CELLULOSE CHEMISTRY AND TECHNOLOGY

MICROWAVE-MEDIATED RAPID OXIDATION AND CATIONIZATION OF COTTON CELLULOSE

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Rapid oxidation and cationization of cotton was carried out with periodate and Girard's Reagent T (GT) under microwave irradiation. The degree of oxidation was increased with an increase in microwave irradiation time and in the amounts of periodate, as evaluated by FTIR and chemical methods. Cationization was carried out both under microwave irradiation and at room temperature for comparison. FTIR, dye sorption and elemental analyses substantiated that imine formation between aldehyde and GT was easier at room temperature, probably due to the reverse reaction at high temperature. Nevertheless, cotton cellulose cationized under microwave irradiation exhibited high hydrophilicity and stability, along with antimicrobial properties. Therefore, this study confirms that rapid and efficient oxidation and cationization of cotton is feasible under microwave irradiation and the obtained material could find various end-use applications.

Keywords: periodate, oxidation, Girard's Reagent T, microwave irradiation, FTIR analysis

INTRODUCTION

Cellulosic fibers are mainly colored by anionic dyes, such as reactive or direct dyes. Because of the presence of zeta potential on the fiber surface in aqueous medium, dyeing of cellulosic fiber requires a high level of salts (sodium chloride or sodium sulfate)of around 30~150 g/dm^3 or 25% on the bath weight. The addition of salts contributes to an easy migration of the dyes into the fiber interior and to dye fixation.[3] However, the use of salt produces severe environmental problems and high-cost desalting processes are necessary to remove the salts from dyeing effluents.[4] On the other hand, cationization, one of the most important processes of cellulose modification, provides cellulose with a highly enhanced affinity towards anionic substances, such as dyes, metal ions and dyeing effluents.[5,6] Therefore, cationization of cellulosic fibers could substantially reduce the salt requirement during dyeing processes.[4-6]

Cationization of cellulose has been commonly carried out in three ways: first, direct reaction can be initiated by a reactive functional group of the cationizing reagent with the hydroxyl groups of cellulose;[2] second, a bifunctional crosslinking agent, such as dimethyloldihydroxyethylene urea, can form bridges between the cationizing reagent and cellulose;[1,7] and third, monomeric or polymeric cationizing reagents can be grafted to cellulose.[8]

Periodate oxidation initiates a selective oxidation, *i.e.*, oxidation of two adjacent secondary hydroxyl groups at C_2 and C_3 in the glucose molecule, producing dialdehyde celluloses (DAC).[1,9,10] Such an oxidation is generally carried out at room or slightly higher temperature, but an extended time (more than 12 hours) is required to ensure the reaction. These DAC could be used for forming derivatives in a further addition reaction.[10] In addition, the DAC could provide antimicrobial properties to cellulose molecules.[14]

In the present study, cotton cellulose was treated by periodate to produce DAC, followed by Girard's Reagent T (GT) treatment for imine formation. Such a treatment provides highly cationized cotton celluloses.[11,12] Since GT has been used for aldehyde evaluation, it is thus expected that the reaction between GT and aldehyde would readily take place.

Furthermore, we also examined the feasibility of using the microwave (MW) irradiation technique during periodate oxidation and cationization. The use of MW irradiation could significantly reduce the reaction time. The treated cotton cellulose (oxidized, oxidized and cationized) specimens were carefully investigated by using Fourier transform infrared (FTIR) spectroscopy, DAC content analysis, dye sorption analyses, elemental analyses (EA), water of imbibition determination, scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, antimicrobial tests and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Cotton fabric (plain weave, 31 x 30 threads/cm^2) was obtained from FITI, Inc. Chemicals were purchased from commercial sources: sodium periodate (SP, $NaIO_4$, 99.5%) and methyl orange ($C_{14}H_{14}N_3NaO_3S$) from Wako Pure Chemical Industries, Ltd., acetic acid (99.5%) from Sam Chun Pure Chemical, hydroxylamine hydrochloride (99%) from Sigma Aldrich Korea, and GT [(carboxymethyl)trimethylammonium chloride hydrazide, or betainehydrazide hydrochloride, $(CH_3)_3N^+CH_2CONHNH_2Cl^-$, 98.0%] from Tokyo Chemical Industry Co., Ltd.

Periodate oxidation

A piece of cotton fabric (ca. 3.0 g) was used as cellulose substrate throughout the study. A 250 mL treating bath, containing SP and cotton fabric, was prepared in DURAN® Heavy-wall beakers. The concentrations of SP were adjusted by using a weight ratio against cotton fabric (1:1, 1.5:1, 2:1, 2.5:1, and 3:1 at SP: cotton weight).The treating bath with the cotton was irradiated for a specific time period by a commercial MW oven (Samsung Electronics, Korea).The beaker was completely covered by a brown Teflon film to minimize the effect of light during the treatment. After irradiation, the fabric sample was rinsed several times with deionized water and dried at 85 °C for 30min in a convection oven (VOS-301SD Rikakikai Co., Ltd., Japan).

Cationizationby GT

Various amounts of GT [0.0025mole (0.42g), 0.005 mole (0.84g) and 0.01 mole (1.68g)] were reacted with the periodate-treated cotton cellulose in two ways: by reaction at room temperature for two hours or under MW irradiation for 1.5 to 20 min. The cotton fabric was then rinsed by deionized water for several times and dried at 85 °C for 30 min in the oven. The fabric sample was then stored in a desiccator until further analysis.

