Crosslinking Reactions of Oxidized Cellulose Fiber. II. Reactions Between Dialdehyde Cellulose and Chito-Oligosaccharides on Lyocell Fabric

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ABSTRACT: Antimicrobial nonfibrillated lyocell fibers were developed by crosslinking reactions between dialdehyde cellulose and chito-oligosaccharides. Partially oxidized lyocell fibers with sodium metaperiodate were successfully crosslinked with two water-soluble chito-oligosaccharides with different molecular weights by Schiff base formation and were reduced with sodium borohydride. Infrared spectroscopy measurements showed the characteristic absorption bands caused by the functional groups of each reaction product. The surface chemical compositions of the modified fibers were analyzed with electron spectroscopy. O_{1s} intensities decreased with the oxidation and crosslinking reaction, whereas N_{1s} intensities increased with the crosslinking reaction. According to the curve fittings, C_{1s} spectra were divided into —CH, —CO—/—CN—, —C=O, and —COO— peaks, and their relative peak areas confirmed the reaction results. The degree of fibrillation of the crosslinked fibers decreased with the oxidation levels and chito-oligosaccharide concentrations and increased with the molecular weight of the chito-oligosaccharide. Furthermore, the chito-oligosaccharide-treated lyocell fibers exhibited antimicrobial activity, especially when treated with a chito-oligosaccharide of a low weight-average molecular weight. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 709–714, 2009

Key words: biofibers; crosslinking

INTRODUCTION

Natural biopolymers play an important role in eco-friendly polymer processes. In particular, chitosan, partially N-deacetylated chitin, is an abundant polymer widely used in physiological, biological, and biomedical applications. Because of its biodegradability, biocompatibility, and antimicrobial activity and the rich reactivity of its amino groups, it is also the most valuable natural substance in textile processes.

Chitosan fibers have been manufactured by wet spinning,[1] dry-jet wet spinning,[2] pseudo-dry spinning,[3] and electrospinning processes,[4] but their dimensional stability and mechanical properties are somewhat undesirable. Therefore, one-step crosslinking reactions in the spinning dope or two-step crosslinking reactions after fiber formation have been introduced with glutaraldehyde or glyoxal,[5,6] vaniline,[7] epichlorohydrin,[8,9] and so forth.

On the other hand, many research groups have developed textile finishing processes with chitosan and have successfully adapted them for commercial use. First, they researched the solubility of chitosan[10] and the antimicrobial activity[11] of fibers treated with chitosans of various molecular weights[12] and different degrees of N-deacetylation.[13] However, the antimicrobial activity of chitosan depends not only on the molecular weight, molecular weight distribution, and degree of deacetylation but also on the test organisms, so it is very difficult to make their relationships clear.

Chitosan has been modified to improve its water solubility and reactivity with textile substrates. Quaternary ammonium salts have been introduced into chitosan for water solubility and increased antimicrobial activity.[14] Carboxylated chitosan derivatives have been used for water solubility and dyeability.[15] The durability of the antimicrobial activity has been improved by the introduction of reactive groups, such as acrylamidomethyl[16] and cyanuric chloride,[17] to substrates. Furthermore, chitosan phosphate treated fabric has exhibited enhanced thermal properties.[18]

Cotton, wool, polypropylene, and polyester have been finished with chitosan and its derivatives by pad–dry–cure and pad–steam processes through the addition of crosslinking agents, such as *N*-methylol compounds (dimethylol dihydroxyethylene urea and dimethyl dihydroxyimidazolidone), poly(carboxylic

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TABLE I
Degree of Oxidation of DAC Fibers

| Sample | Oxidation conditions | | | Degree of oxidation (mmol of NaIO$_4$/g·of fiber) |
	NaIO$_4$ concentration (%)	Solution temperature (°C)	Retention time (h)	
Regular	0	30	4.5	—
DAC-1	0.15	30	4.5	0.092
DAC-2	0.5	30	4.5	0.381
DAC-3	1.0	30	4.5	0.881

acid)s (1,2,3,4-butanetetracarboxylic acid and carboxylic acid), aldehydes (glyoxal and glutaraldehyde), and epichlorohydrin. It is known that chitosan treatments can improve the dyeability of textile materials by anionic dyes because of the cationic nature of chitosan,[19–22] the crease resistance, and the antimicrobial activity.[23–31] In addition, chitosan has been used in pigment and ink-jet printing pastes,[32–35] as a deodorant agent,[36] and as a dyeing wastewater treatment agent.[37,38]

