Antimicrobial and Physical Properties of Woolen Fabrics Cured with Citric Acid and Chitosan

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ABSTRACT: In this study, we used citric acid (CA) as a crosslinking agent, mixed with biopolymer molecular chitosan, to perform a pad–dry–cure treatment on woolen fabrics to study its antimicrobial effects and physical properties with the help of IR spectroscopy, electron microscopy, and differential thermal analysis. From the experimental results, we learned that CA did not crosslink with the woolen fibers if the woolen fabrics were not oxidized by potassium permanganate and that after oxidization, CA produced esterification with the —OH group of the wool and

chitosan and transamidation with the— NH_2 group of the wool to form a crosslink. The surface crosslinks of the oxidized woolen fibers were relatively coarse, which is undesirable for shrink-proofing and yet beneficial for the antimicrobial and antiseptic effects of the woolen fabrics. It had a negative effect on the fabric softness, yellowness, stretching resistance, and elongation percentage. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1999–2007, 2004

Key words: fibers; crosslinking; esterification; FT-IR

INTRODUCTION

To shrink-proof woolen fabrics, an active compound or hyperoxide is often used to oxidize the scales or even to further solidify it through a reaction with a resin to change the directional friction effect and elasticity of the wool and thus produce shrink-proof qualities.¹

For antimicrobial treatments, reagents such as organic silicon quaternary ammonium compounds, halogenated diphenyl ether derivatives, nitrofurantoin, and organic nitrogen compounds are frequently used; among which organic silicon quaternary ammonium compounds are the most common. Antimicrobial activity is achieved by the quaternary ammonium compound cation, which grabs the bacterial anion, destroying the cell wall of the bacteria and causing the interior contents to exude, thus killing the bacteria.

Poly(carboxylic acid) (PCA) is quite effective for antiwrinkle treatments for cotton fabric; by replacing the conventional formaldehyde-type treatment resin, PCA forms a five-membered cyclic anhydride intermediately in the presence of a catalyst and then produces an ester bond with R—OH.^{2–5} The many hydroxyl bonds (e.g., serine, tyrosine) on the wool fiber structure can form ester bonds with PCA and crosslink.⁶ Among the non-formaldehyde-type treatment resins for the esterification crosslinking of cotton fabric, PCA, BTCA (1,2,3,4-butane tetracarboxylic acid), and CA are the most favorable compounds. Although BTCA is very effective, it is very costly. Thus, by reference, we learned that CA is a feasible crosslinking agent.⁷

Chitin is the most abundant substance in nature second only to cellulose; it is distributed widely in insects, shrimp, crab shells, squid, and the cell walls of fungus (eubacteria and various mushrooms).8,9 The molecular weight of chitin is approximately 1,000,000–2,000,000, depending on its source and production conditions. If the acetyl groups on the chitin molecules are completely or partially removed, chitosans are obtained. Because of the amino groups, chitin carries cations under acidic conditions, which give it the ability to lower plasma triglycerides and antimicrobial activity. Recently, it has often been applied as an antimicrobial treatment for textile fibers.^{10–13} Researchers have discovered that woolen fabric may be made shrink-proof by soaking wool in 2-5% chitosan and heating at proper temperatures.^{11,14}

For shrink-proofing and the antimicrobial treatment of woolen fabrics, in addition to conventional methods and those mentioned previously, chitosans can be used to replace resins. Research on the shrink-proofing antimicrobial treatment of woolen fabrics by PCA crosslinking agents and chitosans is scarce.⁶ Thus, this study was devised to use citric acid (CA) as a crosslinking agent to study the antimicrobial treatment of woolen fabrics through the mixture of CA with biopolymer chitosans. In this study, we used

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Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to study the reaction mechanism during crosslinking.^{15,16} Thermal analysis and wash fast and antimicrobial tests were also conducted to evaluate the woolen fabric shrinkproofing antimicrobial treatment.^{6,17–19} At the same time, changes in the softness, yellowness, and mechanical properties of the treated object were also investigated to study the changes in the physical properties of the woolen fabric during heat treatment.^{20–24}

EXPERIMENTAL

Materials

The experimental woolen fabric had a warp density of 52, a weft density of 44, and a yarn number of 48 leno and was scoured for 60 min in 3% NaOH at 50–60°C. Chitosan, with a deacetylation of 90% or above, was produced by OHKA Enterprises Co., Ltd. (Japan). CA was purchased from Shimakyu Food Tech, Inc. (Japan). Acetic acid, sodium hydroxide, alcohol, sodium hypophosphite, and potassium permanganate were all first-grade reagents.

