



**UNION OF ENGINEERS AND TEXTILE
TECHNICIANS OF SERBIA**

**VI INTERNATIONAL SCIENTIFIC CONFERENCE
CONTEMPORARY TRENDS
AND INNOVATIONS IN THE
TEXTILE INDUSTRY**

**VI MEĐUNARODNA NAUČNA KONFERENCIJA
SAVREMENI TRENDovi I
INOVACIJE U TEKSTILNOJ
INDUSTRIJI**

PROCEEDINGS

**EDITOR:
Prof. dr SNEŽANA UROŠEVIĆ**

**Belgrade, 14-15th September, 2023
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Dom inženjera „Nikola Tesla“**



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THE INFLUENCE OF LONG-TERM AGING ON THE PROPERTIES OF TEMPO OXIDIZED COTTON

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ABSTRACT: Cotton yarns were 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) oxidized, i.e., oxidation was carried out in the presence of sodium hypochlorite, sodium bromide and TEMPO, during different time intervals (30, 60 and 120 min). Given that TEMPO oxidized cotton is prone to aging processes, the influence of long-term aging on the properties of TEMPO oxidized cotton yarns was monitored through changes in their content of carboxyl and aldehyde groups, crystallinity index and water retention value, determined immediately after TEMPO oxidations and 10 years later. The content of carboxyl and aldehyde groups was determined by the calcium acetate method, the crystallinity index by the Schwertassek method, and the water retention value by the standard centrifuge method (ASTM D 2402-78, 1978). Aged TEMPO oxidized cotton yarns showed increased content of carboxyl groups, decreased content of aldehyde groups, unchanged crystallinity index and increased water retention value.

Keywords: TEMPO oxidation, cotton, long-term ageing, properties.

UTICAJ DUGOTRAJNOG STARENJA NA SVOJSTAVA TEMPO OKSIDISANOG PAMUKA

APSTRAKT: Pamučne pređe su oksidisane 2,2,6,6-tetrametilpiperidin-1-oksilradikal (TEMPO), tj. oksidisane su sa natrijum-hipohloritom, natrijum-bromidom i TEMPO, tokom različitih vremenskih intervala (30, 60 i 120 min). S obzirom na to da je TEMPO oksidisani pamuk podložan procesima starenja, uticaj dugotrajnog starenja na svojstava TEMPO oksidisanih pamučnih pređa praćen je kroz promene u njihovom sadržaju karboksilnih i aldehidnih grupa, indeksu kristalnosti i sposobnosti zadržavanja vode, određenim neposredno nakon TEMPO oksidacije i 10 godina kasnije. Sadržaj karboksilnih i aldehidnih grupa određen je kalcijum-acetatnom metodom, indeks kristalnosti Schwertassek-ovom metodom, a sposobnost zadržavanja vode standardnom metodom centrifugiranja (ASTM D 2402-78, 1978). Ostarele TEMPO oksidisane pamučne pređe pokazale su povećan sadržaj karboksilnih grupa, smanjen sadržaj aldehidnih grupa, nepromenjen indeks kristalnosti i povećanu sposobnost zadržavanja vode.

Cljučne reči: TEMPO oksidacija, pamuk, dugotrajno starenje, svojstava.

1. INTRODUCTION

Cotton is the one of the most important cotton are from India, Turkmenistan and the Arab economy [1]. Cotton is composed of the molecules linked by hydrogen bonds located at the hydroxyl groups on the C2 and C6 different from glucose units. At the right hydroxyl groups

Mentioned the 1,4-glycosidic composed that cotton O2H-O6

Fig.

1. INTRODUCTION

Cotton is the most prevalent natural raw material used in the textile industry, which is one of the most influential industries in the global economy. Almost 25 million tons of cotton are produced annually in the world, with the largest amount of cotton coming from India, China, the United States, Pakistan, Brazil, Australia, Uzbekistan, Turkey, Turkmenistan, and Burkina Faso [1]. Considering the consumption in the textile industry and the annual production, cotton represents one of the mainstays for the global economy [2].

Cotton is considered the purest plant source of cellulose (about 95%). Figure 1. shows the molecular structure of cellulose generated from repeating glucose units covalently linked by 1,4-glycosidic bonds. In each glucose unit there are three hydroxyl groups located at the C2, C3, and C6 atoms. The hydroxyl group at the C6 atom (primary hydroxyl group) is described as the most reactive, far more than the hydroxyl groups at the C2 and C3 atoms (secondary hydroxyl groups). The glucose units at the ends are different from those inside the cellulose chain. At the left (non-reducing) end, the glucose unit is a closed ring and displays an additional hydroxyl group at the C4 atom. At the right (reducing) end, the glucose unit is an open ring and displays an additional hydroxyl group at the C1 atom and an aldehyde group [3].