In this work, lyocell fiber was crosslinked with chito-oligosaccharide, whereas in our previous research, multifunctional amines were used for the same purpose.[39] Dialdehyde cellulose (DAC) fibers were manufactured by partial oxidation with sodium metaperiodate and crosslinked with water-soluble chito-oligosaccharides to provide soft handle. We produced nonfibrillated and antimicrobial lyocell fiber in which chitosan was bonded chemically to impart durability. Also, Fourier transform infrared (FTIR) spectroscopy, changes in the surface chemical composition, and the degree of fibrillation were studied after oxidation and crosslinking reactions; moreover, the antimicrobial properties were evaluated.

EXPERIMENTAL

Materials

Commercial scoured lyocell fabric (Tongkook Corp., Gumi, Korea) was used in all experiments. Two chito-oligosaccharides with weight-average molecular weights (M_w's) of 1000–2000 and less than 10,000 and with a degree of deacetylation over 85% were obtained from Kitto Life Co., Ltd. (Korea). The oxidation agent sodium metaperiodate (NaIO$_4$) and reduction agent sodium borohydride (Na[BH$_4$]) were all first-grade; they were obtained from Aldrich Chemical Co., Inc., and used without further purification.

Preparation of DAC

Aqueous sodium metaperiodate solutions were prepared (0–1.0 wt %). Lyocell fabrics were stirred gently in these solutions at 30°C for 4.5 h. The degrees of oxidation were estimated by periodate consumption, which was calculated from the ultra-

violet absorbance of residual solutions at 222 cm^{-1} (UV-1601 spectrophotometer, Shimadzu, Kyoto, Japan). After the reactions were stopped with excess ethylene glycol, the samples were washed with warm distilled water and dried under the ambient conditions. The oxidation conditions and the degree of oxidation are shown in Table I.

Preparation of crosslinked lyocell fibers by Schiff base formation

Aqueous chito-oligosaccharide solutions were prepared (0–8 wt %). DAC fabrics were stirred gently in these solutions at 40 or 60°C for 3 h and washed with warm distilled water. After Schiff base formation between DAC and chito-oligosaccharides, the crosslinked fabrics were stirred in 2.0 wt % sodium borohydride solutions at room temperature for 3 h. They were washed with warm distilled water and dried under the ambient conditions. The crosslinking reaction conditions are shown in Table II.

Measurements

FTIR measurement

Potassium bromide pellets mixed with the modified fibers were prepared and scanned with a PerkinElmer Spectrum GX FTIR apparatus (Massachusetts, USA). Infrared spectra of the different samples were recorded and analyzed.

Electron spectroscopy of chemical analysis

Surface chemical compositions of the modified fabrics were evaluated by X-ray photoelectron spectroscopy (XPS) with an Escalab 250 (VG Scientific, West Sussex, United Kingdom). The relative intensities of the C$_{1s}$, O$_{1s}$, and N$_{1s}$ spectra were measured, and through the curve fittings of C$_{1s}$ spectra, the relative peak areas of —CH, —CO—/—CN—, —C=O, and —COO— components were analyzed.

Fibrillation measurement

Fibers were cut into 5-mm lengths, and the cut fibers were placed in a vial containing a 1% NaOH aqueous solution. The vial was shaken vigorously for

TABLE II
Crosslinking Reaction Conditions

Sample	DAC	M_w	Schiff base reaction (chito-oligosaccharide)			Reduction: concentration (wt %)
			Concentration (wt %)	Temperature (°C)	
Regular		—	0.0	40	0.0
Chito-1	DAC-1	1,000–2,000	2.0	40	2.0
Chito-2			5.0	40	2.0
Chito-3			8.0	60	2.0
Chito-4	DAC-2		2.0	40	2.0
Chito-5			5.0	40	2.0
Chito-6	DAC-3		2.0	40	2.0
Chito-7	DAC-1	$\sim 10,000$	2.0	40	2.0
Chito-8	DAC-2		2.0	40	2.0
Chito-9			5.0	40	2.0

30 min. The fibrillated fibers were washed with distilled water on filter paper and dried under the ambient conditions.

