

Multifunctional Processing of Cotton Fabrics with Citric Acid and TiO₂/Chitosan Treatment

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Abstract

Cotton fabrics were heat treated with different concentrations of nano-grade TiO₂ and chitosan processing solution, and analyzed using Fourier Transform Infrared Spectroscopy (FTIR), energy dispersive spectroscopy (EDS), thermogravimetry analysis (TGA) and scanning electron microscopy (SEM). Anti-bacterial, anti-UV and anti-wrinkle properties have also been investigated. FTIR analysis showed that there were a few ester crosslinkages for the –OH residues of chitosan and fibers with the –COOH group of citric acid. However, the EDS analysis indicated the existence of Titanium element on the processed items. The observed increase in the weight ratio and atom content ratio of carbon and oxygen atoms suggested that the processing solution is attached to the cotton fabrics. The SEM observation further confirmed the attachment of TiO₂/Chitosan processing solution on the cotton fabrics. Unprocessed cotton fabrics pyrolyses approximately at 350°C, and after processing, the temperature decreased to 300°C. All processed cotton fabrics possess excellent anti-bacterial and bactericidal effects with an exception for the 4/0 ratio processed fabrics. The anti-UV property of processed cotton fabrics was higher than that without processing, but the entire anti-UV grade was poor; only the processed fabrics with 4/0 ratio yielded the best anti-UV effect. The dry anti-wrinkle angle increased upon increasing the TiO₂ ratio in which the processed fabrics with 3/1 and 4/0 ratios possessed the highest dry anti-wrinkle angle. The wet anti-wrinkle angle, however, increased while increasing the chitosan ratio. The angle of all processed fabrics was higher than that of unprocessed fabrics. Following the rise in curing temperature, the wet anti-wrinkle angle of processed fabrics although tended to increase, it was still lower than that of unprocessed fabrics. The curing temperature did not affect wet the anti-wrinkle angle, but the angle of all processed fabrics was higher than that of unprocessed fabrics.

Keywords: chitosan, anti-bacterial, esterification, FTIR

INTRODUCTION

Although cotton is one of the most popular textiles, it is easy to crumple and shrink with poor rigidity. The traditional way to process non-iron and anti-wrinkle cotton fabrics is using formaldehyde resins to form etherifying crosslinkage. Although the processing can lead to an excellent anti-wrinkle effect, during the heat treatment process, the carcinogenic formaldehyde chemical can be released to harm human health and the environment. To solve this problem, several studies have been carried out in the past few years on non-formaldehyde and polycarboxylic acid, expecting to replace the traditional formaldehyde resin processing¹⁻⁴. Yany applied FTIR to study the esterification between polycarboxylic acid and cotton fibers, and confirmed the formation of five-membered

anhydride intermediates from polycarboxylic acid with sodium hypophosphite (NaHPO₂·H₂O) catalyst. Following the acid anhydride formation, the intermediate esterifies with fiber –OH residues to form a cotton fiber crosslinkage to obtain anti-wrinkle property⁵⁻¹⁵.

In recent years, Nano-TiO₂ has been widely used as a photo-catalyst; it has a strong oxidation activity under sunlight (to oxidize free radicals) that can directly penetrate bacterial cell membrane to drain away the cytoplasm, and further oxidize the nucleus to kill bacteria.¹⁶⁻¹⁷ Titania (TiO₂) is an emerging environment-friendly product, which has the future potential to create a cleaner, more comfortable and high-quality living environment.

Chitin is a nitrogen-containing polysaccharide macromolecule that is widespread in nature. Chitosan is a polysaccharide formed from the polymerization of glucosamine molecules that can be obtained from chitin deacetylation. Chitosan, a cationic macromolecule, has anti-bacterial effect, an addition of which can confer anti-bacterial effect to fibers. Chung and other scholars used citric acid as a crosslinking reagent to study the anti-wrinkle, dyeability and anti-bacterial properties on cotton fibers with the addition of chitosan¹⁸⁻²³. A thorough study on the cotton fabrics has rarely been carried out on the basis of photo-catalyst application with a combination of polycarboxylic acid and Chitosan. Therefore, in this study, the processing of cotton fabrics in the solution containing nano-grade TiO₂, chitosan and citric acid has been investigated under different processing conditions.

