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Application of low-molecular-weight chitosan in durable press finishing

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Abstract

The effect of using low-molecular-weight chitosan (LWCS) for anti-creasing treatments of cotton fabric was studied. The LWCS was mixed with dimethylol dihydroxyl ethylene urea (DMDHEU) to form the finishing agent. The addition of LWCS increased the tensile strength retention (TSR) and creasing resistance of the treated fabrics. The yellowing index and the softness of the treated fabrics became worse when the LWCS molecular weight decreased and the concentration as well as the curing temperature increased. The anti-wrinkle properties of all processed fabrics decreased markedly after washing 20 times. However, the softness of the fabric improved and the strength decreased slightly after the wash treatment.

Keywords: Chitosan; Low-molecular-weight; Textile finishing treatment; DMDHEU; Anti-creasing

1. Introduction

Since cotton fibers contain large amounts of hydroxyl groups they are highly hydrophilic. In addition, the fiber crystallization is low, so that when cotton fibers absorb water, the bonding force among cellulose molecules is reduced markedly, which causes swelling. Therefore, when cotton fabrics are twisted or rubbed when being washed or worn, the cellulose macromolecules shift and undergo plastic deformation. Consequently, the fabric shrinks and wrinkles. The primary method of minimizing creases in cotton fabrics when washed or worn is to use appropriate agents to cross-link the cellulose molecules in the fiber. This prevents the relative displacement of the cellulose molecules in cotton fibers when washed or worn. Crease resistance results from increasing the elasticity of the fibers (Mark, Wooding, & Atlas, 1971).

Chitin that is more than 55% deacetylated is called chitosan, which is a natural polymer. Chitosan has a high molecular weight, usually on the order of tens of thousands or even millions of kDa. Chitin has inter- and intramolecular hydrogen bonding which makes it chemically stable and of low water solubility. Chitosan is soluble only in certain dilute acid solutions which limits its wider use. Chitosan can be hydrolyzed into low molecular weight oligosaccharides. Oligosaccharides have some unique properties compared to chitosan such as microorganism resistance, absorption of anionic dyes, tumor growth inhibition, and cholesterol and blood lipid reduction (Zhao, Zhang, & Zeng, 2003). The molecular structure of chitosan is similar to that of cellulose. Chitosan can be applied as a cotton finish to produce fabrics with properties similar to cellulose fabrics (Yu, 1997). This has become an area of increased research interest.

Current methods for preparing oligosaccharides typically include degradation by acids, yeasts, oxidation and other degradation methods such as irradiation using microwaves and ultrasound. Chitosan hydrolyzes in acidic solutions where the acid acts as a catalyst. The acids typically used to degrade chitosan are either HCl (Hawkins & Davies, 1996) or H_2SO_4 (Maksumov, Denisov, & Makarov, 1990; Nagasawa, Tohica, Inoue, & Tanoura, 1971). Acid catalyzed degradation of chitosan is simple, but the yield is low, the molecular weight distribution of the end

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product is difficult to control, and the separation process is complex. Furthermore, acid degradation of chitosan creates environmental pollution which discourages industrial use. The yeast degradation method uses chitosan-degrading yeast to prepare oligosaccharides. It is carried out in a milder environment, with no other reagents required, so there are no side effects and little pollution as a result. In addition, it is easy to control the degradation progress and the molecular weight distribution of the end product, although this method is expensive and the technology is still primitive, which are obstacles to its application. Oxidization degradation is the most-studied method; it causes rapid degradation and is a simple, inexpensive process with no toxic residues. The primary reagents include H_2O_2 (Chang, Tai, & Cheng, 2001; Fang, Sun, Salisbury, Fowler, & Tomkinson, 1999; Kabal'nova et al., 2001; Takeshi & Tsugio, 1996) and nitride (Yang, Liu, & Guan, 1999); the former is the most common. Other methods of applying an external field can be applied. For example, Li, Liu, and Hsu (2001) reported that γ-rays can degrade chitosan, and that the relative molecular mass drops from 27,140,000 to 2,140,000 kDa, although the disadvantage is that some cross-linking and side-chain reactions occur.

In this study, we used H_2O_2 to degrade chitosan to low-molecular-weight chitosan (LWCS), which was then mixed with an anti-creasing agent to produce the finishing agent, and then applied in the anti-creasing treatment of cotton fabrics. We discuss the influence of LWCS incorporation on the properties of the treated fabrics.

