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ORIGINAL PAPER

Influence of different oxidizing systems on cellulose oxidation level: introduced groups versus degradation model

Emilija Toshikj · Anita Tarbuk · Katia Grgić · Biljana Mangovska · Igor Jordanov

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Abstract Bleached cotton yarns were oxidized by potassium periodate and TEMPO-mediated oxidation systems, with different concentrations and treatment time, to obtain aldehyde and carboxyl oxy-cellulose with different oxidation levels. Oxidized celluloses were further treated with sodium chlorite to convert the created aldehyde to carboxyl groups. The oxidation level was evaluated by assessing the amount of introduced aldehyde and carboxyl groups, the changes in surface morphology and incurred degradation. Functional groups were determined by titration methods, while surface morphology by FTIR-ATR and SEM analyses. Degradation was analysed by determining the mechanical properties, degree of polymerization, alkali solubility and whiteness stability of the cotton samples. It has been established that a properly selected oxidation system, with appropriate working conditions, can provide satisfactory results for achieving low, medium and extensively oxidized celluloses, with a defined degradation profile. For a short treatment time, a higher oxidation level could be achieved by potassium periodate and TEMPO-mediated oxidation with sodium bromide, while by using the bromide-free TEMPO system a longer time was necessary to reach the same oxidation level. The type and oxidation level of the obtained oxy-celluloses influenced their mechanical properties, degree of polymerization, alkaline and whiteness stability. Low-level oxidized celluloses are suitable for producing stable, long-lasting materials with high added value, while extensively oxidized ones are more appropriate for developing disposable products.

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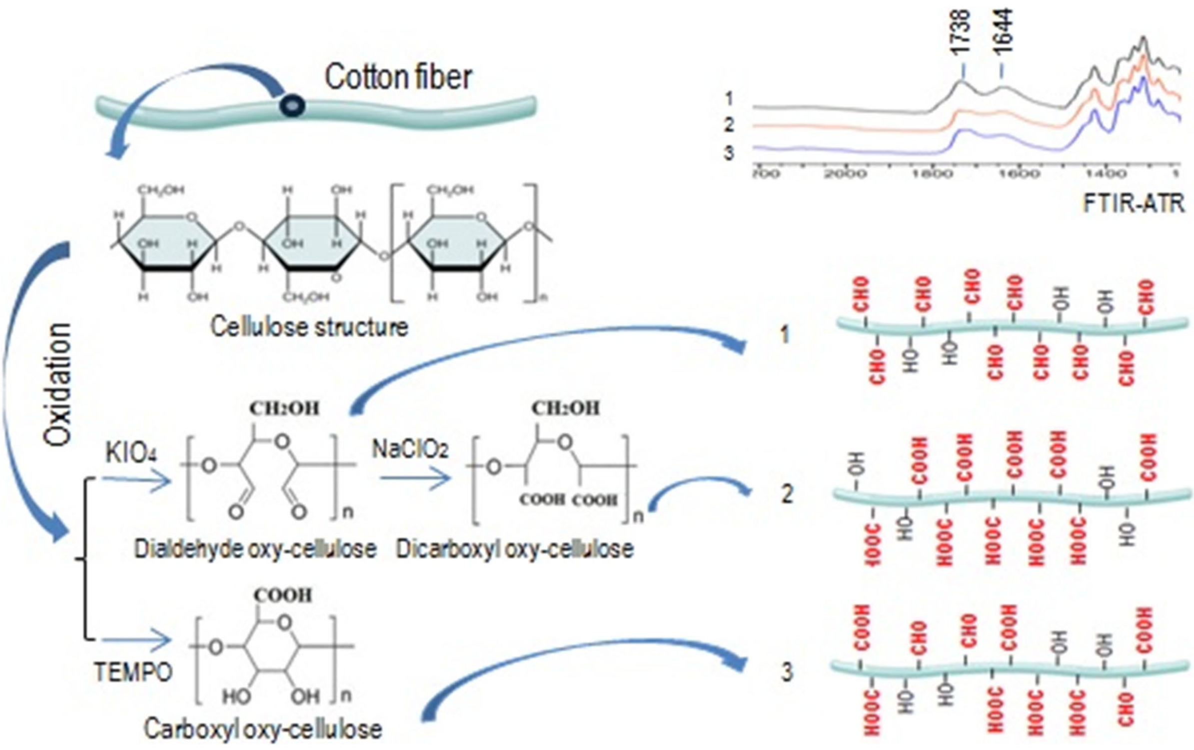
E. Toshikj · B. Mangovska · I. Jordanov (✉)
Department of Textiles, Faculty of Technology and Metallurgy, University Ss. Cyril and Methodius, Ruger Boskovic 16, Skopje, Republic of Macedonia
e-mail: jordanov@tmf.ukim.edu.mk

A. Tarbuk · K. Grgić
Department of Textile Chemistry and Ecology, Faculty of Textile Technology, University of Zagreb, Prilaz baruna Filipovica 28a, Zagreb, Croatia

Graphical abstract



Keywords Cotton · Oxidation · Aldehyde groups · Carboxyl groups · Degradation

Introduction

Cellulose and its modified forms are non-toxic biodegradable polysaccharides, generally considered as the safest and the most acceptable polymer group for utilization in textile, food, pharmaceutical and medical products (Ige et al. 2012). Besides its traditional use (mostly as cotton fibre) for clothes and apparel, cellulose and its modified derivatives have been widely used in various applications, such as artificial kidney membranes, environmentally friendly packaging, coating materials for drugs, blood coagulants, additives for pharmaceutical products, wound dressings, substrates for enzyme immobilisation, stationary phases for HPLC etc. (Kolarova et al. 2013).

The modification of cellulose to make it suitable for such applications and thus to impart an added value to it could be done through physical and chemical pathways. Physical modification includes plasma and corona discharge, UV irradiation or laser treatment, while the chemical one includes acid hydrolysis, oxidation, esterification and etherification, amidation, carbamation etc. (Abo El-Ola et al. 2014; Eyley and Thielemans 2014).

Oxidation is a very promising process for adding new functional groups to cellulose, and it is quite frequently used either to obtain special properties or to alter the existing ones (Coseri et al. 2013; Luo et al. 2015; Tang et al. 2005). It can be selective, achieved with potassium or sodium periodate (Kim and Choi 2014; Strand et al. 2008; Toshikj et al. 2017) or 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (Fraschini et al. 2017; Inamochi et al. 2017; Mishra et al. 2011; Saito et al. 2010; Tang et al. 2005) and phthalimide-*N*-oxy (PINO) (Coseri et al. 2018) or non-selective, using perchloric acid, hydrogen peroxide etc. (Diankova and Doneva 2009; Kramer et al. 2014; Toshikj et al. 2016). Selective oxidation by periodates results in the formation of two aldehyde groups on C_2 and C_3 atoms, that can be further oxidized to carboxyl through treatment by sodium chlorite (Nikolic et al. 2017; Saito and Isogai 2004; Saito et al. 2006), while oxidation by TEMPO leads to the formation of carboxyl groups on C_6 atoms. On the other hand, by combining two of the most common selective oxidation protocols for cellulose, i.e. the nitroxyl mediated and periodate, results in formation of 2,3,6-tricarboxy cellulose (Coseri et al. 2015).

Oxy-cellulose may be used either in the form of water-insoluble cellulose (alone or in combination with other materials, such as polymers, dyes, proteins, collagen, peptides, cells etc.) (Jin et al. 2015; Kanth et al. 2009; Kumari et al. 2016; Pietrucha and Safandowska 2015), or in the form of water-soluble low molecular weight products, for the preparation of which higher than 0.6 mmol/kg carboxyl groups, which corresponds to 75–95% yields, is necessary (Mishra et al. 2012). Each application of oxy-cellulose requires different amounts of newly introduced groups by oxidation. Oxidized cellulose with carboxyl groups less than 25% carboxyl groups is needed for use as immobilizing matrix or carrier for drugs, chemicals, and biological macromolecules (Kumar 2003), 18–21% for hemostatic surgical dressings, gauzes (Stilwell et al. 1996) and 3–13% for absorbable suture textiles (Ashton and Moser 1968). Oxidized cellulose with less than 3% carboxyl groups serves as a non-degradable carrier system, whereas that containing equal or greater than 3% is useful as a biodegradable system (Kumar 2003).

The specific action of oxidizing agents is already quite well understood (Calvini et al. 2006a; Isogai et al. 2018; Perlin 2006; Sang et al. 2017; Sun et al. 2005), contrary to the degradation of oxy-celluloses, which is related to the introduced functional groups (Janjic et al. 2009; Nikolic et al. 2010). As mentioned above, the main purpose of cellulose modification is imparting new characteristics to the materials that can be used for many applications. Materials based on oxidized cellulose are usually used as carrier for disposable and long-lasting textile materials. For the long-lasting materials, they have to withstand many wearing/washing/drying cycles without changing their basic properties and functionalities, especially without changing their mechanical properties. For that purpose, the optimized concentration of the newly introduced groups by oxidation has to be achieved with minimum degradation of the cellulosic materials.