Scanning electron microscopy (SEM) measurement

Fibrillated fiber bundles were photographed with SEM (S-420, Hitachi, Tokyo, Japan). The degree of fibrillation was compared with these SEM images.

Antimicrobial activity

Antimicrobial activities of the modified fibers were evaluated against Gram-positive bacteria (*Staphylococcus aureus*, ATCC 6538) and Gram-negative bacteria (*Klebsiella pneumoniae*, ATCC 4352). According to the bioassay method KS K 0693, an inoculum incubated in a nutrient broth and a nutrient agar broth was prepared with 1.3×10^5 colony forming units (CFU)/mL. The untreated control fabric and each modified fabric were placed in a 30-mL glass flask, and 0.2 mL of the inoculum was added. After incubation at $37 \pm 1°C$ for 18 ± 1 h, these solutions were diluted with a saline solution. Then, 1 mL of the dilute solutions and 20 mL of the nutrient agar broth were incubated at $37 \pm 1°C$ for 24–48 h, and the survival colonies were counted. The percentage reduction was determined with eq. (1):

$$\text{Reduction in CFU (\%)} = \frac{M_b - M_c}{M_c} \times 100 \quad (1)$$

where M_b is the cell number of the control sample and M_c is the cell number of the test sample after incubation for 18 h.

RESULTS AND DISCUSSION

Preparation of the oxidized and crosslinked lyocell fiber

Partial oxidation with periodate results in the cleavage of the C_2—C_3 bond in the glucopyranose ring

and the formation of two aldehyde groups per unit. Also, the aldehyde groups can react with the amino groups of chito-oligosaccharide by Schiff base formation, and the adjacent cellulose chains in the lyocell fibers are crosslinked. Then, the products are stabilized by reduction with sodium borohydride.

FTIR spectroscopy

Infrared spectra of the modified fibers are shown in Figure 1. The oxidized cellulose fiber with periodate exhibited the characteristic absorption band for the C=O stretching vibration at 1723.5 cm^{-1}. After
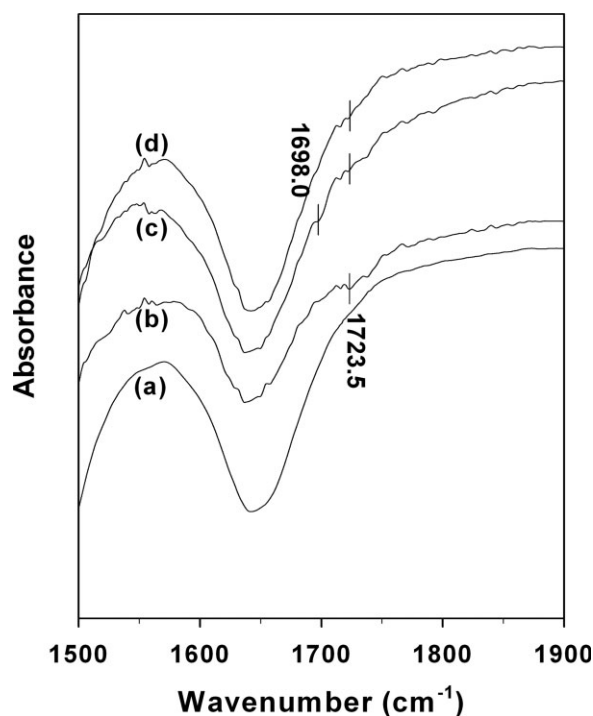

Figure 1 Infrared spectra of the modified cellulose fibers: (a) regular cellulose, (b) oxidized cellulose, (c) crosslinked cellulose, and (d) reduced cellulose.

TABLE III
Relative Intensities of C_{1s}, O_{1s}, and N_{1s} in the XPS Spectra

Sample	Surface chemical composition (%)		
	C_{1s}	O_{1s}	N_{1s}
Regular	66.0	34.0	—
DAC-1	66.5	33.5	—
DAC-2	67.2	32.8	—
DAC-3	68.2	31.8	—
Chito-1	77.6	21.2	1.2
Chito-4	71.4	26.1	2.5
Chito-6	74.3	22.5	3.2
Chito-7	76.2	22.7	1.1
Chito-8	75.9	22.3	1.8

crosslinking with chito-oligosaccharide, the characteristic absorption band for the C=N double bond was exhibited at 1698.0 cm^{-1}, and this band disappeared after the reduction process.