EXPERIMENTAL

Materials

Cotton fabrics with warp density of 144, weft density of 72, warp yarn count of 32 and weft yarn count of 34 were used in this research. Chitosan of 95% deacetylation and citric acid (CA) were purchased from OHKA Enterprises Co., Ltd and Shimakyu Food Tech. Inc. in Japan. The nano-grade TiO₂ (20%) was a product of Nano-Technology Development Co., Ltd in China. Other chemicals such as acetic acid, sodium hydroxide, alcohol, and sodium hypophosphite were research-grade chemicals.

Measurements

Chitosan (1%) was dissolved in 3% acetic acid and 2% citric acid was dissolved in the solution of 30% ethanol and 70% water, to which, 2.1% sodium hypophosphite (SHP:CA molar ratio 1:1) was added. The chitosan solution was first mixed with nano-grade TiO₂, and added to citric acid solution and stirred (liquid ratio = 20:1). The ratio of nano-grade TiO₂ and chitosan concentration was 0/4, 1/3, 2/2, 3/1, and 4/0.

The bleached cotton fabrics were pressed and absorbed with the processing solution using a Rapid Labortex (Taiwan) tenter machine, and pre-processed at 70°C for 5 minutes, followed by curing treatment at

different temperatures, 140°C , 155°C and 170°C , each for 2 minutes. The fabrics were then rinsed in water for 5 minute, soaked in 0.1M NaOH solution for 2 minutes, and rinsed in water again before heat drying at 75°C for 5 minutes.

The processed items were analyzed by an FTIR spectrometer with ATR capabilities (Bio-Rad Digilab UMA400). The chemical composition was carried out using an energy dispersive spectrometer (EDS) in a field emission electron microscope (JSM 6700, Japan). Scanning electronic microscope (SEM, Joel 5610) was used to observe the surface of the cotton fabrics, which were processed in different concentrations of TiO₂/chitosan processing solution at different temperatures. The thermal weight loss of cotton fabrics was examined by a thermo-gravity analyzer (TGA, Dupont 2200) in the range of 20°C ~600°C (20°C /min step). The anti-bacterial experiment was carried out according to the JIS1902-1998 test method of the Japanese Association of Function Evaluation of Textiles (JAFET). The anti-bacterial effects of processed fabrics against *Staphylococcus aureus* have been investigated, and a test sample showing anti-bacterial value > 2.2 is considered to be bacteriostatic whereas that of value > 0 is considered to be bactericidal. The processed items were tested for anti-UV effects using Labsphere UV Transmittance Analyzer (Appendix A-1996) following AS/NIS 4399.

To test the anti-wrinkle property, ASTM D1295-67 method and Monsanto wrinkle restoration test were employed. The size of test fabrics was 1.5cm*4.0cm. The measurement of dry wrinkle restoration angle (DWRA) was conducted horizontally and vertically for five times each to get an average value for each warp and filling so the restoration angle is shown in (W+F)° (W: Warp; F: Filling). The measurement of wet wrinkle restoration angle (WWRA) started with soaking the processed fabrics (1.5cm*4.0cm), five pieces for warp and filling each, in 0.2% sodium carbonate solution at 40°C for 15 minutes, followed by rinsing with water and pat on filter papers to remove an excess of water. Finally, the fabrics were measured by Monsanto method.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR results are shown in Figure 1 and Figure 2. From Figure 1(A), the absorption band at 3337cm⁻¹, 2895 cm⁻¹, and 1153cm⁻¹, respectively, indicated the vibrations of -OH, C-H, and -C-O-C- bonds. Absorptions at 1100cm⁻¹ and 1028 cm⁻¹ are the vibrations of -COH bond. There were a few carboxylate carbonyl bands around 1580 cm⁻¹ suggesting that CA was not esterified with Cell-OH in different concentration ratios of TiO₂/Chitosan and at different curing temperatures. Citric acid before esterification with Cell-OH should form a five-ring anhydride intermediate⁵⁻⁸ that can bond with the -OH residue of chitosan. Moreover, TiO₂ is a hydrophilic oxide that can form chelating compounds with the -OH residue of chitosan or -COOH group of CA reducing the chances of esterification between the -OH group of cellulose and -COOH group of CA. CA have three functional groups that once the central -COOH (α -OH, 2-OH) gets esterified, it is unable to form the five-ring anhydride intermediate and thus loses its activity. CA can bond with two Cell-OH molecules only

