, respectively, in the presence of SHP. However, YI increased to 29.24 compared to the control (19), although at 165°C, YI decreased to an acceptable value of 24.32.

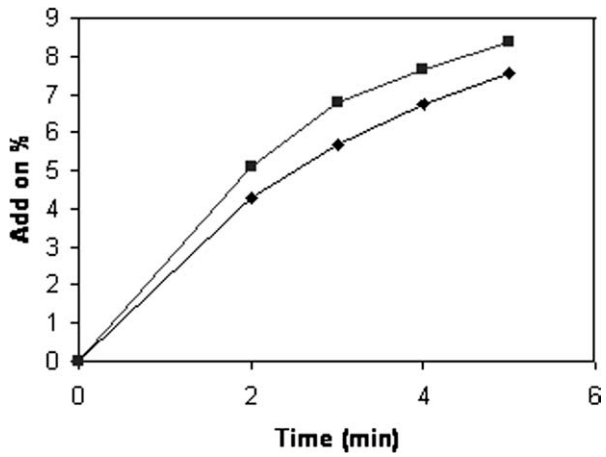


Figure 4 Effect of the curing time on the percentage add-on onto wool fabrics treated with (■) 10% CA/6% SHP and (◆) 10% CA only at 165°C.

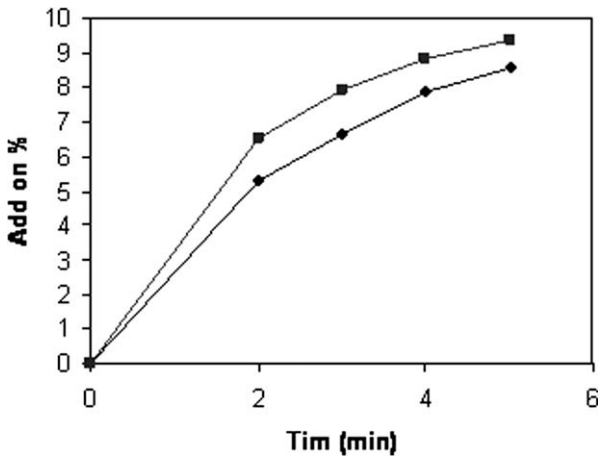


Figure 5 Effect of the curing time on the percentage add-on onto wool fabrics treated with (■) 10% CA/6% SHP and (◆) 10% CA only at 170°C.

It was reported that the dry-heat yellowing of wool was attributed to a dehydration reaction of serine side chain, which led to the formation of unsaturated carbon bonds (Scheme 3).

The significance of the yellowness of wool is one of the disadvantages of wool.

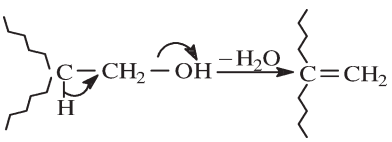
Most treatments have been done to overcome this problem, but in this study, the degree of yellowness was not high enough to badly affect the dyeing process.

So, the best conditions to perform this treatment were chosen as follows: 10% CA, curing temperature of 165°C, and curing time of 5 min.

Effect of CA/chitosan on the percentage add-on of wool

The effect of curing time on the percentage add-on at different temperatures (120–170°C) with a treated solution of 6% CA/1% chitosan is shown later in Figure 7.

Table I demonstrates that YI increased at elevated temperature (170°C) but, at 165°C, had an acceptable value of 23.91 compared to 25.55 at 170°C. From the previous data, we concluded that the best curing time and temperature for this treatment was 5 min and 165°C, respectively. In addition when CA was heated above its melting point of 135°C, unsaturated dicarboxylic and tricarboxylic acids, such as itaconic, citraconic, and aconitic acids, were produced because of dehydration or decarboxylation. This



Scheme 3 Dehydration reaction of wool.

