

Crosslinking Reactions of Oxidized Cellulose Fiber. I. Reactions Between Dialdehyde Cellulose and Multifunctional Amines on Lyocell Fabric

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Received 16 February 2009; accepted 26 May 2009

DOI 10.1002/app.30895

Published online 23 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Fibrillation-controlled lyocell fibers were developed by crosslinking reactions between dialdehyde cellulose (DAC) and multifunctional amines. DAC lyocell fibers were manufactured by partial oxidation with sodium metaperiodate and were successfully crosslinked with two multifunctional amines by Schiff-base formation. The amorphous regions and the char formations, which were characterized by differential scanning calorimetry and thermogravimetric analysis, increased with the degree of oxidation. After the crosslinking reactions, an increase in the amorphous regions also appeared, whereas the thermal stability was somewhat improved by the chain crosslinking. These results were in good agreement with viscosity-average degree of polymerization values in that they diminished with oxidation level and increased with the crosslinking reactions. The water retention value

and moisture regain value decreased with the oxidation and crosslinking levels, which implied that the swellability of fibers and the water absorbency in characteristic sites decreased with them. The increase in the dry crease recovery angle also confirmed the presence of hemiacetal crosslinks in the DAC and amine crosslinks between the DAC and the amines. The fibrillation grade of the crosslinked fibers diminished with oxidation level and the amine concentration. In particular, the fibrillation properties of the crosslinked fibers with 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt were more easily controlled than those of the crosslinked fibers with 2,4,6-triamino-1,3,5-triazine. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 682–690, 2010

Key words: crosslinking; modification; fibers

INTRODUCTION

Lyocell fibers, which are developed from wood pulp in a recyclable, solvent-spun process, are biodegradable fibers with high dry and wet strengths, a low shrinkage, drapability, and inherent luster. The dry-jet/wet-spinning system of lyocell fibers produces highly oriented crystalline regions and weak lateral cohesion between crystallites, which result in fibrillation behavior under mechanical stress in the wet state. The fibrillation of lyocell fibers can produce peach-skin fabrics with the specific finishing process; on the other hand, this adversely affects the dyeing performance and launderability.

The fibrillation control systems of lyocell fibers have long been studied by many textile research groups. They have used conventional crosslinking agents for cellulose, such as dimethylol dihydroxyethylene urea, dimethylol dihydroxyimidazoline, and their modified products,^{1–3} but the application

fields have been restricted because of formaldehyde release. Researchers have developed specific crosslinking agents for lyocell fibers. They have applied triazine derivatives,^{4–7} polycarboxylic acid derivatives,⁸ aminofunctional polysiloxane polymers,⁹ and multifunctional reactive dyes,^{3,4,10} also, combined curing systems with conventional resins, binders, and hardeners have been recommended. Some other attempts to develop fibrillation control techniques were made with pulp blending systems,¹¹ copolymer blending systems,¹² and spinning condition adjustments.¹³

Fibrillation-controlled lyocell fibers have been characterized by their mechanical properties, abrasion resistance, crease recovery angle, water/alkali retention value, and dyeing properties. Also, to evaluate the degree of fibrillation, some specific measurements have been suggested.^{14–16}

On the other hand, cellulose can be partially oxidized with periodate in the powder, paper, and fabric states. The modified dialdehyde cellulose (DAC) has been widely applied for ion-exchange materials,¹⁷ column packing material for chromatography,¹⁸ indicator paper for amines,¹⁹ enzyme immobilization,²⁰ and graft polymerization.²¹

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In this study, we developed a special fibrillation control system for lyocell fibers with DAC and evaluated the fiber properties during oxidation and crosslinking. We obtained DAC lyocell fibers by partial oxidation with sodium metaperiodate and induced crosslinking reactions through Schiff-base formations with multifunctional amines. The oxidized and crosslinked lyocell fibers were characterized by infrared spectroscopy, thermal property testing, degree of polymerization, water retention value (WRV), moisture regain value (MRV), crease recovery angle, and fibrillation behavior.

EXPERIMENTAL

Materials

Commercial lyocell scoured fabric (Tongkook Corp., Gumi, Korea) was used in all experiments. The oxidation reagent (sodium metaperiodate), multifunctional amines (2,4,6-triamino-1,3,5-triazine and 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt), and reduction reagent (sodium borohydride) were all first grade, obtained from Sigma-Aldrich Korea (Yongin, Korea), and used without further purification.

