Anti-Ultraviolet and Physical Properties of Woolen Fabrics Cured with Citric Acid and TiO_2/Chitosan

Sung-Huang Hsieh, Fang-Ru Zhang, Hui-Si Li

Department of Polymer Materials, Kun Shan University of Technology, Tainan 71003, Taiwan, Republic of China

Received 28 April 2005; accepted 24 October 2005
DOI 10.1002/app.23830
Published online 8 March 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This experiment is to research the chemical compositions of the crosslink of the woolen, oxidized with H_2O_2 of various concentrations and temperatures, cured with the citric acid and TiO_2/chitosan liquid of different proportions, and then observed by means of Fourier Transfer Infrared Spectrometer (FT-IR), Scanning Electronic Microscope (SEM), Energy Dispersive Spectrometer (EDS), and Thermo-Gravity Analyzer (TGA). Its antishrinkage, antimicrobes, antiultraviolet, strength, elasticity, softness, and yellowness are also investigated to study the changes in its physical properties. From the result, we can see, under the SEM, the sign of disappearance of woolen scales owing to the destruction by H_2O_2 oxidization; the more H_2O_2 and its oxidization temperature, the more serious their destruction. The phenomenon of crosslink is not obvious after oxidization and curing treatment with TiO_2/chitosan, but it somehow apparently happens to the woolen surface. Because TiO_2/chitosan does not intertwine with the woolen well, which has few effects of heat, the woolen shrinks less with more H_2O_2 and oxidization temperatures. Its antishrinkage is better. But the more wash, the more shrinkage. However, TiO_2 covered with chitosan catches less sunlight, and thus cannot suppress or even kill microbes. The woolen processed with nanometer TiO_2 enhances the effect of antiultraviolet, which is better as the density of TiO_2 increases. The strength and elasticity of the woolen are worse for more H_2O_2 and the higher temperature destroy scales and make the woolen coarse, yellow,and less soft. J Appl Polym Sci 100: 4311–4319, 2006

Key words: crosslinking; esterification; fibers; FTIR

INTRODUCTION

Woolen fabrics are prone to shrinkage and felting, which are often the causes of instability in fabric sizes. In addition, the composition of woolen fabrics is protein fibers; its debris mixed with the sweat from human body provide rich nutrients for the growth and regeneration of bacteria and mold, making the fabrics an agent of disease transmission. Moreover, the micro organisms also cause deterioration in the fabrics; therefore, antishrinkage and antibacterial treatments are essential for the wear-ability of fabrics.[1]

Antishrinkage treatment for woolen fabrics is often conducted and achieved through scale-oxidation by active chemical compounds or superoxide, or in a further treatment, solidification by resin to alter its directional frictional effect or change the elongation rate of the wool.[2,3] Moreover, chemicals used for antishrinkage treatments are pollutants to the environment, especially, the organic substances used in the halogenation process. Moreover, the surface active agents of metal sodium and ammonium sodium, often used in antibacterial processes, are common causes of environmental problems.[4]

Chitosan has a free amino; it has good reaction activity and can be used in an array of treatments. Chitosan can be used to substitute synthetic resin for its functions in antishrinkage, antibacterial, and color enhancement treatments.[5–9] Polycarboxylic acid (PCA) is a good crosslinking agent for antiwrinkle treatments of cotton fabrics.[10,11] In recent years, Nano-TiO_2 has been widely used as a photocatalyst; it triggers oxidation and reduction reactions under ultraviolet light, which achieves not only deodorization but also air-purification and disinfection.[12,13]

According to the aforementioned discoveries, other than the traditional and the above-stated chitosan treatments, antishrinkage and antibacterial treatments for woolen fabrics have rarely been researched on the basis of photocatalyst application, with a combination of polycarboxylic acid and chitosan. Therefore, this research is conducted by processing woolen fabrics with nano-photocatalyst TiO_2 and dispersoid of biopolymer compound chitosan in combination with polycarboxylic acid as the crosslinking agent, in an objective to explore the dispersion of nano-photocatalyst TiO_2 in the treatment liquid[13] and the effect of antishrinkage and antibacterial processes on the physical properties of the subject.[14–16]

Correspondence to: S.-H. Hsieh (f1125146@mail.ksu.edu.tw).

EXPERIMENTAL

Materials

The woolen fabrics used in this experiment are in a dimension of 60 warp 52 fill 48 counts (diagonal pattern), scoured with 3% NaOH under 50–60°C of temperature for 60 min. The chitosan deacetylation is 95%, which is produced by Japanese OHKA Enterprises Co. The citric acid is a product of Japanese Shimakyu Food Tech. Nanometer TiO_2 (20%) is a product of Shenzhen, China Nano Technology Development Co. and other chemicals, acetic acid, sodium hydroxide, alcohol, sodium hypophosphite, and hydrogen peroxide, are regular tester class chemicals.

Measurements

First, 2% of chitosan is ground into powder, dissolved it with 3% ethylic acid, and then mixed with TiO_2/chitosan of 0/4, 1/3, 2/2, 3/1, and 4/0 concentrations, respectively. Then, 2% of citric acid (CA) is dissolved in 30% of ethanol and 70% of water, followed by the addition of 2.1% of sodium hypophosphite (SHP:CA; mole ratio 1:1). The above mixture of TiO_2/chitosan is mixed with citric acid, which produces the final processing solution. The woolen fabrics are pretreated in H_2O_2 (0.5, 1.5, and 2.5%) under a 50°C/pH 9 environment for 50 min and then put through the first wash (70°C, 10 min) and second wash before it is dried in room temperature. The fabrics then undergo a curing treatment according to the aforementioned criteria (a TiO_2/chitosan of 2/2 ratio, curing treatment under 155°C for 2 min). Furthermore, various oxidation temperatures (25, 50, and 75°C) are also applied in conjunction with 1.5% H_2O_2/pH 9 for oxidation for 50 min (curing-treatment criteria are same as earlier).