Analyses of treated cotton cellulose

DAC contents in the periodate-treated cotton were evaluated by the titration method, as described in a previous study.[13] In short, the periodate-treated cotton fabrics were immersed for 2.5 hours in 0.25N hydroxylamine hydrochloride solution containing methyl orange indicator at pH 4. After immersion, the DAC content was analyzed by titration with a standardized solution of 0.1NNaOH to pH 4 until the red-to-yellow end-point. This technique was based on the reaction of hydroxylamine hydrochloride in methyl orange indicator and aldehyde at pH 4. Such a reaction produced a cellulose polyoxime (Cell-(CH=N-OH)$_n$), along with releasing an HCl equivalent for each formyl residue. The released HCl thus could be titrated by an equivalent NaOH solution.[13]

$$\text{DAC content (\%)} = [(M_{NaOH}\ (V_{sample} - V_{control}))/(m/M_w)] \times 100 \qquad (1)$$

where $M_{NaOH}$is the molecular weight of NaOH (40.00 g/mol), V_{sample} is the amount of 0.1 M NaOH solution in the treated cotton (L), $V_{control}$ is the amount of 0.1 M NaOH solution in untreated cotton (L), m is the weight of the specimen (0.1 g), and M_w is the molecular weight of the repeating unit of $(C_6H_8O_5)_n$, in DAC (160.12 g/mol).

In addition, the presence of aldehyde in the periodate-treated cotton was also analyzed by FTIR spectroscopy (Bruker, Vertex 70, USA) with attenuated total reflectance (ATR) attachment in the spectral region of 4000-600 cm^{-1} with 64 scans and 4 cm^{-1} resolution.

In addition, the cationization of the oxidized cotton cellulose was measured by indirect measurement with C.I. Acid Red 4 dye (λ_{max} at 520 nm) sorption and by evaluating the-C=N- peak in imine with FTIR-ATR. The surface reflectance of the oxidized, cationized and acid-dyed cotton was measured by a Color Eye CM-512M3 (Konica Minolta, Japan). Reflectance values were then used to calculate the K/S values by the Kubelka-Munk equation:[1]

$$K/S = (1-R)^2/2R \qquad (2)$$

where R is reflectance of the dyed materials at λ_{max}.

Since common cotton dyeing with direct or reactive dyes requires substantial amounts of salts, one of the objectives in cellulose cationization is to minimize the use of salt in dyeing. Therefore, C.I. Reactive Blue 19 dye (λ_{max} at 600 nm) was also used to investigate the effect of cationization on reactive dyeing. Salt was not added during dyeing.

Dyeing of the cationized cotton fabrics was carried out at 3% on the weight of fiber (owf) and a 30:1 liquor-to-fiber ratio by using acid dye or reactive dye in an IR dyeing machine (Daelim Starlet Co, Ltd., Korea). Dyeing procedures are illustrated in Figure 1.After dyeing, the samples were thoroughly rinsed by distilled water, dried at 85 °C for 30 minutes, and conditioned for at least 24 hours under standard conditions, prior to measuring the K/S values. It should be noted that acid dye was mainly used for quantitative evaluation of cationic groups, while reactive dye was used to examine the efficacy of cationic groups in practical cotton dyeing.

Characterization of oxidized and cationized cotton

The hydrophilic characteristics of periodate-treated and cationized cotton fabrics were measured by determining the water of imbibition. The specimen was completely dried at 85 °C for one hour and weighed (W_d). The specimen was then immersed in distilled water for three hours, followed by centrifuging it at 1,800 rpm for 30 min and its weight was again measured (W_w).The water of imbibition was calculated by the following equation:

$$\text{Water of imbibition (\%)} = \left[\frac{W_w - W_d}{W_d}\right] \times 100 \qquad (3)$$

The thermal characteristics of cotton cellulose were investigated by TGA (Mettler, USA) at 10°C/min within the 25 ° ~ 700 °C range under nitrogen atmosphere. SEM (COXEM, CX-100S, Korea) was employed to study the effect of the treatment on the topological characteristics of cotton. Elemental analysis (Euro Vector E, E/V RE2) was used to determine the amounts of carbon, hydrogen, and nitrogen in the treated cotton cellulose.

The crystalline structure of cotton cellulose was evaluated by X-ray diffraction analysis (D2 PHASER, Bruker, Germany), employing a Cu-Kα (λ= 0.1524nm) source, operating at 30 kV and 10 mA. The sample was scanned at 2°/min with a 0.02 increment in the 2θ range from 40° to 10°. Crystalline index (CI) was calculated as follows:[15,18]

$$\text{CI} = (I_{002} - I_{am})/I_{002} \times 100 \qquad (4)$$

where I_{002} is the height of the crystalline peak and I_{am} is the height of the amorphous shoulder. In addition, the crystallite size L of the refection planes was calculated from the Scherrerequation, as follows:

$$\text{Crystallite size L} = (K \times \lambda)/(\beta \times \cos\theta) \qquad (5)$$

where K is the Scherrer constant of value 0.94, λ is the X-ray wavelength (0.1542 nm), β is the half-height width of the diffraction band, and θ is the Bragg angle corresponding to the planes. Furthermore, the surface chains occupied a layer approximately 0.57 nm thick, so the proportion of the crystallite interior chains was calculated as follows:[15]

$$\text{Crystallite interior chains, X} = (L - 2h)^2/L^2 \qquad (6)$$

where L is the crystallite size for the plane refection, and his the layer thickness of the surface chain (0.57 nm).