However, the influence of commonly used oxidative agents on the mechanical properties of cellulose textile materials has not been studied in depth. TEMPO-mediated oxidation has been widely explored on cellulose pulp (Brodin and Theliander 2012; Inamochi et al. 2017; Shibata and Isogai 2003; Xu et al. 2012), but to a considerably smaller extent on cellulosic textile fibres and fabrics. Several researches have been made to explore the influence of oxidation and added chitosan on regenerated cellulose textile fabrics (Janjic et al. 2009; Zemljic-Fras et al. 2013). Oxidation has been reported to determine a reduction of the average degree of polymerization of cellulose (Toshikj et al. 2016), but did not induce pronounced changes in the crystallinities and crystal sizes of cellulose I (Isogai et al. 2011). The degree of polymerization of cellulose and its evolution during oxidation has remained a fundamental issue of priority interest to numerous researchers (Carrasco-Chinga and Syverud 2014; Saito and Isogai 2004; Saito et al. 2010; Mishra et al. 2011; Coseri 2017) because it strongly correlates with mechanical properties. Less explored topics were the stability of oxidised cellulose in alkaline solutions (commonly used agents in a detergent composition), as well as the effect of oxidation on whiteness stability.

Thus, it is extremely important to be able to determine the kind and the number of functional groups to be added to cellulose, in order to evaluate the polymer-oxidant interactions and their degradation. It should be noted that, for selected applications of oxy-celluloses, the degradation profile as well as alkaline and whiteness stability are important. Moreover, it is also critical to obtain low-, medium- or high-level oxidized cellulose with a defined degradation profile that will fit a selected application. Another role of the oxy-cellulose degradation data is to give a framework of optimal conditions for certain technological processes.

In the present study, K-periodate and the TEMPO mediated system, with and without bromide, were used to prepare low-, medium- and high-level oxidized cotton containing aldehyde or carboxyl groups. Oxidation by K-periodate was carried out varying the concentration of the oxidation agent from 0.1 to 1 g KIO_4/g cellulose for a defined treatment time, while TEMPO mediated oxidation was obtained using the concentration of the oxidation agent most commonly reported in the literature (Nikolic et al. 2017; Saito and Isogai 2004), while varying the treatment time from 15 to 120 min. The oxidised cotton yarns were further treated with sodium chlorite to convert aldehyde to carboxyl groups. Comprehensive research on the influence of the type and level of oxidation on the mechanical properties, surface morphology, degree of polymerisation as well as alkaline and whiteness stability of the oxidised cotton yarns is reported in this paper.

Experimental

Materials

Piled, ring-worsted 100% cotton yarns with 30 × 2 tex linear density and 330 twists/m were used in this study.

Chemicals

Cotoblanc HTD-N-anionic surfactant and Kemonecer NI-nonionic surfactant were purchased from CHT and Kemo–Croatia, respectively. All the other chemicals, namely, potassium periodate, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), sodium bromide, 10% sodium hypochlorite solution, sodium chlorite, Ca-acetate, cupriethylene-diamine (CED), H_2O_2, Na_2SiO_3, NaOH, NaCl, HCl, CH_3COOH, ethanol and phenolphthalein, were purchased from Sigma Aldrich. All the chemicals were of laboratory grade and used without further purification.

Pre-treatment of cotton yarns

Before oxidation, rigorous alkaline scouring and bleaching were done to remove all non-cellulosic components from the cotton yarns. In this way, the reference cotton yarn sample of pure cellulose was obtained.

Alkaline scouring

Scouring was done in a bath with 30:1 liquor ratio (LR) using 20 g/dm^3 NaOH in the presence of 2 cm^3/dm^3 Cotoblanc HTD-N and 1 cm^3/dm^3 Kemonecer NI at 95 °C for 90 min.

Bleaching

Bleaching was done in a bath with 30:1 LR, using 6 cm^3/dm^3 H_2O_2 (30%), 1 cm^3/dm^3 Kemonecer NI, 2 cm^3/dm^3 Na_2SiO_3 at pH 11.2, at 95 °C for 30 min. Both processes were carried out in a Linitest apparatus.

Oxidation

Pre-treated cotton yarns were oxidized with potassium periodate solution in different concentrations, as well as with TEMPO systems, with and without sodium bromide, during different treatment time. Oxidised yarns were further treated with sodium chlorite to convert aldehyde to carboxyl groups.

Oxidation with KIO_4

A 10 g pre-treated cotton yarns was immersed in solution of potassium periodate in 500 cm^3 acetate buffer (pH 4), containing 0.5; 1; 2; 4 and 10 g KIO_4 (i.e.0.05; 0.1; 0.2; 0.4 and 1 g KIO_4/g cellulose). The mixture was then stirred in the absence of light, at 60 °C for 30 min. After completion of the oxidation, the cotton yarns were rinsed five times with cold water for 15 min. Each oxidation was triplicate.

TEMPO-mediated oxidation

The TEMPO oxidation procedure was based on the literature methodology (Nikolic et al. 2017; Saito and Isogai 2004). In brief, for TEMPO/NaBr/NaClO system a 10 g cellulose sample was suspended in 300 cm^3 of distilled water, containing 0.025 g TEMPO and 0.25 g sodium bromide. Subsequently, a designed amount of NaClO solution containing 10% available chlorine, corresponding to 4.84 mmol NaClO per g cellulose, was added to the cellulose yarns under continuous stirring. The pH of this system was maintained at 10.5 by adding a 0.4 M NaOH solution. The oxidation was performed at room temperature for different time intervals of 15, 30, 45, 60 and 120 min. After stirring for a defined time, the oxidation was quenched by adding ethanol (ca. 12 cm^3). The oxidized cotton yarns were washed thoroughly with cold distilled water five times for 15 min. TEMPO/NaClO system was performed according to above described procedure in the absence of sodium bromide. Each oxidation was triplicate.

Conversion of aldehyde to carboxyl groups with sodium chlorite

The oxidized cotton yarns were further treated with sodium chlorite at pH 4–5 for selective conversion of the aldehyde to carboxyl groups according to the literature methodology (Nikolic et al. 2017; Saito and Isogai 2004).

Conversion was carried out by continuous stirring the mixture comprising of 500 cm^3 1 M CH_3COOH, 9.05 g $NaClO_2$ and 10 g never-dried oxidized cotton yarn at room temperature for 12 h, followed by rinsing thoroughly with cold water five times for 15 min.

Testing methods

Determination of carboxyl groups by titration

Determination of carboxyl groups was carried out on the basis of the Ca-acetate method, as reported in the literature (Toshikj et al. 2016). Amounts of 100 cm^3 of distilled water and 60 cm^3 of 0.25 M Ca-acetate solution were added to a 1 g sample. The suspension was allowed to stand for 12 h, under frequent shaking, to facilitate completion of the interchange. Then, a 25 cm^3 portion of the suspension was titrated with 0.01 M sodium hydroxide, using phenolphthalein as an indicator. The quantity of carboxyl groups was calculated using Eq. 1.

$$COOH(mmol/g) = \frac{\frac{(100+60)}{25} \cdot 0.01 \cdot M \cdot V(NaOH)}{m} \quad (1)$$

where 0.01 M is the concentration of NaOH, V is the volume (cm^3) of the NaOH solution used for titration, m is the weight of oxidized or un-oxidized cotton yarns (g), 100 is volume (cm^3) of the distilled water, 60 is volume (cm^3) of the 0.25 M Ca-acetate solution, 25 is volume (cm^3) of the suspension after completion of the interchange.

Determination of carboxyl groups by conductometric titration

Determination of carboxyl groups by conductometric titration was performed as described in the literature methodology (Saito and Isogai 2004). About 110 cm^3 of water and 10 cm^3 of 0.01 M NaCl were added to 0.6 g of dry sample. The pH was adjusted to approximately 2.5, by the addition of 0.1 M HCl. Titration was performed with 0.04 M NaOH solution added at a rate of 0.25 cm^3/min up to a pH of approximately 11, using a WTW Multiline P4 conductometer. Blank titration without any cellulose sample was performed to calibrate the system and to eliminate the effects of impurities. The conductivity was plotted against the volume of NaOH and the carboxyl group quantity was calculated from the titration curve using Eq. 2.

$$COOH(mmol/g) = \frac{V \cdot c}{m} \quad (2)$$

where c is 0.04 M NaOH concentration, V is the volume (cm^3) of the NaOH solution used for titration, m is the weight of sample (g).

Determination of aldehyde groups by the difference between the initial content and that after conversion to carboxyl groups by $NaClO_2$

The amount of aldehyde groups was measured according to the method described in the literature (Nikolic et al. 2017; Saito and Isogai 2004). The samples oxidized with K-periodate and TEMPO were further oxidized with sodium chlorite at pH 4–5 (procedure described above) for selective conversion of the aldehyde groups to carboxyl ones, and the amount of carboxyl groups was determined by the above-mentioned Ca-acetate and conductometric titration methods. The difference in the amount of carboxyl groups before and after the sodium chlorite treatment yields the amount of aldehyde groups.

Fourier transforms infrared spectroscopy-Attenuated total reflectance (FTIR-ATR)

FTIR-ATR spectroscopy was performed on an FTIR-ATR Perkin Elmer Spectrum GX 69,876 spectrometer. 16 scans at a resolution of 4 cm^{-1} were recorded for each sample between 4000 cm^{-1} and 650 cm^{-1}.

Scanning electron microscopy (SEM)

Characterization of surface morphology by scanning electron microscopy (SEM) was carried out on a JEOL JSM-6060 LV (Japan) electron microscope operating at an accelerating voltage of 10 kV and magnification of 5000× on samples previously coated with gold in a scatter coater.