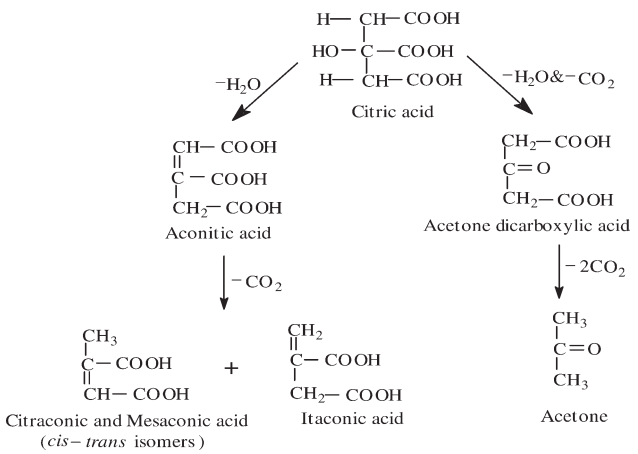
TABLE I
Effect of the Treatment Conditions (Curing Temperature and Time) on the Add-On and YI of the Wool Samples in the Presence of 6% CA/1% Chitosan

Curing temperature (°C)	Time (min)	Add-on (%)	YI
Control	Nil	Nil	19.29
120	1	3.77	20.54
	2	4.08	20.77
	3	4.38	20.99
	5	4.85	21.04
140	1	5.086	21.33
	2	5.33	21.63
	3	6.063	21.80
	5	6.33	21.99
160	1	5.66	22.25
	2	6.56	22.67
	3	6.98	23.02
	5	7.29	23.21
165	1	5.89	23.39
	2	6.79	23.48
	3	7.07	23.75
	5	7.76	23.91
170	1	7.00	27.74
	2	7.55	24.99
	3	8.29	25.01
	5	9.33	25.55

phenomenon gave rise to a yellowing effect. (Scheme 4).

Table II shows that as the chitosan concentration decreased to 0.25%, the add-on was 6.72%, and at 0.5% chitosan, the add-on was at the highest amount, 7.99%; this may have been due to the high viscosity of large concentrations of chitosan (1–3%), which prevented the diffusion of the solution into the wool fibers. That is, the best concentrations used in this treatment were 0.25 and 0.5%

Increasing CA concentration led to an increase in the percentage add-on of wool fabric. The add-on varied from 5.16 to 12.177% as the CA concentration



Scheme 4 Dehydration and decarboxylation reaction of CA.

TABLE II
Effect of the Chitosan Concentrations onto Wool Add-On and YI at 6% CA and 165°C

Chitosan concentration (%)	Add-on (%)	YI
0.25	6.72	23.82
0.5	7.99	23.85
1	7.76	23.91
2	7.54	23.93
3	7.07	23.92

increased from 4 to 10% for 0.25 and 0.5% chitosan, respectively (Fig. 6).

The effect of curing time on the percentage add-on at different temperatures (120–170°C) with a treated solution of 6% CA/1% chitosan is shown in Figure 7. As the curing temperature and time increased, the percentage add-on increased; for 5 min of curing time, the add-on varied from 4.85 to 9.33 at 120–170°C.

The data shown in Table I and Figures 6 and 7 reveal that the best optimum conditions of wool treatment were as follows: 10% CA/0.25% or 0.5% chitosan, no catalyst, and a curing temperature of 165°C for 5 min.

Urea bisulfite solubility test

The urea bisulfite solubility test has been considered to be one of the most common tests for the formation of new permanent crosslinks between wool chains. Urea breaks the hydrogen bonds, whereas the bisulfite breaks the disulfide bonds, which are essential for the stability of wool material.

Table III shows that the percentage weight loss of wool fabric treated with 0.25 and 0.5% chitosan in 2% AA were 50.64 and 50.23%, respectively, which was near to the value of control sample (57.56%). These results may refer to the low percentage chitosan add-on onto the wool fabrics; hence, small amounts of crosslinking between the chitosan and polypeptide chains of wool were formed.

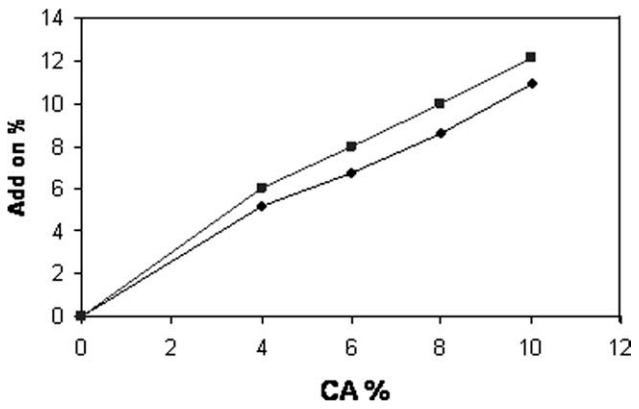


Figure 6 Effect of 10% CA on the percentage add-on onto woolen fabric with (◆) 0.25% and (■) 0.5% chitosan at 165°C.