Antimicrobial tests

The antimicrobial characteristics of the treated cotton were evaluated by KS K 0693 with two microorganisms, such as *Staphylococcus aureus* (ATCC 6538) and *Klebsiella pneumoniae* (ATCC 4352). The reduction of bacteria was calculated as follows:

$$\text{Antimicrobial activity (S)} = \log (M_b / M_a) - \log (M_c / M_a) = \log (M_b / M_c) \qquad (7)$$

$$\text{Reduction of bacteria (\%)} = [(M_b - M_c)/M_b] \times 100 \qquad (8)$$

where M_a is the average number of bacteria in the reference sample immediately after inoculation of the testing bacteria, M_b is the average number of bacteria in the reference sample after incubation for 24 h and M_c is the average number of bacteria in the antimicrobial sample after incubation for 24 h. If the value of M_a is lower than that of M_b, the measurement of the sample is considered to have failed, such a result being caused by natural reduction due to the external environment.[4]

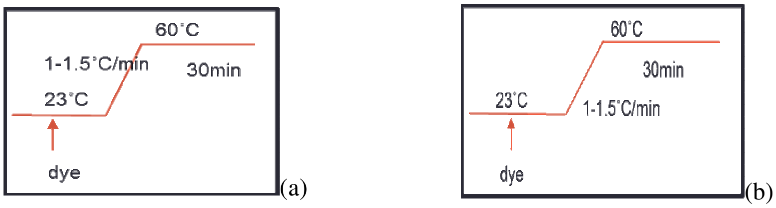


Figure 1: Dyeing procedure for cationized cotton fabrics; (a) acid dyeing at 60 °C, and (b) reactive dyeing at 60 °C

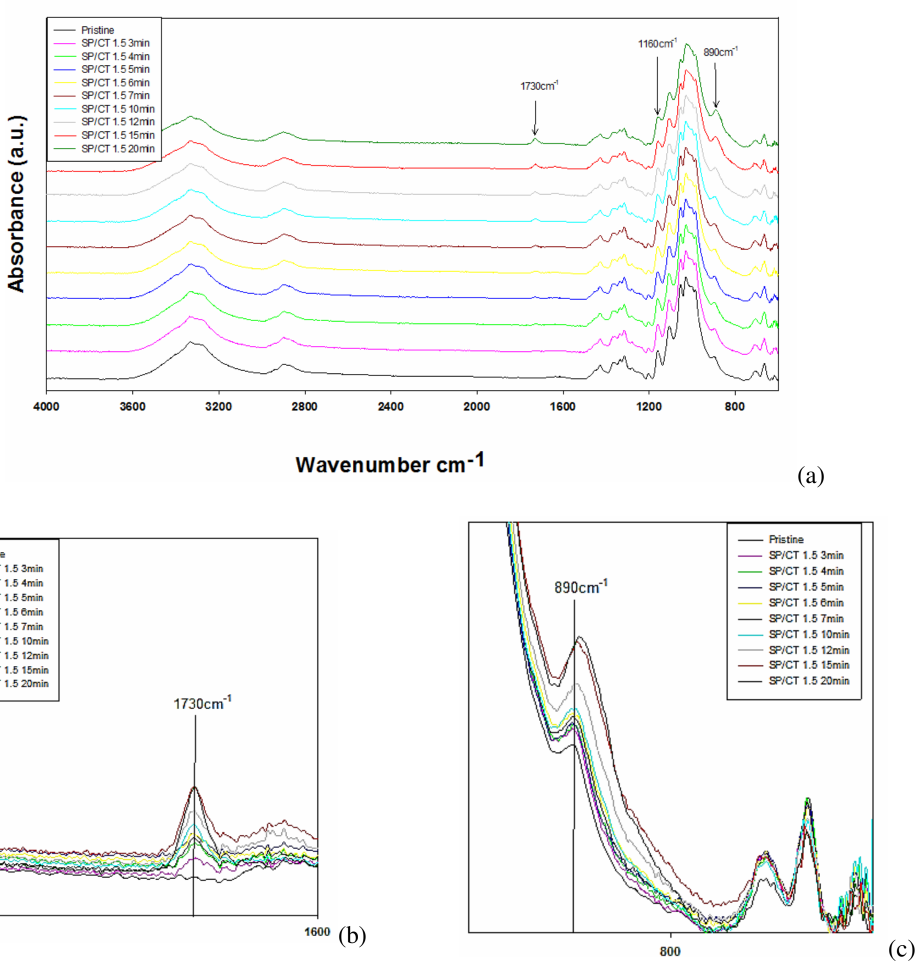
RESULTS AND DISCUSSION

Analyses of oxidized cotton

During SP oxidation, the concentration of SP and the MW irradiation time were the experimental parameters that were varied. The FTIR spectra of cotton fabrics treated at various MW irradiation times and with various ratios of SP/cotton weight are shown in Figures 2 and 3, respectively.

In the spectrum of pristine cellulose, the band at 3300 cm^{-1} corresponding to hydrogen bonded O–H stretching and that at 3000-2800 cm^{-1}

corresponding to sp^3 hybridized C–H stretching may be noticed. The presence of the aldehyde –C=O stretching peak at 1730 cm^{-1} confirm ssuccessful periodate oxidation of cellulose, as shown in Figures 2(b) and 3(b). The aldehyde carbonyl peak intensities increased with the increase in MW irradiation time and in the amount of SP. This increase tended to be greater with the increase in irradiation time, compared to that in SP concentration. Since aldehyde formation in cellulose by periodate oxidation was produced by a cleavage of glucose rings in adjacent C_2-C_3 positions, as shown in Scheme 1, the peak intensities for hydroxyl groups at 3300 cm^{-1} typically decreased with the increase in intensity of the aldehyde carbonyl peak (Figs. 2 and 3). However, such a decrease was smaller than expected, probably because of the formation of hemiacetal. Furthermore, in both cases, the intensity of the absorption peak at 890 cm^{-1}, representing hemiacetal hydroxyl, also enhanced with the increase in SP concentration and MW irradiation time.[1]



(a)

(b)

(c)

Figure 2: FTIR spectra of DAC contents at various MW irradiation times (specimen SP/CT 1.5 3 min was treated at 1.5:1 SP/CT weight ratio for 3 min of MW irradiation)