Degree of polymerization (DP)

The intrinsic viscosity of un-oxidized and oxidized cellulose was determined according to ASTM D 4243-16 (2016) standards in 1.0 M cupriethylene-diamine (CED), and calculated based on the Schultz–Blanschke Eq. 3.

$$\eta\left(cm^3/g\right) = \frac{\frac{\eta_{rel}-1}{c}}{1 + K_{sb}(\eta_{rel} - 1)} \tag{3}$$

where η is intrinsic viscosity (cm^3/g), η_{rel} is the relative viscosity, c is polymer concentration (g/cm^3), and k_{sb} is 0.29 and represent the Schultz–Blanschke coefficient for CED-cellulose system. The relative viscosity, η_{rel}, of the various polymer solutions were determined from the relative values of the viscometrically measured solution and solvent flow times (t and to, respectively) on Ubbelohde viscometer by means of the relationship.

$$\eta_{rel} = \frac{t}{t_0} = \frac{\eta}{\eta_0} \tag{4}$$

The degree of polymerization was calculated from the intrinsic viscosity using the Mark–Houwink–Sakurada Eq. 5

$$[\eta] = K' \cdot DPv^{\alpha} \tag{5}$$

where DPv is average degree of polymerization, η is the intrinsic viscosity and K' (1.33) and α (0.905) are coefficients for a used polymer solvent system (Tosh and Saikia 1997).

The Eq. 5 corresponds to the Eq. 6 for DPv determination.

$$DPv^{0.905} = 0.75 \cdot [\eta] \tag{6}$$

The presented results are the mean values of 3 measurements at a confidence level of 95%.

Mechanical properties

Tensile strength (Fa), elongation at break (ε) and work of rupture (A) were measured on a Tinus Olsen (SDL ATLAS) instrument according to EN ISO 2062 (2009) standard using a test speed of 100 mm/min and gauge length of 300 mm. The presented results are the mean values of 20 measurements at a confidence level of 95%. The mechanical damage was calculated according to Eq. 7.

$$Um = \frac{Fo - F}{Fo} \cdot 100(\%) \tag{7}$$

where U_m is mechanical damage (%), F_0 is tensile strength of pre-treated sample (un-oxidized) (N), F is tensile strength of pre-treated and oxidized sample (N).

Alkali solubility of oxy-cellulose

Alkali solubility of oxy-cellulose was determined according to TAPPI T 212 om-02 (2002) standard. The presented results are the mean values of 3 measurements at a confidence level of 95%.

Whiteness stability of oxy-cellulose

Whiteness stability of oxy-cellulose was determined through the whiteness index (W_{CIE}) and b* colour coordinate according to ISO 105-J02 (1999) standard on an X-Rite Color i7 spectrophotometer. The presented results are the mean values of 20 measurements at a confidence level of 95%.

Results and discussion

Content of functional groups in oxidized celluloses

The oxidation of the cellulose can be defined as its treatment with oxidizing agents that act on the primary (C_6) and secondary (C_2 and C_3) hydroxyl groups oxidizing them to aldehyde or carboxyl ones. As was mentioned above, the type of introduced functional groups is strongly influenced by the type of oxidizing agent as well as treatment conditions comprising concentration of the oxidizing agent, temperature, pH and treatment time.

The amount of aldehyde and carboxyl groups obtained by K-periodate and TEMPO-mediated oxidation systems are shown in Figs. 1 and 2, respectively.

K-periodate acts selectively on the C_2 and C_3 hydroxyl groups of cellulose, oxidizing them to aldehyde by cleaving C_2–C_3 bonds (Calvini et al. 2004, 2006a). The formed aldehyde groups could be further converted to carboxyl ones by treatment with sodium chlorite. The oxidation in this study was conducted with 0.05–1 g K-periodate per g cellulose during constant time of 30 min. These treatment conditions have produced from 50 to 1300 mmol CHO per kg cellulose (depending on the concentration of periodate), which were converted to almost the same quantity of carboxyl groups after sodium chlorite treatment (Fig. 1).

According to the amount of the produced aldehyde groups, we defined three levels of cellulose oxidation: low (obtained with 0.05–0.1 g KIO_4/g cellulose), medium (obtained with 0.2 g KIO_4/g cellulose) and extensive oxidation (obtained with 0.4–1 g KIO_4/g cellulose), which produced oxy-cellulose with low, medium and high amounts of aldehyde groups, respectively.

TEMPO oxidation was carried out with (Nikolic et al. 2017; Saito and Isogai 2004) and without NaBr (Bragd et al. 2000; Fraschini et al. 2017; Shibata and Isogai 2003), during different treatment time under commonly used treatment conditions (Fig. 2). Oxidation by TEMPO with NaBr produced 400–650 mmol COOH/kg cellulose and 100 mmol CHO/kg cellulose, which were further converted to carboxyl groups after treatment with sodium chlorite (Fig. 2a). By the TEMPO-mediated oxidation, the primary C_6–OH groups of cellulose are selectively oxidized to carboxyl groups. At the same time, this system has produced aldehyde groups because TEMPO-mediated oxidation by sodium hypochlorite oxidation leads to scission of glucose units, which results in the formation of aldehyde groups (Dai et al. 2011).

The reaction time during TEMPO-mediated oxidation is significant for obtaining the desired amount of carboxyl groups. In the case of oxidation with NaBr, the reaction rate was fast in the first 15 min and continued to increase slowly after that. In contrast, the oxidation without NaBr had a very slow oxidation rate in the first 60 min, but rapidly increased from 60 to 120 min. However, this oxidation system never reached the level of carboxyl groups obtained by TEMPO with NaBr (Fig. 2b).

The action of the oxidation systems used has resulted in the formation of two extreme types of oxy-celluloses. K-periodate produced mainly aldehyde oxy-cellulose with a negligible amount of carboxyl groups, while the TEMPO-mediated system produced mainly carboxyl oxy-cellulose, with a significant amount of aldehyde groups on the oxidised cotton yarns.

Treating the K-periodate and TEMPO oxidised cotton yarns with sodium chlorite has resulted in the formation of a third type of oxy-cellulose. In both cases, oxy-celluloses enriched only with carboxyl groups have been obtained.

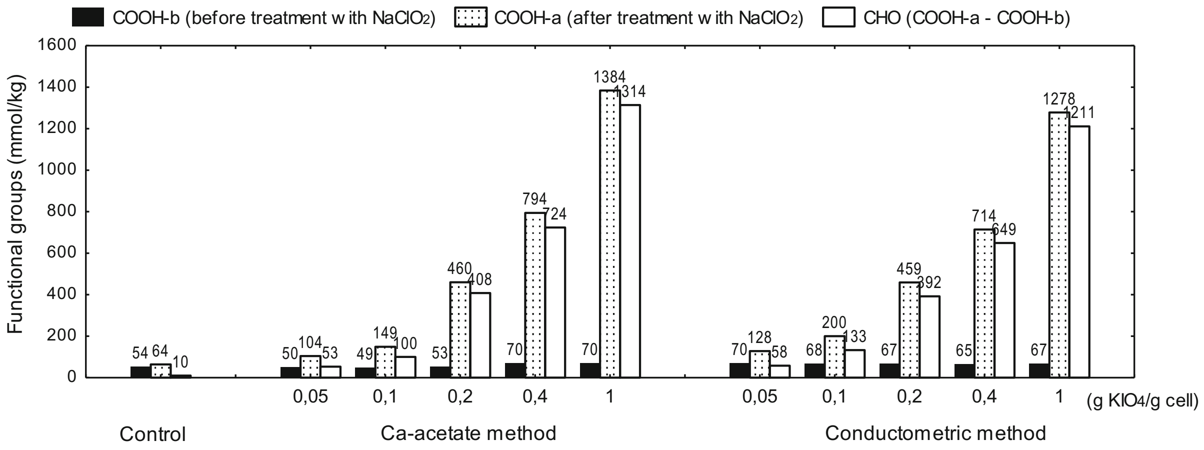


Fig. 1 Carboxyl and aldehyde groups of K-periodate oxidized cotton yarns determined by Ca-acetate and conductometric titration methods before and after treatment with sodium chlorite

