Preparation and Multifunctional Application of *meso*-Chitosan for the Woolen Process

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ABSTRACT: This study used chitosan deacetylated to different degrees to process woolen fabrics via the nanometrization of sodium hydroxide of different concentrations. The analysis and determination of the bacterial resistance, shrink resistance, Fourier transform infrared, and dyeability were then carried out for the processed substances. The particle diameter was measured with light scattering and scanning electron microscopy. It was then reduced with 5% and higher concentrations of NaOH, in which the particle diameter was 150–750 nm. As for bacterial resistance, the processed cloth that was not oxidized by H_2O_2 had better bactericidal and bacteriostatic effects than the cloth that underwent the oxidation process. Chitosan and *meso*-chitosan had a bacterial-resistance effect on the woolen fabrics. The processed cloth also had a better shrink-resistance rate, but the effect of nanometrization was not obvious. For the dyeability of the woolen fabrics, *meso*-chitosan was better than chitosan. The higher degree of deacetylation of chitosan slightly improved the dyeability. The dyeability increased a little as the temperature of the curing treatment rose and the time of the curing treatment was extended. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4080–4086, 2007

Key words: biomaterials; dyes/pigments; fibers; FT-IR; light scattering

INTRODUCTION

Chitin and chitosan are biomaterials that are compatible with organisms and cause little pollution. In recent years, they have been widely applied in industry as raw materials for enzyme immobilization, sewage processes, agriculture, health food, chemical engineering, medicine, and textiles, and they are easy to obtain.[1–5]

Chitosan is the product of the deacetylation of chitin. It can be dissolved in strong and weak organic and inorganic acids. It is more convenient for different kinds of derivatives with chemical coordination.[6–8] Because of its good solubility, it can be converted into colloids, fibers, dew, and membranes.

Woolens are easy to shrink, and this leads to fabrics with unstable sizes. Moreover, woolen fabrics are classified as protein fibers. The exuviations mixed with sweat on the human body easily provide abundant nutrition for the growth and propagation of bacteria and mycetes. They also lead to mildew on the fabric and the diffusion of diseases. In addition, the growth of microorganisms generates a cracking phenomenon. This also leads to discoloration and flaws in the product. Therefore, the processes of shrink resistance and bacterial resistance are very important steps for the wearability of feather fabrics.[9–13]

Materials with particles smaller than 100 nm are nanometer materials, and those with particles smaller than 1 μ are mesometric materials. When the size shrinks to an atomic scale, the electrons and boundary lead to a quantum confinement effect, which is the ratio of the surface area to the volume. This changes many properties of the original material, leading to new particularity or function.[14–16]

Chitosan has an excellent bacterial-resistance effect. Previous research in this laboratory has shown that chitosan and nano-TiO_2/chitosan can confer antibacterial and anti-UV properties onto fabrics,[17,18] and other studies have been conducted on wool.[19–23] Information on the procedure of nanometrization and its application in textiles is not available in the literature, especially concerning its application to processed woolen fabrics. Therefore, we have studied the application of *meso*-chitosan to woolen fabrics to induce a curing treatment and have probed the influence of the degree of processing of *meso*-chitosan on woolen fabrics.

EXPERIMENTAL

Materials

The specifications of the woolen fabrics used in this experiment were as follows: a warp density of 60, a weft density of 52, and a warp and weft yarn count

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TABLE I
Particle Diameters of Chitosan Reduced by Different Concentrations of NaOH and Then Oscillated for 2 h

Deacetylation	NaOH concentration (%)	Particle diameter (nm)
80% chitosan	5	445.23
	15	747.88
	25	411.55
	35	519.50
95% chitosan	5	325.83
	15	146.58
	25	409.91
	35	438.84

of 48 for two strands (twill). A 3% NaOH solution was used to refine the fabrics for 60 min at 50–60°C. The chitosan had deacetylation degrees of 80 and 95%, a viscosity less than 200 MPa s, a degree of polymerization approximately greater than 1290, and a molecular mass approximately greater than 207,000. It was produced by OHKA Enterprises Co., Ltd. (Kao Hsiung, Taiwan). The acidic dyestuff—Bayer Telon Red M-GWN, Bayer Telon Yellow M-4GL, and Bayer Telon Blue M-RLW—was purchased from Dystar. Other reagents, such as acetic acid, sodium hydroxide, hydrogen peroxide, and sodium dithionite ($Na_2S_2O_4$), were all of primary (first-class) quality.