Measurements

A fine powder of 3.5% chitosan was dissolved in 4.0% acetic acid. Then, 4.0% CA was dissolved in a 30% alcohol and 70% water mixture solution, respectively, followed by the addition of 4.0% sodium hypophosphite. The resulting mixture was stirred well to dissolve chitosan with the CA solution to obtain the treatment solution. The curing treatment was carried out according to a pad-dry-cure (Labortex) procedure as follows: woolen fabric \rightarrow treatment solution \rightarrow preprocess (70°C, 5 min) \rightarrow curing reaction (2 min) \rightarrow water rinse (5 min) \rightarrow dry (75°C, 5 min). The curing temperatures were as follows: 90, 105, 120, and 135°C; there was also an uncured sample.

The crosslinking reaction of the woolen fabric and PCA was carried out with the prepared CA treatment solution mentioned previously for curing the woolen fabric with the previous conditions. We carried out the PCA and chitosan reactions by mixing and stirring the CA and the prepared, dissolved chitosans mentioned previously; putting a few drops on a glass slide to create a film; and carrying out the heat treatment reaction under the previous conditions. We carried out the crosslinking treatment of the woolen fabric after the oxidation preprocess by oxidizing the woolen fabric with potassium permanganate at 120°C for 2 min at concentrations of 1, 1.5, 2, 2.5, and 3% and then curing it with a CA solution or chitosan.

We used a Bio-Rad Digilab UMA400 (USA) Fourier spectroscopic analyzer with an attenuated total reflec-

tion microscope. We turned on the computer and chose Digilab Merlin 3.4 access FTIR application software, warmed up the machine for 30 min, poured in nitrogen, and pressed the microscope control. We made sure that the instrument was under IR mode and conducted the calibration, and when the calibration was complete, we placed the sample on the microscope stage, adjusted it until the instrument came into contact with the sample, and began testing. We observed the surface formation of the crosslink under a scanning electron microscope (Jeol 5610, USA). Thermal analysis was conducted with a differential scanning analyzer (PerkinElmer Pyris, USA).

The shrink-proofing measurement was carried out according to ISO 6330-1984(E), in which we used an England Washer (Precision SDL-M223, UK). The area of the original woolen fabric (A_1) sample minus the area after treatment (A_2) divided by area of the woolen fabric multiplied 100% gives the area shrinkage:

Area shrinkage = $(A_1 - A_2)/A_1 \times 100\%$

The antimicrobial test was carried out according to the antimicrobial standard of the Japan Association for the Evaluation of Textile and was measured according to quantification methods JIS L1902-1998. A bacteriostatic value greater than 2.2 means the test sample is bacteriostasic, and an antiseptic value greater than 0 indicates that the test sample is antiseptic.

The wash fast test was carried out according to ISO6330-1984E, with a precision SDL-M223 washer, which conducts 5, 10, 15, and 20 washings, and then the antimicrobial characteristics were measured. Softness measurements were carried out according to CNS1481-L3023 on 2×15 cm test fabric, 5 pieces each of warp-wise and weft-wise fabric. Whiteness and yellowness were measured with a color difference inspector (Nippon ND300A). The stretch test was carried out according to the CNS1481-L3023 wool product test procedure, with a stretch tester with a computer servo control materials testing system (HT-9102, Hung Ta Instrument Co., Ltd.).

RESULTS AND DISCUSSION

FTIR analysis

Wool is composed of a cuticle and cortex and a medulla only in the case of course wool. The cuticle has valine, disulfide bond groups and carboxyl groups, whereas the cortex makes up the main portion of the wool. It is made up of more than 18 amino acids, which can be divided into four distinct groups: cationic, anionic, nonpolar, and polar. The main functional groups include carboxyl (—COOH), amino (—NH₂), and hydroxyl (—OH) groups; thus, the chemical properties were extremely active. In IR spec-



Figure 1 FTIR spectra of the woolen fabrics cured with CA for 2 min: (A) uncured and cured at (B) 90, (C) 105, (D) 120, and (E) 135°C.