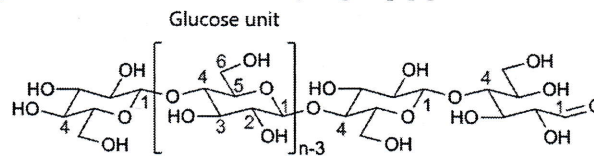


Figure 1: Molecular structure of cellulose. Adapted from [3, 4]

Mentioned hydroxyl groups, together with the oxygen atoms of both the glucose unit and the 1,4-glycosidic bond, form an extensive hydrogen bond network. This network is composed of intra- and intermolecular hydrogen bonds. From Figure 2., it can be seen that cotton (cellulose I polymorph) is characterized by intramolecular O3H–O5' and O2H–O6' hydrogen bonds, and intermolecular O6H–O3'' hydrogen bonds [3].

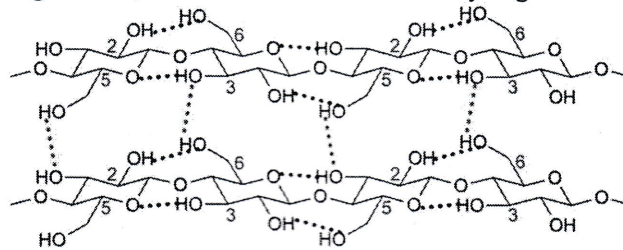


Figure 2: Intra- and intermolecular hydrogen bonds of cellulose in cellulose I polymorph. Adapted from [3, 4]

While intramolecular hydrogen bonds are partly responsible for the linear integrity and rigidity of the cellulose chain, intermolecular hydrogen bonds result in the supramolecular structure of cellulose consisting of crystalline and amorphous regions. The cellulose chains are usually longer than the crystalline regions. As a consequence, one cellulose chain can run from one crystalline region to another, passing through the amorphous regions, thus holding the crystalline regions together (Figure 3) [5].

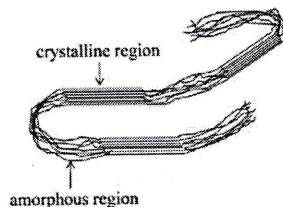


Figure 3: Supramolecular structure of cellulose in cotton. Adapted from [5]

The aggregation of different supramolecular arrangements of cellulose (crystalline and amorphous regions) results in fibrillar elements that have nanometer-scale diameters and micrometer-scale lengths. These are called microfibrils. Further aggregation of microfibrils together results in macrofibrils that have micrometer-scale diameters and millimeter-scale lengths. The morphological structure implies the mutual arrangement of micro- and macrofibrils. In all plants, micro- and macrofibrils are arranged to form plant cell walls that surround the channel (lumen) [3]. Figure 4. shows the morphology of cotton fibers.

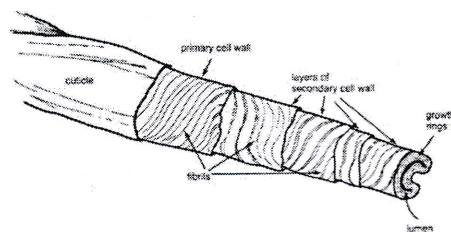


Figure 4: Morphology of cotton fibers. Adapted from [6]

The molecular, supramolecular and morphological structure of cotton described above is meritorious accountable for its chemical reactivity, ie. various possibilities of its chemical modifications. Esterification, etherification and oxidation have been most frequently applied chemical modifications of cotton in recent decades. Among them, TEMPO oxidation has attracted special attention because it provides high reaction efficiency and position selectivity under aqueous and moderate reaction conditions [7]. TEMPO oxidation of cotton in TEMPO/NaBr/NaClO system under alkaline conditions is a complex reaction. Mechanism of TEMPO oxidation of cotton in TEMPO/NaBr/NaClO system is shown in Figure 5. As it can be seen from Figure 5., the

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reaction starts by oxidation of TEMPO to the oxoammonium ion (TEMPO⁺) with NaClO. TEMPO⁺ oxidizes the hydroxyl groups at the C6 atoms of cellulose to aldehyde groups. The reduced TEMPO or N-hydroxy-TEMPO is then oxidized by NaBrO, formed from NaBr by oxidation with NaClO. The aldehyde groups are directly oxidized to the sodium carboxylate groups with NaClO and/or NaBrO. In addition to aldehyde groups formed as intermediates at the C6 atoms in cellulose, a certain amount of aldehyde groups can also be formed as reducing ends of cellulose due to the cleavage of the 1,4-glycosidic bond by β-elimination of cellulose during TEMPO oxidation of cotton in TEMPO/NaBr/NaClO system under alkaline conditions. Depending on the reaction conditions of TEMPO oxidation in TEMPO/NaBr/NaClO system under alkaline conditions, a large number of these aldehyde groups can survive in the final products. Probably the largest number of these aldehyde groups are present as intermediates at the C6 atoms of cellulose [7].

