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Effects of low-molecular-weight chitosan on wool fabric

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ABSTRACT

This study was designed to examine the effect from dyeing wool fabrics when they are first treated with low-molecular-weight chitosan (LWCS). First, we created LWCS from chitosan using different concentrations of hydrogen peroxide, and then we analyzed its properties. The molecular weight and the viscosity of LWCS decreased with increased concentrations of hydrogen peroxide. Next we examined the effect that treatment with LWCS had on the wool fabrics. The shrink-resistance and antibacterial properties of dyed fabrics as well as the color intensity (K/S) were inversely proportional to the LWCS molecular weight and directly proportional to the LWCS concentration. However, the K/S of the treated fabrics peaked when the LWCS concentration reached 4%. Treating fabrics with LWCS before dyeing had a positive effect on dyeing, shrinkage, and antibacterial wash fastness measured after 20 washes.

KEYWORDS

Chitosan;
Degradation;
Wool fabric;
Dyeability;
Shrinkage.

INTRODUCTION

Chitosan is a naturally occurring polymer in chitin with more than 55% deacetylation. Chitosan that is less than 20% polymerized is an oligosaccharide. It has a relatively large molecular mass, usually on the order of tens of thousands or even millions. It has intermolecular and intramolecular hydrogen bonds that lead to stable chemical properties and a low solubility. For example, chitosan is soluble in only a few types of diluted acid solution, and is insoluble in water, which limits its application. Many specialists in the textile industry have reported that chitosan can improve the dye-affinity of wool and silk fabrics by enhancing the rate of dye uptake, leveling, and dye intensity[1-3].

Low-molecular-weight chitosan (LWCS) is soluble in water and highly permeable. Compared to the chitosan polymer, it has other advantages such as resistance to microorganisms, absorption of anionic dye, inhibition of tumor growth, and reduction of cholesterol and blood lipids[4]. This area of study has attracted considerable interest.

Current methods used for the preparation of LWCS include degradation by acid[5-7], yeast, and oxidization, as well as irradiation, microwaves, and ultrasonic waves. Oxidization degradation is the method most studied in recent years. It is a rapid, low-cost, and simple process with no toxic residues. The primary reagents used include hydrogen peroxide[8-10] and nitride[11], with the former being the most common.

Wool fabrics are quite unstable and tend to shrink or crimp easily, and they lose their original shape after

washing and heating. This means that wool fabric items must usually be dry-cleaned, or carefully hand-washed with special detergent. Wool is composed of protein fibers, small pieces of which may break from time to time. These numerous small loose segments mix easily with human sweat to provide an ideal culture medium for the growth of bacteria and molds. If this happens, the fabric can easily be affected by all kinds of microorganisms such as bacteria and mildew that may spread disease and cause the fabric to deteriorate, with discoloration, disintegration, and unpleasant smells. Therefore, the shrink-resistance and antibacterial properties are two very important considerations for wool garments.

In a study on the application of chitin and its derivatives to the antimicrobial finishing of wool and silk fabrics, Takeshi reported that these compounds provide very strong antibacterial protection against *Staphylococcus aureus* in wool and *Escherichia coli* in silk[12]. Erra et al. used chitosan in a finishing process for wool fabrics pretreated with plasma, and discovered that this method added shrink-resistance to the fabrics, and was remarkably helpful in ameliorating the biological problems[13]. Other studies have reported that soaking wool in a 2-5%(w/v) chitosan solution followed by heat-treating makes the fabric shrink-resistant[14].

This aim of this study was to study the effect of LWCS treatment on the dyeability, antibacterial properties, and the shrink-resistance of wool fabrics.

EXPERIMENTAL

1. Materials

Ethanol, hydrochloric acid, and hydrogen peroxide were purchased from Shimaku Medicine, Ltd. Chitosan(85% deacetylation) was obtained from Taiwan Kaohsiung Applied Chemistry Co., Ltd. Sodium lauryl sulfate and acetic acid were supplied by Shimahisashi Pharmaceutical. All were reagent grade. The wool fabrics used as test products were pretreated by the washing and grabbing process. They were supplied by Shun Fu Yai Industrial Co., Ltd.[$48N_w \times 48N_w$, ends(52) and picks(44); 66-inch width]. Anioinic surfactant Penetrating AC supplied by Tai Chieh Co., Ltd. was used as a nonionic surfactant. The C.I. Acid Red 337 dye was provided by Everlight Chemical Industrial Corp., and the Inlev NIA New leveling agent was provided by Jintex Corp.