when the terminal -COOH is esterified. These explains why carboxylate carbonyl band was a few shown on IR diagram, but the TiO₂/Chitosan processing solution diffuse into molecule structure on fabrics.

EDS Analysis

From Figure 3 and Table 1, the energy position for the atoms, carbon, oxygen, and titanium were found at 0.2774, 0.5249, and 0.4522 respectively. As shown in the diagram, titanium is located at the position 0.4522 suggesting its presence on the processed items. The weight ratio and atom content ratio of carbon and oxygen were increased after processing. This indicates that the processing solution adhered on to the cotton fabrics. From the previously described IR data, whether an esterification proceeded could not be confirmed. This may be due to the enlargement of textile apertures at high-temperature treatment . This allows some of the TiO₂/Chitosan processing solutions on the fabric surface to diffuse into molecular structure. In Figure 3 and Table 1, chitosan nitrogen was not detected probably because it was a trace component that could not be detected, or it existed outside the range of measurement on the cotton fabrics. The existence of platinum (Pt) was due to the remaining of sample gilding.

SEM Observation

As shown in Figure 4, after processing, TiO₂/Chitosan was confirmed to distribute in spot form on the cotton fabrics, which were processed in 2/2 ratio of TiO₂/Chitosan solution at 155°C . The IR spectrum described previously does not show any esterification. This should be the outcome when TiO₂/Chitosan adheres to the fabric surface after processing, the textile apertures become larger during the high curing temperature, allowing TiO₂/Chitosan processing solution to penetrate to the apertures easily. This point is proved in the following experiments.

TGA Analysis

The TGA results of cotton fabrics which were processed in citric acid (2%) and different concentrations of processing solution, and heat treated under different curing temperatures are shown in Figures 5 and 6. The unprocessed cotton fabrics began to pyrolyze at 350°C and at the same time, the weight began to decrease. After processing, the cotton fabrics pyrolyzed approximately at 300°C . The pyrolysis of processed cotton fabrics was advanced during high-temperature treatment because TiO₂/Chitosan processing solution had very few crosslinking bonds with cotton fabrics resulting in little heat impact. As shown in figure 6, while curing temperature increases, the pyrolysis temperature decreases. After pyrolysis, the remaining weight of all processed items is higher than that of cotton fabrics because the processed items contain a small amount of titanium.

Anti-Bacterial Property Analysis

From Table 2 showed that all displayed excellent anti-bacterial and bactericidal effects. The fabrics processed in 4/0 ratio possess the poorest anti-bacterial property, indicating that pure chitosan (in 0/4 ratio) is more anti-bacterial as compared to pure titania. Chitosan contains amine groups, which are positive under acidic conditions. This allows it to be anti-bacterial. The 4/0 processed fabrics did not show any bactericidal property because TiO₂ could not elaborate the oxidation function, so that the fabrics only have anti-bacterial effects but

have no bactericidal effects.

Ultraviolet Protection Analysis

The data in Table 3 showed that it had a higher ultraviolet protection factor than blank cotton fabrics because the metal oxides such as TiO₂ have a higher refractive index, and nano-graded metal oxides can reflect ultraviolet light more easily. The fabrics processed in different ratios of TiO₂/Chitosan showed a similar ultraviolet protection effect. The fabrics processed in 4/0 ratio showed the best ultraviolet protection property because the processing solution did not contain chitosan leading to the diffusion of some TiO₂ into the fabric and it could reflect ultraviolet light more easily.