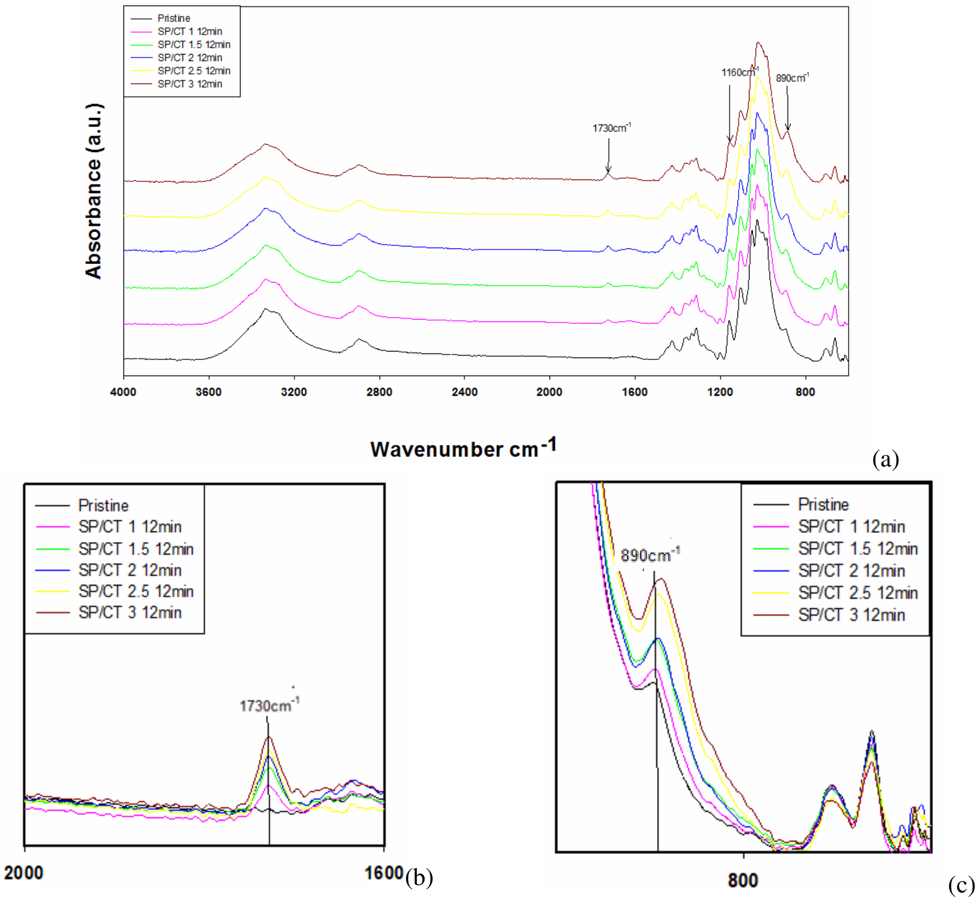


Figure 3: FTIR spectra of DAC contents at various SP/cotton mole ratios

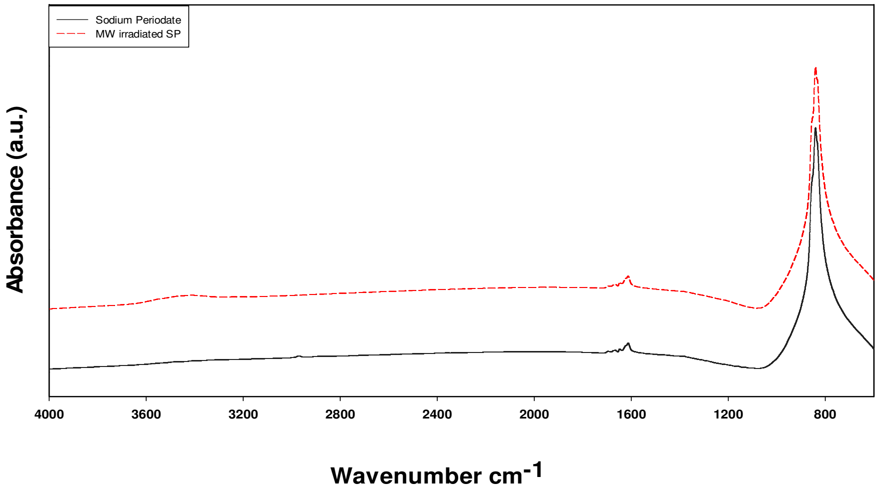


Figure 4: FTIR spectra of sodium periodate before and after MW irradiation

To investigate the stability of periodate under MW, the SP solution (SP/cotton 1.5:1) was irradiated for 12 min, and then subjected to solidification in an evaporator, prior to measuring the FTIR spectra by the KBr pellet method. As shown in Figure 4, the FTIR spectra of the SP before and after MW irradiation were practically the same, showing the main absorption peak at around 800 cm^{-1}. Since periodate could be transformed from IO_4^- to IO_3^- during the oxidation reaction of glucose, the peak should be identical, unless the decomposition of SP occurred.

Therefore, this result confirmed the stability of SP under MW irradiation under the reaction conditions used in the current study, suggesting the feasibility of the proposed process of rapid cellulose oxidation using SP under MW irradiation.

To investigate the DAC contents in the periodate-treated cotton in more detail, the intensity of the aldehyde C=O stretching peak at 1730 cm^{-1} was normalized by the asymmetry C-O-C stretching peak at 1160 cm^{-1} in the cellulose molecule (Fig.5). DAC contents were almost linearly proportional to the increase in MW irradiation time and in the amount of periodate, as shown in Figure 5 (a) and (b).