The H_2O_2 oxidation-treated woolen fabrics are submerged in the processing solution and padded with the Rapid Labortex tenter machine. After pretreatment (70°C, 5 min), the fabrics undergo a curing treatment under 140, 155, and170°C for 2 min, followed by a wash (room temperature, 5 min), alkaline treatment (0.1*M* NaOH, 2 min), and drying (75°C, 5 min).

The surface structures of the above woolen fabrics (treated with various H_2O_2 concentrations, oxidation temperatures) and crosslinking fabrics are then observed under an electronic microscope (SEM Joel 5610). The aforementioned crosslinking fabrics are also analyzed through an Energy Dispersive Spectrometer (EDS) of an emissive-type electron microscope (JSM 6700, JAPAN) for their chemical compositions, as well as a Fourier spectrometer equipped with Microscope ATR (FT-IR, Bio-Rad Digilab FTS-40, USA) for an infrared spectrum. The thermogravity losses of the woolen fabrics are measured by a Thermo-Gravity Analyzer (TGA, Dupont 2200).

According to the I.W.S.TM31 standards, the crosslinking fabrics are washed by a Launder (Precision SDL-M223, UK), following the ISO 7A and ISO 5A sequences for one, two, and three times before the shrinkage rate is recorded. The shrinkage area (%) can be derived through the following: the area of the original woolen fabric samples ($A1$) minus the area of the treated woolen fabric samples ($A2$) divided by the area of the original woolen fabric samples ($A1$) and times 100%. The antibacterial experiment is conducted using the JIS L1902–1998 Quantitative Testing Method of the Japan Association For the Evaluation of Textile (JAFET) antibacterial standards, in which a bacterial-repression rate >2.2 means that the object has bacteria-repression effect and a bactericide value >0 indicates antiseptic effect. The above crosslinking fabrics tested by Labsphere UV Transmittance Analyzer (Appendix A-1996) according to the AS/NIS 4399 standards derives the following antiultraviolet ray index:

Range of Anti-UV Index	Level of Anti-UV
15–24	Good
25–39	Very good
40–50,50$^+$	Fine

A computer server tension tester (HT-9102, Hung Ta Instrument Co. Ltd, Taiwan) is used to conduct the tension test for the crosslinking fabrics, according to the CNS1481, L3023 Woolen Fabric Testing method. A softness tester is used to test its softness, using the 45° Cantilever method of the CNS1481, L3023 Softness Testing method; where a smaller value indicates higher softness. A chromatic aberration machine (NIPPON ND300A) is also used to analyze the degrees of yellowing.

RESULTS AND DISCUSSION

Effects of concentrations and temperatures on H_2O_2 treatments

Woolen fabrics pretreated with H_2O_2 oxidation treatment have oxidation concentration of 0.5, 1.5, and 2.5% and oxidation temperature of 25, 50, and 75°C. The original fabrics seen under an electronic microscope, as shown in Figure 1, indicate no damages to the scales. However, the woolen fabrics, after being oxidized by H_2O_2, as seen in Figure 2, under various oxidation temperature, as seen in Figure 3, show marks of scale disappearances after the scales are damaged by H_2O_2, along with the increases in the concentrations of H_2O_2 and oxidation temperatures. After oxidation, the woolen fabrics are cured with citric acid (2%) and various concentrations of TiO_2/chitosan (155°C, 2 min). As seen in Figure 4, the treated fabrics have obvious TiO_2/chitosan adhesions after the surface scales are damaged by H_2O_2.

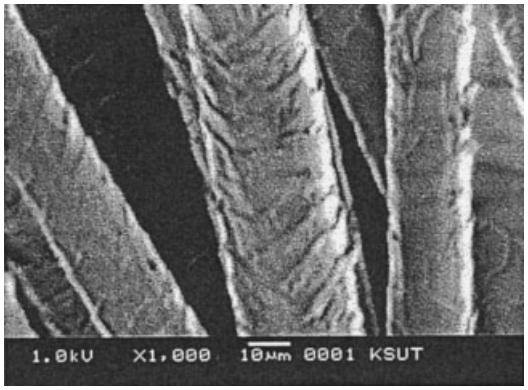

Figure 1 SEM photographs of woolen fabrics (×l000).

Energy dispersion spectrum (EDS) analysis

The woolen fabrics, treated with H_2O_2 (1.5%, 50°C) oxidation and cured with citric acid (2%) and TiO_2/chitosan, are analyzed for their chemical compositions by an Energy Dispersion Spectrometer (EDS) of an emissive-type electron microscope (JSM 6700, JAPAN). The locations of element energy are as follows: C, 0.2774; O, 0.5249; N, 0.3924; Ti, 0.4522 and 4.5089; and S, 2.3075. Figure 5 reveals that the 0.4522 location has Ti element, but it is not shown in the element composition chart. It is probable because the Ti element is undetectably micro or this location does not contain Ti element. It is also possible that the Ti element adheres onto other parts of the woolen fabric. The presence of TiO_2 can be proved through the following physical characteristics.