2. Methods

Preparation of LWCS

Two grams of chitosan were dissolved in 100mL of 0.1M HCl, stirred for 30min, and added to a 5%, 10%, or 15%(v/v) solution of hydrogen peroxide(H_2O_2). The mixture was stirred for 4h at 50^0C and vacuum-filtered. The upper residue was rinsed to neutral with distilled water, and then baked and weighed. Ethanol was added to the lower solution, left for 24 h to precipitate, and then filtered, dried, and weighed. This produced low-molecular-weight, water-soluble chitosan, which we refer to as C5, C10, and C15, corresponding to the 5%, 10%, and 15% concentrations, respectively, of H_2O_2 used in the process.

Application of LWC

We mixed weights of 0.5g, 1g, 2g, 4g, 6g, and 8g of C5, C10, and C15 LWCS with distilled water in different concentrations in the range 0.5-8% to prepare a finishing solution. We added 1 g/L penetrating AC and stirred for 30 min. The woolen fabrics were impregnated with the finishing solution for 10min at room temperature. This was followed by squeezing to a wet pickup of 85%, pinning on a frame without tension, drying at 80^0C for 5min, and then curing at 100^0C for 2min. The samples were bagged at ambient conditions after curing.

Dyeing of pretreated fabrics

Take the acid dye of 3% on weight of fiber, join the leveling agent of 1g/L, liquor ratio is 1:20, the acetic acid will adjust the pH of the liquid dye to about 4.5, then will prepare puts into the steel bottle of dyeing machine over its wool fabrics, dyed at 90^0C for 45min, then washed and dried, finally bagging, need to be measured related property.

Analysis and measurement

We recorded Fourier transform infrared attenuated total reflection mode (FT-IR/ATR) spectra of the LWCS with a Bio-Rad Digilab FTS-200 spectrometer and a mercury-cadmium-telluride(MCT) detector. A diamond crystal was used as the internal reflectance element.

Single beam spectra were the result of 64 scans and the spectral resolution was 4cm^{-1}. Detection of the LWCS ^{1}H-NMR chemical shift was tested using a Bruker AMX-400 L-NMR analyzer. A Bruker-AXS D8 was used for X-ray powder diffraction, with parallel beam optics, a Cu-target scintillation counter, and sampler changer with rotation. The samples were run with a 40kV, 100mA, 2-60^{0}C theta/2 theta, 0.01^{0}C step size and a counting time of 5s. Viscosity of the LWCS was measured at 25^{0}C using a Wurtz viscometer based on a 1g/L sample in a 0.1M acetic acid, 0.2M NaCl solution. The molecular weight was calculated using the Mark-Houwink equation, $[\eta]=K[Mv]\alpha$, with $K=1.81\times10^{-3}$cm^3/g and $\alpha=0.93$[1]. Element analysis of LWCS was performed on an Elementar Vario EL analyzer. The K/S of the treated fabrics was measured with a Nippon ND 300A color-difference meter. The treated fabrics were tested for their shrink-resistance properties using the AATCC TM 187-2001 method described in TABLE 1.

The antibacterial properties of the samples were tested using the Japanese Association for the Functional Evaluation of Textiles (JAFET) method JIS1902-1998. The following equations were used to calculate the bacterial growth and bacteriostatic and bactericidal values:

$$\text{Bacterial growth (F)} = \log (M_b/M_a) \quad (1)$$

An F value >1.5 would indicate statistical significance.

$$\text{Bacteriostatic value (S)} = \log (M_b/M_c) \quad (2)$$

An S value >2.2 would suggest that the sample has a bacteriostatic effect.

$$\text{Bactericidal value (L)} = \log (M_a/M_c) \quad (3)$$

An L value >0 would suggest that the sample has a bactericidal effect. M_a is the bacterial number in the sample of a non-treated fabric immediately after rinsing. M_b is the bacterial number in the sample of a non-treated fabric after culturing for 18-24h. M_c is the bacterial number in the sample of the treated fabric after culturing for 18-24h.