Furthermore, Figure 6 shows the DAC content of cotton fabric measured by a hydroxylamine hydrochloride solution.[13] Figure 6(a) reveals that the DAC content in cotton generally increased with MW irradiation time. The results also show that too short irradiation time, such as 4 min or less, did not increase the DAC content in cotton, and the increase in DAC was much slower at longer irradiation times. These analytical results derived from both FTIR and DAC content analyses verify that a minimal level of energy is needed to initiate the reaction between IO_4^- and vicinal hydroxyl groups in the glucose ring. Contrarily, a linear relationship (r^2=1) is clearly observed between DAC contents and SP/cotton weight ratios, as shown in Figure 6(b).Therefore, these analyses clearly substantiate that periodate oxidation of cellulose, *i.e.* DAC content, was influenced by both MW irradiation time and concentration of periodate. In addition, a high level of DAC content could be achieved within a very short period of time by using the MW irradiation process.

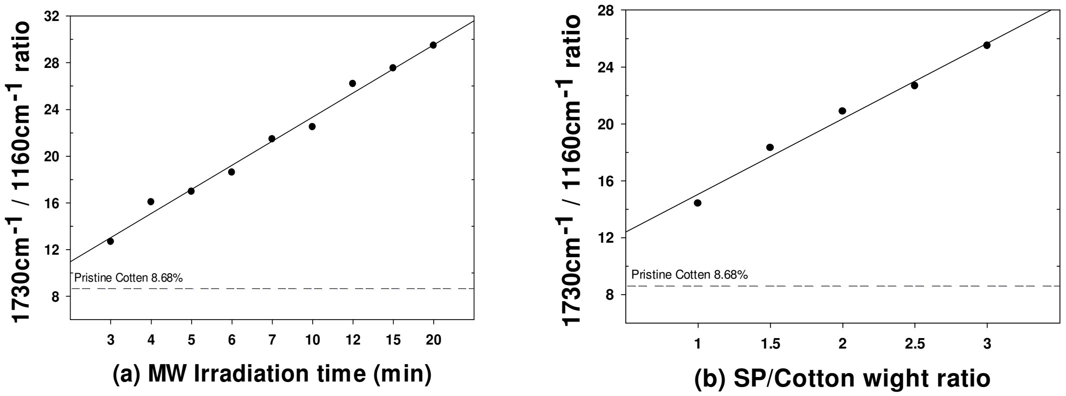


Figure 5: Analyses of FTIR peaks (a) 1730 cm^{-1} (C=O)/1160 cm^{-1} (C-O-C) ratios at different MW irradiation times ($r^2 = 0.91$), (b) 1730 cm^{-1} (C=O)/1160 cm^{-1} (C-O-C) ratios at different SP/cotton weight ratios ($r^2 = 0.95$)

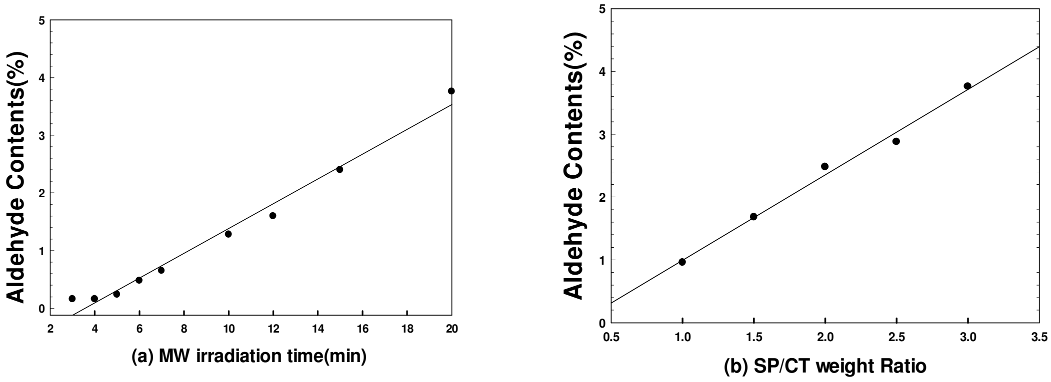


Figure 6: Analyses of DAC content in cotton fabrics; (a) at various MW irradiation times ($r^2 = 0.94$), and (b) at different SP/cotton weight ratios ($r^2 = 1$)

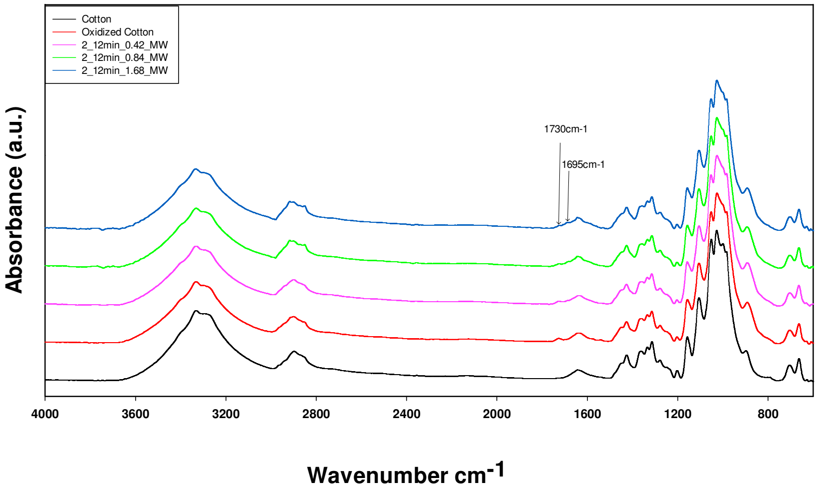


Figure 7: FTIR spectra of cotton fabrics treated by periodate, followed by cationization with various amounts of GT for 1.5 min MW irradiation