Measurements

The woolen fabrics were treated with H_2O_2 (2%) at 50°C for 50 min (pH = 9, bath ratio = 30 : 1), washed with water at 70°C for 10 min, dried at room temperature, and prepared for the process.

Chitosan samples with different degrees of deacetylation (80 and 95%) were dissolved in a 3% acetic acid solution. Then, the chitosan solution was loaded into a sprayer, sprayed in an aqueous alkaline solution (5, 15, 25, and 35% NaOH) for reduction for 30 min at a high speed, and evenly stirred. It was reduced to a chitosan suspension, subjected to a sedimentation process with gravity (0–4000 rpm; DSC-15125D, Taipei, Taiwan), and washed with deionized water repeatedly to acquire a neutral solution. The appropriate concentration was modulated to obtain a *meso*-chitosan suspension that was neutral and milk-white. A Delta (Tainan, Taiwan) DC80H ultrasonic oscillator was used to oscillate the chitosan suspension for 2 h, and then the particle diameter was measured with a ALV/CGS-3 (Langen, Germany) dynamic static state light scattering apparatus and a JEOL 5610 (Japan) scanning electron microscope.

We dissolved the *meso*-chitosan samples with 80 and 95% degrees of deacetylation (1, 2, and 3%) in a 3% acetic solution to obtain the processing liquids. Using a Rapid Labortex (Taipei, Taiwan) tenter machine, we took precut pieces of woolen fabric oxidized by H_2O_2 and soaked each piece in one kind of the processing solution for 20 min, using the two-dip, two-nip process. After the soaking process, the treated fabric pieces were cured either at different temperatures (85, 105, and 115°C) for 2 min or for different times (1, 2, and 2.5 min) at 105°C; this was followed by a series of finishing treatments: rinsing with water for 5 min and drying in an oven for 5 min at 25°C. A Rapid (Taipei, Taiwan) GD-02 dyeing machine was used earlier to place 0.5 g of $Na_2S_2O_4$ and NaOH into a steel cylinder; then, water was added (to 200 mL), and the steel was sleeked for 30 min at 120°C. The red acidic dyestuff (2%) was used to modulate the liquid dye with a bath ratio of 1 : 30; it was then put into the steel cylinder, and the woolen fabric was dyed for 60 min at 100°C. The color strength (K/S) value was measured with a Hunterlab K/S 45/O-L computer color analyzer.

The IR spectrum of the processed cloth was analyzed with a Bio-Rad (United States) Digilab FTS-40 Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflection microscope. The aforementioned fabrics were also analyzed with an energy-dispersive spectrometer of an emissive-type electron microscope (model 6700, JSM, Japan). According to CNS Standard 8038 L3138 F1, the processed fabrics were washed with an SBF (Taipei, Taiwan) ES-951 launder. The original sample area of the woolen fabric minus the processed area divided by the original area of the woolen fabric was multiplied by 100 to obtain the dimensional shrinking rate, which was measured three times for the sample to calculate the mean value. The processed woolen fabric agreed with the Japanese Association for the Functional Evaluation of Textiles

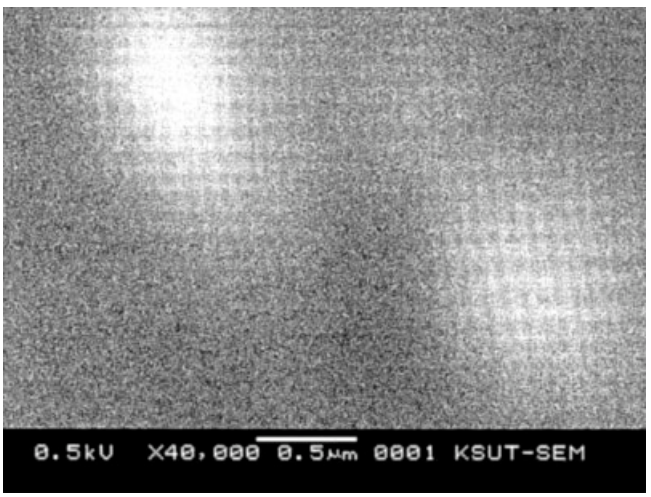

Figure 1 SEM photograph (40,000×) showing the particle diameter of 95% deacetylated chitosan that was reduced by 25% NaOH, nanometrized, and then oscillated for 2 h to generate a suspension.