Preparation of DAC

Aqueous sodium metaperiodate solutions were prepared with three different concentrations (0, 0.5, and 1.0 wt %). Lyocell fabrics were stirred gently in these solutions at 30 or 35°C for 4.5 or 7 h. The degree of oxidation values were estimated by periodate consumption calculated from the UV absorbance of residual solutions at 222 cm^{-1} (Shimadzu UV-1601 spectrophotometer, Kyoto, Japan). After the reactions were stopped with excess ethylene glycol, the samples were washed with warm distilled water and dried under ambient conditions. The oxidation conditions and the degrees of oxidation are shown in Table I.

Preparation of the crosslinked lyocell fibers by Schiff-base formation

Aqueous triamine solutions were prepared at different concentrations (0–2.0 wt %). The DAC fabrics

were stirred gently in these solutions at 30, 40, 50, and 80°C for 3 h and washed with warm distilled water. After Schiff-base formation between the DAC and multifunctional amines, the crosslinked fabrics were stirred in 0–4.0 wt % sodium borohydride solutions at room temperature for 3 h. They were washed with warm distilled water and dried under ambient conditions. The crosslinking reaction conditions are shown in Table II.

Measurements

Fourier transform infrared (FTIR) measurement

Potassium bromide pellets of the modified fibers were prepared and scanned with a PerkinElmer FTIR model Spectrum GX (Waltham, MA). Infrared spectra of the different samples were recorded and analyzed.

Thermal analysis

The thermal properties of the oxidized cellulose fibers were evaluated by differential scanning calorimetry (DSC; SSC-5200, Seiko Instruments, Inc., Tokyo, Japan). The samples were scanned from 40 to 150°C at 20°C/min under a nitrogen flow (70 mL/min) and then quenched and scanned for the second time from 40 to 400°C at 5°C/min under the same purging conditions.

Also, thermogravimetric analysis (TGA; Tyris 6, PerkinElmer) was used to study the thermal stability of the modified cellulose fibers at 10°C/min under an air flow (20 mL/min).

Viscosity measurement

The viscosity-average degree of polymerization (DP_V) of the modified cellulose fibers was obtained through intrinsic viscosity ($[\eta]$) values measured in 0.5M CuEn (cupriethylenediamine solution) with an Ubbelohde viscometer. The $[\eta]$ values were determined by the extrapolation of the reduced viscosity at zero concentration by a straight line, which was measured in six dilute solutions (5.00, 4.00, 3.33, 2.50, 1.92, and 1.56 mg/mL) at 25°C. DP_V was calculated as follows:

TABLE I
Degree of Oxidation of the 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	0.5	30	4.5	0.371
DAC-2	1.0	35	4.5	0.881
DAC-3	1.0	35	7.0	1.198

TABLE II
Crosslinking Reaction Conditions

Sample	Schiff-base reaction			Reduction
	Triamine	Concentration (wt %)	Temperature (°C)	Concentration (wt %)
Regular	—	0	40	0
DAC-1	Mel-1	0.5	40	1.0
	Mel-2	1.0	40	2.0
	Mel-3	2.0	80	4.0
DAC-2	Mel-4	1.0	40	2.0
	Mel-5	2.0	80	4.0
DAC-3	Mel-6	1.0	40	2.0
DAC-1	Sam-1	0.1	30	0.2
	Sam-2	0.2	30	0.4
	Sam-3	0.5	50	1.0
DAC-2	Sam-4	0.2	30	0.4
	Sam-5	0.5	50	1.0
DAC-3	Sam-6	0.2	30	0.4

$$\overline{DP}_V^{0.905} = 0.75[\eta]_{\text{CuEn}} (\text{cm}^3/\text{g}) \quad (1)$$

WRV and MRV

The modified fibers (0.5 g) were soaked in distilled water and deaerated in a vacuum oven at 20°C for 24 h. The fibers were centrifuged in a tube with stainless steel mesh at 1000 rpm for 20 min and weighed (W_1). The fibers were dried in a vacuum oven at 40°C for 24 h, kept in a desiccator containing calcium chloride/phosphorous pentoxide for 24 h, and weighed (W_0). These fibers were also kept in a desiccator containing a water/sulfuric acid solution at a fixed 65% relative humidity for 48 h and weighed (W_2). WRV and MRV were calculated as follows:

$$\text{WRV}(\%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

$$\text{MRV}(\%) = \frac{W_2 - W_0}{W_0} \times 100 \quad (3)$$

Crease recovery measurement

The dry crease recovery angle (DCRA) was measured according to KS K 0550 (the Monsanto method).

Fibrillation measurement

Fibers were cut to a 5-mm length, and the cutting fibers were placed in a vial containing a 1% NaOH aqueous solution. The vial was translated at 300

turns/min for 30 min. The fibrillated fibers in the swelling state were photographed with an optical microscope and graded from 5 (very highly fibrillated) to 0 (no fibrillated) according to standard grading photographs (Fig. 1).