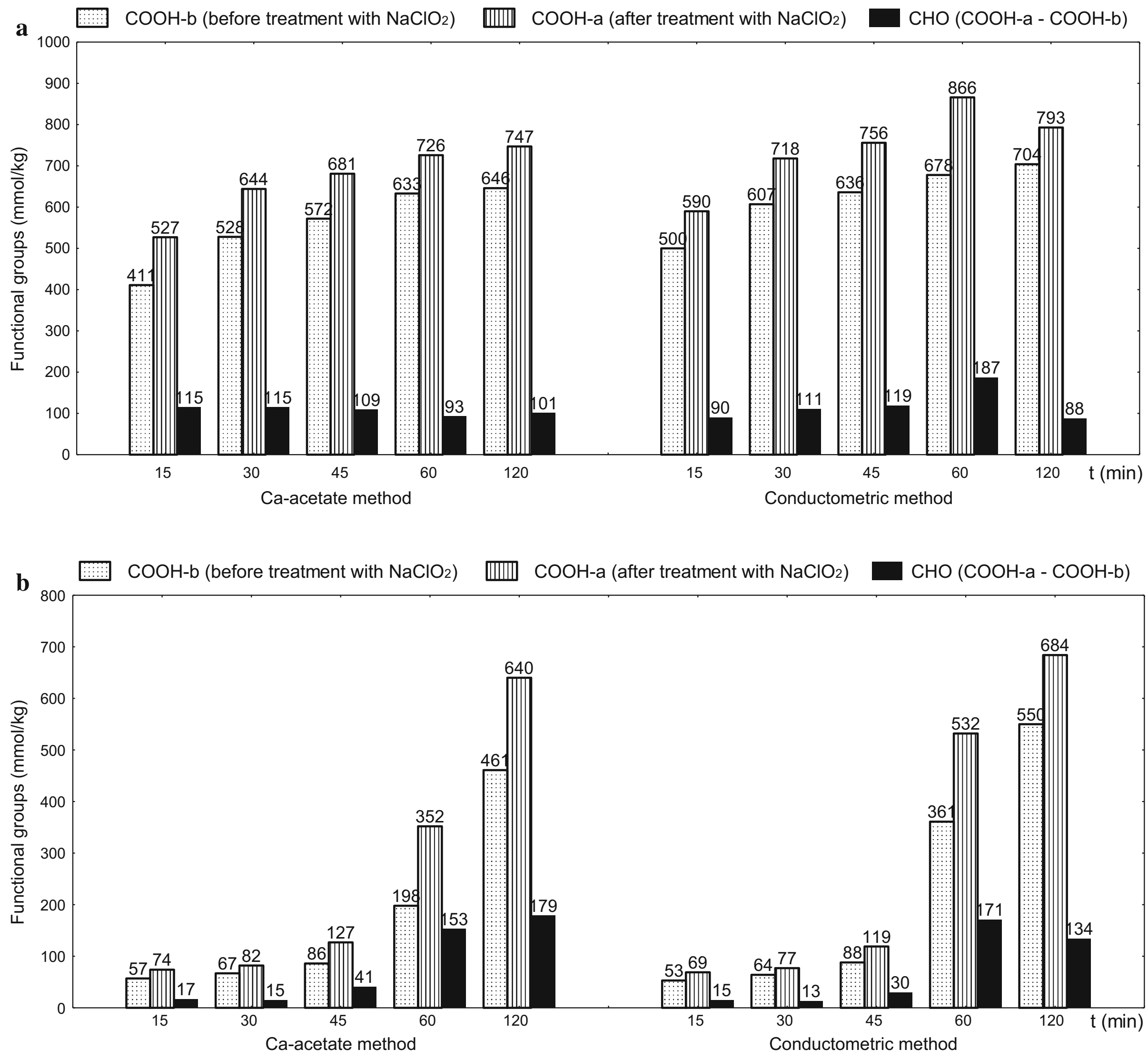


Fig. 2 **a** Carboxyl and aldehyde groups of TEMPO/NaBr/NaClO-mediated oxidized cotton yarns with NaBr determined by Ca-acetate and conductometric titration methods before and after treatment with sodium chlorite. **b** Carboxyl and aldehyde groups of TEMPO/NaClO-mediated oxidized cotton yarns without NaBr determined by Ca-acetate and conductometric titration methods before and after treatment with sodium chlorite

FTIR-ATR analyses

FTIR-ATR spectroscopy was used to characterize the surface of cellulose before and after oxidation (Fig. 3a–c). It may be remarked that the FTIR-ATR spectra of differently-oxidized celluloses show typical cellulose pattern, which is also noted for the un-oxidized control sample. The identification of the functional groups in the oxidized samples is complicated because the aldehyde, keto and carboxyl groups of the oxy-cellulose absorb in a very narrow region of the spectrum, between 1720 and 1780 cm^{-1} (Sivakova et al. 2008; Li et al. 2011). The typical band of aldehyde groups appears at 1733 cm^{-1} (Sivakova et al. 2008; Zhang et al. 2017). The un-oxidized control sample (Fig. 3a) did not show any carboxyl or aldehyde signal in the FTIR-ATR spectrum. In addition, low- and high-level K-periodate oxidized samples before treatment with $NaClO_2$ showed similar FTIR-ATR spectra with those of the un-oxidized ones.

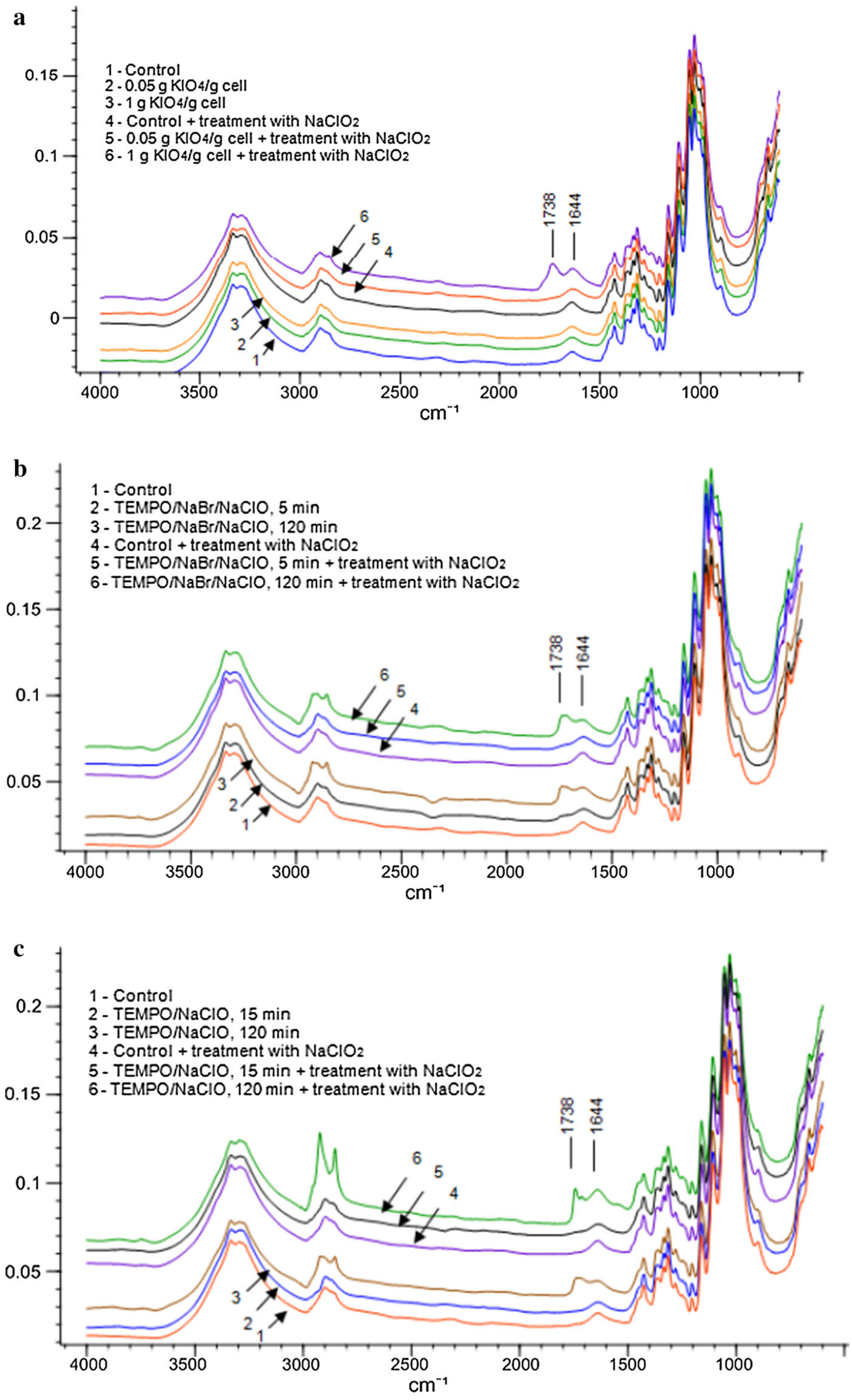


Fig. 3 **a** FTIR-ATR spectra of control, low and extensively oxidized cotton yarns by K-periodate before and after treatment with sodium chlorite. **b** FTIR-ATR spectra of control, low and extensively oxidized cotton yarns by TEMPO/NaBr/NaClO-mediated oxidation system before and after treatment with sodium chlorite. **c** FTIR-ATR spectra of control, low and extensively oxidized cotton yarns by NaBr free TEMPO/NaClO-mediated oxidation system before and after treatment with sodium chlorite

For aldehyde oxy-cellulose, the identification of the aldehyde groups is more difficult, since di-aldehyde cellulose can exist in partly or completely hydrated forms that do not contain peak of the aldehyde carbonyl (Calvini et al. 2006b; Zhang et al. 2017).

To confirm the presence of aldehyde groups, aldehyde oxy-cellulose were treated with sodium chlorite to convert aldehyde to carboxyl groups. This treatment strongly increased absorbance at 1738 cm^{-1} (Fig. 3a) corresponding to C=O stretching frequency of carboxyl groups in their acidic form (Calvini et al. 2006b). The intensity of the 1738 cm^{-1} peak of the oxidized sample with 1 g KIO_4/g cellulose and treated with sodium chlorite is more obvious than the sample oxidized with 0.05 g KIO_4/g cellulose and treated with sodium chlorite. These results (Fig. 3a) revealed that the introduced aldehyde groups with K-periodate were successfully converted to carboxyl by sodium chlorite treatment.