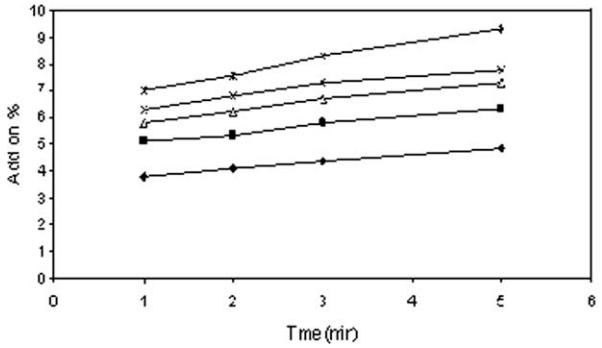


Figure 7 Effect of different curing conditions (time and temperature) on the add-on of wool samples treated with 6% CA/1% chitosan at (◆) 120, (■) 140, (△) 160, (×) 165, and (*) 170°C.

On the other hand, the percentage weight loss of the urea bisulfite solubility test for the modified wool fabric treated with 10% CA only was 12.25% compared to 57.56% for the control sample. This result could be attributed to the formation of a new amide linkage between amino groups of the wool chains and carboxylic groups of CA.

The urea bisulfite solubility test also clarified that the percentages weight loss of the wool fabric modified with a mixture of CA/chitosan was 32.45 and 29.58% for chitosan concentrations of 0.25 and 0.5%, respectively, compared to that treated with 10% CA only (12.25%). These results could have been attributed to the presence of chitosan with CA, which enhanced the reaction between the carboxylic groups of CA and wool and hydroxyl and the amino groups of chitosan; accordingly, new terminal esters and amides linkages were formed.

CRA

DCRA measurement

The treatment of wool fabric with a mixture of CA and chitosan improved CRA from 295° for the control sample to different values, depending on the concentrations of CA and chitosan (Table IV).

TABLE III
Effect of the Treatment Conditions of the Urea Bisulfiite Solubility Test on the Modified and Control Wool Fabric Cured at 165°C for 5 min

Treatment conditions	Add-on (%)	Weight loss (%)
Control	Nil	57.56
2% AA/0.25% chitosan	0.5	50.64
2% AA/0.5% chitosan	0.7	50.23
10% CA	7.541	12.25
10% CA/0.25% chitosan	10.9	32.45
10% CA/0.5% chitosan	12.18	29.854

TABLE IV
Effect of the 10% CA/Chitosan Concentrations on the DCRA and YI of Modified Wool Fabrics Cured at 165°C for 5 min

Treatment condition	Add-on (%)	Weight loss (%)
Control	Nil	57.56
2% AA/0.25% chitosan	0.5	50.64
2% AA/0.5% chitosan	0.7	50.23
10% CA	7.541	12.25
10% CA/0.25% chitosan	10.9	32.45
10% CA/0.5% chitosan	12.18	29.854

The treatment of wool fabrics with 0.25 and 0.5% chitosan dissolved in 2% AA had a low effect on the DCRA because of the low percentage add-on onto wool fabrics. However, the dissolution of the same chitosan concentration in 10% CA increased DCRA to 322 and 326°, respectively, and this proved that CA acted as a crosslinking agent between chitosan and the wool fabric (Table IV).

Tensile strength and elongation

The effect of wool fabrics treated with CA and mixture of CA/chitosan on the tensile strength and elongation is shown in Table V.

The modification of wool by CA alone, chitosan, or a CA/chitosan mixture created new esters and amides linkages into wool and increased the tensile strength of wool in the following order: CA (10%) > CA/chitosan (10%/0.5%) > CA/chitosan (10%/0.25%) > chitosan (0.5%) > chitosan (0.25%).

The addition of CA only greatly increased the tensile strength of wool to 17.64% compared to that of chitosan alone; the latter showed a slight increase in the tensile strength to 1.13–1.83%. The mixture of CA and chitosan increased the percentage tensile strength to 12.02–16.98%, which was lower than that of CA alone. The tensile strength of fabric treated with chitosan in AA was the same of that of the control, and this may have been due to the low percentage add-on onto the wool fabric.