2. Experiment

2.1. Materials

Ethanol, HCl, H_2O_2, and $MgCl_2$, sodium lauryl sulfate all reagent class, were purchased from Shimaku Medicine (Japan). Dimethylol dihydroxyl ethylene urea (DMDHEU; solids 30%) was obtained from Taiwan Cyanamid (Taipei, Taiwan), and chitosan (85% deacetylated) was obtained from Taiwan Kaohsiung Applied Chemistry (Kaohsiung, Taiwan). The cotton fabrics (from Yi Hwa Textile, Tainan, Taiwan), 40 s × 40 s ends (100), and picks (80), were desized, scoured, and bleached. A non-ionic type softening agent (Ablusoft NB-150) was purchased from Taiwan Surfactant Company (Taiwan).

2.2. Methods

2.2.1. Preparation of LWCS

Two grams of chitosan were dissolved in 100 ml 0.1 M HCl and stirred for 30 min. Then, H_2O_2 was added in one of five concentrations (5%, 7.5%, 10%, 12.5%, or 15%). The mixture was heated and stirred at 60 °C for 2 h and then vacuum filtered. The upper residue was neutralized with distilled water, baked, and weighed. Ethanol was added to the lower solution, which was left for 24 h to precipitate, after which it was filtered, dried, and weighed. This gave low-molecular-weight water-soluble chitosans denoted by C5, C7.5, C10, C12.5, and C15.

2.2.2. Application of LWCS

LWCS of different molecular weights (C5, C10, and C15) was added to 10 ml of distilled water and stirred for 15 min to allow it to dissolve completely. Then, 8 g DMDHEU, 0.8 g $MgCl_2$, and 3 ml softener were added and the solution was stirred for 15 min. Finally, distilled water was added to the beaker until the volume totaled 100 ml. Cotton fabric (20 × 24 cm) was immersed in the finishing solution using a 'two-dips two-nips method', and was shaken in an ultrasonic shaker. The immersed white cloth was press-absorbed (pick-up = 80%), pre-dried for 5 min at 80 °C, cured at various temperatures (130, 140, and 150 °C), rinsed and dried, and then wrapped in a polyethylene (PE) bag and stored for later analysis.

2.2.3. Analysis of the LWCS and treated fabrics

Fourier transform infrared/attenuated total reflectance (FT-IR/ATR) spectra of the LWCS were recorded with a Digilab FTS-200 spectrometer (Bio-Rad, Hercules, CA, USA) using an MCT detector. A diamond crystal was used as the internal reflectance element. Single beam spectra were obtained from 64 scans, and the spectral resolution was 4 cm^{-1}. Detection of the ^1H NMR chemical shift of LWCS was tested using an AMX-400 L NMR analyzer (Bruker, Berlin, Germany). A Bruker AXS D8 was used for X-ray powder diffraction (parallel beam optics, Cu target, scintillation counter, sampler changer with rotation). The samples were run at 40 kV, 100 mA, 2–60° $\theta/2\theta$, 0.01° step size, and 5 s counting time. The viscosity and molecular weight of the LWCS were measured as follows: viscosity was measured at 25 °C with a Wurtz viscometer based on a 1 g/L sample in 0.1 M acetic acid and 0.2 M NaCl. The molecular weight was calculated from the Mark–Houwink equation, $[\eta] = K[Mv]^{\alpha}$, where $K = 1.81 \times 10^{-3}$ cm^3/g, $\alpha = 0.93$ (Zhao et al., 2003). Element analysis of the LWCS was measured with a Vario EL III analyzer (Elementar, Hanau, Germany). The anti-creasing angle of dried treated fabrics was measured using the ASTMD1295-61 Monsanto method; mechanical performance was tested with an Alphaten 400 tensile tester according to the ASTM370 standard, and the softness and yellowing index were examined with an INTECO softness tester with a 45° tilted workbench and Nippon ND 300A spectrophotometer (Nippon Denshoku Industries, Tokyo, Japan), respectively. Investigations on the leaching behavior were performed at 40 °C using a Rapid H-type dyeing machine. As washing solution a 1% aqueous solution of sodium lauryl sulfate (SLS) with pH 7 was used. After a leaching 20 min the textile samples were rinsed intensively with water, dried at room temperature and physical properties again investigated after 20 times wash.