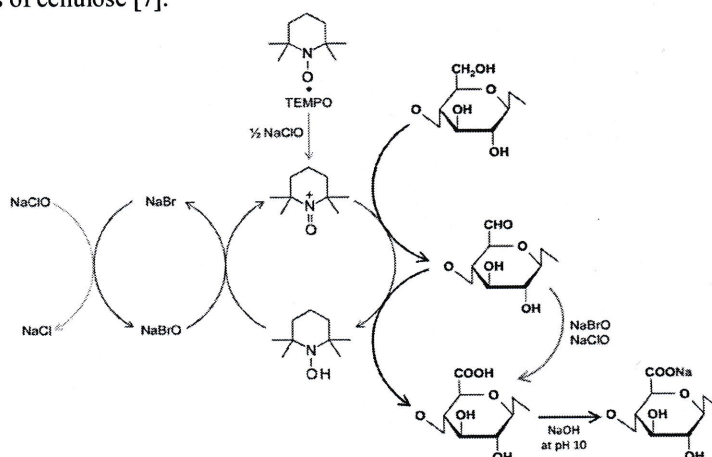


Figure 5: TEMPO oxidation of cotton in TEMPO/NaBr/NaClO system under alkaline conditions [4, 7]

By TEMPO oxidation of cotton in TEMPO/NaBr/NaClO system under alkaline conditions, only the hydroxyl groups at the C6 atoms present on crystalline cellulose microfibril surfaces are converted to the sodium carboxylate groups. The high crystallinity and the original crystalline microfibril structure of cotton cause highly position-selective oxidation of the hydroxyl groups at the C6 atoms to the sodium carboxylate groups without oxidation of the cellulose molecules inside the crystalline cellulose microfibrils. Consequently, the degradation of the molecular, supramolecular and morphological structure of cotton during TEMPO oxidation in TEMPO/NaBr/NaClO system under alkaline conditions is minimized [8].

The properties of TEMPO oxidized cotton have been widely determined by various conventional analytical and instrumental techniques. However, in spite of the fact that TEMPO oxidized cotton is prone to aging processes, there is no enough literature data



about the influence of long-term aging on the properties of TEMPO oxidized cotton. In this paper, the influence of long-term aging on the properties of TEMPO oxidized cotton yarns in TEMPO/NaBr/NaClO system under alkaline conditions was monitored through changes in their content of carboxyl and aldehyde groups, crystallinity index and water retention value, determined immediately after TEMPO oxidations and 10 years later.

2. MATERIALS AND METHODS

2.1. Materials

Combed cotton yarn with linear density of 20 tex was used in this study as starting material. TEMPO, sodium bromide and 13 % sodium hypochlorite solution were p.a. grade and used without further purification.

2.2. Preparation of TEMPO oxidized cotton yarns

10 g of cotton yarn was suspended in 750 mL water containing 0.025 g of TEMPO and 0.25 g of sodium bromide. Subsequently, a designed amount of NaClO corresponding to 2.42 mmol NaClO·g⁻¹ cotton yarn, was added to the cotton slurry under continuous stirring. The pH of cotton slurry was maintained at 10.5 at room temperature by adding 0.5 M NaOH. After stirring for a designed time (30, 60 and 120 min), TEMPO oxidation was quenched by adding ethanol. TEMPO oxidized cotton yarns were washed thoroughly with water and dried at room temperature.

2.3. Aging of TEMPO oxidized cotton yarns

A part of each TEMPO oxidized sample was packed into filter paper and zip bag and stored in the dark at standard conditions for a period of ten years (2013–2023). Given that cellulose fibers stored under standard conditions do not biodegrade, the samples were stored in contact with filter paper which buffers humidity in zip bags as a precautionary measure.

Oxidation conditions and sample denotations of TEMPO oxidized and aged TEMPO oxidized cotton yarns are listed in Table 1.