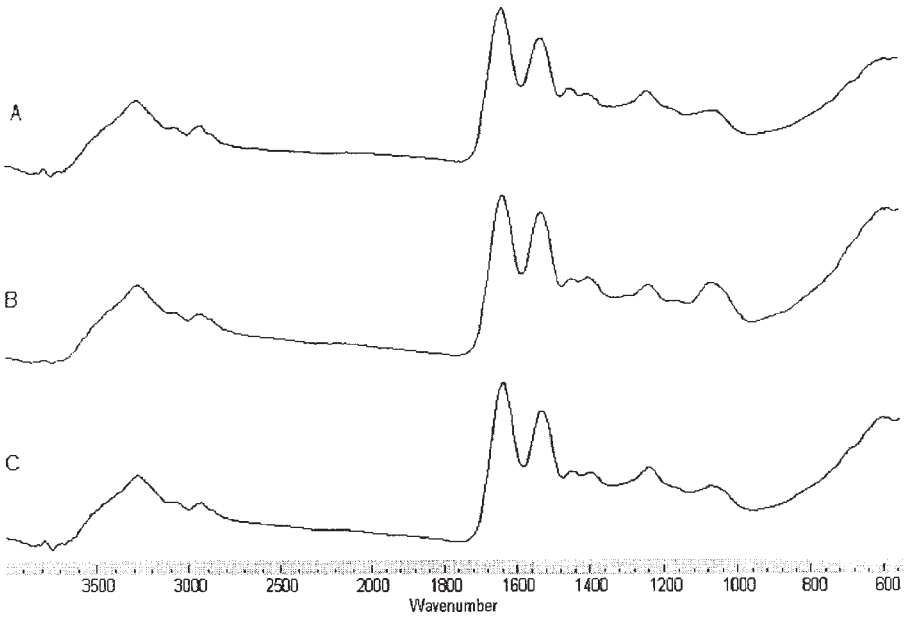

Figure 2 IR illustration of woolen fabrics oxidized with H_2O_2 (2.0% and 50°C) and treated with different types of chitosan: (A) original woolen fabrics, (B) chitosan, and (C) *meso*-chitosan (reduced with 25% NaOH).

(JAFET) standard of bacterial resistance, and this was followed by the JIS L1902-1998 quantitative method to measure the bacterial-resistance effect of the processed cloth to *Staphylococcus aureus* (ATCC 6538P); bacteriostatic activity greater than 2.2 indicated that the sample had a bacteriostatic effect, and bactericidal activity greater than 0 indicated that the sample had a bactericidal effect.

RESULTS AND DISCUSSION

Analysis of the light scattering particle diameter

The particle diameter was measured with a ALV/C GS-3 (Langen, Germany) dynamic static state light scattering apparatus (Malvern). Table I shows the particle diameter of chitosan (between 150 and 750 nm) after nanometrization. The NaOH concentration did not affect the degree of nanometrization of chitosan. However, Table I shows that 5% NaOH could adequately nanometrize chitosan of a higher deacetylation degree to a lesser particle diameter. When the deacetylation was 80% with 15% NaOH, the particle diameter was 747.88 nm. This may be the measurement of particle aggregates because of the uneven scattering of *meso*-chitosan after it was dissolved with acetic acid, vibrated, and scattered.

Analysis of the scanning electron microscopy (SEM) particle diameter

The particle diameter was measured with a JEOL 5610 scanning electron microscope. Figure 1 shows that the particle diameter of 95% deacetylated chitosan was 500 nm via the reduction of 25% NaOH and oscillation for 2 h. Fuzziness diffusion was present in the perimeter of the particle diameter due to the resolution of the testing machine. Therefore, the actual size of the particle diameter was near 400 nm and matched the light scattering data.