3. Results and discussion

3.1. Elemental analysis and viscosity and molecular weight measurements

After H_2O_2 treatment, the molecular weight and viscosity of the chitosan decreased and continued to decrease as more H_2O_2 was added (Table 1). This was due to the degradation of the chitosan molecular chain by H_2O_2, which oxidizes the —OH and —NH_2 groups into —COOH groups. Therefore, the N content of the LWCS decreased as the H_2O_2 volume increased, while the O content increased (Table 1). The C and H contents did not change significantly, except for C15. For C15, O had the largest percentage increase compared to the other elements, indicating that C15 degradation occurred.

3.2. FT-IR analysis

Fig. 1A shows the absorption peaks of the —CONH and —CN groups attributable to the chitin remaining in the original chitosan at 1574 and 1330 cm^{-1}, respectively. Fig. 1B–D shows the spectra of C5, C10, and C15, respectively. A significant peak was observed at 1600–1630 cm^{-1} due to C=O absorption, which was probably attributable to a new side chain group in the LWCS, corroborating previous reports (Lu, Wei, & Peng, 2004). The oxidation of chitosan under stronger conditions might cause the degradation of amides to form carboxylic acid (ion) and amine groups, which have absorption bands at 1600–1640 cm^{-1}. This results from the progressive oxidization of the —CN groups. Similarly, the hydroxyl group near the ring might also be oxidized to form carboxylic acid (ion).

3.3. ^{1}H-nuclear magnetic resonance (NMR) analysis

Fig. 2 shows the ^{1}H NMR spectrum of C15. There was an absorption peak at 1.91 ppm (H-7) and 3.16 ppm (H-2), four absorption peaks at 3.57–3.80 ppm (H-3, H-4, H-5, and H-6), and a peak at 4.75 ppm (H-1). The absorption peaks of the protons were similar to the ^{1}H NMR absorption data on chitosan reported by Mars and Kui (1996); Table 2 and Scheme 1); therefore, the structure of LWCS after H_2O_2 degradation in this experiment was similar to that of the original chitosan.

3.4. X-ray detection of LWCS

Fig. 3 shows LWCS after treatment with various concentrations of H_2O_2. The LWCS diffraction peak differed from that of chitosan when 2θ was 11° or 21° (Fig. 3A), and chitosan had a diffraction peak when 2θ is 11°, whereas the LWCS diffraction peak disappeared gradually as the H_2O_2 concentration rose (Fig. 3B–D). In addition, chitosan had obvious diffraction peaks at 21.2°, 23.4°, and 26.3°. The latter two peaks occur because the chitosan contains some chitin. The peaks at 23.4° and 26.3° disappeared in the LWCS. The C15 diffraction peak shifted to 22.4°, while the 2θ diffraction peaks of C10 and C5 shifted to 22.5° and 22.4°, respectively, suggesting that increasing amounts of H_2O_2 change the crystallographic structure of LWCS.

3.5. Influence of LWCS molecular weight and concentration on the properties of the treated fabrics

The crease recovery angle of fabrics treated with LWCS was better than that of untreated fabrics (Table 3). In addition, the dry crease recovery angle became more pronounced as the LWCS molecular weight decreased, because in addition to reacting with DMDHEU in the fiber molecules, chitosan cross-linked the fibers to form a network matrix. The lower-molecular-weight chitosan also penetrated the fibers more easily, promoting anti-creasing in the treated fabrics. LWCS generates an ether reaction with the hydroxyl radicals in the fibers, forming a two-dimensional structure that improved the crease resistance of the fabrics (Hsiao & Chen, 1996; Pigman & Horton, 1970). LWCS penetration or encapsulation improved the strength of treated fabrics, and the tensile strength retention (TSR) decreased as the LWCS concentration increased, probably because higher LWCS concentrations created more fiber bridging and were more likely to cause stress accumulation. Nevertheless, the LWCS molecular weight did not have a significant impact on the strength of the treated fabrics. Regarding its impact on the yellowing index and softness, the table