Anti-Wrinkle Property Analysis

The anti-wrinkle property analysis of cotton fabrics, which were processed in different concentrations of TiO₂/Chitosan processing solution and cured at different temperatures, was carried out and the results are shown in Table 4. The dry wrinkle restoration angle increased along with the increase in TiO₂ ratio in which the processed fabrics with the 3/1 and 4/0 ratios had a larger dry wrinkle restoration angle compared to the unprocessed fabrics. To explain this, the -OH residue of chitosan did not esterify with the -COOH group of CA to form crosslinking bonds that was useless to anti-wrinkle property of processed items. Contrarily, the increase in the TiO₂ ratio enhanced the dry wrinkle restoration angle. This resulted in that the processed fabrics with 3/1 and 4/0 ratios had a larger dry wrinkle restoration angle, compared to the unprocessed fabrics. The wet wrinkle restoration angle, however, increased while chitosan ratio was increased. As compared to original fabrics, all processed fabrics had a larger wet wrinkle restoration angle. Although only a few chitosan molecules were bound to cotton fabrics, as chitosan ratio increased to diffuse into the fiber apertures, the amount of chitosan bound more or less increased. The tensile strength of wet cotton fabrics is stronger than that of dried fabrics, and hydrogen bonding was formed. These are beneficial to wet wrinkle restoration angle. While the curing temperature was increased, though dry wrinkle restoration angle tended to increase, it was still lower than that of original fabrics or even lower than the pre-heat temperature 70°C. The reason is the same as that described previously. Esterification did not proceed so the rise of curing temperature was not beneficial to dry wrinkle restoration angle as well as to wet wrinkle restoration angle. It was due to the fact that wet fabrics have stronger tensile strengths that together with the formation of hydrogen bonding are advantageous to wet wrinkle restoration angle compared to original fabrics.

CONCLUSIONS

Cotton fabrics after processed in different concentrations of TiO₂/Chitosan processing solution and cured at different temperatures were tested and the following conclusions have been drawn.

1. As suggested by the FTIR analysis, only a few ester crosslinkages were formed for the -OH residue of chitosan and cellulose with the -COOH group of citric acid. However, EDS analysis revealed the existence of titanium on processed items, and the weight ratio and element content of carbon and oxygen were both increased. Therefore, it can be concluded that the processing solution was attached to cotton fabrics.
2. SEM further indicated that TiO₂/Chitosan adhered to

the surface of cotton fabrics after processing.

3. From the physical analysis that the best processing conditions to obtain the optimal anti-wrinkle, UV-protection and bactericidal properties was in 3/1 ratios of TiO₂/Chitosan.

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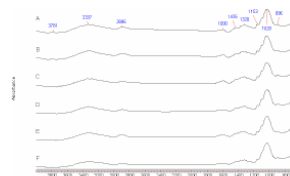


Figure 1 The IR spectra of cotton fabric cured with different concentration ratios of TiO₂/Chitosan processed solution. (A:Control, B:0/4, C:1/3, D:2/2, E:3/1, F:4/0)

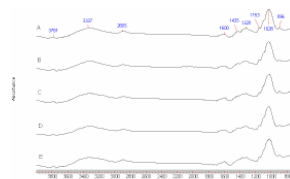


Figure 2 The IR spectra of cotton fabric treated with TiO₂/Chitosan processed solution of concentration ratio (2/2) and cured at different temperatures. (A: Control, B: 70°C, C:140°C, D:155°C, E:170°C)

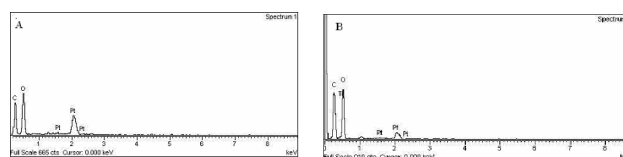


Figure 3 The EDS charts of processed cotton fabric. (A: Control, B: (2/2)TiO₂/Chitosan)

Table 1 The EDS analysis of cotton fabric cured with (2/2)TiO₂/Chitosan processed solution of concentration ratio.