Infrared spectrum (IR) analysis

The woolen fabrics, oxidized with H_2O_2 (1.5%, 50°C) and cured with citric acid (2%) and TiO_2/chitosan, generate the following results as shown in Figures 6 and 7. Location 1641 cm^{-1} has C—O stretch, location 1522 cm^{-1} has —N—H stretch, location 3270 cm^{-1} has —NH and —NH_2 stretch, and location 2929 cm^{-1} has C—H(or —CH_2—) stretch. Location 3270 cm^{-1} indicates the —NH_2 of fiber and chitosan. Figure 6 shows that when the curing temperature is at 140°C, a better chitosan binding volume is indicated, and the C—H (or —CH_2—) at location 2929 cm^{-1} also increases along with the curing temperature, which also means an increase in the binding volume.

Polycarboxylic acid is capable of forming esterification with the —OH base of woolen fibers and chitosan, and triggers amidation with —NH_2 to crosslink one another.[17,18] The reaction mechanism is shown as follows:

$$R—COOH + HO—W \rightarrow R—CO \cdot O—W$$

$$R—COOH + H_2N—W \rightarrow R—CO \cdot NH—W$$

R is the main chain of polycarboxylic acid and W is the main chain of woolen fiber.

As seen in Figure 6, no noticeable esterification and amidation occurred, because citric acid and TiO_2/chi-

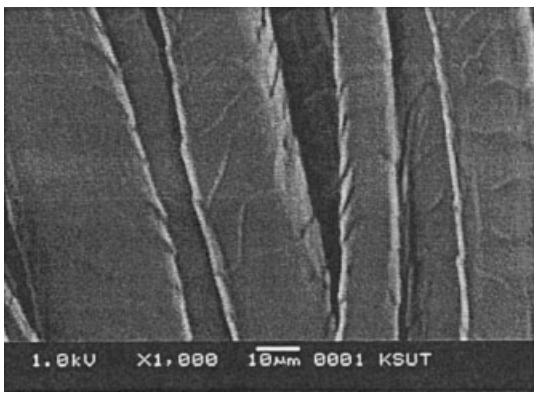

Figure 2 SEM photographs of woolen fabrics oxidized with H_2O_2 (2.5%, 50°C; ×l000).

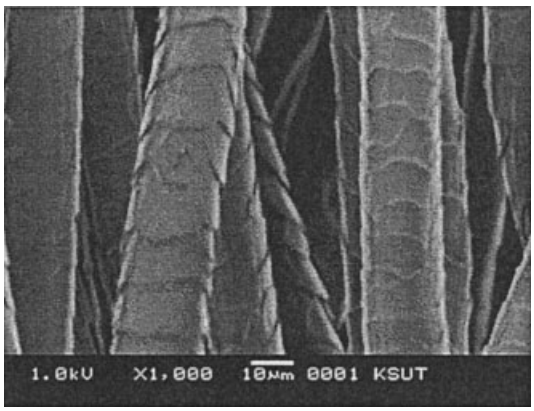

Figure 3 SEM photographs of woolen fabrics oxidized with H_2O_2 (1.5%,75°C; ×l000).

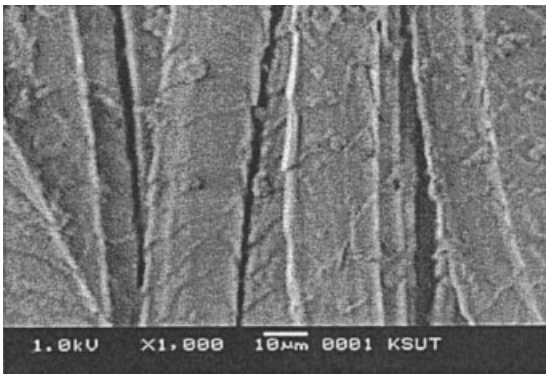

Figure 4 SEM photographs of woolen fabrics oxidized with H_2O_2 (1.5%, 50°C) and cured with citric acid (2%) and 4/0 TiO_2/chitosan solutions (×1000).

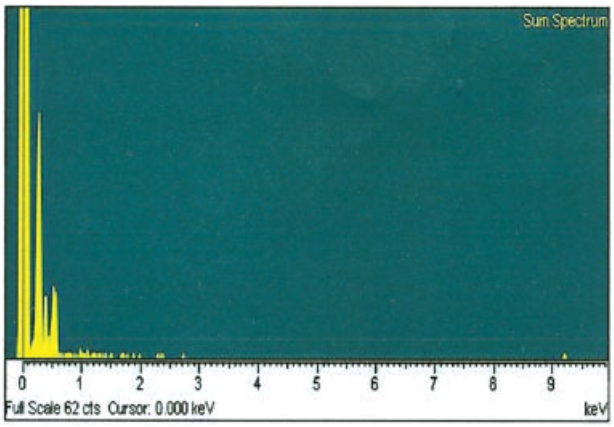

Figure 5 EDS chart of woolen fabrics oxidized with H_2O_2 (1.5%, 50°C) and cured with citric acid (2%) and 2/2 TiO_2/chitosan solutions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tosan have less crosslinking with woolen fiber. In addition, Figure 7 shows that when the concentration of TiO_2 rises to 2/2, higher concentration of chitosan (—NH_2) is formed at location 3292 cm^{-1}. Conversely, when the concentration of TiO_2 rises to 4/0, less quantity of chitosan is found at location 3285 cm^{-1}, and no noticeable esterification or amidation is detected.