troscopy, the main characteristic appeared between 1000 and 1700 cm⁻¹, including amide I (\sim 1670 cm⁻¹), amide II (\sim 1540 cm⁻¹), amide III (\sim 1270 cm⁻¹), and S—O contraction (\sim 1100 cm⁻¹).^{15,16}

PCA, after the introduction of the catalyst $(NaH_2PO_2 \cdot H_2O)$, becomes a five-membered cyclic anhydride intermediate. To form a cyclic anhydride, there must be a pair of adjacent —COOH groups. After the cyclic anhydride is formed, it produces esterification with the -OH on wool (or the chitosan -OH), at the same time releasing a -COOH group, but if the middle position (α -OH, 2-OH) carboxyl produces esterification, then it cannot form a five-membered cyclic anhydride intermediate and, thus, forfeits its activity. If it forms an ester and not in the middle, there are still two carboxyl groups able to form another cyclic anhydride; thus, it can produce bonding with the wool —OH (or chitosan —OH) again.^{5,7} CA can undergo esterification with the wool -OH group crosslink.^{15–17,20} The reaction mechanism is as follows:

$$R - COOH + HO - W \rightarrow R - CO \cdot O - W$$
$$R - COOH + H_2N - W \rightarrow R - CO \cdot NH - W$$

where R is the CA backbone and W is the wool backbone.

The woolen fabric was cured for 2 min with CA under different temperatures. The results, displayed in Figure 1, show that despite the change in curing temperature, its spectroscopic data was similar to that of a blank woolen fabric; no reaction occurred. This was caused by the cuticle and rigid scales on the surface of woolen fiber; when the fabric was oxidized with potassium permanganate during the preprocess, the results are displayed in Figure 4(C), which is shown later. At 1033 cm⁻¹, there was S—O contraction, which was increased by oxidation; at 1634 cm⁻¹, there was C—O contraction. At 1533 cm⁻¹, there was C—N and N—H contraction, which meant that the PCA —COOH group and —OH, —NH₂ groups of the wool fiber became —COO— and —CONH— increased; in other words, there was an increase in crosslinking.

The CA —COOH group can undergo esterification and transamidation with the —OH, and $-NH_2$ groups of chitosan as follows:

$$R$$
—COOH + HO—Chitosan \rightarrow

R—CO·O—Chitosan

$$R$$
—COOH + H_2N —Chitosan \rightarrow

R—CO·NH—Chitosan

CA and the chitosans were heat-treated for 2 min. The IR analysis of the film is displayed in Figure 2. As shown in Figure 2, at 1701 cm⁻¹, there was a -CO- contraction; at 1637 cm⁻¹, there was a -CONH- contraction; at 1149 cm⁻¹, there was a -CN, COH contraction; and at 1032–1078 cm⁻¹, there was a $C-NH_2$ contraction, displaying a PCA -COOH group, and chitosan -OH and $-NH_2$ groups formed -COO- bonds and -CONH- bonds, which were especially evident at 120°C.



Figure 2 FTIR spectra of chitosan cured with CA for 2 min: (A) uncured and cured at (B) 90, (C) 105, (D) 120, and (E) 135°C.

The curing treatment results for the woolen fabric treated with CA and the chitosan treatment solution for 2 min are shown in Figure 3. Figure 3 was similar to Figure 1, which means that it did not react with woolen fibers, owing to the cuticle and rigid scales hindrance on the surface of woolen fiber. When oxidizing with potassium permanganate during preprocessing and then carrying out the curing treatment, we obtain the results shown in Figure 4(C). When the woolen fibers were oxidized and heat-treated with chitosan at 120°C for 2 min, the IR spectra [Fig. 4(D)] showed a vibration at 1624 cm⁻¹ corresponding to —CONH—, showing that the chitosan —NH₂ group

and the —COOH group of the woolen fibers reacted with each other.

SEM analysis

The results of woolen fabric cured at 120°C for 2 min with CA and chitosan are shown in Figure 5. There was no obvious sign that CA or chitosans adhered to the woolen fabric because of the obstruction caused by the rigid scales on the surface and cuticle of the woolen fabric, and so there was no obvious adherence of chitosan to the surface of the fiber. The woolen fabric oxidized by KMnO₄ (1.5%), as shown in Figure



Figure 3 FTIR spectra of the woolen fabrics cured with CA and chitosan for 2 min: (A) uncured and cured at (B) 90, (C) 105, (D) 120, and (E) 135°C.