Table 1: Oxidation conditions and sample denotations of TEMPO oxidized and aged TEMPO oxidized cotton yarns

Oxidation conditions			Sample denotations
Concentration of NaClO, mmol·g ⁻¹ cotton yarn	τ, min	Aging, years	TEMPO oxidized cotton yarn
2.42	30	0	Co1
	60	0	Co2
	120	0	Co3
	30	10	Co1 _{aged}
	60	10	Co2 _{aged}
	120	10	Co3 _{aged}

2.4. Determination of content of carboxyl and aldehyde groups

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2.6. Determination of water retention

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The content of carboxyl groups was determined by the modified calcium acetate method described by Praskalo et al. [9]. Briefly, 0.5 g of cotton yarn was treated with 0.01 M HCl for 1 h and then washed thoroughly with distilled water. Then, 50 mL distilled water and 30 mL 0.25 M calcium acetate solution were added to the yarn. After standing for 2 h with frequent shaking, portions of 30 mL of the liquid were titrated with 0.01 M sodium hydroxide, and phenolphthalein was used as an indicator. The content of carboxyl groups in cotton yarn (COOH) is calculated as follows:

$$COOH = \frac{80 \cdot 0.01M \cdot V(NaOH)}{m \cdot (1 - \frac{w}{100})}, \text{ mmol} \cdot \text{g}^{-1} \text{ cotton yarn} \quad (1)$$

Where 0.01 M is concentration of NaOH, $V(NaOH)$ is volume (mL) of NaOH solution used for titration, m is weight of cotton yarn (g), and w is moisture content (%).

The content of aldehyde groups (CHO) was determined according to a modified method described by Parks and Hebert [10, 11]. Aldehyde groups of cotton yarn are oxidized with sodium chlorite to carboxyl groups. Namely, 1g of cotton yarn was added to a mixture containing 0.905 g of NaClO_2 , 10 mL 5 M CH_3COOH and 50 mL distilled water. After shaking the mixture at room temperature for 48 h, the yarn was washed thoroughly with distilled water. The carboxyl groups formed by oxidation with sodium chlorite were considered as aldehyde groups present in cotton yarn. Those groups were determined by the modified calcium acetate method mentioned above.

2.5. Determination of crystallinity index

The crystallinity index was determined by the *Schwertassek* method [12]. 0.3 g of cotton yarn was treated with 2 mL iodine solution (5 g of I_2 + 40 g of KI + 50 mL H_2O) for 3 min. After that, 100 ml saturated sodium sulphate solution was added and the mixture was shaken for 1 h. The concentration of iodine in cotton yarn and blank was determined by titration with 0.02 M sodium thiosulphate. The concentration of iodine in cotton yarn (CI) is calculated as follows:

$$CI = \frac{(a-b) \cdot 2.04 \cdot 2.54}{m \cdot (1 - \frac{w}{100})}, \text{ mg} \cdot \text{g}^{-1} \text{ cotton yarn} \quad (2)$$

Where a is volume (mL) of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for blank titration, b is volume (mL) of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for cotton yarn solution titration, m is weight of cotton yarn (g), and w is moisture content (%). According to *Schwertassek*, iodine absorption takes place in amorphous regions. The ratio of CI (per 1 g of cotton yarn) to 412 (mg of iodine absorbed per 1 g of methyl cellulose) represents the amorphous fraction. The crystallinity index of the cotton yarn (CrI) is calculated as follows:

$$CrI = 100 - \left(\frac{CI}{412} \cdot 100 \right), \% \quad (3)$$

2.6. Determination of water retention value

Water retention value of cotton yarn was determined in triplicate by the standard centrifuge method (ASTM D, 2402-78). This method is based on determining the amount of water that cotton yarn absorbs and retains under defined conditions. Water retention value of cotton yarn (WRV) is calculated as follows:



$$WRV = \frac{m_1 - m_2}{m_2} \cdot 100, \% \quad (4)$$

Where m_1 (g) is the mass of cotton yarn after centrifuging and m_2 (g) is the mass of dry cotton yarn.

3. RESULTS AND DISCUSSIONS

3.1. Influence of long-term aging on the content of carboxyl and aldehyde groups of TEMPO oxidized cotton

The content of carboxyl and aldehyde groups is one of the most important parameters of the molecular structure of TEMPO oxidized cotton [7, 8]. From Table 2. it can be seen that the content of carboxyl groups of TEMPO oxidized cotton yarns determined immediately after TEMPO oxidations is 0.178 mmol·g⁻¹·cotton yarn for Co1, 0.277 mmol·g⁻¹·cotton yarn for Co2 and 0.456 mmol·g⁻¹·cotton yarn for Co3. After aging for 10 years, an increase in the content of carboxyl groups was detected: 0.008 mmol·g⁻¹·cotton yarn for Co1_{aged}, 0.028 mmol·g⁻¹·cotton yarn for Co2_{aged} and 0.036 mmol·g⁻¹·cotton yarn for Co3_{aged}. The detected increase in the content of carboxyl groups of TEMPO oxidized cotton yarns after 10 years aging indicates the conversion of aldehyde groups into carboxyl groups.

