

CATIONIZATION OF PERIODATE-OXIDIZED COTTON CELLULOSE WITH CHOLINE CHLORIDE

JOO YONG KIM and HYUNG-MIN CHOI

*Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul,
Republic of Korea 156-743*

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To find a more efficient and practically feasible cationization process for cellulose, periodate oxidation followed by a reaction with choline chloride was carried out in cotton. FTIR spectra revealed the presence of aldehyde carbonyl groups in periodate-oxidized cotton. The cationized cotton fabrics were dyed by acid dye to confirm the presence of cationic groups. Elemental analyses also indicated the presence of cationic groups. In general, oxidation temperature is an important factor in determining the oxidation effectiveness and, consequently, cationization. This oxidation-cationization process proved to be practically feasible and environmentally desirable as an alternative cationization of cotton.

Keywords: periodate oxidation, cationization, choline chloride, FTIR analysis

INTRODUCTION

Cationization is one of the most important modifications for cellulose. Its cationization is mainly carried out to improve affinity toward anionic substances, such as dyes in conventional textile processing and metal ions or unfixed dyes in effluent treatment.¹⁻⁷ Since cotton, the most popular textile material, is usually dyed by anionic dyes, such as reactive and direct dyes, modifying cotton fibers with cationic charges prior to dyeing is an attractive route to improving dye-fiber affinity.^{1,2} Furthermore, various cationized cellulosic materials, such as rice hulls, soybean hulls, and saw dust, have been examined in controlling toxic heavy metals in effluent waters.⁶⁻⁹

Cellulosic materials are commonly cationized in three ways: firstly, a direct cationization of cellulose using a chemical compound with suitable functional groups that react with cellulose hydroxyl groups. A representative compound for this approach includes N-(3-chloro-2-hydropropyl) trimethylammonium chloride.^{1,2} The second approach involves the addition of binding agent, such as dimethyloldihydroxyethylene urea,

which reacts both with cellulose hydroxyl and the functional group of cationic agent.⁶ This process is mainly used for textile application since the common textile pad-dry-cure process can be employed. The third approach utilizes graft polymerization to introduce monomeric or polymeric cationizing agents within the cellulose, but it is not commercially applicable.¹⁰ Each process has advantages and disadvantages, but none of these processes has been commercially adopted yet. Therefore, a better process is yet to be developed in the cationization of cellulose.

Partial oxidation of cellulose by periodate can lead to the selective cleavage at C-2 and C-3 vicinal hydroxyl groups within glucose to yield dialdehyde units.¹¹⁻¹⁴ This process can be carried out at room temperature or slightly elevated temperature.¹¹ The dialdehyde cellulose is an important derivative for additional reactions¹² as this is further reacted easily with inexpensive cationizing agents, such as choline chloride (CC). The commercial pad-dry-cure process can be applied in the reaction between dialdehyde cellulose and CC.

Therefore, in this paper, cotton cellulose was first periodate-oxidized and subsequently cationized with CC. The produced celluloses can increase reactivity toward anionic dyes or can be used as membrane with potentially high affinity.^{1,6} CC is an inexpensive and non-toxic chemical approved as food additive by the Food and Drug Administration of U.S.A.⁶ The cationized cellulose produced was analyzed as to its characteristics by FTIR, elemental analysis, SEM, dye affinity and tearing strength measurement.

EXPERIMENTAL

Materials

A plain weave cotton fabric was purchased from Sombe, Inc. Chemicals, such as sodium periodate, choline chloride, aluminum sulfate, glycerol, acetic acid, and C. I. Acid Red 4, were of analytical grades and purchased from Aldrich Chemicals. Deionized water was used throughout the study.

Periodate oxidation

An amount of 10 g of cellulosic material was placed in 500 mL water and 21.4 g (0.2 mol) sodium periodate was added, unless otherwise noted. The mixture was gently stirred in the dark and oxidized at room temperature or 50 °C for an appropriate time. After oxidation, the sample was suspended in 0.1 mol/L aqueous glycerol solution for 0.5 h and washed up to neutral. Finally, the sample was washed by deionized water for 24 h and then air-dried.