Figure 4 FTIR spectra of woolen fabrics cured with different treatments at 120°C for 2 min: (A) woolen fabric, (B) cured with CA and chitosan, (C) oxidized and cured with CA and chitosan, and (D) oxidized and cured with chitosan.

6, showed that after the woolen fabric scales were damaged by $KMnO_4$, the surface scales disappeared. The results of the oxidizing and curing treatment (120°C, 2 min) of the sample with CA and chitosan are shown in Figure 7. Once the surface of the scales on the woolen fabric were damaged by $KMnO_4$, the chitosan adhered to the woolen fabric. The oxidized woolen fabric after the curing treatment (120°C, 2 min) with chitosan is shown in Figure 8. As shown in Figure 8, the woolen fabric after oxidation with chitosan obviously adhered to the woolen fabric surface.

Differential scanning calorimetry (DSC) analysis

The heat treatment DSC curve of the woolen fabric before oxidation by potassium permanganate and af-



Figure 6 SEM photographs of the woolen fabrics oxidized with potassium permanganate $(300 \times)$.

ter oxidation by CA and chitosan is shown in Figure 9. Because the woolen fabric was a highly hydrophilic fiber, as shown in Figure 9(A), with increasing temperature, the vaporization of the water molecule heat flux also increased to about 100 and 200°C to approximately a 230°C peak, which was α -keratin crystallization melting with a 230°C maximum. From 230 to 275°C, there was another peak; this was the temperature at which the other components of the woolen fibers decomposed.²⁵ The B curve in the figure represents the woolen fabric before oxidation and the curing treatment with CA and chitosan. Because woolen fabric was hindered by scale, when it was cured with CA, crosslinking was rarely produced; thus, its DSC results were identical to those of pure woolen fabric. However, for the woolen fabric oxidized by potassium permanganate and then cured with CA and chitosan,



Figure 5 SEM photographs of the woolen fabrics $(300 \times)$.



Figure 7 SEM photographs of the woolen fabrics oxidized with potassium permanganate and then cured with CA and chitosan at 120° C for 2 min ($300 \times$).



Figure 8 SEM photographs of the woolen fabrics oxidized with potassium permanganate and then cured with chitosan at 120° C for 2 min ($300 \times$).

in the DSC results, as shown in Figure 9(C), the first peak (\sim 230°C) was shorter than the next peak (\sim 275°C), whereas the second peak was not as obvious. This showed that the woolen fabric oxidized the scale and cuticle were seriously damaged because of the decomposition of α -keratin crystallization rapidly on heating.

TABLE I Antimicrobial Activity of the Woolen Fabrics Cured with CA and Chitosan for 2 min

Curing temperature	Bacterial growth activity value	Antimicrobial value	Antiseptic value	
Control fabric cured at				
120°C	2.75	<0	<0	
Uncured	_	<0	<0	
90°C	_	<0	<0	
105°C	_	<0	<0	
120°C	_	0.49	<0	
135°C		<0	<0	

Antimicrobial analysis

For woolen fabric, according to the Japan Association for the Evaluation of Textile antimicrobial standard, a bacteriostatic value greater than 2.2 means that the test sample is bacteriostasic, and an antiseptic value greater than 0 means that the sample possesses antiseptic effects. In the experiment, as Table I shows, when the bacteriostatic value was less than 0 and the antiseptic value was less than 0, the chitosan did not adhere to the fabric, which resulted in no antimicrobial or antiseptic properties. The woolen fabric possessed a scale structure, which protected the inner cortex when it reacted with the PCA crosslinking



Figure 9 DSC curves of the woolen fabrics cured with different treatments at 120°C for 2 min: (A) control, (B) cured with CA and chitosan, and (C) oxidized and cured with CA and chitosan.