Scanning electron microscopy measurement

The fibrillated fibers were washed with distilled water several times and dried under ambient conditions. The fibrillated fiber bundles were photographed with scanning electron microscopy (Hitachi S-420, Tokyo, Japan).

RESULTS AND DISCUSSION

Preparation of the oxidized and crosslinked fibers

The partial oxidation of cellulose with periodate resulted in the cleavage of the C₂—C₃ bond in the glucopyranose ring and the formation of two aldehyde groups per unit. The aldehyde groups could react with amino groups by Schiff-base formation, so the adjacent cellulose chains in the lyocell fibers were crosslinked with multifunctional amines. The products were stabilized by a reduction process with sodium borohydride (Scheme 1).

FTIR spectroscopy

The infrared spectra of the modified fibers are shown in Figure 2. The absorption bands of the crosslinked fibers at 1555 cm⁻¹ were characterized by N—H deformation vibration, and the absorption

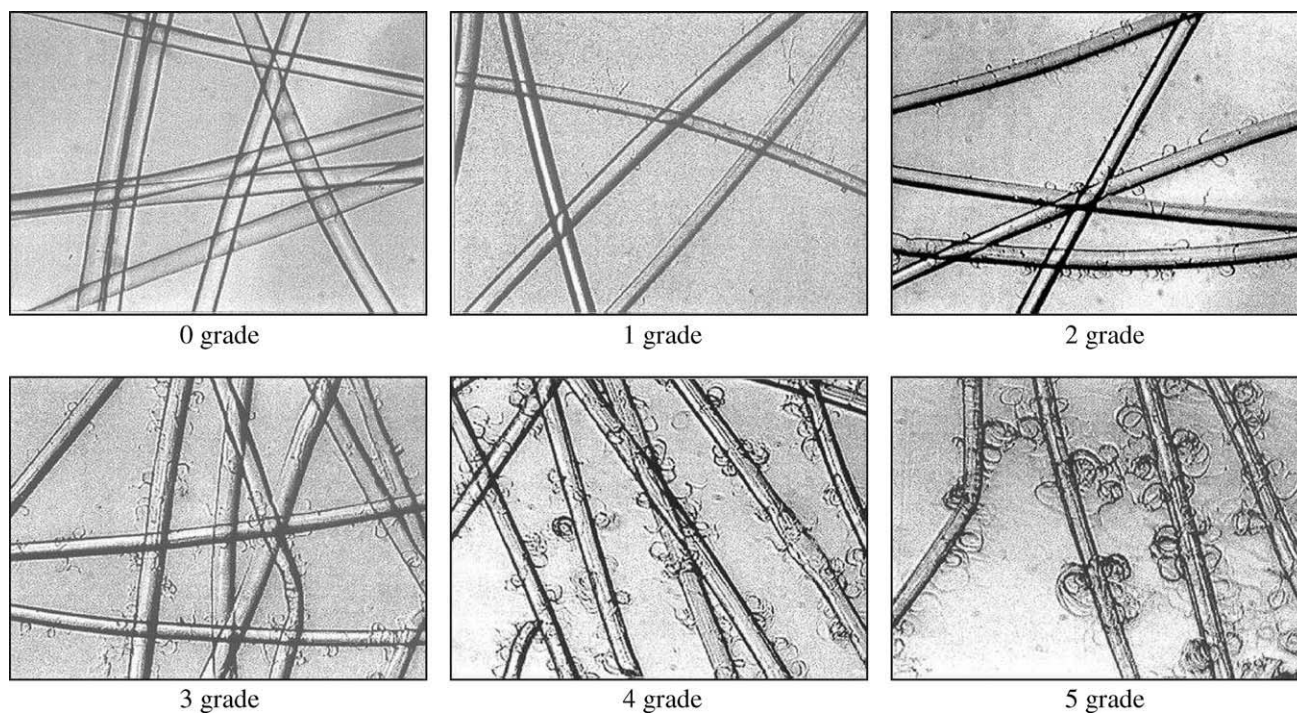


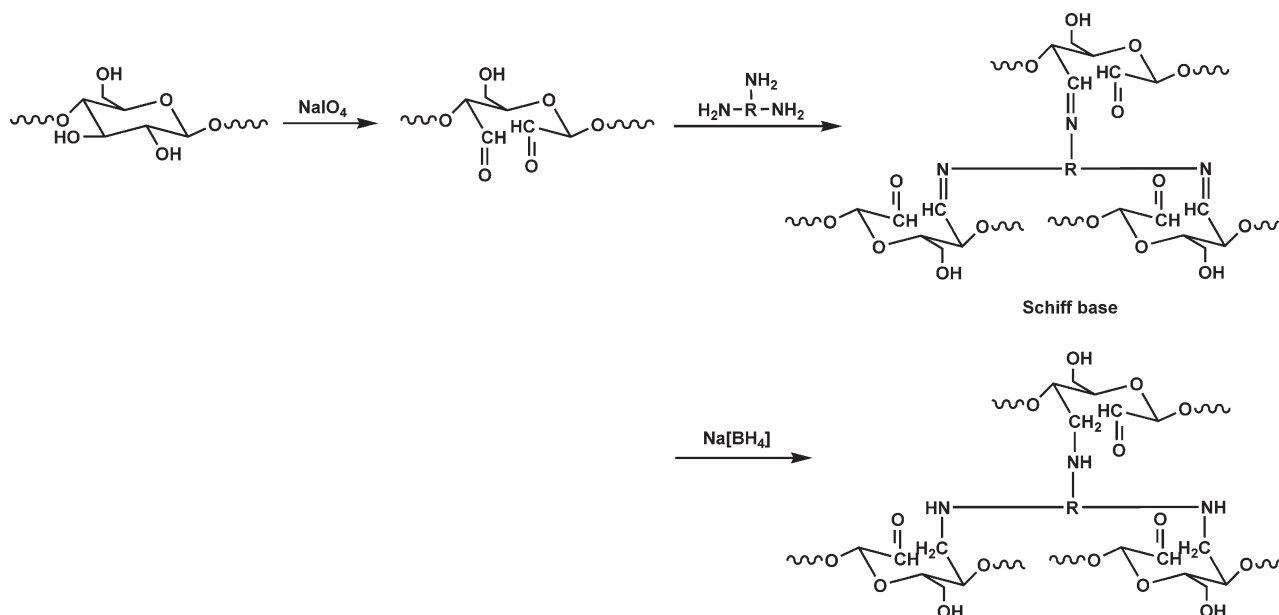
Figure 1 Standard fibrillation grade.

bands at 1115 cm^{-1} were characterized by C–N stretching vibrations. We knew that the multifunctional amines were successfully introduced into the modified fibers.

DSC of the oxidized fiber