Cationization of cotton

The oxidized cellulose specimen was impregnated in the aqueous bath containing CC (20 g/L) and aluminum sulfate catalyst (10 g/L) for cationization. The liquor-to-fabric ratio was 30:1. The sample was then padded to a wet pick-up of 80-85%, dried at 85 °C for 10 min, and cured at 140 °C for 2 min in the laboratory curing oven (LTH type, Werner Mathis AG,

Switzerland). The treated sample was then thoroughly washed until neutral and finally air-dried. The fabrics were stored in a standard environment (21±1 °C, 65%±2%) for future analyses.

Analyses of oxidized and cationized cotton

Elmendorf tearing strength was measured to evaluate the strength of the oxidized cotton. Three replications were used in tearing strength evaluation. An FTIR spectroscope (Jasco, FT/IR-6300, Japan) with an attached ATR was used to analyze the cotton fabrics in the spectral region of 4000-600 cm⁻¹ with 54 scans at 4 cm⁻¹ resolution. Thermogravimetric analysis (TG/DTA6200, Seiko, Japan) of the treated cotton was carried out from 50 °C to 650 °C with a 10 °C/minute heating rate in a nitrogen atmosphere (50 cm³/min). Scanning electron microscopy (SEM) (COXEM, CX-100S, Korea) was used to study the topological effect of oxidation and subsequent cationization of cotton. Elemental analysis (Euro Vector E, E/V RE2) was employed to determine the presence of nitrogen in cationized cotton.

Sorption of C. I. Acid Red 4 dye was used to evaluate the presence of cationic groups within the treated cotton cellulose. A dyeing solution containing acid dye (10 g/L) and sodium sulfate (6 g/L) was prepared and the pH of the dyebath was adjusted to 3~4 with an acetic acid solution (0.1 mol/L) at a 30:1 liquor-to-fabric ratio. Dyeing was carried out in a stainless tube of the IR dyeing machine (Daelim Starlet Co, Ltd., Korea). A detailed dyeing process illustration is provided in Figure 1.

After dyeing, the reflectance of the dyed fabric was measured by Minolta Color Eye CM-512M3 (Japan) and the K/S value was calculated according to the Kubelka-Munk equation:²

$$K/S = (1-R)^2/2R \tag{1}$$

where R is the reflectance of the sample at the wavelength of maximum absorption.

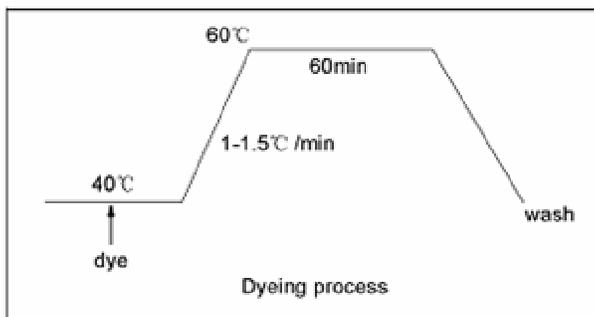


Figure 1: Dyeing process for cationized cellulose

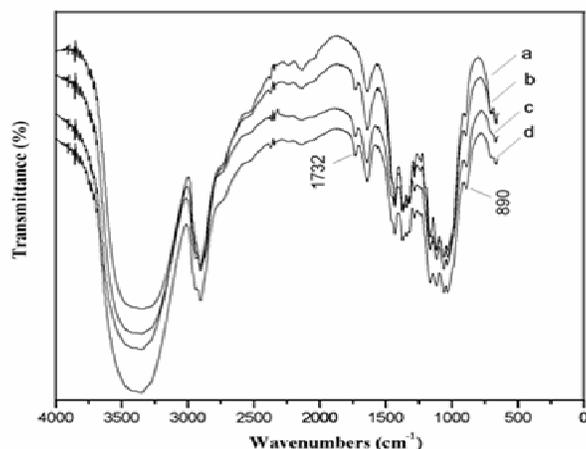


Figure 2: FTIR spectra of samples (at room temperature): a) untreated; b) 10 h; c) 20 h; d) 30 h