Investigations on the leaching behavior were performed at 40^{0}C using a Rapid H-type dyeing machine. A 1% aqueous solution of sodium lauryl sulfate SDS with a pH of 7 was used as a washing solution. After leaching for 20min, the textile samples were thoroughly rinsed with water, and then dried at room temperature. The physical properties investigated again after 20 wash cycles.

TABLE 1: Accelerated machine program settings[1]

Program operation	Number of cycles	Time per cycle, s	Temperature, °C
Wash	1		60
Agitation time		165	
Rinse/dry			60
Agitation time		45	
Spin time		35	
Dry time		240	

[1]The air pressure was 3.8 bars, and the water level was 3L.

TABLE 2: Molecular weight, viscosity and element analysis of LWCS

Sample	H_2O_2 (ml)	Elemental composition(%)				η(ml/g)	Mv
		N	C	H	O		
Chitosan		7.40	39.06	6.22	47.32	293.474	240,500
C5	5.0	6.39	37.56	7.01	49.02	64.628	77,210
C7.5	7.5	6.36	36.95	6.98	49.71	34.944	40,100
C10	10.0	6.35	36.83	6.94	49.88	14.081	15,090
C12.5	12.5	6.33	36.93	6.90	49.94	8.455	8,720
C15	15.0	5.92	35.77	6.59	51.72	7.762	3,650

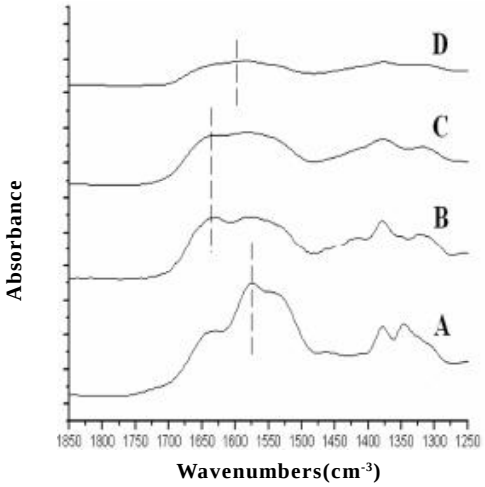


Figure 1: FT-IR of chitosan and LWCS (a) chitosan (C0), (b) C5, (c) C10, (d) C15

RESULTS AND DISCUSSION

Elemental analysis and measurement of viscosity and molecular weight

As TABLE 2 shows, the molecular weight and viscosity of chitosan decreased as more H_2O_2 was used. This was due to the degradation of the chitosan molecular chain, which caused the -OH and -NH_2 groups to be oxidized into -COOH groups. As the H_2O_2 increased, the nitrogen content of the LWCS decreased and oxygen content increased. The carbon and hydrogen contents did not show a significant change, except

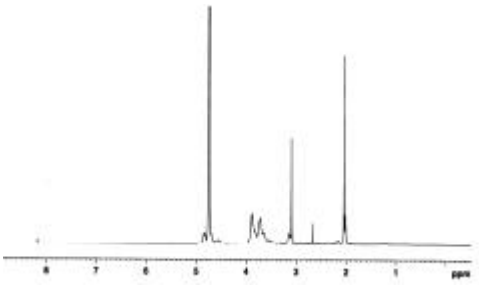


Figure 2: ^{1}H-NMR of LWCS (C15)