Surface chemical composition

Relative intensities of C_{1s}, O_{1s}, and N_{1s} in XPS spectra of the oxidized and crosslinked lyocell fibers are shown in Table III. O_{1s} intensities slightly decreased with the degree of oxidation. After crosslinking with chito-oligosaccharide, O_{1s} intensities decreased because of dehydration, and the N_{1s} component was introduced by amino groups of chito-oligosaccharide. N_{1s} intensities increased with the degree of oxidation, and the values of fibers treated with a high-M_w chito-oligosaccharide were a little smaller than those fibers treated with a low-M_w chito-oligosaccharide. From this result, we determined that the crosslinking reactions occurred more easily with highly

oxidized lyocell and low-molecular-weight chito-oligosaccharide.

Furthermore, curve fittings of C_{1s} spectra are shown in Figure 2. The C_{1s} peak of untreated cellulose was divided into three peaks [Fig. 2(a)]: the —CH peak at 285 eV (p-1), the —CO— peak at 286.5 eV (p-2), and the —COO— peak at 288.5 eV (p-4). Periodate oxidation caused a new —C=O peak in the C_{1s} spectra [Fig. 2(b)]: the —CH peak at 285 eV (p-1), the —CO— peak at 286.5 eV (p-2), the —C=O peak at 287.7 eV (p-3), and the —COO— peak at 288.9 eV (p-4). The crosslinked and reduced cellulose exhibited the same four separate peaks [Fig. 2(c)]: the —CH peak at 285 eV (p-1), the —CO— and —CN— peak at 286.5 eV (p-2), the —C=O peak at 287.7 eV (p-3), and the —COO— peak at 288.9 eV (p-4). However, the relative peak area of p-3 was smaller and that of p-2 was larger than those of the oxidized cellulose because of Schiff base formation with the chito-oligosaccharide.