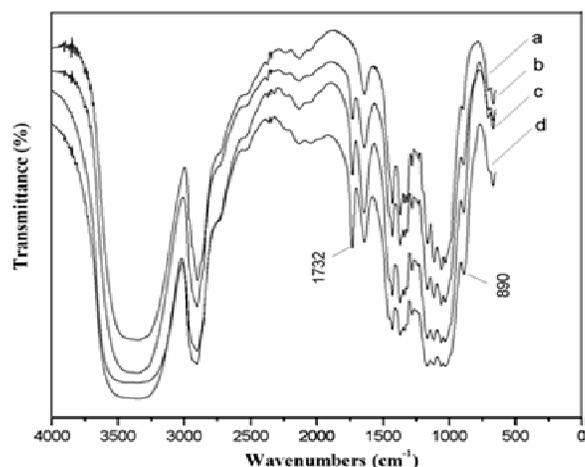


Figure 3: FTIR spectra of samples (at 50 °C): a) untreated; b) 2 h; c) 5 h; d) 8 h

RESULTS AND DISCUSSION

FTIR analyses of oxidized and cationized cellulose

Figures 2 and 3 represent the FTIR spectra of the periodate-oxidized samples. The cellulose samples were oxidized under two sets of oxidizing conditions in this study, one was oxidized at low temperature for a long time (Fig. 2), and the other specimen was oxidized at high temperature for a short time (Fig. 3). The characteristic cellulose peaks, such as 3300 cm^{-1} for hydrogen bonded O–H stretching, and $3000\text{--}2800\text{ cm}^{-1}$ region for sp^3 hybridized C–H stretching, are noted in all the samples, as expected. In addition, periodate-oxidized

celluloses show an absorption peak at 1732 cm^{-1} assigned to C=O stretching of aldehyde groups.

As shown in Table 1, the intensity of the 1732 cm^{-1} peak in dialdehyde cellulose enhanced with the increase in the oxidizing time, but there was hemiacetal formation between aldehyde and the neighboring hydroxyl groups (or water) at the same time.¹²⁻¹⁵ The presence of hemiacetal was further confirmed by the peak at 890 cm^{-1} in the spectra. The intensity of this peak was also enhanced after oxidation.

It should be noted that the intensity of the peak at 1732 cm^{-1} in dialdehyde cellulose was stronger in the samples oxidized at high temperature for a short time than in the samples oxidized at low temperature for a long time. The main parameters

that could affect the efficiency of oxidation are oxidant concentration, oxidation time, and temperature.¹³ Among them, the oxidation temperature was therefore more effective to enhance the oxidation than the oxidation time, because higher temperature accelerated the oxidizing reaction between IO_4^- and vicinal hydroxyl groups.^{11,12}

Meanwhile, the absorption peaks at 1054 cm^{-1} ($-\text{OH}$ distortion vibration), 1203 cm^{-1} ($-\text{OH}$ in-plane bending), 1108 cm^{-1} ($\text{C}-\text{H}$ deformation stretch vibration), and 1160 cm^{-1} (asymmetry $\text{C}-\text{O}-\text{C}$ stretch vibration) became weak after oxidation. This tended to indicate a partial decomposition of cellulose during sodium periodate oxidation.¹³⁻¹⁵

Table 1
FTIR peak analyses of cotton fabrics oxidized at $50\text{ }^\circ\text{C}$

Samples	Area of peaks	
	1732 cm^{-1}	890 cm^{-1}
Untreated	0	0.12
Oxidized for 2 h	0.93	0.27
Oxidized for 5 h	1.52	0.31
Oxidized for 8 h	3.24	0.44