Analysis of FTIR

Wool is composed of 18 amino acids, which are divided into four kinds: positive group, negative group,

TABLE II
EDS Analysis of Woolen Fabrics Cured with Processing Solutions of Chitosan and *meso*-Chitosan

Original woolen fabric			Wool and chitosan			Wool and *meso*-chitosan		
Element	wt %	atom %	Element	wt %	atom %	Element	wt %	atom %
C	39.12	51.64	C	31.92	54.70	C	38.42	49.27
N	17.41	19.14	N	9.53	14.27	N	17.52	19.28
O	28.28	27.86	O	20.97	26.96	O	31.86	30.41
Pt	15.19	1.36	Pt	37.58	4.06	Pt	12.20	1.04
Total	100			100			100	

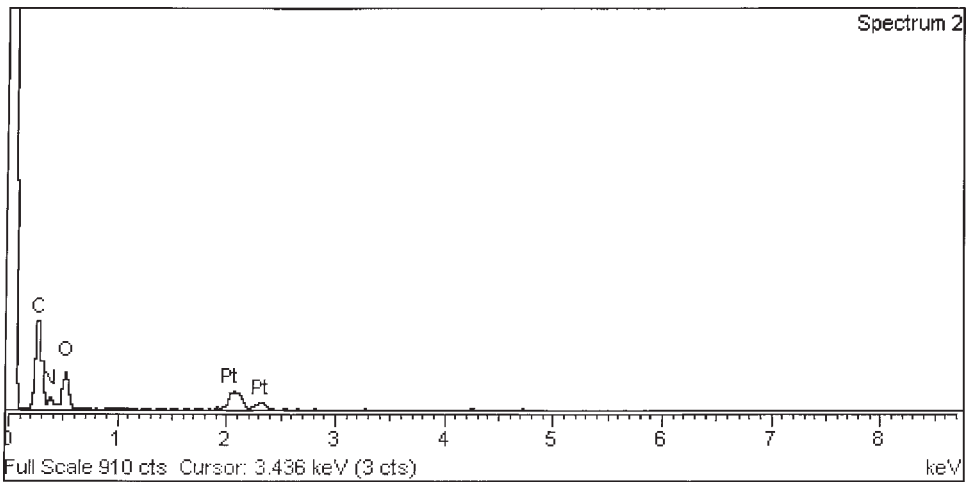

Figure 3 EDS chart of woolen fabrics.

nonpolar, and polar-uncharged groups. The functional groups mainly have the carboxyl group (—COOH), amino group (—NH), and hydroxyl group (—OH), and they lead to labile chemoactivity. Figure 2 shows that the vibration of C—OH occurs at 1050 cm^{-1}, the vibration of C=O occurs at 1631 cm^{-1}, and the vibration of —NH— occurs at 1531 cm^{-1} in the amide group (—CO·HN—); the vibration of C—H (—CH_2—) is at 2934 cm^{-1}, and the vibration of —NH is at 3285 cm^{-1}. Figure 2 does not show the crosslinking of the —OH group of chitosan and the —COOH group of the woolen fiber. However, *meso*-chitosan and chitosan have the same combination with the woolen fabric. This can be proven by the following energy-dispersive spectrometry (EDS) analysis and physical properties derived from experimentation.

Analysis of EDS

The woolen fabrics were analyzed for their chemical compositions with an emissive-type energy-dispersion spectrometer (Table II). Figure 3 shows the EDS analytical results for the woolen fabrics, whereas Figures 4 and 5 present the EDS results for the wool samples, where were heat-treated with chitosan or *meso*-chitosan, respectively. The energy position of each atom was as follows: C was at 0.2774, O was at 0.5249, and N was at 0.3924. According to Figures 4 and 5 and Figure 2, for the woolen fabrics after the curing treatment with *meso*-chitosan, the N and O atomic contents were higher than those of woolen fabrics cured with chitosan as well as the untreated woolen fabrics. The rise of the N atomic content indicated an increase in the —NH_2 residue of chitosan. The increase in the O atomic content suggested that the —OH residue of chitosan increased. As the particle diameter of *meso*-chitosan was small, when the woolen fabrics were heat-treated, the aperture size increased, and this allowed *meso*-chitosan to enter, leading to an increase in the N and O atomic contents.