Table 1
Molecular weight, viscosity, and element analysis of LWCS

Samples	H_2O_2 (ml)	Elemental composition (%)				η (ml/g)		Mv	
		N	C	H	O	M[a]	SD[b]	M	SD
Chitosan		7.40	39.06	6.22	47.32	293.47	35.22	240,500	12,550
C5	5.0	6.39	37.56	7.01	64.628	64.63	9.58	77,210	5200
C7.5	7.5	6.36	36.95	6.98	34.944	34.94	4.86	40,100	3505
C10	10.0	6.35	36.83	6.94	14.081	14.08	3.52	15,090	2020
C12.5	12.5	6.33	36.93	6.90	8.455	8.46	2.24	8720	685
C15	15.0	5.92	35.77	6.59	7.762	7.76	2.13	3650	320

[a] Mean value.
[b] Standard deviation.

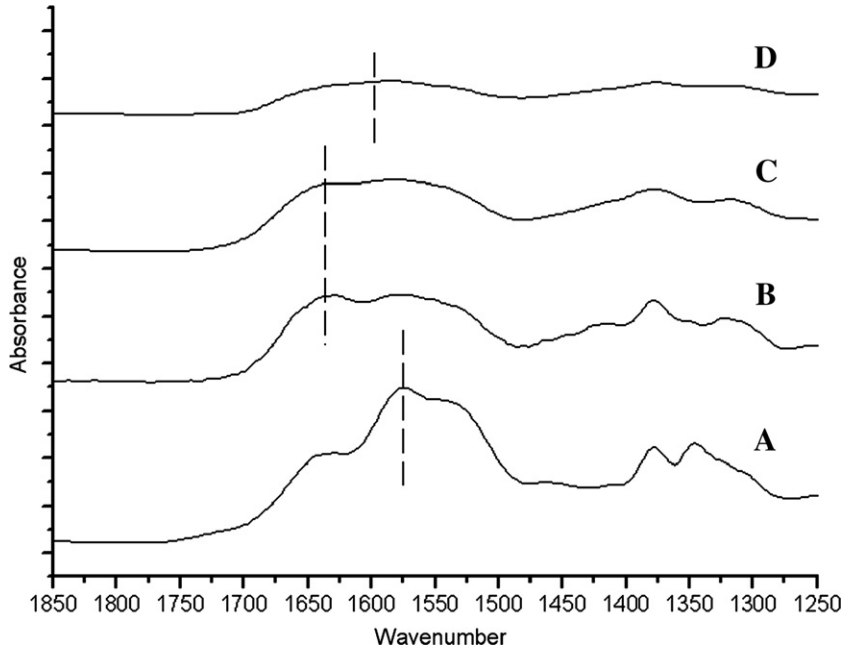


Fig. 1. FT-IR spectra of chitosan and LWCS: (A) chitosan (C0), (B) C5, (C) C10, (D) C15.