Wool dyeing

Table VI shows that the modification of wool fabrics with CA only, chitosan, or a mixture of CA and chitosan highly increased the exhaustion and *K/S* of both the reactive and acid dyes compared to the control (Table VI). However, at the same time, it was found that the treatment of wool fabric with chitosan/10% CA had dye exhaustion and *K/S* values higher than that of chitosan/2% AA (Table VI). This may have been due to the high percentage add-on (10.9–12.18%) for the chitosan dissolved in 10% AA on the fabric, which was higher than that of the former (0.5–0.7%), and thus increasing the content of the amino groups from chitosan onto the fabrics modified in the presence of CA which acts as crosslinking agent.

These results may have been due to the strong chemical bonds formed between the anions in both dyes, which were the sulfonic and chlorine groups for the reactive dye, sulfonic groups for the acid dye, and protonated amino groups in the fabrics in addition to the hydrogen bonds formed between the —NH of the dye and carboxylic groups of wool.

TABLE V
Effect of the Wool Fabric Treatment Conditions on the Tensile Strength and Elongation Cured at 165°C for 5 min

Treatment conditions (%)	Add-on (%)	Tensile strength (10^3 gm)	Tensile strength increase (%)	Elongation (%)
Control	Nil	43.014	—	34.04
2% AA/0.25% chitosan	0.5	43.501	1.13	32.01
2% AA/0.5% chitosan	0.7	43.8	1.83	30.819
10% CA	7.541	50.6	17.64	33.5
10% CA/0.25% chitosan	10.9	48.18	12.01	22.694
10% CA/0.5% chitosan	12.18	50.318	16.98	20.847

Antimicrobial activity

Table VII shows that 10% CA had an antibacterial resistance of 14.16 mm against *Escherichia coli* and *Staphylococcus aureus*. It was found that the presence of chitosan in the treatment bath containing 10% CA increased the microbial resistance to a high extent, that is, 31 mm for *E. coli*, 34 mm for *S. aureus*, 16 mm for *Candida albicans*, and 17 mm for *Aspergillus*

TABLE VI
Effect of the Wool Treatment Conditions on the Percentage Exhaustion and *K/S* of the Modified and Control Washed Wool Fabric with Acid and Reactive Dyes (Cured at 165°C for 5 min)

		Exhaustion (%)		*K/S*	
Treatment conditions	Add-on (%)	Acid Red 1	Reactive Red 24	Acid Red 1	Reactive Red 24
Control	nil	0.5	6.63	6.17	12.58
2% AA/0.25% chitosan	0.5	78.41	83.03	22.34	14.11
2% AA/0.5% chitosan	0.7	80.22	85.91	24.49	15.37
10% CA	7.541	93.1	87.37	28.15	19.48
10% CA/0.25% chitosan	10.9	84.5	90.15	26.33	23.36
10% CA/0.5% chitosan	12.18	86.3	97.9	27.06	26.34

TABLE VII
Resistance of the Wool Fabric Treated with (a) 10% CA/0.5% Chitosan, (b) 2% AA/0.5% Chitosan to Microorganisms, and (A) 10% CA

Sample	Inhibition zone diameter (mm/mg of sample)			
	Escherichia coli (Gram negative)	*Staphylococcus aureus* (Gram positive)	*Candida albicans* (fungus)	*Aspergillus flavus* (fungus)
Control	0.0	0.0	0.0	0.0
10% CA (A)	14	16	0.0	0.0
10% CA/0.5% chitosan (a)	31	34	16	17
2% AA/0.5% chitosan (b)	0.0	0.0	0.0	0.0