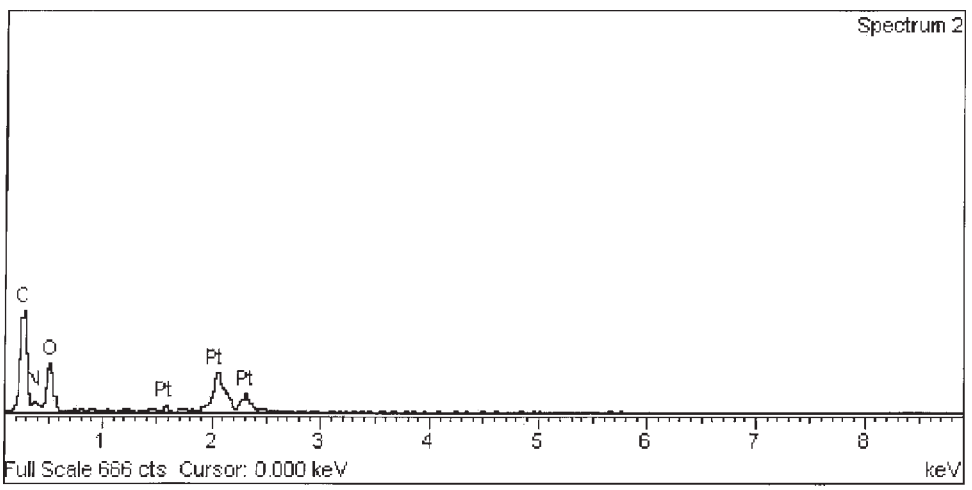

Figure 4 EDS chart of woolen fabrics cured with chitosan.

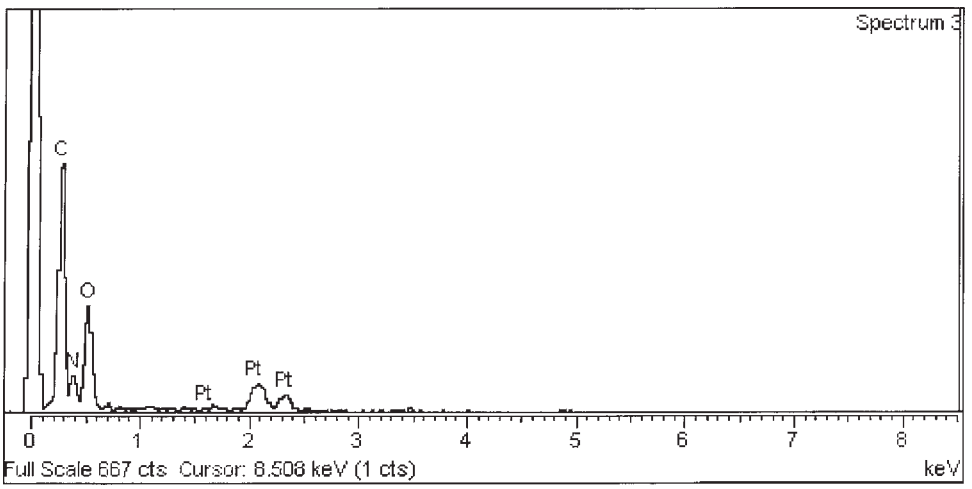

Figure 5 EDS chart of woolen fabrics cured with *meso*-chitosan.

Analysis of the bacterial resistance

The bacterial resistance of the cloth processed with chitosan samples of different degrees of deacetylation and concentrations is shown in Tables III and IV. Table III shows that the processed cloth oxidized by H_2O_2 had bactericidal and bacteriostatic effects. Even the control cloth oxidized by H_2O_2 had bactericidal and bacteriostatic effects. This meant that it could not be proven that the bacterial resistance of chitosan to woolen fabric was not due to the oxidation of woolen fabrics via 2% H_2O_2. Table IV shows that the processed cloth not oxidized by H_2O_2 had the same bactericidal and bacteriostatic effects as the oxidized one. The control woolen fabric that was not oxidized by H_2O_2 did not have bacterial resistance, and this revealed that *meso*-chitosan and chitosan had bactericidal and bacteriostatic effects. The pores of the woolen fiber were aggrandized when the woolen fabric was processed at 105°C, and this made it easy for chitosan and *meso*-chitosan to penetrate the interior of the fiber. This showed the good bactericidal and bacteriostatic effects of chitosan. Chitosan bore a cation of the amino group, which attracted the negative charges of the cell walls of bacteria and fungi to one another. This result bound the latitude of the organism and led to the blocking of breeding. Then, it came to an antibiotic effect. Table III shows that all the bacteriostatic values were greater than 5.82, and the antibacterial values were greater than 2.9. All the woolen fabrics cured with chitosan and *meso*-chitosan under various conditions were tested