Thermogravimetric analysis (TGA)

After being oxidized by H_2O_2 (1.5%, 50°C), the woolen fabrics are cured with citric Acid (2%) and TiO_2/chitosan (2/2) solutions. The relationships between various curing temperatures and TGA are shown in Figure 8, and the relationships between curing treatments with various concentrations of TiO_2/chitosan solutions and TGA are shown in Figure 9. As can be

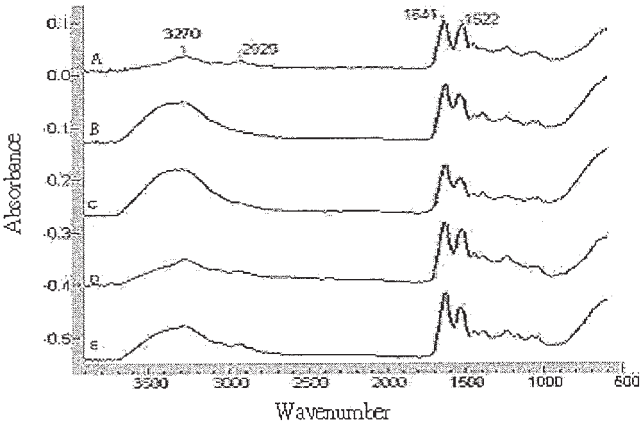

Figure 6 IR curves of different curing temperature for the woolen fabrics oxidized with H_2O_2 (1.5%, 50°C) and cured with citric acid (2%) and 2/2 TiO_2/chitosan solution (A, original fabric; B, uncured (70°C); C, l40°C; D, 155°C; and E, 170°C).

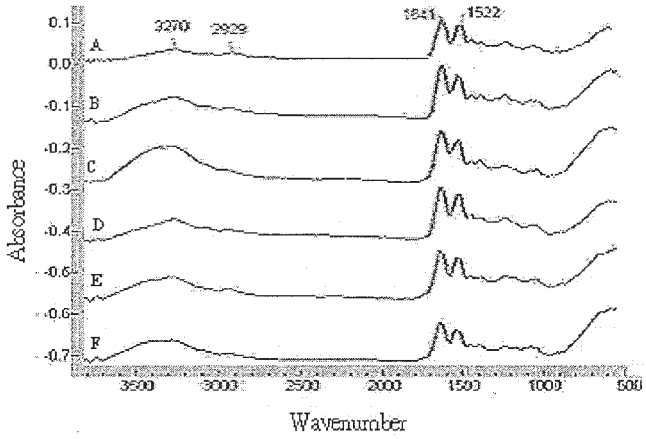

Figure 7 IR curves of different concentrations ratio of TiO_2/chitosan solutions after the woolen fabrics are oxidized with H_2O_2 (1.5%, 50°C) and cured with citric acid (2%) and various concentrations ratio of TiO_2/chitosan solutions. (A, original woolen fabrics; B, 0/4; C, 1/3; D, 2/2; E, 3/1; and F, 4/0).

seen, the untreated (blank) woolen fabric began the thermocracking reaction at ~280°C and the weight became reduced. On the other hand, woolen fabrics treated with the solutions were found to have neither delayed nor advanced thermocracking reactions. This is because citric acid and TiO_2/chitosan have less crosslinking with woolen fiber; therefore, heat has minimal effect on the treated fabrics.

Anti-bacterial analysis

According to the JAFET Antibacterial Standards, antibacterial value >2.2 indicates that the samples are bacterial repressive, and bactericide value >0 indicates that the test samples are bactericidal. From Table I, we can see that after being oxidized by H_2O_2 (1.5%, 50°C) and cured with citric Acid (2%) and various concentrations of TiO_2/chitosan solutions, the antibacterial value of the woolen fabric is less than 2.2 and the bactericide value is smaller than 0. Both indicate that the sample is neither antibacterial nor bactericidal. However, the antibacterial value tends to increase as the concentration of TiO_2/chitosan solutions increase. The postculture bacteria count (M_c), value of the woolen fabric before treatment is $2.77E + 7$, and after the samples are treated with 0/4 ratio TiO_2/chitosan solution, the bacterial count is lowered to $1.45E + 7$. Chitosan contains positive amino ions; therefore, it is capable of interfering with the negatively charged surface of the bacteria cells, thus causing the bacteria to lose protein and die. Moreover, along with the increase in TiO_2, the antibacterial value increases, indicating a moderate level of bacterial repressiveness. When the TiO_2/chitosan ratio reaches 4/0, only $2.25E + 6$ of bacterial value remains. The