The results of the DSC analysis of the partially oxidized lyocell fibers are shown in Figure 3 and Table III. Two broad endothermic peaks appeared in each

curve. The former one (endo I) was at $120\text{--}170^\circ\text{C}$ and was caused by the molecular motions of amorphous regions, and the latter one (endo II) was at $200\text{--}250^\circ\text{C}$ and was caused by the facilitated thermal scission of covalent bonds, which led to the generation of volatile substances.^{22,23} The endothermic enthalpy values of these peaks became larger and the peak temperature became lower according to the increase in the degree of oxidation. Furthermore, a main endothermic peak started at 280°C (endo III)



Scheme 1 Reaction mechanism of Schiff-base formation between DAC and multifunctional amines.

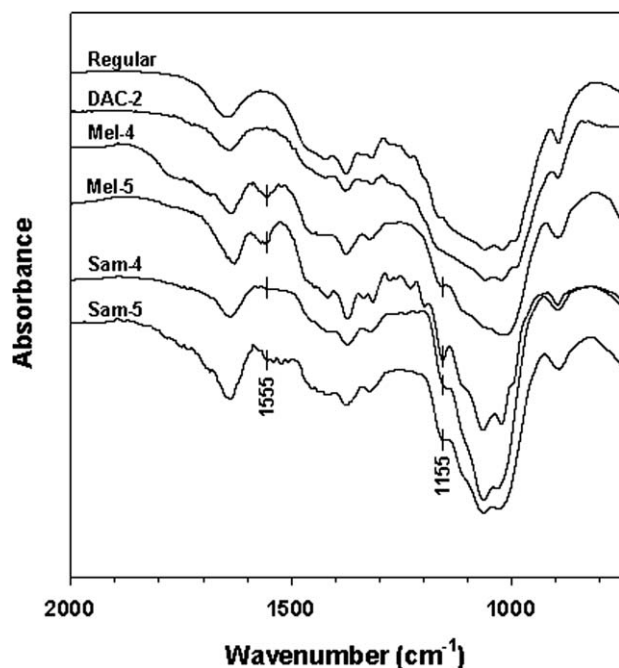


Figure 2 Infrared spectra of the modified cellulose fibers.

and was characterized by the decomposition of cellulose through the formation of levoglucosan (1,6-anhydro- β -D-glucopyranose). This peak shifted to a lower temperature and the enthalpy values decreased with increasing degree of oxidation. The following exothermic peak (exo I) due to char formation moved to a lower temperature, and the exothermic enthalpy values increased according to the oxidation levels.