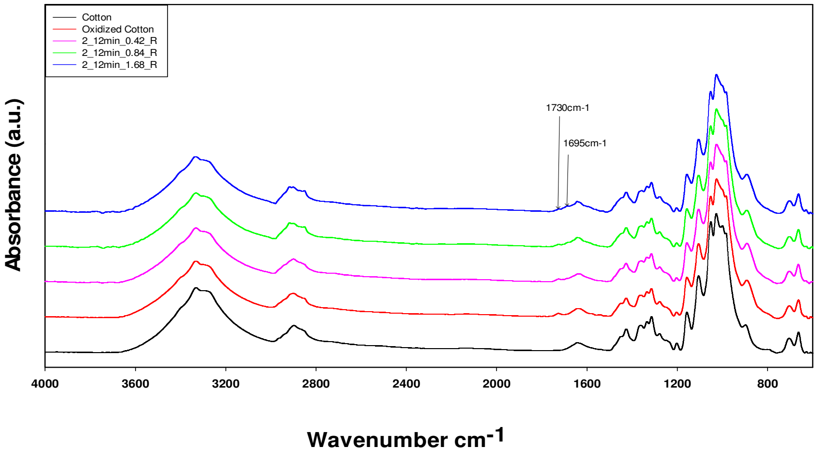
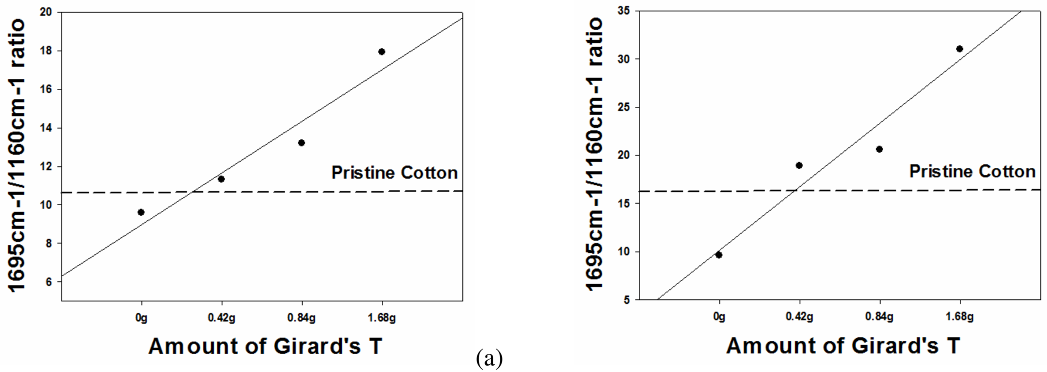


Figure 8: FTIR spectra of cotton fabrics treated by periodate, followed by cationization with GT at room temperature for 2 h

Analysis of cationized cotton

The mechanism of the periodate and GT treatments of cotton cellulose is shown in Scheme 1. FTIR spectra in Figures 7 and 8 reveal that the aldehyde carbonyl peaks at 1730 cm^{-1} decreased and the -C=N- imine peaks at 1695 cm^{-1} increased, regardless of the treatment conditions. To study the effect of different cationization conditions, the intensity of the imine peak at 1695 cm^{-1} was normalized by the cellulose peak intensity at 1160 cm^{-1}, as shown in Figure 9. Surprisingly, the peak intensity ratios were higher for the specimens reacted with GT at room temperature than for those subjected to MW irradiation, regardless of GT concentrations. Therefore, the results clearly substantiate that cationization by MW irradiation is more rapid, but the formation of imine is greater during the reaction at room temperature. This verifies that the reaction of dialdehyde cellulose and GT occurred readily, and thus high energy MW irradiation caused an adverse effect, probably promoting a reverse reaction.

The K/S values of cotton fabrics dyed by C.I. Acid Red 4 depended on the cationization process. Figure 10 indicates that untreated cotton cellulose resulted in a K/S value of almost zero at 520 nm λ_{max}, whereas the cationized specimen showed very high K/S values, indicating strong ionic interactions between quaternary ammonium compounds and the sulfonate group in acid dye (its chemical structure is shown in Scheme 2).[2] The K/S values of all the GT-treated cotton fabrics increased with the increase in the amounts of GT, regardless of the cationization conditions. The substantially greater K/S values for the cotton fabrics that reacted with GT at room temperature, compared to those subjected to MW irradiation, regardless of the amounts of GT, again justify the results of the FTIR analyses discussed above.



(a) (b)

Figure 9: Analyses of FTIR peaks (a) 1695 cm^{-1} (C=N)/1160 cm^{-1} (C-O-C) ratios for 12 min of MW irradiation, (b) 1695 cm^{-1} (C=N)/1160 cm^{-1} (C-O-C) ratios at room temperature

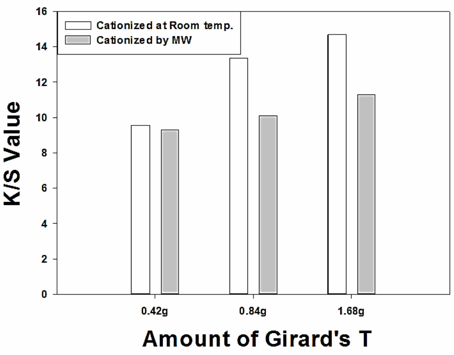


Figure 10: K/S values of cationic cotton celluloses dyed by C.I. Acid Red 4 at 3% owf

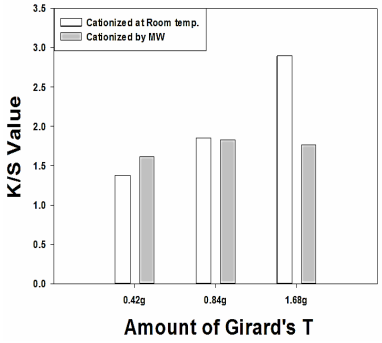


Figure 11: K/S values of periodate-treated and cationized cotton fabrics dyed by C.I. Reactive Blue 9