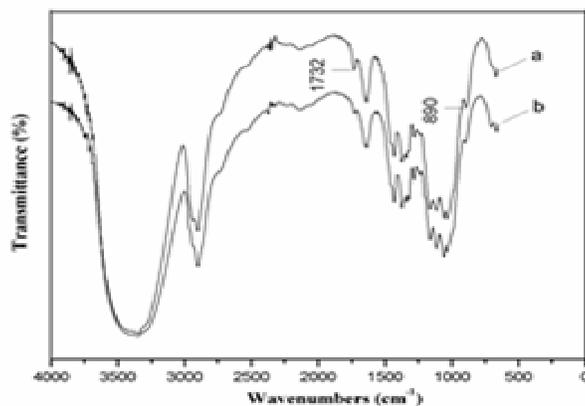


Figure 4: FTIR spectra of samples: a) oxidized at room temperature for 20 h; b) cationized by CC

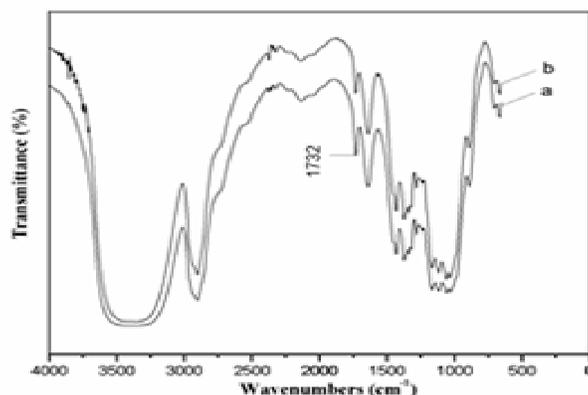


Figure 5: FTIR spectra of samples: a) oxidized at $50\text{ }^\circ\text{C}$ for 5 h; b) cationized by CC

Table 2
Elemental analyses of oxidized and cationized cotton at room temperature

Elements	N (%)	C (%)	H (%)	O (%)
Oxidized for 3 days	0.035	40.942	6.151	47.837
Oxidized for 2 days & cationized	0.104	40.367	6.060	49.004
Oxidized for 3 days & cationized	0.647	40.149	6.232	47.735

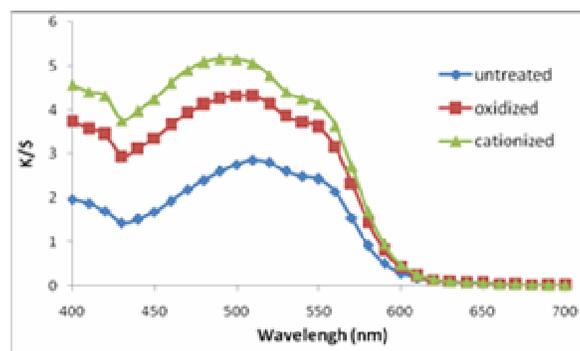


Figure 6: K/S values of cotton fabrics oxidized at room temperature for 20 h

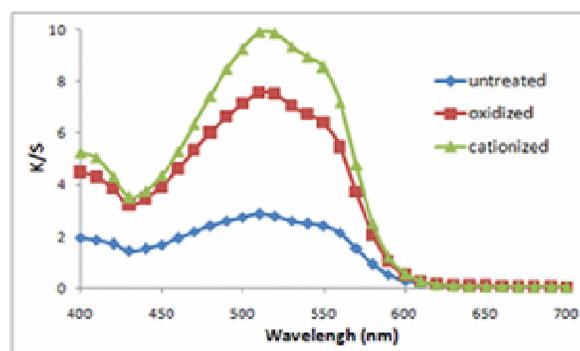


Figure 7: K/S values of cotton fabrics oxidized at 50 °C for 5 h

Figures 4 and 5 illustrate the FTIR spectra of the oxidized and cationized cellulose. The presence of the attached CC to oxidized cellulose was not confirmed by FTIR as shown in spectra, *i.e.*, no C-N bond. This was most likely because of the presence of quaternized nitrogen. However, the intensity of the peaks around 1732 cm^{-1} and 890 cm^{-1} became weak, indicating a decrease in aldehyde contents after cationization.

Evidence of quaternization

The evidence of quaternized cellulose was investigated in two ways: elemental analysis and staining method. As shown in Table 2, nitrogen content was considerably increased after oxidation followed by cationization. This indicated the presence of CC within cotton.