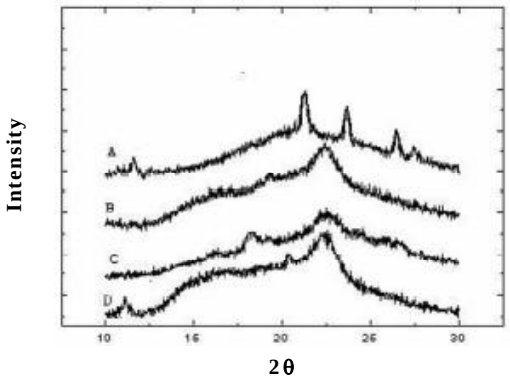


Figure 3: X-ray of chitosan and LWCS (a) chitosan (C0), (b) C15, (c) C10, (d) C5

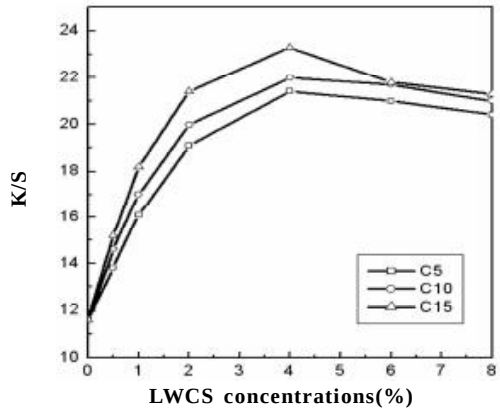
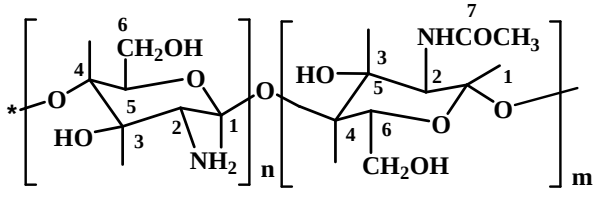


Figure 4: Effect of LWCS concentration on the K/S of the treated fabrics. The K/S of pretreated fabrics with 1% chitosan was 14.75



SCHEMATIC 1

in C15, in which the oxygen increased more percentage-wise than the other elements, indicating the obvious degradation that had taken place.

TABLE 3: ^{1}H-NMR chemical shift for Chitosan and LWCS in D_2O solution

	H-1	H-2	H-3	H-4	H-5	H-6	H-7
Chitosan[a]	4.87	3.18	3.78	3.83	3.74	3.87	2.07
Chitosan[b]	4.80	3.16	3.61	3.78	3.72	3.82	2.02
LWCS(C15)	4.75	3.16	3.57	3.66	3.71	3.80	1.91

[a]Reference 1; [b]Chitosan in this study

FT-IR analysis

Figure 1(a) shows the absorption peak of the -CONH group to be at 1574cm^{-1}. This was due to the residual chitin. Figures 1(b), 1(c) and 1(d) show the spectra of C5, C10, and C15, respectively. A significant peak at 1600-1630cm^{-1} was due to C=O absorption, probably in a new side-chain group of LWCS as reported elsewhere[11]. The oxidation of chitosan under harsher condition might cause the degradation of amide to form carboxylic acid (ion) and amine groups, whose absorption bands are at about 1600-1640cm^{-1}. In the meantime, the hydroxyl group near the ring might also be oxidized to form carboxylic acid (ion).

^{1}H-NMR analysis

Figure 2 shows a ^{1}H-NMR spectrum of C15. An absorption peak occurred at 3.16 ppm (H-2) and four more at 3.57-3.80ppm (H-3, H-4, H-5, and H-6). An H-7 absorption peak was observed at 1.91ppm and an H-1 absorption peak at 4.75ppm. Comparing this to the ^{1}H-NMR absorption data of chitosan from the reference[12], in TABLE 3 and Schematic 1 we observe that no significant difference exists in the proton absorption peaks. Therefore, the structural formula of LWCS created by the H_2O_2 degradation in this experiment was similar to that of the original chitosan.

X-ray detection of LWCS

Figure 3 shows low-molecular-weight chitosan produced with various concentrations of H_2O_2 solution. The LWCS absorption peak is different from that of chitosan for 2θ^{0}C of 11^{0}C or 21^{0}C. In figure 3(a), chitosan has a diffraction peak for 2θ of 11^{0}C, whereas the LWCS diffraction peak disappears gradually as the H_2O_2 concentration rises, as figures 3(b), 3(c), and 3(d) show. In addition, chitosan showed an obvious diffraction peak at 21.2^{0}C, while the C15 diffraction peak shifted to 22.4^{0}C, and the 2θ diffraction peaks of C10 and C5 shifted to 22.5^{0}C and 22.4^{0}C, respectively. We

inferred that increased amounts of H_2O_2 changed the crystallographic structure of chitosan.

Effect on the color intensity

Figure 4 shows that fabrics dyed after treatment with LWCS had higher K/S values than those of fabrics dyed without the LWCS treatment. The K/S value increased as the LWCS molecular weight decreased, and increased as the LWCS concentration increased. This occurred because the reduction of the molecular weight of LWCS increased the uptake of dye through osmosis. However, when the concentration of LWCS exceeded 4%, the K/S value was immediately reduced since the viscosity of LWCS increases with increased concentration, which worked against the uptake of dye by osmosis.