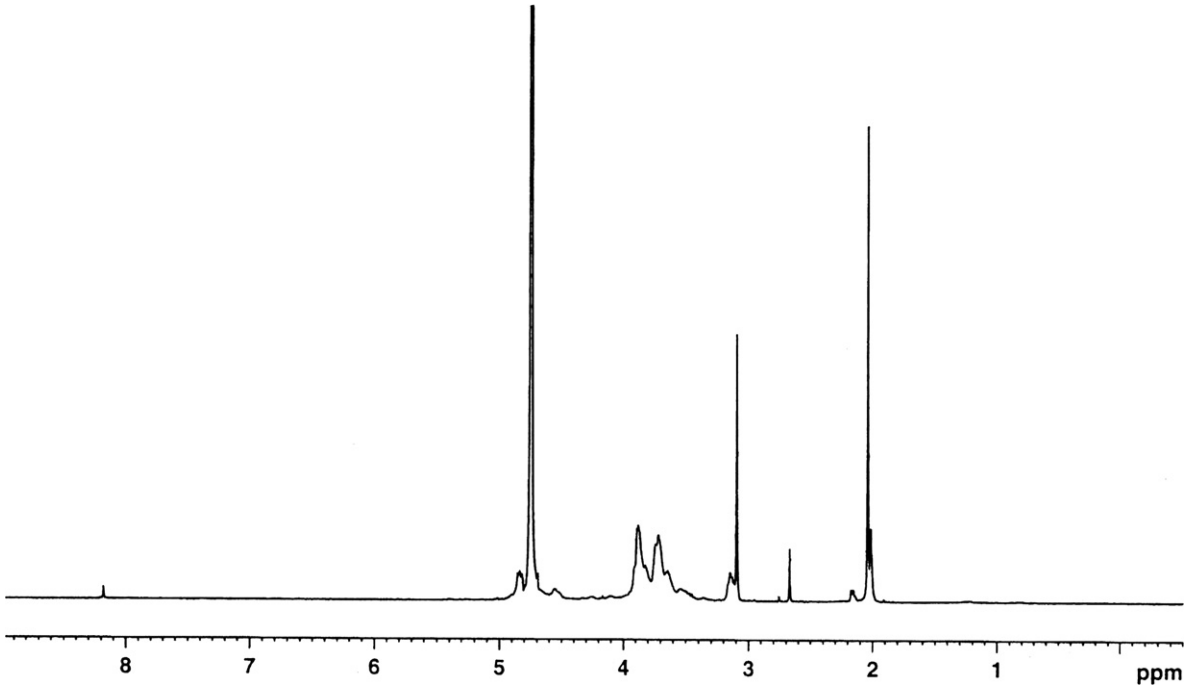


Fig. 2. ^{1}H NMR spectra of LWCS (C15).

shows that the degree of yellowing deteriorated as the LWCS molecular weight decreased. This resulted from the process of LWCS preparation, which resulted in a higher H_2O_2 concentration that led to more oxidation of the chitosan. The softness improved as the LWCS molecular weight decreased, because LWCS penetrated the fibers more easily and less of the yarn surface was covered.

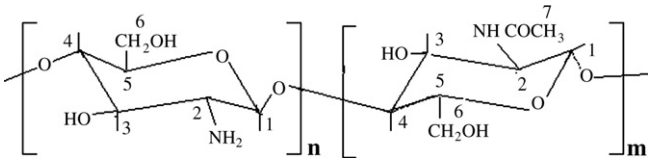
3.6. Influence of cure temperature and time on the properties of treated fabrics

The dry crease recovery angle increased with the curing temperature, curing time, and LWCS concentration (Table 4). However, the TSR changed in a manner opposite to that of the yellowing index, as higher temperatures or longer curing times oxidized the fibers more easily, which

Table 2
^{1}H NMR chemical shifts for chitosan and LWCS in D_2O solution

Samples	H-1		H-2		H-3		H-4		H-5		H-6		H-7	
	M[c]	SD[d]	*M*	SD	*M*	SD	*M*	SD	*M*	SD	*M*	SD	*M*	SD
Chitosan[a]	4.87	–	3.18	–	3.78	–	3.83	–	3.74	–	3.87	–	2.07	–
Chitosan[b]	4.80	1.02	3.16	0.68	3.61	0.85	3.78	0.88	3.72	0.92	3.82	0.96	2.02	0.44
LWCS (C15)	4.75	0.98	3.16	0.64	3.57	0.86	3.66	0.90	3.71	0.92	3.80	0.95	1.91	0.37

[a] Chang et al. (1999).
[b] Chitosan in this study.
[c] Mean value.
[d] Standard deviation.



Scheme 1. Structure of 85% deacetylated chitosan.

reduced their strength. Conversely, the wrinkle recovery angle of the treated fabrics was better, because with higher treatment temperatures or longer times cotton fiber molecules swell more and finishing solution can enter more easily. The finishing agents react more with the fibers and adhere to the fiber molecules, improving the dry wrinkle recovery angle of the fabrics. In addition, since more cross-linking occurs when the reaction between the fibers and finishing agent is more active with a higher curing temperature or longer curing time, the treated fibers become hardened and straightened, resulting in a greater loss of the tensile strength of fabrics. Moreover, a long curing time enhances the hydrolysis of fibers in acid catalysts, reducing the tensile strength of the fabrics. As the table also shows, the degree of yellowing of the treated fabrics worsened at increased curing temperatures and longer curing times because the fibers and chitosan undergo more oxidization. No significant difference was observed between the two treated groups in terms of the feel of the fabric, although the LWCS-treated fabrics generally felt slightly rougher than the non-LWCS-treated fabrics.