Figure 3b, c show the FTIR-ATR spectra of the samples before and after TEMPO-mediated oxidation with (Fig. 3b) and without sodium bromide (Fig. 3c). It is clear that characteristic absorbance at 1738 cm^{-1} region appears in oxidized sample (Fig. 3b, c). The band is absent in the control and low oxidized, but can be detected in the extensively oxidized samples. Moreover, intensity markedly increases with increasing degree of oxidation, which is consistent with the reported FTIR spectra of TEMPO-mediated oxy-celluloses (Habibi et al. 2006; Tang et al. 2017). The intensity of this peak (1738 cm^{-1}) on the samples treated for 120 min is stronger than on the samples treated for 15 min using both TEMPO systems, indicating a higher amount of carboxyl groups and extensively degree of oxidation.

Generally, according to the literature, the absorbance at about 1735 cm^{-1} is characteristic for carboxyl groups in acidic form (Calvini et al. 2006b; Tang et al. 2017), while 1610 cm^{-1} is assigned to the sodium carboxylate form (Ifuku et al. 2009; Marković et al. 2018).The results (Fig. 3a–c) indicate only the presence of the carboxyl groups in their acidic form because all oxidized samples (using K-periodate and TEMPO systems with and without sodium bromide) were treated with hydrochloric acid after oxidation, for removing the ionic metals existing in the fibres.

SEM analyses

The oxidation could be responsible for changes in the oxidized cellulose surface morphology as well. The results of surface imaging of the differently treated cotton yarns are presented in Fig. 4a, b. The control sample has clearly defined fibrils on the fiber surface, indicating completely removed cuticle. SEM images reveal that the obtained oxy-cellulose also possesses fibrillar surface. Although the cellulose was obviously damaged after oxidation, the surface characteristics of the oxidized cellulose before and after sodium chlorite treatment did not change significantly.

Mechanical properties

Tensile strength, elongation at break and work of rupture were used to evaluate mechanical properties and to calculate the damage of differently oxidized cotton yarns (Table 1). Decreasing tensile strength and work of rupture of the oxidised cotton yarns are evident after using all the oxidizing systems. Increasing concentration of K-periodate leads to a decrease of tensile strength and work of rupture of the produced aldehyde oxy-cellulose. The degree of mechanical degradation, calculated as the difference between tensile strength values before and after oxidation, has shown that the cotton yarns were damaged up to 65% when using the maximum concentration of periodate in this study. Even at a low concentration, of 0.05 g periodate per g cellulose, the tensile strength of the oxidized cotton yarns decreased by 33%.

Tensile strength values of the TEMPO oxidised cotton yarns, with and without sodium bromide, are also given in Table 1. As the duration of the treatment rises, the tensile strength and work of rupture decrease up to 77%. It is evident that shorter treatment time with the TEMPO mediated system, with the addition of sodium bromide, caused more damage than without it. Surprisingly, the damage is similar for both TEMPO systems after 120 min treatment time. The same observations have been made when the introduced groups were analysed. As the concentration of periodate and the treatment time with the TEMPO oxidizing systems are increased, the amount of the produced groups is higher.

The mechanical properties and the introduced aldehyde and carboxyl groups correlate very well. For K-periodate oxidation, tensile strength correlates with the aldehyde groups obtained with Ca-acetate (− 0.94) and conductometric titration (− 0.94). Moreover, there are also good correlations between the introduced groups and work of rupture. For TEMPO-mediated oxidation, tensile strength correlates with the carboxyl groups obtained by Ca-acetate (− 0.96) and conductometric titration (− 0.98).

During the oxidation, the glucoside units of cellulose are attacked by the oxidizing agents, resulting in the formation of new functional groups, as well as in the scission of molecular chains, which subsequently leads to a decrease of mechanical properties and DP (discussed below).

K-periodate and TEMPO oxidized cotton yarns were further treated with sodium chlorite to convert aldehyde to carboxyl groups. The mechanical properties of these samples are given in Table 1. It is evident that, after conversion, mechanical properties are additionally lightly decreased. The tensile strength of the periodate oxidized cellulose additionally decreases to 9%, while that of the TEMPO oxidized ones decreases up to 10.7%, depending on the presence of NaBr and treatment time. The treatment of aldehyde oxy-cellulose with sodium chlorite is a good path for converting aldehyde to carboxyl groups,

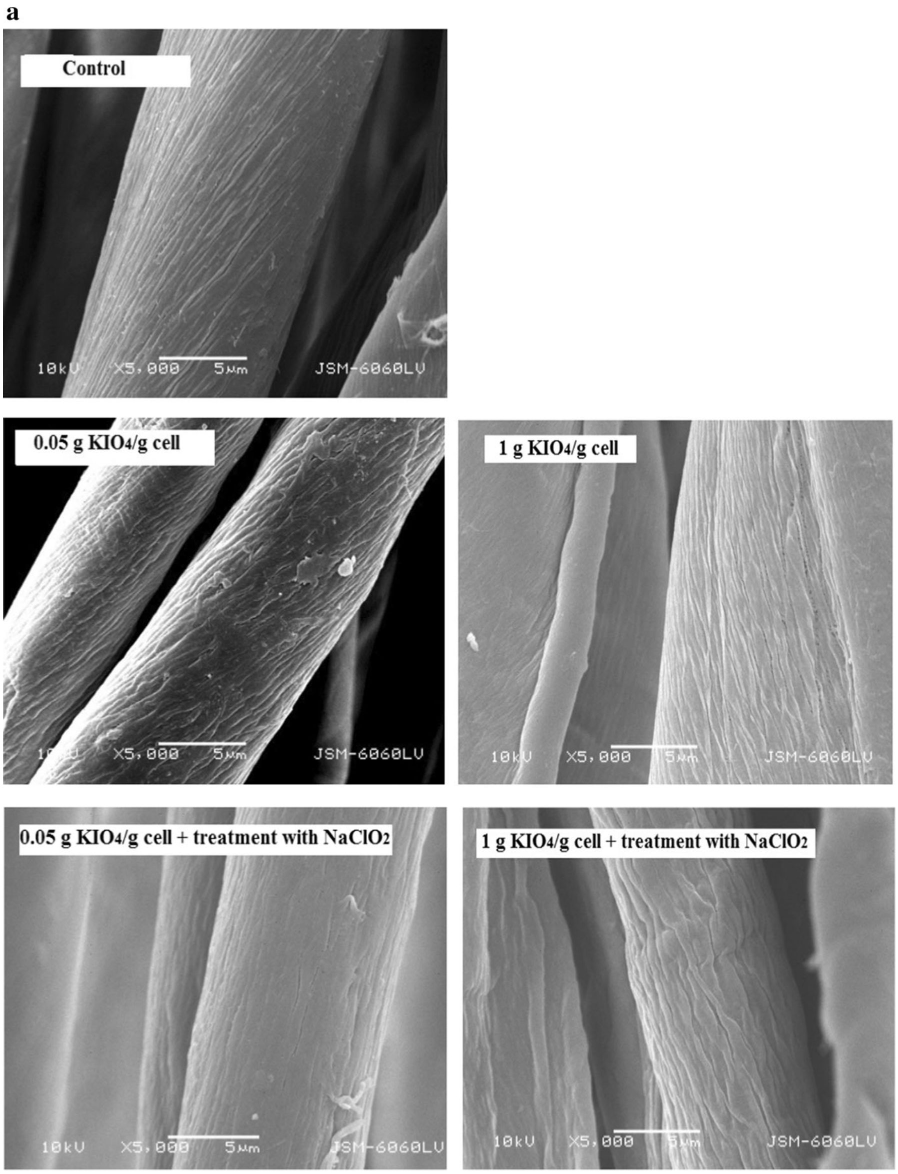


Fig. 4 **a** SEM images of control, low and extensively oxidized cotton yarns with K-periodate before and after treatment with sodium chlorite. **b** SEM images of control, low and extensively oxidized cotton yarns with TEMPO/NaBr/NaClO-mediated oxidation system before and after treatment with sodium chlorite