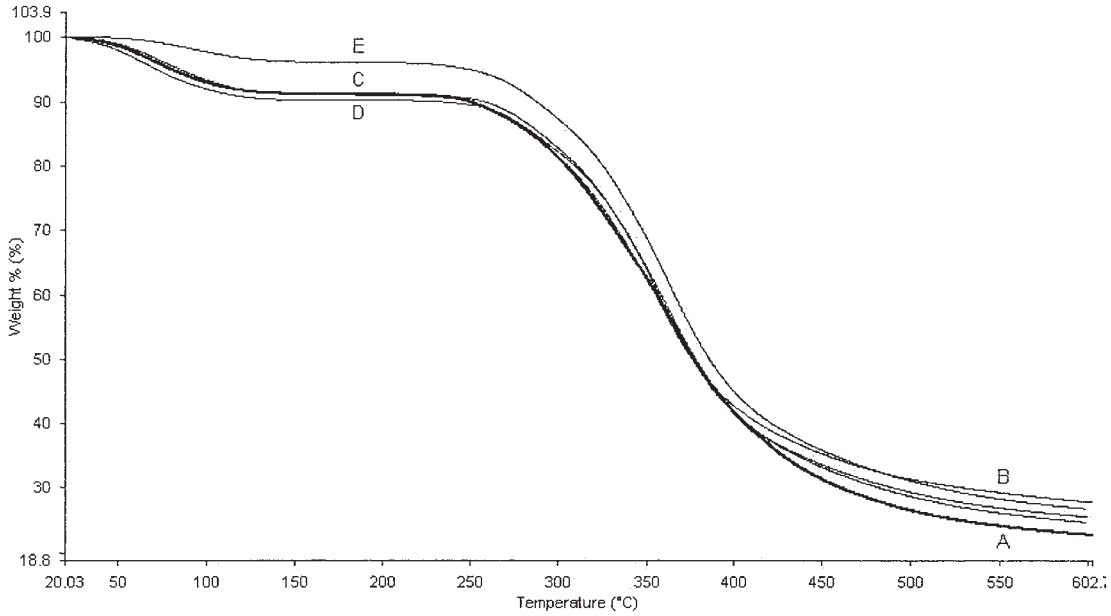

Figure 8 TGA curves of different curing temperature for the woolen fabrics oxidized with H_2O_2 (1,5%, 50°C) and cured with citric acid (2%) and 2/2 TiO_2/chitosan solution (A, original woolen fabrics; B, 70°C; C, 140°C; D, 155°C; E, 170°C).

finding reveals that TiO_2 has a large impact on the antibacterial effect; especially, when nano-TiO_2 photocatalyst is under strong sunlight, TiO_2 triggers strong oxidation reaction (free oxygen and hydrogen radicals), which penetrates directly into the membrane of the cells and causes the protein in the cells to be drawn out. In effect, oxidation of the nucleus eliminates effectively the bacteria. However, from the experiment, we see that neither chitosan nor TiO_2 has taken effect. The main causes are that a very scarce quantity of chitosan binds with the fibers of the woolen fabrics, so do TiO_2, and TiO_2 wrapped in the chitosan, thus receiving very little sunlight. From Table II, we can see that as the number of washes increases, both the antibacterial and bactericide values are less than 0, which indicates that the fabric is neither antibacterial nor

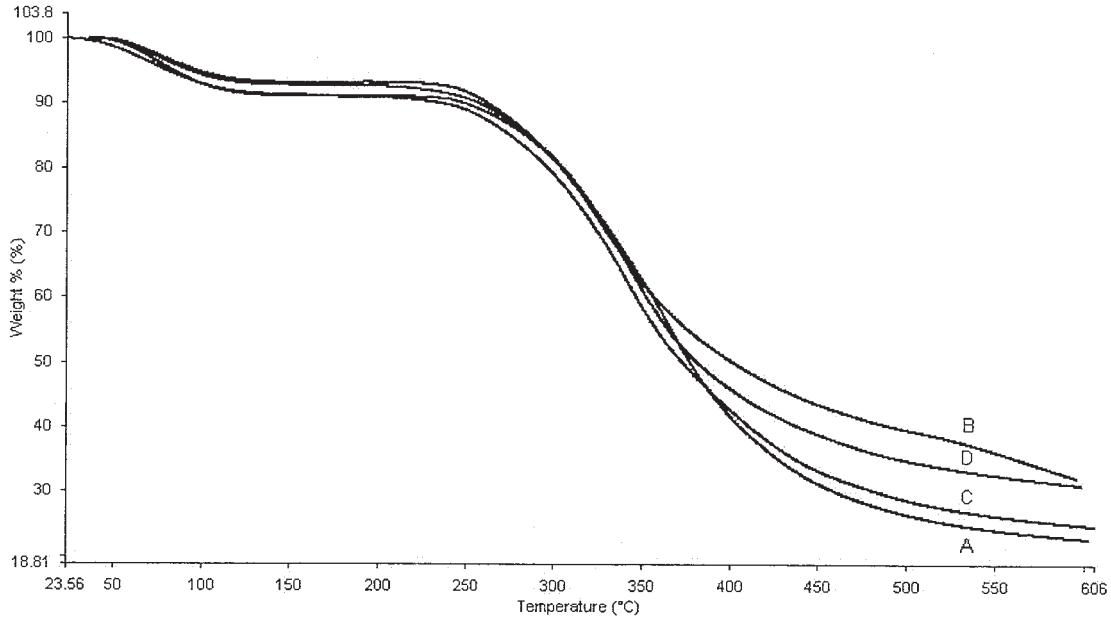

Figure 9 TGA curves of different concentrations ratio of TiO_2/chitosan solutions after the woolen fabrics are oxidized with H_2O_2 (1.5%, 50°C) and cured with citric acid (2%) and various concentrations ratio of TiO_2/chitosan solutions. (A, original woolen fabrics; B, 0/4; C, 2/2; D, 4/0).