3.7. Durable press property

Durable press is one of the most important properties for cotton fabrics on anti-wrinkle treatment. From Table 5, the anti-wrinkle property of all process fabrics is decreased obviously after washing 20 times, because the internal cross-linking of fiber molecule was broken. When LWCS was added leading to the net structure formed in the molecular structure of the fiber (Yu, 1997), the break of cross-linking was reduced. Therefore, the treated fabrics with LWCS still maintained better anti-wrinkle. On the other hand, the softness of the fabric was improved,

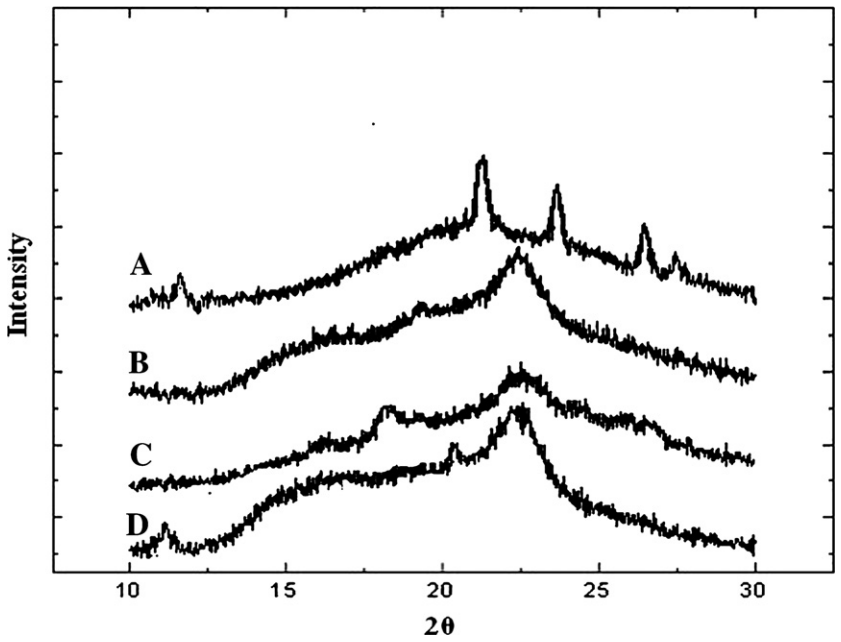


Fig. 3. X-ray spectra analysis of chitosan and LWCS: (A) chitosan (C0), (B) C15, (C) C10, (D) C5.

Table 3
Properties of various fabrics treated with LWCS different LWCS

Type of LWCS	LWCS conc. (%)	DCRA (W + F)°		TSR (%)		Yellow index		Stiffness (cm)	
		M[a]	SD[b]	*M*	SD	*M*	SD	*M*	SD
Control[c]		285	25.4	52.5	12.5	4.8	1.2	4.8	1.1
C5	0.5	285	26.2	65.7	16.3	4.8	1.2	4.9	1.0
	1.0	287	26.4	60.6	14.2	5.0	1.1	5.2	1.1
	2.0	293	26.6	56.8	14.0	5.2	1.3	5.5	1.3
	3.0	297	28.2	52.9	12.8	5.9	1.4	5.8	1.4
C10	0.5	287	24.8	63.9	16.2	4.6	0.8	4.8	1.0
	1.0	290	26.8	59.7	14.8	4.8	1.1	5.3	1.1
	2.0	297	27.4	55.3	13.8	5.7	1.4	5.4	1.1
	3.0	302	30.4	54.1	13.2	6.5	1.8	5.6	1.4
C15	0.5	290	28.2	63.3	16.7	5.0	1.1	4.8	0.8
	1.0	297	28.6	60.7	15.4	5.9	1.3	5.0	1.0
	2.0	301	29.4	56.4	14.2	6.8	1.8	5.1	1.0
	3.0	307	31.8	53.7	14.0	7.2	2.0	5.2	1.1

[a] Mean value.
[b] Standard deviation.
[c] DMDHEU, 8%; $MgCl_2$, 0.8%; softening agent, 3 ml; pick-up, 80%; drying, 80 °C × 5′; curing, 150 °C × 3′.