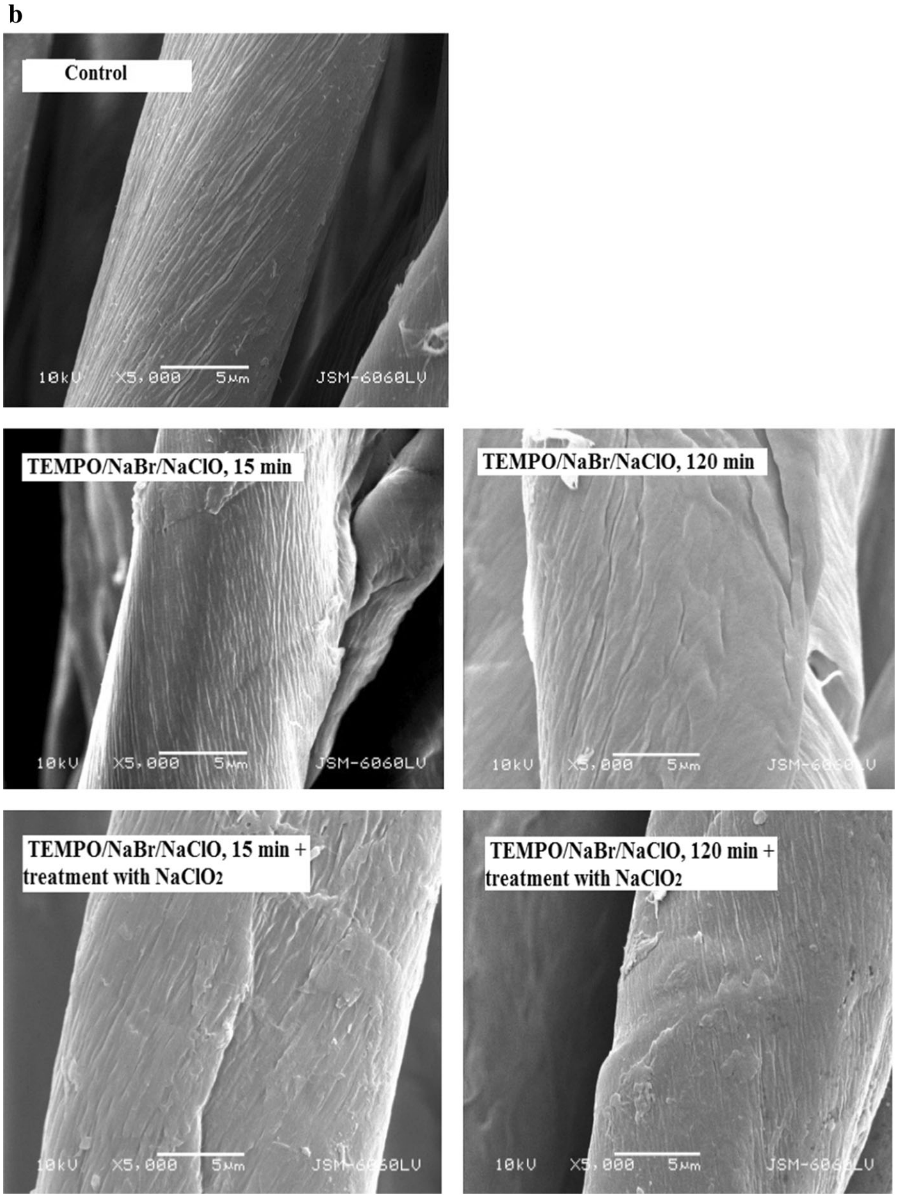


Fig. 4 continued

but it is absolutely not necessary to treat carboxyl oxycellulose with sodium chlorite, because no additional carboxyl groups are formed in the samples, while their mechanical properties are slightly decreased.

Degree of polymerization

The degree of polymerization of the oxidized yarns presented in Table 2, have lower DP than the control sample (DP 1733). The results have shown that DP depends on the type of the oxidizing agent, its concentration and the time of oxidation. The lowest DPs are observed on K-periodate oxidized cotton yarns, which have values between 384 (min. concentration of K-periodate) and 36 (max. concentration of K-periodate). On the other hand TEMPO/NaBr/NaClO oxidized yarns have higher values for DP than K-periodate. TEMPO oxidized cotton yarn has 186

Table 1 Tensile strength, elongation at break, work of rupture and mechanical damage of K-periodate and TEMPO-mediated oxidized cotton yarns before and after treatment with sodium chlorite

Treatment	Time (min)	Concentration (g KIO_4/g cell)	Before treatment with $NaClO_2$				After treatment with $NaClO_2$			
			Fa (N)	ε (%)	A (mJ)	Um (%)	Fa (N)	ε (%)	A (mJ)	Um (%)
Control			9.7	16.2	159.4		7.7	14.2	112.2	
KIO_4	30	0.05	6.5	11.5	80.2	− 33.0	6.8	14.4	98.6	+ 4.6
		0.1	5.6	13.6	74.3	− 42.3	5.1	12.9	66.3	− 8.9
		0.2	4.8	14.1	64.2	− 50.5	4.6	12.5	60.0	− 4.2
		0.4	4.1	13.2	51.3	− 57.7	4.4	12.4	56.8	+ 7.3
		1	3.4	12.5	39.1	− 65.0	3.1	8.6	31.4	− 8.8
TEMPO	15		3.3	11.7	37.2	− 66.0	3.2	9.4	33.9	− 3.0
NaBr	30		2.9	10.8	32.8	− 70.1	2.8	7.1	24.3	− 3.5
NaClO	45		2.9	10.4	32.9	− 70.1	2.7	8.3	26.7	− 6.9
	60		2.8	8.2	25.6	− 71.1	2.5	7.2	19.7	− 10.7
	120		2.6	9.9	27.1	− 73.2	2.4	9.2	24.9	− 7.7
TEMPO	15		6.4	13.8	91.3	− 34.0	6.4	10.4	80.9	0.0
NaClO	30		5.1	12.2	66.6	− 47.4	4.8	11.6	61.3	− 5.9
	45		3.7	10.8	44.1	− 61.9	3.7	10.7	43.6	0.0
	60		2.9	9.1	26.4	− 70.1	3.1	8.7	31.6	+ 6.9
	120		2.2	7.7	19.4	− 77.3	2.1	7.3	17.3	− 4.6

Table 2 Degree of polymerization of K-periodate and TEMPO-mediated oxidized cellulose before and after treatment with sodium chlorite

Treatment	Time (min)	Concentration (g KIO_4/g cell)	DP_v	
			Before treatment with $NaClO_2$	After treatment with $NaClO_2$
Control			1733.8	1382.7
KIO_4	30	0.05	384.3	368.9
		0.1	256.7	245.5
		0.2	211.7	164.4
		0.4	72.3	129.1
		1	36.3	103.2
TEMPO	15		186.6	195.8
NaBr	30		143.4	173.9
NaClO	45		133.3	190.1
	60		106.0	178.0
	120		152.2	162.2
TEMPO	15		748.1	760.9
NaClO	30		629.5	637.6
	45		569.0	599.8
	60		443.5	448.5
	120		140.1	194.5

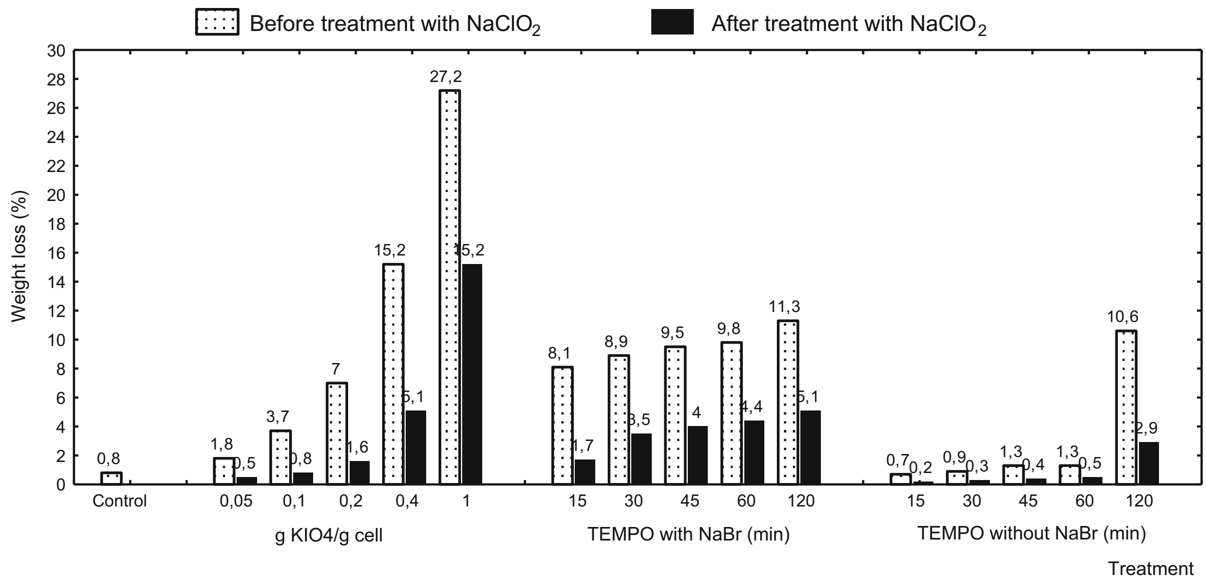


Fig. 5 Alkali solubility of oxidised cotton yarns obtained by K-periodate and TEMPO-mediated oxidation systems before and after treatment with sodium chlorite

value of DP achieved for 15 min. After 30 min treatment time, the DP is 143, so this value is higher than medium to high K-periodate oxidized cotton yarns. After 120 min treatment, the DP of 152 is still higher than the DP of oxy-cellulose obtained with the maximum concentration of K-periodate for 30 min treatment time (Table 2).

Sodium bromide has strong influence on the degree of polymerization of TEMPO oxidized cotton yarns. The decrease of DP was more prominent in the case of the oxy-celluloses obtained by TEMPO oxidation with NaBr, compared to the samples oxidized without NaBr. Differences are remarkable for a treatment time of up to 60 min, but, surprisingly, the same values are obtained with and without NaBr after 120 min of treatment.

Oxidation with periodate is highly specific and leads to selective cleavage of the C_2–C_3 bond of the glycoside ring forming aldehyde groups on them. During the oxidation, additional reactions of alkoxy-fragmentation of the oxidized units have occurred, decreasing the DP of cellulose. TEMPO oxidation may depolymerise cellulose to some extent by cleavage the 1–4 β-glycoside bonds of cellulose through β-elimination reaction under alkaline conditions (pH 10.5) due to the presence of sodium hypochlorite (Calvini et al. 2004), decreasing the DP of carboxyl-cellulose (Saito and Isogai 2004).