TABLE III
Bacterial Resistance of Woolen Fabrics Oxidized by H_2O_2 (2.0% and 50°C) and Treated with Processed Solutions of Different Concentrations of Chitosan

Chitosan concentration (%)		Ma	Mb	Mc	Bacterial growth activity value	Antibacterial value	Bactericide value
Test blank cloth		1.57×10^4	1.31×10^7	—	2.92	—	—
Original woolen fabric[a]		—	—	< 20	—	> 5.82	> 2.90
80% chitosan	1	—	—	< 20	—	> 5.82	> 2.90
	2	—	—	< 20	—	> 5.82	> 2.90
	3	—	—	< 20	—	> 5.82	> 2.90
95% chitosan	1	—	—	< 20	—	> 5.82	> 2.90
	2	—	—	< 20	—	> 5.82	> 2.90
	3	—	—	< 20	—	> 5.82	> 2.90
80% *meso*-chitosan	1	—	—	< 20	—	> 5.82	> 2.90
	2	—	—	< 20	—	> 5.82	> 2.90
	3	—	—	< 20	—	> 5.82	> 2.90
95% *meso*-chitosan	1	—	—	< 20	—	> 5.82	> 2.90
	2	—	—	< 20	—	> 5.82	> 2.90
	3	—	—	< 20	—	> 5.82	> 2.90

The concentration of the plant bacteria was 0.79×10^5.

[a] Oxidized by H_2O_2 (2.0% and 50°C).

Ma, The number of bacteria recovered from the inoculated control at the beginning of contact time; Mb, The number of bacteria after 18 hrs inoculation of the control; Mc, The number of bacteria after 18 hrs inoculation of the sample.

TABLE IV
Bacterial Resistance of Woolen Fabrics Treated with Processed Solutions with Different Concentrations of Chitosan

Chitosan concentration (%)		Ma	Mb	Mc	Bacterial growth activity value	Antibacterial value	Bactericide value
Test blank cloth		2.4×10^4	1.8×10^7	—	2.9	—	—
Original woolen fabric		—	—	5.6×10^7	—	<0	< 0
80% chitosan	2	—	—	< 20	—	> 6.0	> 3.1
95% chitosan	2	—	—	< 20	—	> 6.0	> 3.1
80% *meso*-chitosan	2	—	—	< 20	—	> 6.0	> 3.1
95% *meso*-chitosan	2	—	—	< 20	—	> 6.0	> 3.1

The concentration of the plant bacteria was 1.2×10^5.

for antibacterial properties, and the results showed that the microbial counts after 18–24 h of incubation were all less than 20. After calculation, their bacteriostatic and antibacterial values were very high and identical. The bacteriostatic and antibacterial values displayed in Table IV are also due to the same reasons.

Analysis of the shrinkage resistance

Table V shows that processing with chitosan reduced the shrinking-rate effect in comparison with the unprocessed woolen fabric. However, the variation in chitosan or *meso*-chitosan was limited. This showed that oxidation might lead to shrinkage. The shrinkage rate decreased at higher concentrations. Because of the woolen scales on the surface of the wool, it was easy to generate a directional friction effect and make the woolen fabric shrink. When the wool was treated with a processed solution of chitosan, the fricative coefficients of the right and contrary directions were reduced. Thus, the fricative coefficient effect was reduced, and the milling shrinkage was lowered. As shown in Table V, the curing treatment with 1% *meso*-chitosan gave rise to 8% shrinkage; this indicated that the abnormal result may have resulted from errors in the experimental measurement.