The second method to confirm the presence of cationic groups was to use a dyeing method with an acid dye. After quaternization, the dyeing was carried out at $60\text{ }^{\circ}\text{C}$. Since the thermal property of cellulose generally decreased after oxidation,¹⁵ we chose to use a lower dyeing and curing temperature during the experiment.

Figures 6 and 7 show the K/S value of the samples. The K/S value is directly related to the color intensity of the fabric. A higher K/S value means greater absorption in dyeing. The K/S value of cationized cellulose around 520 nm was greater than that of oxidized cellulose, indicating higher absorption of C. I. Acid Red 4 in the cationized cellulose. Cationic cellulose had an outstanding capacity of adsorption of anionic groups in the dye through the ionic bond between

cationized cellulose (Cell-R-N⁺(CH₃)₃Cl⁻) and acid dye (Dye-SO₃⁻).^{1,2} This revealed that the reaction occurred between CC and dialdehyde cellulose. It should be also noted that the dialdehyde cellulose showed a greater K/S value than that of untreated cellulose. This was probably due to the degradation of cellulose during oxidation resulting in greater sorption of acid dyes.

Meanwhile, we found that the K/S value of the dialdehyde cellulose oxidized at high temperature for a short time was higher than that of the samples oxidized at low temperature for a long time. The aldehyde contents of the dialdehyde cellulose increased under stronger oxidizing conditions, which was confirmed by the FTIR spectra. Higher aldehyde contents meant generation of more reactions between CC and the acid dye used.

Additional characteristics of oxidized and cationized cellulose

Table 3 displays the thermal characteristics of dialdehyde cellulose after periodate oxidation.

Generally, the thermal degradation temperature of untreated cotton in nitrogen is about 280 °C and a rapid weight loss occurs at 330-380 °C.^{15,17} But the thermal degradation characteristics of oxidized cellulose were different, and its thermal decomposition temperature shifted to lower temperature and was continuously reduced with the increase in oxidant concentration. After cationization of dialdehyde cellulose, the temperature for rapid weight loss was decreased even further (Table 3). This demonstrated that the degradation of cellulose occurred due to the acid catalyst employed.

The degradation that occurred during periodate oxidation was further examined by tearing strength measurement. Figure 8 indicates that the room temperature oxidation for a long time resulted in a lower strength reduction than that of the fabrics oxidized at high temperature for a short time. Nevertheless, the surface characteristics of the oxidized fabrics did not change significantly, as shown in the SEM micrographs of oxidized cellulose (Figure 9).

Table 3
TGA analyses of oxidized (50 °C) and cationized cotton fabrics

Properties	Oxidation conditions (concentration of NaIO ₄ and time)					
	untreated	1.5 g/L, 1 h	5.0 g/L, 1 h	15.0 g/L, 1 h	21.4 g/L, 1 h	5 g/L, 1 h, cationized
Rapid weight loss temperature (°C)	342.2	335.6	327.6	314.0	298.3	270.2

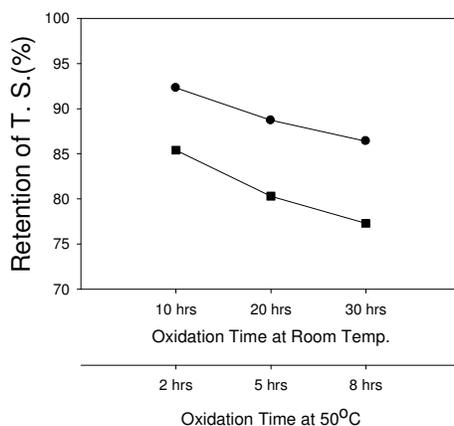


Figure 8: Retention of tearing strength of cotton fabrics oxidized at room temperature (●) and at 50 °C (■)