Fibrillation property

The fibrillation tendency of the modified lyocell fibers was efficiently controlled by the crosslinking reactions between DAC and chito-oligosaccharide. SEM images of the fibrillated fibers are shown in Figures 3 and 4, and the degree of fibrillation was compared with the relative number of fibrils on the fiber surface. The degree of fibrillation decreased in proportion to the degree of oxidation and the chito-oligosaccharide concentration. With a high-M_w chito-oligosaccharide, the possibility of crosslinking reactions between adjacent cellulose chains decreased, and it facilitated the splitting of the fibrils of the fiber.
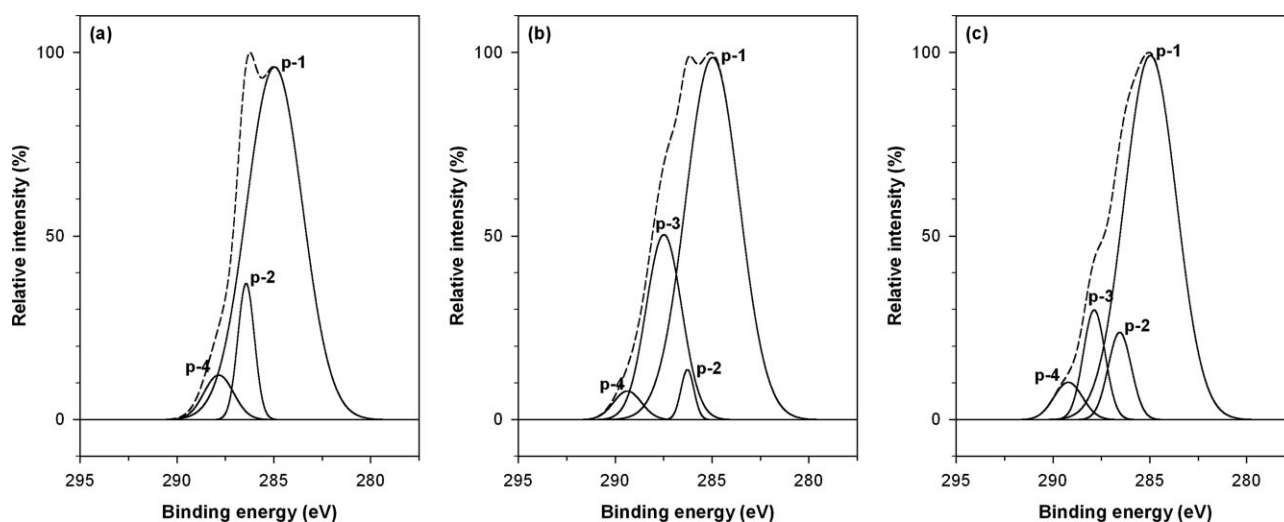
Figure 2 Curve fitting of C_{1s} spectra: (a) regular cellulose, (b) oxidized cellulose, and (c) crosslinked and reduced cellulose.
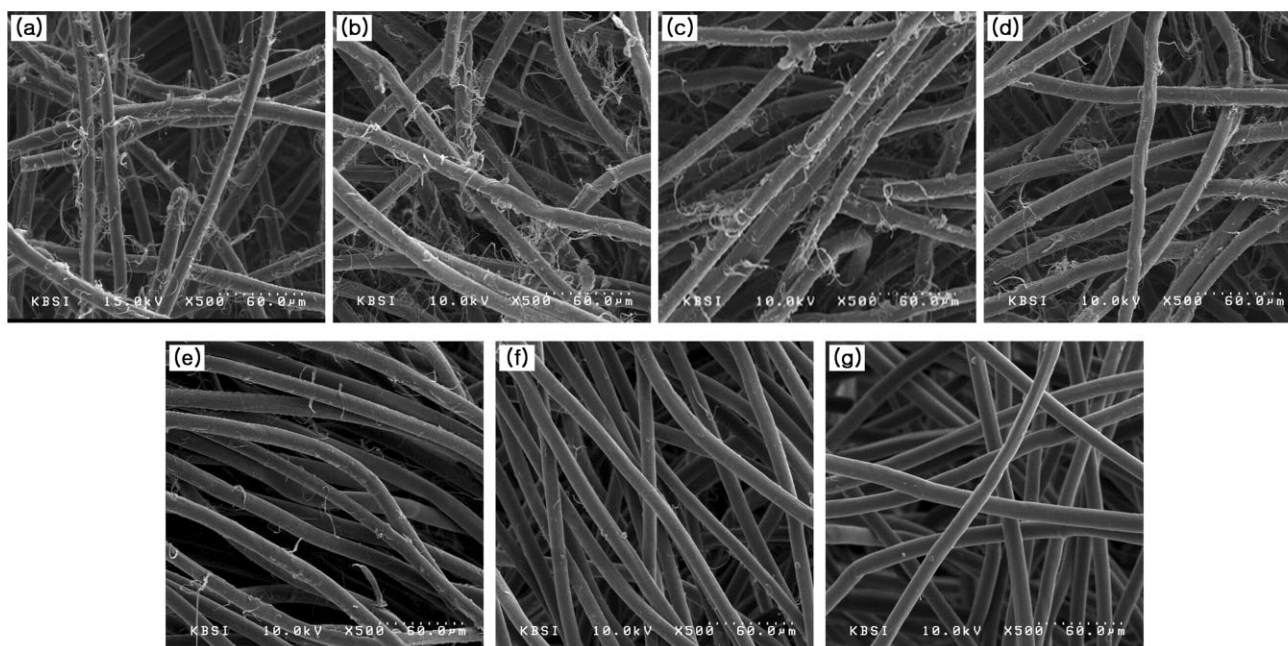
Figure 3 Morphology of fibrillated lyocell fibers after crosslinking with low-M_w chito-oligosaccharide: (a) regular, (b) Chito-1, (c) Chito-2, (d) Chito-3, (e) Chito-4, (f) Chito-5, and (g) Chito-6.

Antimicrobial activity

Lyocell fibers crosslinked with a chito-oligosaccharide had antimicrobial activity against *S. aureus* and *K. pneumoniae* because of the successful introduction of a chito-oligosaccharide with amino groups (Fig. 5). However, the reduction rates of the crosslinked fibers with a high-M_w chito-oligosaccharide were somewhat lower than those of the fibers crosslinked with a low-M_w chito-oligosaccharide; this was caused by the decrease in the crosslinking reactivity.