There are strong coefficients of correlation between the DP and the amount of aldehyde groups after oxidation with K-periodate, measured by the Ca-acetate method (− 0.91) and conductometric titration (− 0.91). After TEMPO oxidation with NaBr, the coefficient of correlation between DP and aldehyde groups (determined by conductometric titration) is − 0.86.

The DP values of oxy-celluloses after conversion of aldehyde to carboxyl groups by treating with sodium chlorite are also shown in Table 2. The samples oxidized with 0.05–0.2 g KIO_4 per g cellulose have slightly lower DP after conversion, while highly oxidized oxy-celluloses (obtained with 0.4 and 1 g KIO_4 per g cellulose) have higher DP after conversion.

TEMPO oxidized cotton yarns with and without NaBr have higher DP after treatment with $NaClO_2$ too. The same phenomenon has been observed by Mishra et al. (2011, 2012). They noted that a possible reason for this effect could be the presence of aldehyde groups generated during the oxidation process, which may have rendered the cellulose polymers vulnerable to depolimerization in the highly alkaline CED solution used for the viscosity determination. Treatment with $NaClO_2$ converted the aldehyde groups to carboxyl and thus eliminating any kind of possible damage due to the highly alkaline conditions during CED viscosity measurement.

Table 3 Whiteness index and b* colour coordinate of oxidized cotton yarns obtained by K-periodate and TEMPO-mediated oxidation systems before and after treatment with sodium chlorite

Treatment	Time (min)	Concentration (g KIO_4/g cell)	WI_{CIE} and b*			
			Oxidized		After treatment with $NaClO_2$	
			b*	WI_{CIE}	b*	WI_{CIE}
Control			1.41	82.65	0.80	88.65
KIO_4	30	0.05	2.01	79.52	0.75	85.85
		0.1	2.33	77.90	0.68	85.99
		0.2	2.18	78.26	0.51	85.80
		0.4	2.24	77.48	0.65	85.87
		1	2.60	75.37	0.64	83.28
TEMPO	15		0.86	80.95	0.29	86.46
NaBr	30		0.54	82.79	0.29	86.13
NaClO	45		0.76	82.35	0.33	86.17
	60		0.96	82.20	0.30	86.86
	120		0.79	80.48	0.23	84.16
TEMPO	15		0.98	77.79	0.68	85.87
NaClO	30		1.06	77.99	0.55	85.52
	45		1.09	75.12	0.41	86.02
	60		1.07	77.84	0.37	86.85
	120		0.90	77.33	0.18	85.65

Alkali solubility of oxy-celluloses

The results of alkali solubility determined as weight loss after treatment with sodium hydroxide are shown in Fig. 5. More damaged cellulose should have higher alkali solubility or higher weight loss after the treatment with the alkali solution. Alkali solubility is a good method for determining the resistance of oxidized cellulose to washing cycles. More damaged cellulose could be hydrolysed and solubilised even during the first several washing cycles.

Alkali solubility increased with an increasing amount of aldehyde and carboxyl groups of the oxy-celluloses obtained by K-periodate and TEMPO, respectively (Fig. 5). The alkali solubility of K-periodate oxidized cotton yarns lies in the range of 1.8% (0.05 g KIO_4/g cellulose) to 27% (1 g KIO_4/g cellulose). Low to medium K-periodate oxidized cotton yarns have lower alkali solubility than the TEMPO oxidised ones with sodium bromide. Alkali solubility rapidly increased to extensively oxidized periodate oxy-cellulose, even higher than on TEMPO oxidised.

Alkali solubility of TEMPO oxidised cotton yarns linearly increased with treatment time, so after 120 min, it is still lower (up to 11%) than that of the most extensively oxidized periodate oxy-cellulose (27.2%). Alkali solubility was more prominent in the case of the oxy-celluloses obtained by TEMPO oxidation with NaBr than without it. Generally, TEMPO oxidation without NaBr leads to low alkali solubility, except the case of the sample treated for 120 min. It proved the significant influence of NaBr in the TEMPO oxidation reaction.

After conversion of aldehyde to carboxyl groups by sodium chlorite, the alkali solubility of the samples decreased. It confirms previous mentioned observation noted by Mishra et al. (2011, 2012) for obtaining higher DP of the oxidized samples after treatment with sodium chlorite. They noted that the presence of aldehyde groups may have rendered the cellulose polymers vulnerable to depolimerization in the highly alkaline CED solution used for the viscosity determination. The alkali solubility method is similar as viscosity determination in CED alkaline solution. This is reason why conversion of aldehyde to carboxyl groups leads to lower alkali solubility and makes carboxyl reach oxidized samples more stable in alkaline conditions. This phenomenon could also explain higher alkali solubility of K-periodate oxidized than TEMPO oxidized cotton.

Whiteness stability of oxy-celluloses

The results for whiteness index and b* colour coordinate (CIELab colour coordinate system) of the control and oxidized samples are presented in Table 3. In the CIELab colour system, b* represents the blue–yellow colour coordinate. Negative values indicate more blue, while positive ones–more yellow colour. The control sample has a WI_{CIE} of 82.65 and b* of 1.41. While WI_{CIE} decreased, the value of b* increased upon increasing concentration of K-periodate. It means that by increasing the amount of the created aldehyde groups, some damage occurs, causing a decrease of the whiteness and leading to more yellow samples. TEMPO with NaBr oxidized samples have slightly lower whiteness index than the control and substantially less yellowness, as indicated by the lowest b* values. When TEMPO without NaBr is applied to cotton yarns, oxy-celluloses with lower whiteness are produced than with NaBr. The yellowness of those yarns lies between the values for K-periodate and TEMPO with NaBr oxidized oxy-celluloses.

As mentioned above, sodium chlorite treatment was performed in order to selectively convert aldehyde to carboxyl groups in all the oxidized samples. Sodium chlorite is also used as a bleaching agent for bleaching textile materials. After the sodium chlorite treatment, the whiteness of all the samples (K-periodate and TEMPO oxidised) increased, and b* values decreased. It suggests that, although sodium chlorite is a good bleaching chemical, probably the conversion of aldehyde to carboxyl groups also improved the whiteness of the cotton yarns.

Conclusions

Different levels of oxidation, as well as type of functional groups, have been achieved by properly selected oxidation systems, while controlling the concentration of the oxidants and treatment time. Higher oxidation levels for a shorter treatment time were achieved by K-periodate and TEMPO-mediated oxidation system with sodium bromide, while for a longer treatment time by the bromide-free TEMPO-mediated oxidation system. The oxidation systems used have led to the formation of two extreme types of oxy-celluloses. K-periodate produced mainly aldehyde oxy-cellulose, with a negligible amount of carboxyl groups, while the TEMPO-mediated system produced mainly carboxyl oxy-cellulose with significant amount of aldehyde groups present on the oxidized cotton yarns. Treating the K-periodate and TEMPO oxidized cotton yarns with sodium chlorite has resulted in the formation of a third type of oxy-cellulose containing almost exclusively carboxyl groups.

The type and oxidation level of oxy-celluloses influenced their mechanical properties, degree of polymerization, alkaline and whiteness stability. Oxy-celluloses with a low level of aldehyde and carboxyl groups are less sensitive to an alkaline solution and showed slight tensile strength loss, followed by medium and extensively oxidized oxy-celluloses. Celluloses with a low level of oxidation are suitable for producing stable long-lasting materials with high added value, while extensively oxidized ones are applicable for disposable products. The present study reports the results of a comprehensive fundamental exploration of the cotton behaviour under the action of different oxidation systems, which we believe can serve as a contribution to the scientific community with a research interest in developing cellulosic textile materials for different applications.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval All appropriate international, national and/or institutional guidelines for the care and use of animals were followed.

References

Abo El-Ola AMS, Moharam EM, Eladwi MM, El-Bendary AM (2014) Optimum conditions for polyamide fabric modification by protease enzyme produced by Bacillus sp. Indian J Fibre Text Res 39:65–71

Ashton HW, Moser EC (1968) Oxidized cellulose product and method for preparing the same. United States Patent No. US3364200A

ASTM D 4243-16 (2016) Standard test method for measurement of average viscometric degree of polymerization of new and aged electrical papers and boards. In: Annual Book of ASTM Standards. American Society for Testing and Materials, Philadelphia, PA

Bragd LP, Besemer CA, van Bekkum H (2000) Bromide-free TEMPO-mediated oxidation of primary alcohol groups in starch and methyl α-D-glucopyranoside. Carbohydr Res 328:355–363

Brodin WB, Theliander H (2012) Absorbent materials based on kraft pulp: preparation and material characterization. BioResources 7:1666–1683

Calvini P, Conio G, Lorenzoni M, Pedemonte E (2004) Viscosimetric determination of dialdehyde content in periodate oxycellulose. Part I. Methodology. Cellulose 11:99–107

Calvini P, Conio G, Princi E, Vicini S, Pedemonte E (2006a) Viscosimetric determination of dialdehyde content in periodate oxycellulose Part II. Topochemistry of oxidation. Cellulose 13:571–579

Calvini P, Gorassini A, Luciano G, Franceschi E (2006b) FTIR and WAXS analysis of periodate oxycellulose: evidence for a cluster mechanism of oxidation. Vib Spectrosc 40:177–183

Carrasco-Chinga G, Syverud K (2014) Pretreatment-dependent surface chemistry of wood nanocellulose for pH-sensitive hydrogels. J Biomater Appl 29:423–432