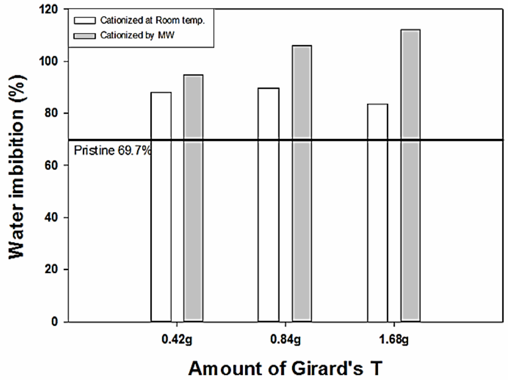
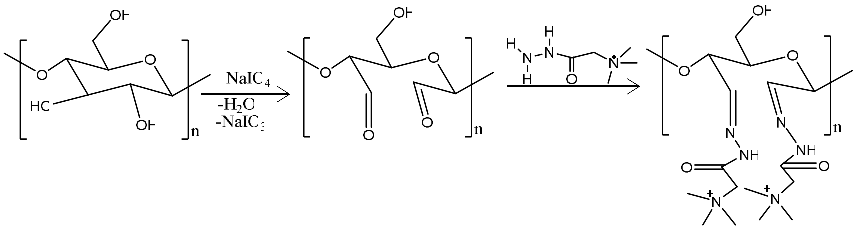
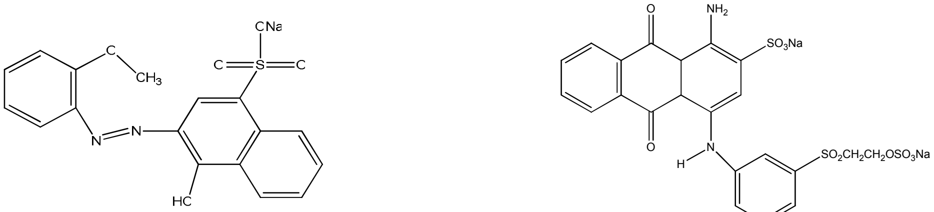


Figure 12: Analysis of water of imbibition



Scheme 1: Potential mechanism of cellulose periodate oxidation and cationization



C.I. Acid Red 4

C.I. Reactive Blue 19

Scheme 2: Chemical structures of the dyes used in this study

Table 1
Elemental analyses of oxidized and cationized cotton (1.68 g GT)

Treatment condition	N (%)	C (%)	H (%)
Pristine	0.00	43.07± 0.07	6.20±0.06
Room temperature	1.38± 0.133	42.25± 0.095	6.12±0.09
12 min MW irradiation	0.435± 0.004	42.51± 0.06	6.07±0.11

Figure 11 shows the K/S values of oxidized and cationized cotton fabrics dyed with the vinyl type reactive dye (Scheme 2).The pristine cotton again shows no affinity toward this dye. Since alkali was not used in the current dyeing procedure, the dye could behave as an acid dye rather than as a reactive dye, because of the presence of two strong anionic sulfonate groups. Therefore, the cationic treatment of cotton could considerably improve the affinity toward this particular dye. Furthermore, it must be noted that the K/S values of the dyed cotton fabrics were much greater (163.9%) in the cotton cationized by 1.68 g of GT at room temperature than in that subjected to MW irradiation with the same amount of GT. However, at lower concentration of GT, the K/S value of the treated cotton fabric was higher in the MW irradiated cationized specimen.

To investigate the effectiveness of the two cationization processes in more detail, we also carried out elemental analysis, as shown in Table 1.The results clearly demonstrate that the nitrogen content of cotton cationized at room temperature was more than three times greater than that of the cotton subjected to MW irradiation with 1.69 g GT. This again validates that the reaction between aldehyde and GT was more favorable at room temperature than at MW irradiation, especially with a high concentration of GT.

Water of imbibition

Cationic cotton could be expected to present greater hydrophilicity than pristine cotton, due to the presence of the quaternary ammonium group in GT. As shown in Figure 12, the water of imbibition value significantly increased upon cationization (pristine: 69.7%). Cotton fabrics cationized at MW irradiation surprisingly gave a higher water of imbibition value than those reacted at room temperature. This finding is opposed to the results we obtained by other analytical methods: greater amounts of GT were generally fixed to cotton at room temperature treatment.

The water of imbibition on cotton could be influenced by both chemical and physical factors. Therefore, in addition to the presence of the hydrophilic quaternary ammonium group, the number and type of pores could also determine the sorption of sorbates, such as water or dye molecules. Since oxidation and cationization processes of cotton were carried out with repeated drying and wetting at different temperatures, the MW irradiation could preferentially decrease large size pores.[16] MW irradiation had thus less influence on sorption of small molecules (water), whereas sorption of large molecules (dye) decreased. Furthermore, the cotton fabrics treated at room temperature for 2 hours tended to display a greater surface damage, even with fiber cleavage sometimes, than those subjected to MW irradiation. These effects could all influence the low water of imbibition values for the specimens cationized at room temperature.

X-ray diffraction analysis

Figure 13 demonstrates that the oxidation and cationization treatment of cotton cellulose destroyed its crystalline structures. Table 2 lists the amount of crystalline area within cotton cellulose (CI), the size of crystallites (L), and the numbers of chains in the crystallites (X), as recorded from the XRD spectra. In general, regardless of the treatment method, all the crystallite values, such as CI, L and X, decreased compared with those recorded for the pristine cellulose. The replacement of hydroxyl groups by aldehyde and/or quaternary ammonium groups within cellulose could significantly reduce the number of intra- and/or inter-hydrogen bonding interactions. This would substantially decrease the crystalline area and crystallite size, along with the number of crystallite chains. Such a decrease was generally greater for the cellulose molecules treated at room temperature for a longer time period. Also, minor peak shifts at the (200) plane toward a lower degree were observed, and this was due to the increased amorphous peak around 19º, affecting the major diffraction peak at (200).[18]

Thermal analysis

TGA results in Figure 14 demonstrate that cationized cotton fabrics presented lower thermal stability than pristine cotton, with a low degradation temperature (<200 °C), regardless of the cationization process. In addition, the peak decomposition temperatures in the 1st derivative for cationized cotton were also lower (346 °C), compared with those of pristine sample (359 °C). This verified that a certain level of cellulose degradation occurred upon oxidation and cationization. However, the amounts of residue at 700 °C in both cationized samples were higher than that of the pristine sample, presumably due to the addition of GT.