TABLE I
The Relationships Between the Concentrations of TiO_2/Chitosan Solutions and Antibacterial Characteristics after the Woolen Fabrics Are Oxidized with H_2O_2 (1.5%, 50°C) and Cured with Citric Acid (2%) and Various Concentrations of TiO_2/Chitosan Solutions

TiO_2/chitosan	M_a	M_b	M_c	Bacterial growth activity value	Antibacterial value	Bactericide value
Test blank cloth	$2.23E+4$	$1.15E+7$[a]	—	2.71	—	—
Control	—	—	—	—	<0	<0
0/4	—	—	$1.45E+7$	—	<0	<0
1/3	—	—	$3.58E+6$	—	0.51	<0
2/2	—	—	$7.13E+6$	—	0.21	<0
3/1	—	—	$5.86E+6$	—	0.29	<0
4/0	—	—	$2.25E+6$	—	0.71	<0

Concentration of plant bacteria, $1.11\ E+5$.
[a] $E+7 = 10^7$.

bactericidal. The postculture bacteria count (M_c) increases along with the increase in the number of washes, which shows that the TiO_2/chitosan solution crosslinked on the surface of the fibers gets washed off after repeated washes, thus increasing the bacteria count.

Anti-UV analysis

Woolen fabrics, after being oxidized with H_2O_2 (1.5%, 50°C) and cured with various concentrations of TiO_2/chitosan, are then tested by a Labsphere UV Transmittance Analyzer, according to the AS/NIS 4399 standards. The results are shown in Table III. Along with the increase in TiO_2, the anti-UV effect increases. This is because metal oxidants like TiO_2 are high reflectors,[15] and under the nano size, the reflectors reflect even more ultraviolet rays.

Antishrinkage and wash-ability analysis

Owing to the scale structure of the woolen surface, woolen fabrics are prone to Directional Friction Effect (DFE), which causes the fabrics to contract. Woolen fabrics oxidized with various concentrations of H_2O_2 produce the results shown in Table IV. Higher concentration of H_2O_2 damages the scales of woolen fabrics more seriously. Therefore, the shrinkage area goes down as the concentration of H_2O_2 goes up. Woolen fabrics oxidized with H_2O_2 (1.5%) under various temperatures produce the results shown in Table IV. The higher the oxidation temperature is, the easier the scales are damaged, and therefore, the better the oxidation effects are. Furthermore, the shrinkage area is also lowered as the oxidation temperatures increase. Table IV shows that the shrinkage area of woolen fabrics, treated with various curing temperatures, increases slightly as the curing temperatures increases. Maximum increase is achieved at the point of 170°C, because after being treated at high heat, the woolen fabrics contract, which enhances the shrinkage area; therefore, the most suitable curing temperature lies between 140 and 155°C. Woolen fabrics oxidized with H_2O_2 (1.5%, 50°C) and cured with various concentrations of TiO_2/chitosan yield the results shown in Table V. As the concentration of TiO_2 increases, the shrinkage area increases, since increase in the concentration of TiO_2 means decrease in the concentration of chi-

TABLE II
The Relationships Between the Number of Washes and Antibacterial Characteristics after the Woolen Fabrics Are Oxidized with H_2O_2 (1.5%, 50°C) and Cured with Citric Acid (2%) and Various Concentrations of TiO_2/Chitosan Solutions

Wash number	TiO_2/chitosan	M_a	M_b	M_c	Bacterial growth activity value	Antibacterial value	Bactericide value
	Test blank cloth	$2.23E+4$	$1.15E+7$	—	2.71	<0	<0
1	0/4	—	—	$1.81E+6$	—	0.80	<0
	2/2	—	—	$2.19E+7$	—	<0	<0
	4/0	—	—	$1.91E+7$	—	<0	<0
3	0/4	—	—	$2.45E+7$	—	<0	<0
	2/2	—	—	$2.33E+7$	—	<0	<0
	4/0	—	—	$2.53E+7$	—	<0	<0

Concentration of plant bacteria, $1.11\ E+5$.

TABLE III
The Relationships Between the Concentrations Ratio of TiO_2/Chitosan Solutions and Anti-UV Characteristics after the Woolen Fabrics Are Oxidized with H_2O_2 (1.5%, 50°C) and Cured with Citric Acid (2%) and Various Concentrations Ratio of TiO_2/Chitosan Solutions

TiO_2/chitosan	Anti-UV index	Level of anti-UV
0/4	31	Very good
1/3	32	Very good
2/2	32	Very good
3/1	40	Fine
4/0	50	Fine

Anti-UV index of control woolen fabrics, 18 (Good).

tosan, which increases the shrinkage area. This reveals that chitosan bound with the surface of the fabrics is effective in reducing the shrinkage area. Although oxidation by H_2O_2, which damages the scales of the woolen fabrics, produces the effect of minimizing shrinkage area, it also causes esterification and induces crosslinking between the —OH of chitosan and —COOH of woolen fiber, thus enabling the chitosan to bind with the woolen fibers. In addition, the shrinkage area brought about by the aforementioned criteria is all smaller than that of untreated woolen fabrics.

Woolen fabrics, under various criteria, washed with a British-made Precision SDL-M22 launder according to the ISO 7A and ISO 5A procedures, produce the results shown in Table V. Increase in the number of washes affects the shrinkage area. More washes cause more chitosan to come off the surface of the woolen fabrics, thus increasing the shrinkage area. Nonetheless, the shrinkage areas are still lower than that of the original woolen fabrics.