The thermal decomposition process of cellulose has been regarded as two competitive pathways.²⁴ At a relatively low temperature (<250°C), the dehydration pathway followed by chain scission and char formation is predominant. At high temperatures, the depolymerization pathway of cellulose yields tar (levoglucosan), which further decomposes with the formation of char. The former is known to mainly occur in amorphous regions, and the latter occurs in crystalline regions. Char yield is affected not only by char formation through the dehydration pathway but also by the secondary degradation of levoglucosan. As mentioned for the DSC results, the endother-

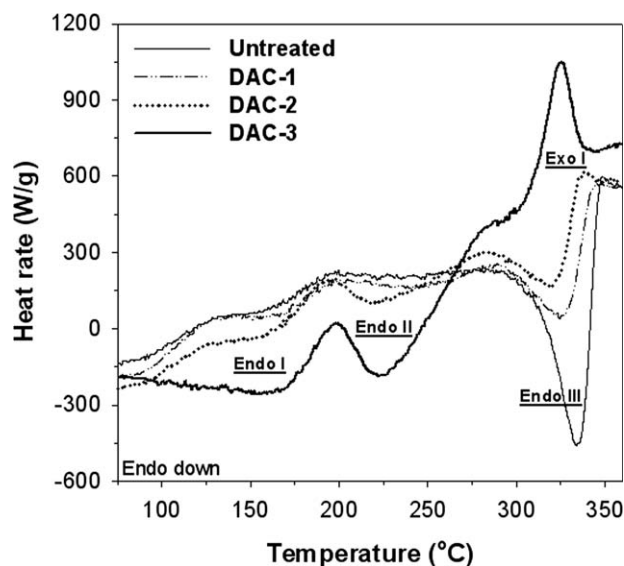


Figure 3 DSC curves of the oxidized fibers.

mic enthalpy values of endo I and endo II increased and those of endo III decreased with periodate oxidation. Their peak temperatures decreased with it. Therefore, it was apparently proven that the amorphous regions of the internal fibers increased with periodate oxidation. Also, as shown by the increase in the exothermic enthalpy values of exo I, the char formation by heat degradation increased with periodate oxidation.

TGA of the oxidized and crosslinked fiber

The TGA and differential thermogravimetry (DTG) curves and data are shown in Figure 4 and Table IV. The onset temperature of thermal decomposition corresponded to endo I and endo II (the dehydration pathway) in the DSC curve, and the first peak temperature of the DTG curve corresponded to endo III (the depolymerization pathway). These two values diminished with periodate oxidation. The first step weight loss between 150 and 400°C decreased with the oxidation levels, so the char formation at 400°C increased. The residue after char oxidation at 550°C became larger according to the oxidation levels. These thermogravimetric results of the oxidized

TABLE III
DSC Results for the Oxidized Lyocell Fibers

Sample	Endo I		Endo II		Endo III		Exo I	
	T_{\max} (°C)	ΔH (W/g)	T_{\max} (°C)	ΔH (W/g)	T_{\max} (°C)	ΔH (W/g)	T_{\max} (°C)	ΔH (W/g)
Regular	166.8	1,455	242.2	1,059	334.3	20793	348.3	593
DAC-1	166.1	2,070	238.4	2,647	324.2	9412	347.6	489
DAC-2	164.7	3,017	233.4	5,578	320.6	5705	338.2	947
DAC-3	158.3	11,660	232.9	15,084	—	—	324.9	7380

ΔH = enthalpy; T_{\max} = maximum temperature.