Antimicrobial tests

GT-cationized cotton fabrics under MW irradiation showed 99.9% bacterial reduction due to the presence of the quaternary ammonium group. In addition, the periodate-treated cotton also showed 99.9% bacterial reduction, indicating high antimicrobial characteristics. A previous study pointed out that periodate-treated cellulose also exhibited an antimicrobial property initially, but it disappeared rapidly in a short period of time.[14] In addition, cationized specimens treated under MW irradiation were generally more stable under acidic conditions than the specimens treated at room temperature.

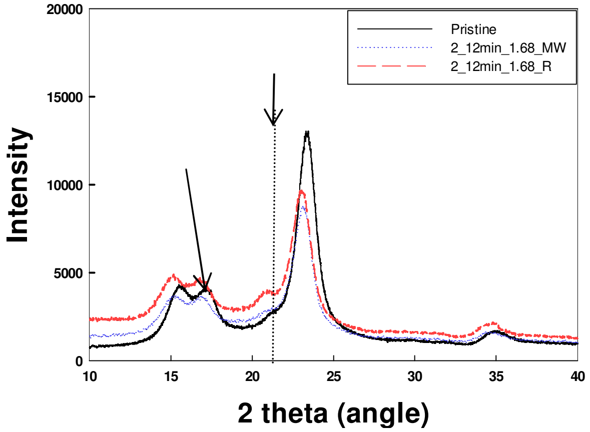


Figure 13: XRD spectra of cationized cotton celluloses

Table 2
Crystalline index (CI), crystallite size (L) and crystallite interior chains (X) of cationized cellulose derived from XRD spectra

Specimens	CI	L (nm)	X
Pristine	85.29	6.11	0.61
MW	75.38	5.34	0.62
Room temperature	71.22	4.51	0.56

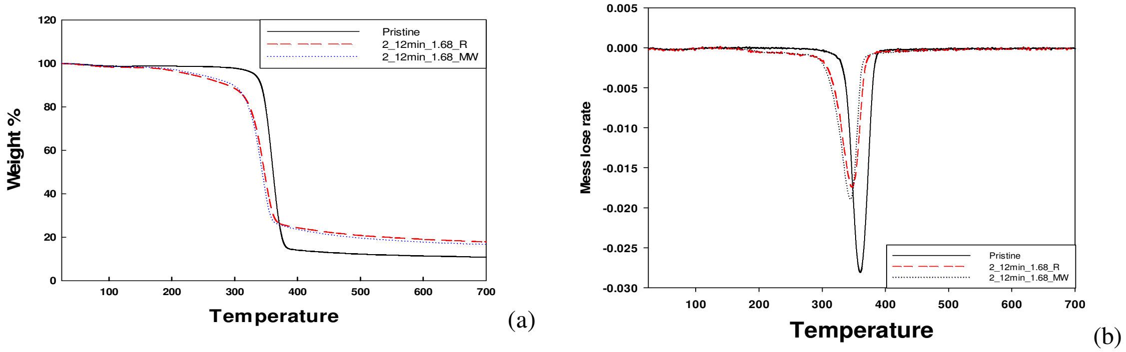


Figure 14: TGA curves of cationized cotton fabrics; (a) TGA curve and (b) 1st derivative curve

Table 3
Antimicrobial test results

Specimen	Bacterial reduction (%)	
	Staphylococcus aureus	*Klebsiella pneumoniae*
Pristine	32.6	20.1
Oxidized cotton	99.9	99.9
MW cationized cotton	99.9	99.9

CONCLUSION

A rapid, yet efficient periodate oxidation of cotton cellulose was carried out under MW irradiation. Oxidized cellulose was confirmed by FTIR analysis, which showed the presence of the absorption peaks at 1730 cm^{-1} assigned to carbonyl and at 890 cm^{-1} corresponding to hemiacetal hydroxyl. The intensities of both peaks increased with an increase in MW irradiation time and in the amount of SP, while the increase with irradiation time tended to be greater. In addition, the assessment of the DAC content by hydroxylamine hydrochloride also demonstrated similar results.

The dialdehyde celluloses formed were cationized with GT both under MW irradiation and at room temperature. The results obtained in FTIR analysis of peak ratios, the sorption study with acid and reactive dyes, as well as elemental analyses all substantiated that the cationization under MW irradiation was much more rapid and stable than that at room temperature, but the amounts of imine found in the specimens were generally greater after the latter treatment. This could be due to the occurrence of a reverse reaction at high temperature. Similar results were obtained regardless of the GT concentration. However, a greater water of imbibition value was found for the specimens cationized under MW irradiation, which suggested different pore size effects induced by the two cationization processes.

The evaluation of the crystalline structure and thermal properties of the treated cotton all substantiated that a certain level of degradation occurred during oxidation and cationization, regardless of the treatment conditions. In addition, cationized cotton celluloses expressed very high antimicrobial characteristics. Therefore, the proposed procedure of rapid formation of oxidized and cationized cotton presenting high anionic dye affinity, high hydrophilicity and high antimicrobial properties could be feasible by treating cotton with peroxide and GT under MW irradiation.

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