Effect on the antibacterial and shrink-resistance properties

Under weak acid conditions, the amine groups of chitosan change into -NH_3^+ anions, which interact with the cell wall of bacteria and hinder the growth of the microorganism[15]. TABLE 4 shows that the antibacterial properties of the pretreated fabrics were better than those of the untreated fabrics. This occurred because the molecular weight of LWCS is low and so the osmotic effect is strong. The antibacterial properties of the fabrics increased with increasing LWCS concentrations, reaching a peak at 4%. Further increases in LWCS concentration caused little change in the antibacterial properties.

The shrinkage of the untreated fabrics in both the warp and the weft direction was greater than that of the treated fabrics, as shown in TABLE 4. The treated fabrics had reactive polymers completely covering the fiber scales and possibly may have had even a thin protective membrane layer on the surface. This means that the tightness of the yarn, the structure of the fabric, and weaving density tended to restrict the movement of individual fibers. Under such circumstances, the fibers in the treated fabric would, of course, become much more resistant to outside forces and not slip against each other. In other words, the fabric would become more shrink-resistant[17]. We also noted that shrinkage in the warp direction was always greater than in the weft direction because the warp yarn was stretched more tightly than the weft yarn during weaving, which is the main reason why wool fabrics are likely to shrink when heated. The shrink-resistance of treated fabrics improved with reduction of the LWCS molecular weight and with the increase in LWCS concentration.

TABLE 4: The anti-bacterial and shrinkage properties of treated fabrics.

LWCS conc. (%)	Anti-bacterial property		Shrinkage (%)	
	Bacteriostatic value	Bactericidal value	Warp	Weft
Control[2]	4.5	2.4	6.57	5.36
0	0	<0	11.67	8.61
0.5	3.7	2.4	6.13	5.07
1.0	4.8	2.5	5.56	4.89
2.0	5.2	2.9	5.02	4.66
4.0	5.7	3.0	4.20	4.52
6.0	5.8	3.1	3.74	4.01
8.0	6.0	3.1	3.19	3.28

[1]pretreated with C15, [2]pretreated with chitosan

TABLE 5: Wash fastness of treated fabric[1]

Samples	Before washing					After washing 20 times				
	K/S	Anti-bacterial		Shrinkage (%)		K/S	Anti-bacterial		Shrinkage (%)	
		A[4]	B[5]	Warp	Weft		A[4]	B[5]	Warp	Weft
0[2]	11.56	0	<0	11.8	8.6	9.04	0	<0	13.6	9.7
4.0	23.52	5.7	3.0	5.7	3.0	20.86	5.1	2.6	6.2	3.2
Control[3]	14.75	4.5	2.4	6.6	5.4	12.17	4.0	2.3	7.3	6.1

[1]Pretreated with C15; [2]Unpretreated fabric; [3]Pretreated with chitosan; [4]Bacteriostatic value; [5]Bactericidal value.

Wash fastness

TABLE 5 shows the color-fastness of treated fabrics after they had been washed 20 times. The color-fastness of the untreated fabrics was very poor. The fabric treated with LWCS showed an 11.3% reduction in K/S compared to 17.5% for the fabric treated with chitosan. The LWCS-treated fabric had a shrinkage of 6-10% compared to 11-13% for the chitosan-treated fabric. The ion binding of the dye in the treated fabric resulted in better color-fastness, and the dyed fabrics exhibited superior antibacterial properties after treatment with chitosan or LWCS.

CONCLUSIONS

This study was designed to examine the effect of LWCS treatment on the dyeing of wool fabrics and resulted in important findings. First, the molecular weight and the viscosity of LWCS decreased with increased concentrations of H_2O_2. Second, the K/S, shrink-re-

sistance, and antibacterial properties of dyed fabrics were inversely proportional to increases in the LWCS molecular weight, and directly proportional to LWCS concentration. This was true only up to a LWCS concentration 4%, at which point the K/S of the treated fabrics peaked. Third, treatment of fabrics with LWCS before dyeing had a positive effect on dyeing, shrinkage, and antibacterial wash fastness measured after 20 washes.

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