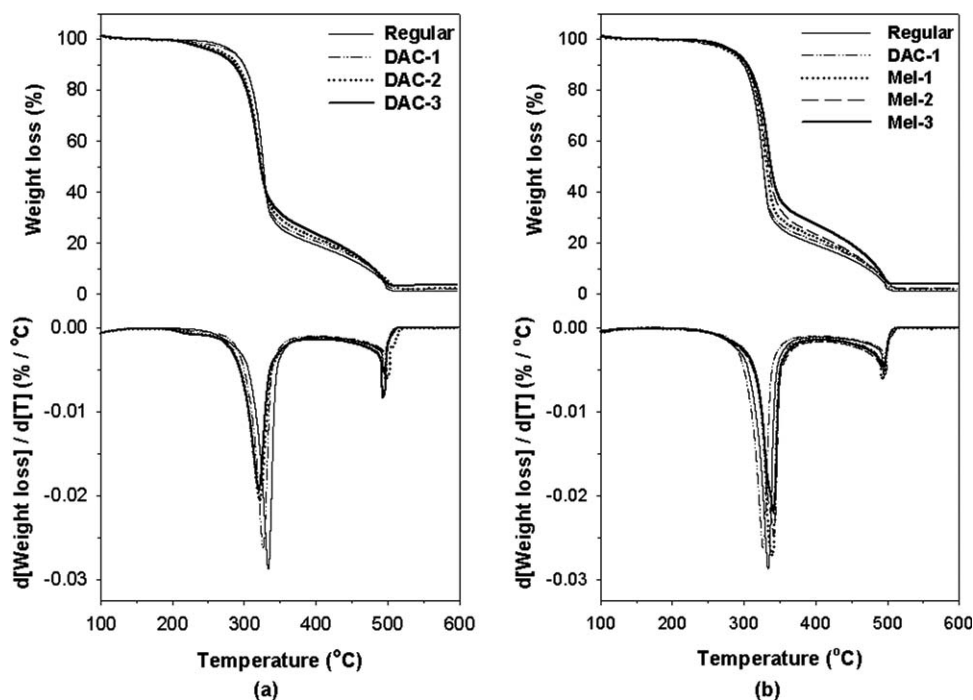


Figure 4 TGA and DTG curves of (a) the oxidized fibers and (b) the crosslinked fibers.

fibers are in good agreement with the DSC results, which was for the amorphous regions and the char formation increased with periodate oxidation.

After the reactions between the DAC and multifunctional amines, the first-step weight loss also decreased, and the second-step weight loss and the residue increased. On the other hand, the onset temperature and first peak temperature of the DTG curves increased with the amine concentration. We

determined that the crosslinking reactions between the oxidized cellulose and amines increased the amorphous regions; however, the molecular chain mobility was somewhat restricted by chain crosslinking, so the thermal stability increased. In particular, the crosslinked fibers with 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt exhibited similar results with a small amount of amines to those of the fibers crosslinked with 2,4,6-triamino-1,3,5-triazine.

TABLE IV
Thermogravimetric Results for the Modified Lyocell Fibers

Sample	TGA curve				DTG curve	
	Onset temperature	First step of weight loss ^a	Second step of weight loss ^b	Residue ^c	First peak temperature	Second peak temperature
Regular	310.4	80.7	18.2	1.1	333.3	494.3
DAC-1	309.2	79.2	18.8	2.0	326.2	495.0
Mel-1	310.5	77.8	20.0	2.2	339.8	492.7
Mel-2	311.2	76.4	21.0	2.6	341.7	494.8
Mel-3	313.5	72.5	23.6	3.9	341.3	494.8
Sam-1	310.8	78.5	18.9	2.6	335.2	493.6
Sam-2	311.3	76.2	20.4	3.4	335.2	491.5
Sam-3	315.1	71.8	23.7	4.5	340.8	492.3
DAC-2	298.0	77.9	19.8	2.3	321.8	498.8
Mel-4	302.4	75.3	22.2	2.5	333.7	492.6
Mel-5	301.8	73.0	23.1	3.9	335.2	490.6
Sam-4	301.9	74.9	22.2	2.9	331.6	493.7
Sam-5	304.1	71.7	24.6	3.8	337.2	495.3
DAC-3	296.5	76.3	20.1	3.5	320.7	493.6
Mel-6	296.9	74.2	22.3	3.5	336.4	491.4
Sam-6	298.5	70.0	25.9	4.1	342.8	492.2

^a Weight loss (%) between 150 and 400°C.

^b Weight loss (%) between 400 and 550°C.

^c Residual weight (%) at 500°.

TABLE V
 \overline{DP}_V , Water Absorbency, Crease Recovery, and Fibrillation Properties of the Modified Lyocell Fibers

Sample	\overline{DP}_V	WRV (%)	MRV (%)	Crease recovery angle ($^\circ$) ^a	Fibrillation grade
Regular	1265	69.9	6.67	227	5
DAC-1	996	58.2	6.28	235	—
Mel-1	1014	54.8	6.13	239	4
Mel-2	1079	51.3	6.05	253	4
Mel-3	1032	45.2	5.89	247	2
Sam-1	1056	52.1	6.16	240	3
Sam-2	1093	52.7	5.98	248	2
Sam-3	1164	44.9	5.79	266	1
DAC-2	861	52.9	6.08	248	—
Mel-4	890	44.3	6.00	276	3
Mel-5	949	44.7	5.77	268	2
Sam-4	953	41.5	5.95	258	2
Sam-5	976	39.6	5.8	274	2
DAC-3	754	47.8	5.74	266	—
Mel-6	817	39.1	5.61	288	0
Sam-6	882	36.7	5.58	281	0

^a $w + f$.