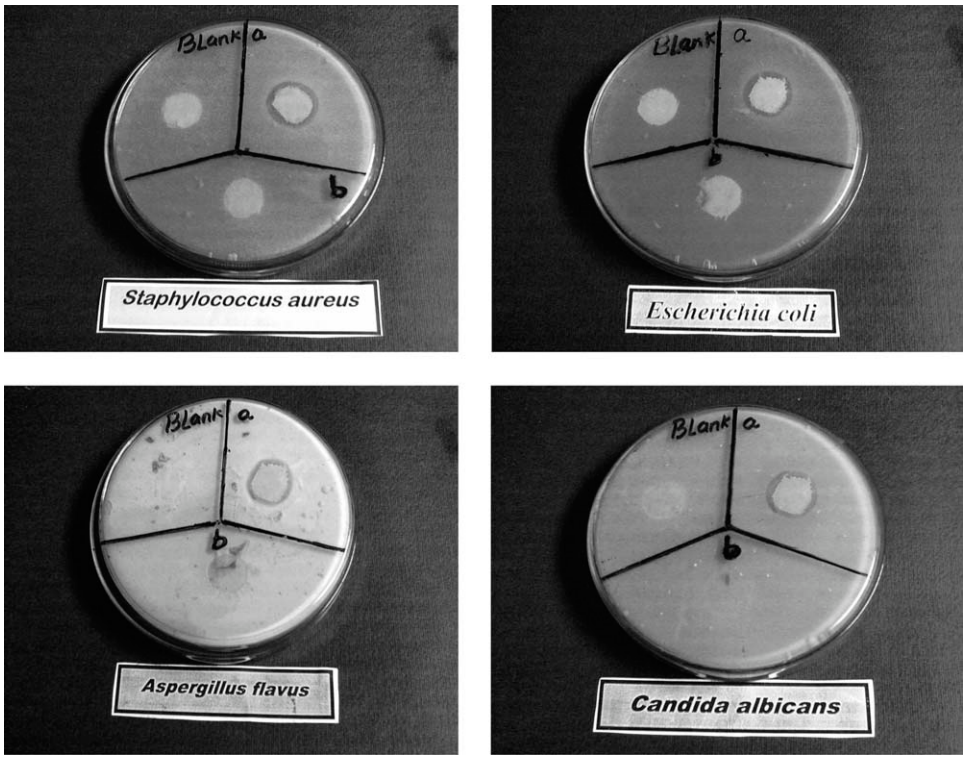


Figure 8 Antimicrobial activity of the wool fabrics treated with chitosan: (Blank) sample treated with 10% CA, (a) sample treated with 10% CA/0.5% chitosan, and (b) sample treated with 2% AA/0.5% chitosan.

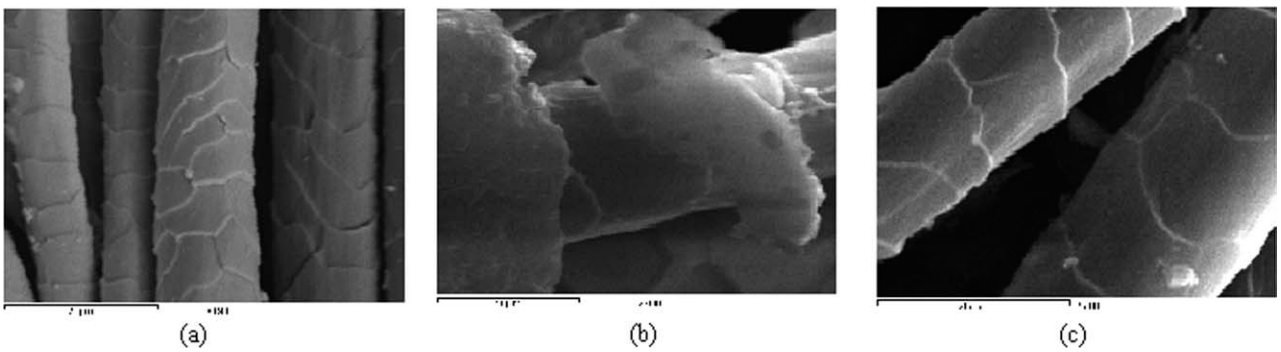


Figure 9 SEM of Wool Fabric (a) untreated control sample, (b) wool fabric modified with a mixture of 10% CA/0.5% chitosan, and (c) wool fabric modified with a mixture of 2% AA/0.5% chitosan.

flavus, whereas the treatment of wool fabric with 2% AA/0.5% chitosan had no effect on the microorganisms at all. This result could be attributed to the slight add-on of chitosan onto wool fabric treated with 2% AA compared to that treated with 10% CA/0.5% chitosan.

Morphology of the wool fabric

The surface of wool fabric was observed with SEM [Fig. 9(a–c)].The control wool sample (a), clearly showed the overlapping wool scales. The modified wool sample (a) with a mixture of 10% CA/0.5 chitosan confirmed the grafting of wool by chitosan because enormous grafts were formed on the wool surface, although the wool sample modified with 2%AA/0.5% chitosan (c) revealed that small amounts of grafts were seen on the wool surface.