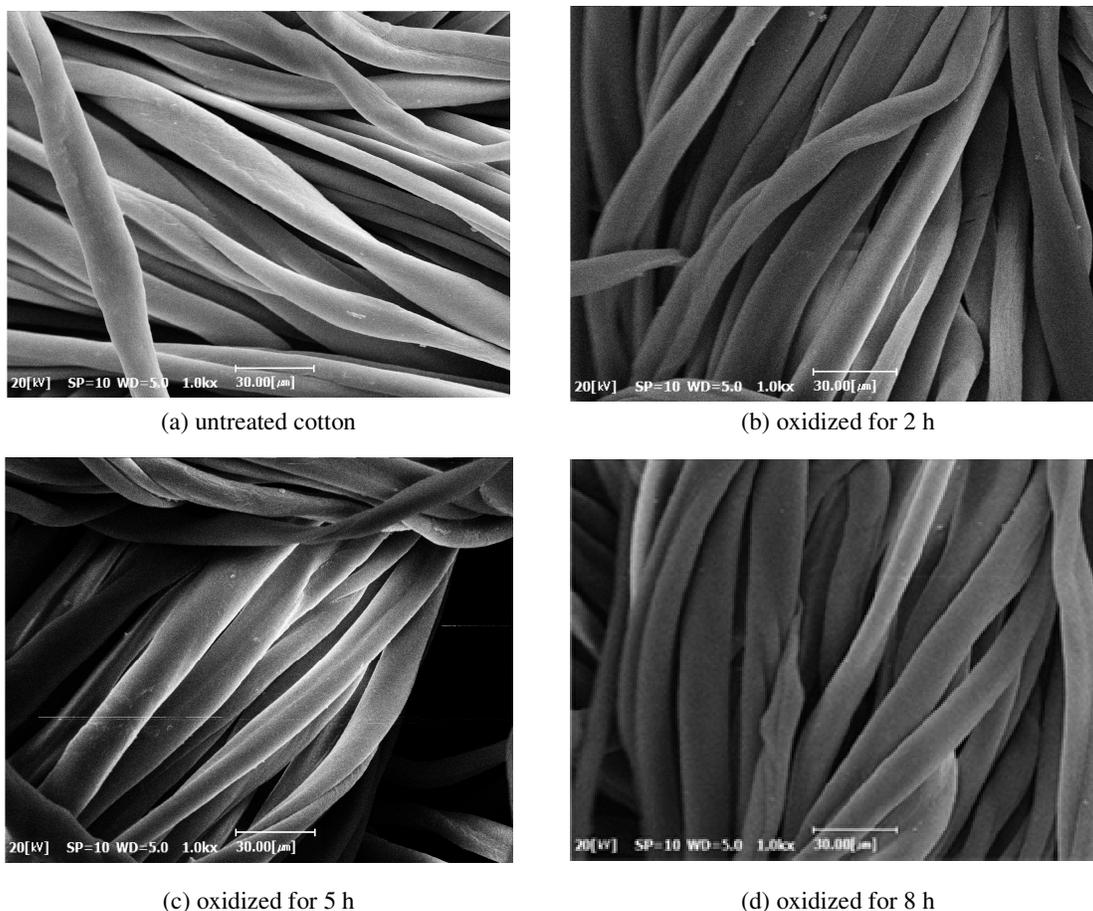


Figure 9: SEM micrographs of periodate-oxidized cotton fabrics at 50 °C

CONCLUSION

In this paper, cotton fabric was oxidized by sodium periodate at first, and the cationization cellulose was prepared from dialdehyde cellulose by reaction with choline chloride. FTIR analyses indicated the presence of aldehyde groups after oxidation. Cationization was confirmed by elemental analyses along with dyeing with acid dye. After dyeing, the K/S value of cationized cellulose was greater than that of oxidized cellulose. The higher dye sorption of the cationized cotton was attributed to the ionic bonding between the cationic groups in cationized cellulose and anionic groups in acid dye. The higher the oxidizing temperature was, the greater the K/S value of the samples.

However, oxidation and cationization both resulted in a certain level of degradation of cellulose. This was confirmed by thermal analysis and tearing strength measurement. No significant change however was observed in the surface

characteristics of the treated cotton, as examined by SEM.

Therefore, this alternative oxidation-cationization process with choline chloride could be used as an efficient and practical cationization method offering better environmental safety than a conventional cationization process.

Corresponding author: hchoi@ssu.ac.kr

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