\overline{DP}_V

The \overline{DP}_V values of the modified cellulose fibers are shown in Table V. We determined that the \overline{DP}_V values decreased with periodate oxidation because of partial depolymerization during the ring-opening process and were somewhat recovered with the crosslinking reactions between adjacent cellulose chains. The crosslinked fibers with 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt had larger values than the fibers crosslinked with 2,4,6-triamino-1,3,5-triazine.

WRV and MRV

The fibers soaked in distilled water were vacuum-deaerated to remove air in the fiber interspaces. The fully wetted fibers were swollen by expansion with absorbed water molecules in the amorphous regions. After centrifugation, the mechanically held water in the interfiber spaces was successfully removed, so we determined that the WRVs implied the swellability of fibers. The oxidized fibers with periodate had lower WRV than the regular lyocell fibers (Table V). By the previous results of thermal analysis, we determined that the amorphous regions increased with oxidation, so it was proven that more densely packed molecular structures through the reduction of molecular weight diminished the swellability of the oxidized fibers. As is generally known, the crosslinked cellulose fibers also exhibited a decrease in WRV, which was caused by the swellability reduction by the network crosslinking structures.²⁵

MRV is also shown in Table V, which was closely related to the total sites of water absorption in the fiber internal surface. The oxidized fibers had lower

MRVs than regular fiber because the aldehyde groups were less prone to absorb water molecules than hydroxyl groups. The crosslinked fibers exhibited a small reduction in MRV, which was due to the introduction of amine linkages between the DAC and multifunctional amines.

Pearson's correlation analyses were performed with the statistical software package SPSS PC (version 12.0). The results were considered statistically significant at a correlation coefficient of 0.860 and a significance probability of 0.000 in the relation between WRA and MRA.

Crease recovery angle

The DCRA values of the modified cellulose fabrics are shown in Table V. It is well known that DACs have hemiacetal crosslinks between aldehyde groups and hydroxyl groups in the neighbor molecular chains,²⁶ these links are easily broken at very high moisture contents.²⁷ DCRA of the oxidized fabrics increased with the oxidation levels because these crosslinks somewhat enabled the recovery of the creases. After the reactions with multifunctional amines, we also determined that the crosslinking reactions took place between the DAC and amines. These reactions resulted in an increase in DCRA due to these network structures.²

Pearson's correlation analyses were performed with the statistical software package SPSS PC (version 12.0). The results were considered statistically significant at a correlation coefficient of -0.878 and a p value of 0.000 in the relation between WRA and DCRA and at a correlation coefficient of -0.867 and a p value of 0.000 in the relation between MRA and DCRA.