Coseri S (2017) Cellulose: to depolymerize… or not to? Biotechnol Adv 35:251–266

Coseri S, Biliuta G, Simionescu B, Kleinschek-Karin S, Ribitsch V, Harabagiu V (2013) Oxidized cellulose-survey of the most recent achievements. Carbohydr Polym 93:207–215

Coseri S, Biliuta G, Zemljic LF, Srndovic JS, Larsson PT, Strnad S, Kreze T, Naderi A, Lindstrom T (2015) One-shot carboxylation of microcrystalline cellulose in the presence of nitroxyl radicals and sodium periodate. RSC Adv 104:85889–85897

Coseri S, Biliuta G, Simionescu B (2018) Selective oxidation of cellulose, mediated by *N*-hydroxyphthalimide, under a metal-free environment. Polym Chem 9:961–967

Dai L, Dai H, Yuan Y, Sun X, Zhu Z (2011) Effect of TEMPO oxidation system on kinetic constants of cotton fibers. BioResources 6:2619–2631

Diankova MSV, Doneva DM (2009) Analysis of oxycellulose obtained by partial oxidation with different reagents. Bulg Chem Commun 41:391–396

EN ISO 2062 (2009) Textiles - Yarns from packages - Determination of single-end breaking force and elongation at brake using constant rate of extension (CRE) tester (ISO 2062:2009). International Organization for Standardization, Geneva, Switzerland

Eyley S, Thielemans W (2014) Surface modification of cellulose nanocrystals. Nanoscale 6:7764–7779

Fraschini C, Chauve G, Bouchard J (2017) TEMPO-mediated surface oxidation of cellulose nanocrystals (CNCs). Cellulose 24:2775–2790

Habibi Y, Chanzy H, Vignon RM (2006) TEMPO-mediated surface oxidation of cellulose whisker. Cellulose 13:679–687

Ifuku S, Tsuji M, Morimoto M, Saimoto H, Yano H (2009) Synthesis of silver nanoparticles template by TEMPO-mediated oxidized bacterial cellulose nanofibers. Biomacromol 10:2199–2209

Ige OO, Umoru EL, Aribo S (2012) Natural products: a minefield of biomaterials. ISRN Mater Sci 2012:1–20

Inamochi T, Funahashi R, Nakamura Y, Saito T, Isogai A (2017) Effect of coexisting salt on TEMPO-mediated oxidation of wood cellulose for preparation of nanocellulose. Cellulose 24:4097–4101

ISO 105-J02 (1999) Textiles - Tests for colour fastness - part J02: Instrumental assessment of relative whiteness. International Organization for Standardization, Geneva, Switzerland

Isogai A, Saito T, Fukuzumi H (2011) TEMPO-oxidized cellulose nanofibers. Nanoscale 3:71–85

Isogai A, Hänninen T, Fujisawa S, Saito T (2018) Review: catalytic oxidation of cellulose with nitroxyl radicals under aqueous conditions. Prog Polym Sci 86:122–148

Janjic S, Kostic M, Vucinic V, Dimitrijevic S, Popovic K, Ristic M, Skundric P (2009) Biologically active fibers based on chitosan-coated lyocell fibers. Carbohydr Polym 78:240–246

Jin LQ, Sun QC, Xu QH, Xu YJ (2015) Adsorptive removal of anionic dyes from aqueous solutions using microgel based on nanocellulose and polyvinylamine. Bioresour Technol 197:348–355

Kanth SV, Ramaraj A, Rao RJ, Nair BU (2009) Stabilization of type I collagen using dialdehyde cellulose. Process Biochem 44:869–874

Kim YJ, Choi MH (2014) Cationization of periodate-oxidized cotton cellulose with choline chloride. Cellul Chem Technol 48:25–32

Kolarova K, Vosmanska V, Rimpelova S, Svorcik V (2013) Effect on plasma treatment on cellulose fiber. Cellulose 20:953–961

Kramer A, Milanović J, Korica M, Nikolić T, Asanović K, Kostić M (2014) Influence of structural changes induced by oxidation and addition of silver ions on electrical properties of cotton yarn. Cellul Chem Technol 48:189–197

Kumar V (2003) Powdered oxidized cellulose. United States Patent No. US6627749B1

Kumari S, Mankotia D, Chauhan GS (2016) Crosslinked cellulose dialdehyde for congo red removal from its aqueous solutions. J Environ Chem Eng 4:1126–1136

Li H, Wu B, Mu C, Lin W (2011) Concomitant degradation in periodate oxidation of carboxymethyl cellulose. Carbohydr Polym 84:881–886

Luo CC, Wang H, Chen Y (2015) Progress in modification of cellulose and application. Chem Ind Eng Prog 34:767–773

Marković D, Korica M, Kostić M, Radovanović Ž, Šaponjić Z, Mitrić M, Radetić M (2018) In situ synthesis of Cu/Cu_2O nanoparticles on the TEMPO oxidized cotton fabrics. Cellulose 25:829–841

Mishra PS, Thirree J, Manent SA, Chabot B, Daneault C (2011) Ultrasound-catalyzed TEMPO-mediated oxidation of native cellulose for the production of nanocellulose: effect of process variables. BioResources 6:121–143

Mishra PS, Manent SA, Chabot B, Daneault C (2012) Production of nanocellulose from native cellulose-various options utilizing ultrasound. BioResources 7:422–436

Nikolic T, Kostic M, Praskalo J, Pejic B, Petronijevic P, Skundric P (2010) Sodium periodate oxidized cotton yarns as carrier for immobilization of trypsin. Carbohydr Polym 82:976–981

Nikolic T, Korica M, Milanovic J, Kramar A, Petronijevic Ƶ, Kositc M (2017) TEMPO-oxidized cotton as a substrate for trypsin immobilization: impact of functional groups on proteolytic activity and stability. Cellulose 24:1863–1875

Perlin AS (2006) Glycol-cleavage oxidation. Adv Carbohydr Chem Biochem 60:183–250

Pietrucha K, Safandowska M (2015) Dialdehyde cellulose-crosslinked collagen and its physicochemical properties. Process Biochem 50:2015–2111

Saito T, Isogai A (2004) TEMPO-mediated oxidation of native cellulose the effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions. Biomacromol 5:1983–1989

Saito T, Okita Y, Nge TT, Sugiyama J, Isogai A (2006) TEMPO-mediated oxidation of native cellulose: microscopic analysis of fibrous fractions in the oxidized products. Carbohydr Polym 65:435–440

Saito T, Hirota M, Tamura N, Isogai A (2010) Oxidation of bleached wood pulp by TEMPO/NaClO/NaClO$_2$ system: effect of the oxidation conditions on carboxylate content and degree of polymerization. J Wood Sci 56:227–232

Sang X, Qin C, Tong Z, Kong S, Jia GW, Liu X (2017) Mechanism and kinetics studies of carboxyl group formation on the surface of cellulose fiber in a TEMPO-mediated system. Cellulose 24:2415–2425

Shibata I, Isogai A (2003) Depolymerization of cellourinic acid during TEMPO-mediated oxidation. Cellulose 10:151–158

Sivakova B, Beganskienė A, Kareiva A (2008) Investigation of damaged paper by ink corrosion. Mater Sci (MEDŽIAGOTYRA) 14:51–54

Stilwell LR, Whitmore JE, Saferstein GL (1996) Calcium-modified oxidized cellulose hemostat. United States Patent No. US005484913A

Strand S, Šauper O, Jazbec A, Kleinschek SK (2008) Influence of chemical modification on sorption and mechanical properties of cotton fibers treated with chitosan. Text Res J 78:390–398

Sun B, Gu C, Ma J, Liang B (2005) Kinetic study on TEMPO-mediated selective oxidation of regenerated cellulose. Cellulose 12:59–66

Tang A, Zhang H, Chen G, Xie G, Liang W (2005) Influence of ultrasound treatment on accessibility and regioselective oxidation reactivity of cellulose. Ultrason Sonochem 12:467–472

Tang Z, Li W, Lin X, Xiao H, Miao Q, Huang L, Chen L, Wu H (2017) TEMPO-oxidation cellulose with high degree of oxidation. Polymers 9:421–430

TAPPI T 212 om-02 (2002) One percent sodium hydroxide solubility of wood and pulp. Technical Association of the Pulp and Paper Industry, Peachtree Corners, GA

Tosh NB, Saikia NC (1997) Mark–Houwink–Sakurada constants for cellulose-paraformaldehyde/dimethyl sulphoxide system. Indian J Chem Technol 4:247–250

Toshikj E, Jordanov I, Dimova V, Mangovska B (2016) The influence of non-selective oxidation on differently pre-treated cotton yarns. Mater Sci (MEDŽIAGOYRA) 22:429–434

Toshikj E, Jordanov I, Dimova V, Mangovska B (2017) Influence of various pre-treatment processes on selective oxidation of cotton yarns. AATCC J Res 4:22–28

Xu M, Dai H, Sun X, Wang S, Wu W (2012) Influence of buffer solution on TEMPO-mediated oxidation. BioResources 7:1633–1642

Zemljic-Fras L, Sauperl O, Kreze T, Strnad S (2013) Characterization of regenerated cellulose fibers antimicrobial functionalized by chitosan. Text Res J 83:185–196

Zhang L, Ge H, Xu M, Cao J, Dai Y (2017) Physicochemical properties, antioxidant and antibacterial activities of dialdehyde microcrystalline cellulose. Cellulose 24:2287–2298