CONCLUSIONS

This study revealed that the modification of wool fabric with chitosan and CA/chitosan greatly improved the wool properties. Thus, strong covalent bonds were created on wool fabric because of the grafting of CA/chitosan. The improvement of wool properties included increases in DCRA, percentage dye exhaustion, *K/S* of dyes using acid and reactive dyes, tensile strength, and biocidal activity of wool to some species of bacteria, such as *E. coli* and *S. aureus*, and fungal activity, that is, *C. albicans* and *A. flavus*. The grafting of wool fabric was confirmed by the urea bisulfite solubility test and SEM; this confirmed the ecofriendly application of chitosan to human wool and to the environment.

References

1. Juliá, M. R.; Pascual, E. Agro-Food-Industry Hi-Tech 2000, (November/December), 11, 34.
2. Juliá, M. R.; Pascual, E.; Erra, P. J Soc Dyer Colorist 2000, 116, 62.
3. Zhang, Z.; Chen, L.; Ji, J.; Huang, Y.; Chen, D. Text Res J 2003, 73, 1103.
4. Sekiguchi, S. In Food Hydrocolloids: Structures, Properties and Functions; Nishinari, K., Doi, E., Eds.; Plenum: New York, 1994; p 71.
5. Pascual, E.; Juliá, M. R. J Biotechnol 2001, 89, 289.
6. Vichez, S.; Manich, A. M.; Jovancic, P.; Erra, P. Carbohydr Polym 2008, 71, 515.
7. Giri Dev, V. R.; Venugopal, J.; Sudha, S.; Deepika, G.; Ramakrishna, S. Carbohydr Polym 2009, 75, 646.
8. Jeong, Y. J.; Cha, S. Y.; Yu, W. R.; Park, W. H. Text Res J 2002, 72, 71.
9. Tonin, C.; Roncolato, G.; Innocenti, R.; Ferrero, F. J Nat Fibers 2007, 4, 77.
10. Jocica, D.; Výlchez, S.; Topalovic, T.; Navarro, A.; Jovancic, P.; Rosa Juliá, M.; Erra, P. Carbohydr Polym 2005, 60, 51.
11. Roberts, G. A. F.; Wood, F. A. J Biotechnol 2001, 89, 297.
12. Dutkiewiez, J. U.S. Pat. 6,197,322 B1 (2001).
13. Filipowaska, B.; Walawska, A.; Rybicki, E. Ind Text 2000, 1317, 21.
14. Liu, X. F.; Guan, Y. L.; Yang, D. Z.; Li, Z.; Yao, K. D. J Appl Polym Sci 2001, 79, 1324.
15. Sc-Kwon Kim. Chitin, Chitosan, Oligosaccharides & their dervatives. Elsevier Publisher: London, 1989, p 373.
16. Ralston, G. B. Biochem Biophys Acta 1964, 93, 652.
17. Hsieh, S. H.; Huang, Z. K.; Huang, Z. Z.; Tsen, Z. S. J Appl Polym Sci 2004, 94, 1999.
18. Vikhoreva, G. A.; Shablyukova, E. A.; Kil'deeva, N. R. Fiber Chem 2001, 33, 206.
19. Yang, C. Q.; Wang, X. Text Res J 1996, 66, 595.
20. Gawish, S. M.; Ramadan, A. M.; Abo El-Ola, S. M.; Abou El-Kheir, A. A. Polym Plast Technol Eng 2009, 48, 701.
21. Muanza, D. N.; Kim, B. W.; Euler, K. L.; Williams, L. Int J Pharmacog 1994, 32, 337.
22. Int Wool Text Org Test Method 1996, 11–65 (E).
23. Grayer, R. J.; Harbone, J. B. Photochemistry 1994, 37, 19.
24. Irob, O. N.; Moo-Toung, M.; Anderson, W. A. Int J Pharmacopia 1996, 34, 87.
25. Jawetz, E.; Melnick, J. L.; Adelberg, E. A. Lange Medical: Los Altos, CA, 1974.
26. Chaudhary, A. N.; Smith, B. AATCC Rev 2003, 3(1), 27.
27. Simpson, W. S.; Grawshaw, G. H. ''Wool Science and Technology,'' Wood head Publisher, Chapter 5; p 132, 2002.