Table 4
Properties of various fabrics treated with LWCS under different curing conditions

Curing temp. (°C)	Curing time (min)	LWCS[a] conc. (%)	DCRA (W + F)°		TSR (%)		Yellow index		Stiffness (cm)	
			M[c]	SD[d]	*M*	SD	*M*	SD	*M*	SD
Control[b]			285	25.4	52.5	12.5	4.8	1.2	4.8	1.1
130	3	0.5	285	26.2	65.7	16.3	4.8	1.2	4.9	1.0
		1.0	287	26.4	60.6	14.2	5.0	1.1	5.2	1.1
		2.0	293	27.4	56.8	14.0	5.2	1.3	5.5	1.3
		3.0	297	28.2	52.9	12.8	5.9	1.4	5.8	1.4
140	3	0.5	287	24.8	63.9	16.2	4.6	0.8	4.8	1.0
		1.0	290	26.8	59.7	14.8	4.8	1.1	5.3	1.1
		2.0	297	27.4	55.3	13.8	5.7	1.4	5.4	1.1
		3.0	302	30.4	54.1	13.2	6.5	1.8	5.6	1.4
150	3	0.5	290	28.2	63.3	16.7	5.0	1.1	4.8	0.8
		1.0	297	28.6	60.7	15.4	5.9	1.3	5.0	1.0
		2.0	301	29.4	56.4	14.2	6.8	1.8	5.1	1.0
		3.0	307	31.8	53.7	14.0	7.2	2.0	5.2	1.1
150	1	2.0	287	27.8	62.5	16.2	6.2	1.4	5.0	0.8
	2		294	29.0	60.1	15.4	6.5	1.4	5.1	0.7
	3		301	29.4	56.4	14.2	6.8	1.8	5.1	1.0
	5		310	32.4	51.2	11.8	7.5	2.1	5.2	0.9

[a] LWCS is C15.
[b] DMDHEU, 8%; $MgCl_2$, 0.8%; softening agent, 3 ml; pick-up, 80%; drying, 80 °C × 5′; curing, 150 °C × 3′.
[c] Mean value.
[d] Standard deviation.

because process agent was cleaned. The strength of the fabric was decreased after washing 20 times, but not obviously.

4. Conclusions

In this study, we degraded chitosan into LWCS using various concentrations of H_2O_2. The LWCS was then mixed with DMDHEU to form the finishing agent, which was used for the anti-creasing treatment of cotton fabrics. We evaluated the influence of LWCS incorporation on the properties of the treated fabrics, and reached the following conclusions. FT-IR and ^1H NMR analyses confirmed that the LWCS structure was similar to that of the original chitosan. The crystallographic structure of chitosan was damaged by H_2O_2 degradation. In addition, the molecular weight and viscosity of the LWCS decreased as the H_2O_2 concentration increased. The dry crease recovery angle and strength of the LWCS-treated fabrics were better than those of the non-LWCS-treated fabrics, and the yellowing index and softness decreased. The anti-creasing property of the treated fabrics improved as the LWCS molecular weight decreased, the concentration increased, and the cure temperature increased, while the strength, yellowing index,

Table 5
Durable press properties of various treated fabrics after 20 washing times

Curing temp. (°C)	Curing time (min)	LWCS[a] conc. (%)	DCRA (W + F)°		TSR (%)		Yellow index		Stiffness (cm)	
			M[c]	SD[d]	*M*	SD	*M*	SD	*M*	SD
Control[b]			285	24.4	52.5	12.8	4.8	1.0	4.8	1.2
150	3	1.0	280	24.2	58.7	14.6	5.6	1.2	4.7	1.0
		2.0	283	24.4	55.2	14.0	6.3	1.7	4.8	1.0
		3.0	291	26.8	52.4	12.6	6.7	2.0	5.0	1.1
150	1	2.0	271	23.5	60.2	16.2	5.8	1.4	5.0	0.8
	2		279	24.2	58.7	14.4	6.0	1.6	4.9	0.7
	3		283	24.4	55.2	14.0	6.3	1.7	4.8	1.0
	5		288	25.2	49.1	11.7	7.1	2.2	5.2	1.2

[a] LWCS is C15.
[b] DMDHEU, 8%; $MgCl_2$, 0.8%; softening agent, 3 ml; pick-up, 80%; drying, 80 °C × 5′; curing, 150 °C × 3′.
[c] Mean value.
[d] Standard deviation.

and softness changed in the opposite direction. The anti-wrinkle property of all process fabrics is decreased obviously after washing 20 times, the softness of the fabric was improved, and the strength of the fabric was decreased, but not obviously.

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