Physical property analysis

Woolen fabrics oxidized with H_2O_2 and cured with citric acid (2%) and TiO2/chitosan (2/2) produce the results shown in Table IV. The strength of the fabrics appears to be lower when H_2O_2 is at the concentration rate of 2.5%, and elongation increases along with the increase in the concentration of H_2O_2. This is due to the fact that the surface scales of the woolen fabrics are damaged by the oxidation effect of H_2O_2; therefore, the strength is lowered and elongation increased. As seen in Table IV, the strength–elongation is lowered along with the increase in oxidation temperature, which heightens the activity of H_2O_2 oxidation, thus increasing the damages to the scales and lowering the strength–elongation. From Table IV, we also derive that better strength–elongation is achieved when the curing temperature reaches 140°C, and thereafter the strength–elongation goes down as the curing temperature goes up because better esterification effect is achieved at 140°C. From Table IV, we can see that better strength–elongation is achieved when the TiO_2/chitosan ratio is at 1/3, and after 2/2 the strength–elongation rate goes down. When the ratios are at 0/4 and 1/3, the solution contains less TiO_2, that is, the concentration of chitosan is higher. During curing treatment, the —COOH of the woolen fibers forms more crosslinks, thus achieving higher strength–elongation. On the other hand, when the solution concentrations are at 3/1 and 4/0, increase in TiO_2 content, that is decrease in chitosan concentration, induces less crosslinking, thus reducing the strength–elongation. From Table V, we can see that the smaller the values in the table are, the better the softness is, implying that the degree of softness decreases with increasing concentration of H_2O_2. This is because higher concentration of H_2O_2 causes more damages to the surface scales of the woolen fabrics, and more damages to the scales cause roughness on the surface. As seen in Table IV, as the oxidation temperature increases, degeneration in softness occurs because higher oxidation temperature causes more damages to the surface scales;

TABLE IV
The Relationships Between Physical Properties and the Different Oxidized Condition with H_2O_2 for Woolen Fabrics Cured with Citric Acid (2%) and 2/2 Concentrations Ratio of TiO_2/Chitosan Solutions

Oxidized condition with H_2O_2	Shrinkage area (%)	Strength (kg f/mm^2)	Elongation (%)	Softness (cm)	Yellowness (Yi)
Control	22.3	2.36	44.16	5.27	18.79
Concentrations of H_2O_2 (%)					
0.5	19.9	2.45	48.92	4.97	6.82
1.5	17.3	2.51	50.63	4.97	6.73
2.5	16.3	2.52	51.51	6.67	5.14
Oxidized temperature (°C)					
25	18.4	2.57	53.02	5.37	10.97
50	20.6	2.47	49.68	4.32	6.03
75	13.4	2.41	49.43	9.23	6.22
Curing temperature (°C)					
Uncured (70°C)	13.7	2.37	45.53	4.43	5.62
140	14.1	2.51	50.63	6.77	9.63
155	14.0	2.44	48.94	5.87	17.69
170	15.5	2.28	45.77	5.27	22.57

TABLE V
The Relationships Between Physical Properties and the Different Concentrations Ratio of TiO_2/Chitosan Solutions after the Woolen Fabrics Are Oxidized with H_2O_2 (1.5%, 50°C) and Cured with Citric Acid (2%) and Various Concentrations Ratio of TiO_2/Chitosan Solutions

TiO_2/chitosan	Wash number	Shrinkage area (%)	Strength (kg f/mm^2)	Elongation (%)	Softness (cm)	Yellowness (Yi)
Control	1	22.3	2.63	44.16	5.27	18.79
	2	29.17				
0/4	1	12.00	2.42	50.12	7.43	14.91
	2	13.70				
	3	14.60				
1/3	1	14.00	2.48	51.83	4.93	17.83
	2	16.10				
	3	18.00				
2/2	1	14.00	2.40	52.17	5.80	15.83
	2	16.10				
	3	19.30				
3/1	1	17.70	2.23	43.65	4.10	18.02
	2	19.80				
	3	22.40				
4/0	1	16.60	2.21	43.01	3.87	12.68
	2	21.80				
	3	25.30				

therefore, the fabrics are less soft. Again, from Table IV, we derive that the worst softness is produced when the curing temperature reaches 140°C, and as the curing temperature increases, the softness increases. This is because when the temperature reaches 140°C, chitosan binds better with the fibers; therefore, the surface of the fabrics appears to be hard and in turn produces less favorable softness. From Table IV, we can see that when the ratio reaches 0/4, less favorable softness is achieved, but when the TiO_2 ratio is gradually increased to 4/0, better softness is achieved. This is because when the ratio is at 0/4, the solution contains the most chitosan, which forms the most crosslinking with the fibers; therefore, the worst softness is produced. However, when the ratio is reversed at 4/0, the result is also reversed. As seen in Table IV, along with the increase in H_2O_2 concentration, the degree of yellowing increases as well, because increase in the concentration of H_2O_2 causes more damages to the surface scales of the woolen fabrics; therefore, higher degree of yellowing occurs. Table IV shows that when the oxidation temperatures are at 50 and 75°C, the degrees of yellowing are highly close and low; blank woolen fabrics are registered at 18.79%. Moreover, when the oxidation temperature reaches above 50°C, oxidation bleach effect is detected; this effectively lowers the degree of yellowing to the fabrics. From Table IV, we can also see that along with the increase in curing temperature, the degree of yellowing increases as well. This is because when the curing temperature goes up, chitosan forms crosslinking with the fibers; and when the temperature is too high, the fibers degenerate because of the heat and causes higher degree of yellowing. Table V shows that when the TiO_2/chitosan concentration ratio is at 4/0, lower degree of yellowing is detected, because when the ratio is at 4/0, the solution contains only TiO_2 (no chitosan to form crosslinks with the fibers), resulting in lower degree of yellowing. Since other ratios of the solution contain more or less chitosan and chitosan tends to form crosslinking with the fibers, the degrees of yellowing are higher.