CONCLUSIONS

Solvent-spun lyocell fibers have unique fibrillation properties because of their fine molecular structure. We introduced crosslinking reactions between water-soluble chito-oligosaccharides and cellulose chains to impart antifibrillation and antimicrobial properties. First, we determined that the aldehyde groups of the oxidized cellulose could react with the amino groups in the chito-oligosaccharide by Schiff base formation. The absorption bands of infrared spectroscopy showed the characteristics of the reaction products after periodate oxidation, the crosslinking reaction with the chito-oligosaccharide, and the reduction with sodium borohydride. According to the surface chemical analysis by XPS, the oxidation resulted in a reduction of the O_{1s} intensities, and the crosslinking reaction resulted in a reduction of the O_{1s} intensities and an increase in the N_{1s} intensities. Also, the curve fitting of C_{1s} spectra showed the occurrence of the oxidation and the crosslinking reaction. The fibrillation tendency of the
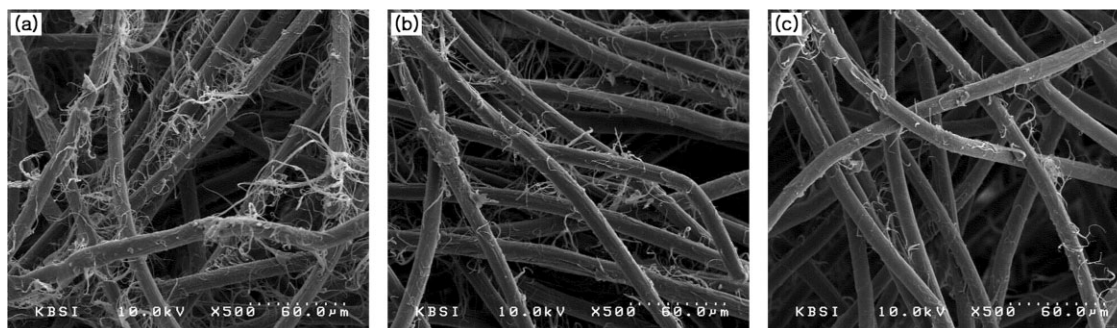
Figure 4 Morphology of fibrillated lyocell fibers after crosslinking with high-M_w chito-oligosaccharide: (a) Chito-7, (b) Chito-8, and (c) Chito-9.
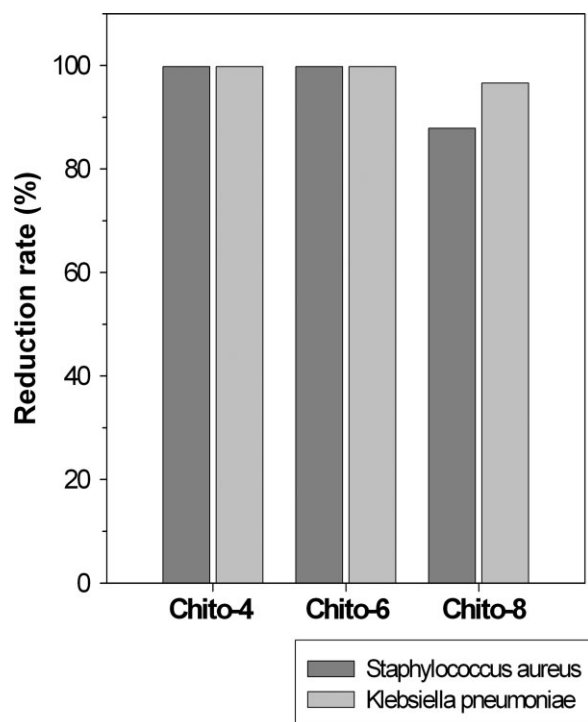
Figure 5 Reduction rate of the chitosan-crosslinked fibers.

crosslinked fibers was diminished by the oxidation levels and chito-oligosaccharide concentrations, especially with a low-M_w chito-oligosaccharide. Furthermore, the antimicrobial activity was achieved by crosslinking reactions with chito-oligosaccharides and was superior when the fibers were treated with a low-M_w chito-oligosaccharide.

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