TABLE II Washing Rounds Versus Antimicrobial Relation of the Woolen Fabrics Oxidized with Potassium Permanganate and Then Cured with Chitosan at 120°C for 2 min				
Wash number	Bacterial growth activity value	Antimicrobial value	Antiseptic value	

Wash number	activity value	value	value	
Control fabric				
120°C	2.75	<0	<0	
1	_	3.57	0.82	
5	_	2.60	< 0	
10	_	1.52	< 0	
15	_	0.58	< 0	
20	—	1.72	<0	

TABLE IV Properties of the Woolen Fabrics Cured with CA and Chitosan for 2 min

Curing temperature	Softness			Shrinkage
	Warp	Weft	Yellowness	area (%) ^a
Control fabric cured at 120°C	39.2	41.4	12.36	7.1083
Uncured 90°C 105°C 120°C 135°C	30.6 31.7 40.1 37.4 33.6	35.0 45.6 40.4 36.4 37.2	27.19 27.78 22.83 23.28 30.68	16.0231 16.7950 15.6732 14.6047 12.8229

^a Control shrinkage area = 6.1142%.

agent and chitosan heat treatment. We hoped to produce esterification between the woolen fabric and PCA/chitosan, so the other free carboxyl would form an amide bond between the chitosan amino group or wool amino group and become fixed. Because of the scale hindrance, it could not completely react with the hydroxyl and amino group crosslinks within the wool fiber, which resulted in poor crosslinking, so we added PCA, which caused the chitosan to be unable to adhere.

The woolen fabric first underwent a potassium permanganate preprocess, which caused the scale to oxidize and resulted in regional damage of the scale and increased the crosslinking reaction. These were then treated with the previous method to serve as a means of comparison, as shown in Tables II and III. Table II displays the antimicrobial properties of the oxidized woolen fabric on curing treatment with chitosan. The tests showed that a bacteriostatic value of greater than 3.57 and an antiseptic value of greater than 0.82 allowed the chitosan to adhere to the fabric and produced antimicrobial and antiseptic properties. Because the amino groups of the chitosans in the treatment agent easily formed a quaternary amine salt, which could catch the anionic bacteria and cause its

TABLE III Washing Rounds Versus Antimicrobial Relation of the Woolen Fabrics Oxidized with Potassium Permanganate and Then Cured with CA and Chitosan at 120°C for 2 min

Wash number	Bacterial growth activity value	Antimicrobial value	Antiseptic value	
Control fabric cured at				
120°C	2.75	<0	< 0	
1	_	0.16	<0	
5	_	0.08	<0	
10	_	0.12	<0	
15	_	<0	<0	
20	—	0.12	<0	

cell wall to stop growing, it showed antimicrobial properties. Also, for the woolen fabric oxidized by potassium permanganate and then cured with CA and chitosans (Table III), the resulting fabric was antimicrobial but not antiseptic, meaning that it did have crosslinks, but because of the damage done to scales, the chitosan was affected by CA and woolen fabric crosslinking, which resulted not only in a decrease in amount but also caused them shield each other; therefore, the antimicrobial antiseptic nature of the chitosan was not as good as pure chitosan crosslinked with the woolen fabric.

Wash fast analysis

Woolen fabric under various conditions of heat treatment was wash-tested multiple times according to ISO 6330-1984(E) with a precision SDL-M223 wash machine (UK). The results are illustrated in Tables II and III. The antimicrobial nature decreased with increasing number of washings. The more the washings there were, the more chitosans detached from the woolen fabric, and its antimicrobial effect decreased, but after 20 washings, it maintained decent antimicrobial properties, revealing a good crosslinking effect.

Physical property analysis

The softness of the woolen fabrics treated with the CA and chitosan solution and cured for 2 min under different temperature is shown in Table IV. The smaller the value is, the better the softness was. The fabric good softness, and the curing temperature did not have a significant effect. For the woolen fabric oxidized with potassium permanganate and then cured with the CA and chitosan treatment solution, the results are given in Table V. Regardless of the curing temperature, the softness was poorer than that of the original fabric, and this fabric displayed serious stiffening because the scale of the woolen fabric was damaged when oxidized. —COOH of PCA and —NH₂ or

IABLE V				
Properties of the Woolen Fabrics Oxidized with				
Potassium Permanganate and Then Cured with CA and				
Chitosan for 2 min				

Curing temperature	Softness			Shrinkage
	Warp	Weft	Yellowness	area (%) ^a
Control fabric cured at				
120°C	39.2	41.4	12.36	7.1083
Uncured	71.0	70.6	40.38	19.9590
90°C	77.6	96.8	50.54	19.0152
105°C	100.0	106.4	55.96	22.5051
120°C	76.8	100.8	58.76	23.3431
135°C	104.6	117.8	52.55	28.4491

^a Control shrinkage area = 6.1142%.