Analysis of *K*/*S*

Table VI shows that the woolen fabric oxidized by H_2O_2 and cured with the *meso*-chitosan solution had a better pigmentation effect as a result of the nanometrization of chitosan. Because the pore of the woolen fiber was aggrandized when it was processed at a high temperature, it was easy for *meso*-chitosan to enter the interior of the woolen fiber. The pigmentation effect of chitosan was worse than that of the control woolen fabric because it was not easy to enter the interior of the fiber pore. Chitosan was easy to crack because of the absence of a crosslinking agent. Besides, the woolen fabric oxidized by H_2O_2 showed the destruction of some amino acids on the surface. This reduced dye fixity. It was also observed that processing with 95% deacetylated *meso*-chitosan was slightly superior to processing with 80% deacetylated *meso*-chitosan.

Analysis of the curing-treatment conditions

The processing of cloth of woolen fabrics was conducted at different temperatures and for different times of the curing treatment; this was followed by staining with red, yellow, and blue (the three original colors). Table VII shows that the dyeability of *meso*-chitosan was better than that of chitosan. The dyeability increased as the temperature and time of the curing treatment increased. The pore was aggrandized as the temperature was raised; this made it easy for *meso*-chitosan to interpenetrate the interior

TABLE V
Shrink Resistance of Woolen Fabrics Treated with Processed Solutions with Different Concentrations of Chitosan and *meso*-Chitosan

Deacetylation	Concentration (%)	Shrinkage rate (%)	
		meso-Chitosan	Chitosan
80% chitosan	1	8	5
	2	5	5
	3	5	5
95% chitosan	1	4	6
	2	6	5
	3	5	4

The concentration for the original woolen fabrics was 7%.

TABLE VI
Dyeability of Woolen Fabrics Treated with Processed Solutions with Different Concentrations of Chitosan and *meso*-Chitosan

Deacetylation	Concentration (%)	*K*/*S*[a]	
		meso-Chitosan	Chitosan
80% chitosan	1	37.60	31.55
	2	35.83	30.86
	3	36.08	32.89
95% chitosan	1	38.37	31.95
	2	36.83	33.11
	3	37.38	31.80

[a] Bayer Telon Red M-GWN was used (wavelength = 530 nm). For the original woolen fabrics, *K*/*S* was 31.20.

TABLE VII
Dyeability of Woolen Fabrics Cured Under Different Curing Conditions with Different Acid Dyes in Processing Solutions of Chitosan and *meso*-Chitosan

		K/S					
		Blue[a]		Yellow[b]		Red[c]	
Curing condition		*meso*-Chitosan	Chitosan	*meso*-Chitosan	Chitosan	*meso*-Chitosan	Chitosan
Original woolen fabric		18.26		16.98		31.20	
Curing temperature (2 min)	85°C	24.66	20.20	20.57	18.05	32.16	31.55
	115°C	24.89	22.08	22.90	20.89	38.29	34.28
Curing time (105°C)	1.0 min	24.63	20.52	22.46	20.39	34.99	32.10
	2.5 min	24.71	20.67	22.72	20.99	37.24	33.86

[a] Bayer Telon Blue M-RLW (wavelength = 630 nm).
[b] Bayer Telon Yellow M-4GL (wavelength = 400 nm).
[c] Bayer Telon Red M-GWN (wavelength = 530 nm).

of the woolen fiber. A prolonged time for the curing treatment also allowed *meso*-chitosan to interpenetrate the interior of the woolen fiber. Chitosan could not easily interpenetrate the holes of the woolen fabrics because the molecules were larger. Its dyeability was worse than that of *meso*-chitosan.

CONCLUSIONS

Woolen fabrics oxidized by H_2O_2 and cured with different types of deacetylated chitosan or processing solutions of *meso*-chitosan of different concentrations proceeded to their curing treatment. The following conclusions were drawn from the experiments:

1. A 5% NaOH solution could adequately nanometrize chitosan to 150–750 nm.
2. Crosslinking between *meso*-chitosan and woolen fibers was not obvious, but some chitosan and *meso*-chitosan entered the interior of the woolen fiber pores.
3. The woolen fabric processed with chitosan or *meso*-chitosan had a bacterial-resistance effect; the woolen fabric also had a bacterial-resistance effect via the oxidation of H_2O_2.
4. The effect of the shrinking rate was reduced after chitosan was used in the processing, but the effect of nanometrization was not obvious.
5. Chitosan could indeed improve the dyeability after nanometrization.
6. The dyeability increased when the temperature was raised and the time of the curing treatment was prolonged.

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