Cotton			Cotton + TiO ₂ /Chitosan (2/2)		
Element	Weight %	Atomic %	Element	Weight %	Atomic %
C	26.13	48.23	C	36.10	48.86
O	37.28	48.09	O	48.92	49.72
Ti	--	--	Ti	0.66	0.22
Pt	34.59	3.68	Pt	14.32	1.19
Totals	100		Totals	100	

Table 2 Bacterial resistance of cotton fabric cured with different concentration ratios of TiO₂/Chitosan processed solution.

TiO ₂ /Chitosan	Ma	Mb	Mc	Bacterial growth activity value	Antibacterial value	Bactericide value
Test blank cloth	1.5×10^4	9.3×10^6	--	2.8	--	--
Control	--	--	2.3×10^3	--	<0	<0
0/4	--	--	1.0×10^2	--	5.0	2.2
1/3	--	--	5.4×10^2	--	4.2	1.4
2/2	--	--	3.3×10^1	--	5.4	2.6
3/1	--	--	2.3×10^2	--	4.6	1.8
4/0	--	--	2.3×10^4	--	2.6	<0

Concentration of plant bacteria: 0.7×10^5

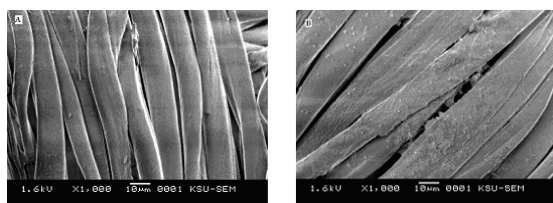


Figure 4 The SEM photographs of processed cotton fabric (1000 folds). (A: Control, B: (2/2)TiO₂/Chitosan)

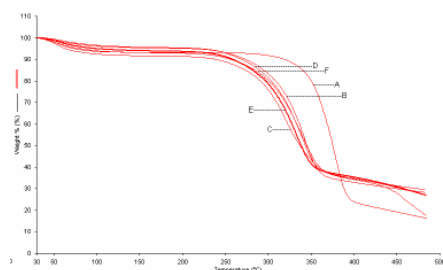


Figure 5 The TGA spectra of cotton fabric cured with different concentration ratios of TiO₂/Chitosan processed solution. (A: Control, B:0/4, C:1/3, D:2/2, E:3/1, F:4/0)

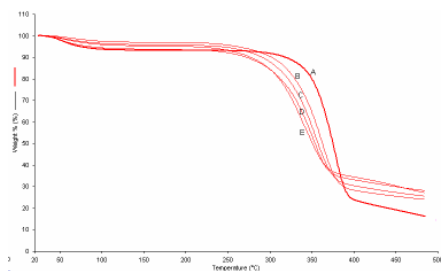


Figure 6 The TGA spectra of cotton fabric cured with TiO₂/Chitosan processed solution of concentration ratio (2/2) and cured at different temperatures. (A: Control, B:70°C, C:140°C, D:155°C, E:170°C)

Table. 3 UV resistance of cotton fabric cured with different concentration ratios of TiO₂/Chitosan processed solution.

TiO ₂ /Chitosan	Anti-UV Index	Level of Anti-UV
Control	11	General
0/4	18	Good
1/3	18	Good
2/2	16	Good
3/1	15	Good
4/0	30	Very good

Table 4 Anti-wrinkle properties of cotton fabric cured with different concentration ratios of TiO₂/Chitosan processed solution and cured at different temperatures.

Processing conditions		Anti-wrinkle angle	
		Dry (W+F) ⁰	Wet (W+F) ⁰
TiO ₂ /Chitosan (%)	Control	178.0	165.4
	0/4	100.0	216.0
	1/3	119.4	207.2
	2/2	154.0	208.0
	3/1	184.2	206.0
	4/0	200.2	173.0
Curing temperatures (°C)	70 (pre-heat)	164.4	182.2
	140	132.0	204.2
	155	133.0	208.0
	170	149.2	202.0