-OH within the woolen fibers may have formed acylamino groups or ester crosslink bondings, decreasing the softness. Also, the oxidized woolen fabric, directly cured with chitosan, as shown in Table VI, had better softness than those in Table V; chitosan had a softening effect on the oxidized surface of the woolen fibers. For the woolen fabrics in the CA and chitosan treatment solution, which were cured for 2 min under different temperatures, the yellowness is displayed in Table IV. Regardless of the curing temperature, the yellowness was greater than that for the original woolen fabrics. For the oxidized woolen fabric, which was then cured with CA and chitosan treatment solution (Table V), the yellowness increased regardless of the treatment temperature. For the oxidized woolen fabric directly cured with chitosan, the yellowness was poor, as shown in Table VI. Because the wool itself had scales, it produced a a differential frictional effect (DFE); thus, the woolen fabric shrank. As shown in Table IV, the curing treatment did not influence the shrink-proof properties of the fabric. The area shrinkage was approximately the same as a blank sheet. The shrinkage of the woolen fabrics after curing with CA and chitosan is shown in Table IV. The surface

TABLE VI Properties of the Woolen Fabrics Oxidized with Potassium Permanganate and Then Cured with Chitosan for 2 min

Curing temperature	Softness			Shrinkage
	Warp	Weft	Yellowness	area (%)
Control fabric cured at				
120°C	39.2	41.4	12.36	7.1083
Uncured	48.4	59.2	29.87	16.9088
90°C	41.0	42.8	49.14	14.5492
105°C	45.6	52.4	34.66	14.7702
120°C	47.5	64.4	29.10	17.0328
135°C	53.4	59.4	37.32	18.5826

^a Control shrinkage area = 6.1142%.



Figure 10 Stress–strain curves of the woolen fabrics (warp) cured with different treatments at 120°C for 2 min: (A) control, (B) cured with CA and chitosan, (C) oxidized and cured with CA and chitosan, and (D) oxidized and cured with chitosan.

crosslinking of CA and wool after the curing treatment gradually turned rigid, causing it to shrink even more. For the woolen fabric oxidized by potassium permanganate (1.5%) and cured with CA and chitosan, the area of shrinkage is shown in Table V; both were worse than before oxidation because after the scales were damaged, CA and the woolen fabric produced better esterification and transamidation, which made the surface of the woolen fabric more coarse, as under microscopic observation, and thus increasing its tendency to shrink. The results of the oxidized woolen fabric directly cured with chitosan, shown in Table VI, reveal that the area shrinkage was undesirable. The woolen fabric before and after oxidation was cured for 2 min at 120°C with the CA and chitosan treatment solution; its stretching resistance and elongation percentage curve is shown in Figure 10. After oxidation, its stretching resistance and elongation percentage were the poorest; oxidized woolen fabric that was cured with the treatment solution was next; the one that was oxidized and directly cured with chitosan was better; and the nonoxidized one treated with the CA and chitosan treatment solution was even better but was still worse than the nonoxidized woolen fabric. From this, we learned that once the woolen fabric was oxidized, the surface scales were damaged, which greatly decreased its tensile strength.

CONCLUSIONS

1. Because of the scale, when the woolen fabric was cured with CA or the CA and chitosan treatment solution, no crosslinking was produced. After the woolen fabric was oxidized by preprocessing with potassium permanganate and cured with the CA and chitosan treatment solution, esterification and transamidation were produced.

- 2. For the woolen fabric before oxidation, as shown by microscopic observation, CA did not crosslink with the woolen fabric, and once oxidized, there were crosslinks with CA.
- 3. The thermal analysis of woolen fabric cured with CA and chitosan before oxidation was similar to that of the pure woolen fabric; after oxidation, its α -keratin crystallization was heated, and decomposition occurred even more rapidly.
- 4. The woolen fabric cured with CA and chitosan before oxidation did not possess antimicrobial or antiseptic properties. When oxidized and cured with CA and chitosan, the woolen fabric obtained antimicrobial properties. The antimicrobial effect decreased with the frequency of washing.
- 5. For the woolen fabric oxidized by KMnO₄ and cured with CA and chitosan, shrinkage increased instead. For the woolen fabric, no matter if it was oxidized, once it produced crosslinks on heat treatment with the CA and chitosan treatment solution, the softness became poorer, the yellowness worsened, and the stretching resistance and elongation percentage declined; it deteriorated especially after it was oxidized.

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