CONCLUSIONS

Experiments on woolen fabrics oxidized with various concentrations and various oxidation temperatures with H_2O_2 and cured with citric acid and various concentrations of TiO_2/chitosan solutions produce the following results.

1. As observed under an electronic microscope, along with increases in the concentration and oxidation temperature, more surface scales of the woolen fabrics are found damaged after they are oxidized with H_2O_2. Fabrics, cured with citric acid and TiO_2/chitosan solutions, are found to have solution residues on the surface as the concentration of nano-TiO_2 increases. However, the IR analysis did not detect noticeable crosslinking reactions.
2. Different curing temperatures and different concentrations of TiO_2/chitosan solutions yield no heat effects on the woolen fabrics; results of their heat-cracking effect are similar to that of the blank samples.
3. Woolen fabrics oxidized with H_2O_2 and cured with citric acid and TiO_2/chitosan solutions

show increases in the anti-UV indexes as the concentration of TiO_2 increases.

4. Woolen fabrics oxidized with H_2O_2 show a decline in the shrinkage area with increase in the oxidation concentration and oxidation temperature. However, as the curing temperature increases, the shrinkage area increases as well. The fabrics cured with TiO_2/chitosan solutions are found to have increase in their shrinkage area when the concentration of TiO_2 increases. The shrinkage area is also found to increase after repeated washes, but the rates are all lower than that of the original fabrics.
5. Nano-TiO_2/chitosan solutions produce neither antibacterial nor bactericidal effects.
6. The strength goes down as the concentration of H_2O_2 increases, but the elongation rate appears to be otherwise. Strength–elongation rate declines as the oxidation temperature rises. Higher strength–elongation is achieved when the concentration of TiO_2/chitosan is at the ratio of 1/3, but lower rates are recorded after the concentration reaches above 2/2. Better strength–elongation rate is achieved when the curing temperature is at 140°C and the rate goes down as the temperature of curing treatment goes up.
7. Softness declines with increasing concentration of H_2O_2 and oxidation temperature, and less favorable softness is produced when the curing temperature reaches 140°C. Along with the increase in curing temperature, softness improves. When the TiO_2/chitosan ratio is at 0/4, less favorable softness is produced, but when the TiO_2 ratio is increased to 4/0, better softness is achieved.
8. The degree of yellowing increases as the concentration of H_2O_2 and curing temperature increase, when the TiO_2/chitosan ratio is at 4/0, less yellowing occurs, while other ratios produce higher degrees of yellowing.

References

1. Mark, H.; Wooding, N. S.; Wiley, S. M. Chemical Aftertreatment of Textiles; Wiley: New York, 1971; p 520.
2. Jocic, P. D.; Molina, R.; Julia, M. R.; Erra, P. Textile Res J 2001, 71, 948.
3. Pascual, E.; Julia, M. R. J Biotechnol 2001, 89, 289.
4. Kim, Y.-H.; Choi, H.-M.; Yoon, J.-L. Textile Res J 1998, 68, 428.
5. Davidson, R. S.; Xue, Y. J Soc Dyers Colour 1994, 110, 24.
6. Jocic, P. D.; Julia, M. R.; Erra, P. J Soc Dyers Colour 1997, 113, 25.
7. Erra, P.; Molina, R.; Jocic, P. D.; Julia, M. R. Textile Res J 1999, 69, 811.
8. Julia, M. R.; Pascual, E.; Erra, P. J Soc Dyers Colour 2000, 116, 62.
9. Masri, M. S.; Randall, V. G.; Pittman, A. G. Conference on Chitin and Chitosan; MIT Press: Cambridge, MA, 1978; p 306.
10. Yang, C. Q.; Wang, X. Texile Res J 1996, 66, 595.
11. Martel, B.; Weltrowski, M.; Ruffin, D.; Morcellet, M. J Appl Polym Sci 2002, 83, 1449.
12. Stamataskis, P.; Palmer, B. R. J Coat Technol 1990, 62, 95.
13. Dmitriuk, A. V.; Soloveva, N. D.; Timofeev, N. T. Glass Phys Chem 1993, 19, 33.
14. Jeong, Y. J.; Cha, S. Y.; Yu, W. R.; Park, W. H. Textile Res J 2002, 72, 70.
15. Choisnard, L.; Bigan, M.; Deau, D. B.; Dhulster, P.; Leman, B.; Guillochon, D. J Appl Polym Sci 2003, 89, 535.
16. Freddi, G.; Innocenti, R.; Arai, T.; Shiozaki, H.; Tsukada, M. J Appl Polym Sci 2003, 89, 1390.
17. Church, J. S.; Corino, G. L.; Woodhead, A. L. Biopolymer 1997, 42, 7.
18. Wojciechowska, E.; Wlochowicz, A.; Weselucha-Birczynska, A. J Mol Struct 1999 ,511/512, 307.