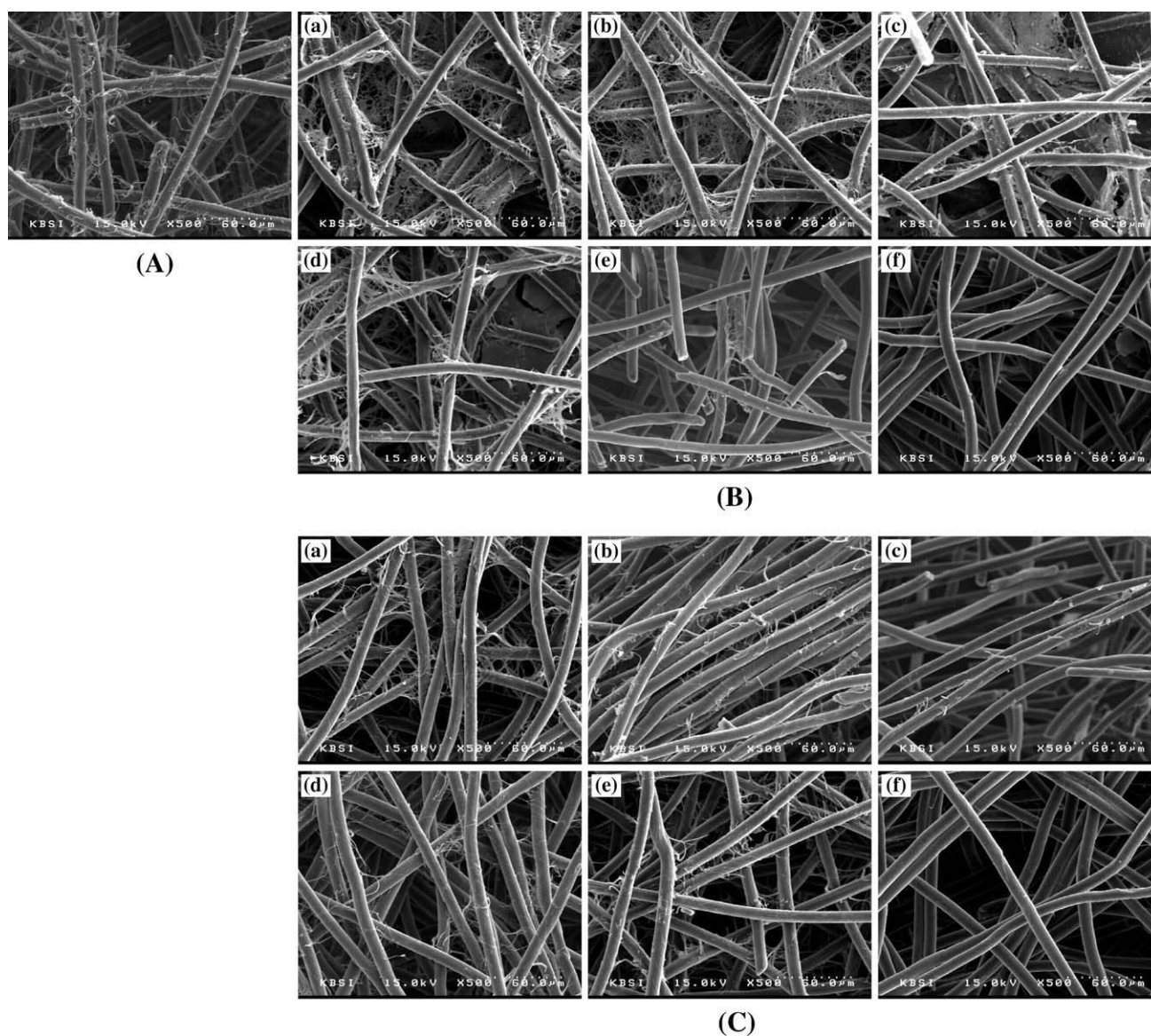


Figure 5 Morphology of the fibrillated lyocell fibers: (A) and (f) Mel-6], and (C) fibers crosslinked with 4-hydroxy-regular fibers, (B) fibers crosslinked with 2,4,6-triamino-1,3,5-2,4,6-triaminopyrimidine sulfate salt [(a) Sam-1, (b) Sam-2, triazine [(a) Mel-1, (b) Mel-2, (c) Mel-3, (d) Mel-4, (e) Mel-5, (c) Sam-3, (d) Sam-4, (e) Sam-5, and (f) Sam-6].

Fibrillation properties

It is well known that the fibrillation tendency of lyocell fibers diminishes with the crosslinking reactions of cellulose chains. As shown in Table V, the fibrillation grade decreased in proportion to the degree of oxidation and the amine concentration. We determined that the crosslinking reactions successfully occurred between the DAC and multifunctional amines and were more effective at relatively high oxidation levels and amine concentrations. Particularly in the case where 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt was used, the fibrillation was easily controlled with a small amount of amines. The SEM images also showed the fibrillation reduction phenomena by the reactions between partially

oxidized cellulose and the multifunctional amines (Fig. 5).

CONCLUSIONS

Partially oxidized lyocell fibers (DAC) were produced by sodium metaperiodate oxidation, and two aldehyde groups were introduced into the glucopyranose unit through the cleavage of the C_2-C_3 bond. According to thermal analysis, the amorphous regions increased with oxidation level. Thermal depolymerization occurred more easily, and char formation increased in the oxidized fibers. \overline{DP}_V of the oxidized fibers decreased with oxidation level, which induced WRV drops because of the

swellability reduction. MRV also decreased because of the introduction of aldehyde groups, but the hemiacetal crosslinks in DAC increased DCRA of the oxidized fabrics.

DAC fibers could be crosslinked with multifunctional amines (2,4,6-triamino-1,3,5-triazine and 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt) by Schiff-base formation. From TGA, we determined that the amorphous regions increased with the crosslinking reactions between the oxidized cellulose and amines; however, the molecular chain mobility was somewhat restricted by chain crosslinking. The reduction of WRV and MRV implied that the crosslinking reactions were successfully introduced, so the formation of amine crosslinkages induced the decreasing of swellability and water absorption sites. These crosslinked fabrics also exhibited high DCRA values. Furthermore, we confirmed the crosslinking reactions from photographs of the fibrillated fibers. The fibrillation grade of the crosslinked fibers decreased with oxidation level and amine concentration. Particularly for the case in which 4-hydroxy-2,4,6-triaminopyrimidine sulfate salt was used, the degree of fibrillation was easily reduced under milder conditions.

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