Table 2: Content of carboxyl and aldehyde groups, crystallinity index and water retention value of TEMPO oxidized and aged TEMPO oxidized cotton yarns

Sample denotations	COOH, mmol·g ⁻¹ ·cotton yarn	CHO, mmol·g ⁻¹ ·cotton yarn	CrI, %	WRV, %
Co1	0.178*	0.186*	94.09*	34.47*
Co2	0.277*	0.138*	94.57*	37.76*
Co3	0.456*	0.156*	95.12*	53.70*
Co1 _{aged}	0.186	0.164	94.09	35.51
Co2 _{aged}	0.305	0.095	94.57	38.93
Co3 _{aged}	0.492	0.104	95.13	55.86

* Previously reported in [13]

It is important to point out that the aging of TEMPO oxidized cotton is not only an aldehyde-consuming process, but also an aldehyde-generating process. Namely, due to the cleavage of the 1,4-glycosidic bond by the hydrolysis of cellulose chains during aging, new reducing ends of cellulose are formed and, consequently, a certain amount of aldehyde groups. These aldehyde groups formed during aging and aldehyde groups formed during TEMPO oxidation are oxidized together into carboxyl groups [14]. From Table 2. it can be seen that the content of aldehyde groups of TEMPO oxidized cotton yarns determined immediately after TEMPO oxidations is 0.186 mmol·g⁻¹·cotton yarn for Co1, 0.138 mmol·g⁻¹·cotton yarn for Co2 and 0.156 mmol·g⁻¹·cotton yarn for Co3. If we compare these values with the values detected after 10 years aging (Table 2.), it is clearly that aging for 10 years reduced the content of aldehyde groups: 0.022 mmol·g⁻¹·cotton yarn for Co1_{aged}, 0.043 mmol·g⁻¹·cotton yarn for Co2_{aged} and 0.052 mmol·g⁻¹·cotton yarn for Co3_{aged}. The detected decrease in the content of aldehyde groups of

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3.2. Influence of cotton Crystallinity TEMPO represents Degradation known to after TEM words, from cotton yarn

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TEMPO oxidized cotton yarns after 10 years aging confirms the conversion of aldehyde groups into carboxyl groups. In addition to this decrease in the content of aldehyde groups due to the conversion of aldehyde groups into carboxyl groups, the decrease in the content of aldehyde groups also can be a consequence of the consumption of aldehyde groups groups by cross-linking [14].

By comparing the changes in the content of carboxyl and aldehyde groups after 10 years aging, it is evident that only part of the aldehyde groups is converted into carboxyl groups. In the case of the sample with the most pronounced changes in the content of carboxyl and aldehyde groups after 10 years aging, i.e. Co3_{aged}, the content of aldehyde groups decreased for 0.052 mmol·g⁻¹·cotton yarn, and the content of carboxyl groups increased for 0.036 mmol·g⁻¹·cotton yarn. The noticed gap in the content of aldehyde groups can be explained by the fact that aldehyde groups can be predominantly masked as hemiacetal and hemialdal moieties [15].

3.2. Influence of long-term aging on the crystallinity index of TEMPO oxidized cotton

Crystallinity, as one of the most important parameters of the supramolecular structure of TEMPO oxidized cotton, is expressed as the crystallinity index. The crystallinity index represents the mass ratio of the crystalline regions in the total dry sample [8, 16]. Degradation of the supramolecular structure of cotton during TEMPO oxidation is known to be minimal. Thus, the supramolecular structure of cotton remains very stable after TEMPO oxidation [7, 8]. The results from Table 2. confirms that fact. In other words, from Table 2. it can be seen that the crystallinity index of TEMPO oxidized cotton yarns remains unchanged after 10 years aging.

3.3. Influence of long-term aging on the water retention value of TEMPO oxidized cotton

The water retention value is a parameter of TEMPO oxidized cotton that is influenced by its molecular, supramolecular and morphological structure. It represents the amount of water retained in TEMPO oxidized cotton after its soaking in water and subsequent centrifugation. It was found that the water retention value of TEMPO oxidized cotton is influenced to the greatest extent by the content of carboxyl groups and the crystallinity index. More precisely, the increased water retention value of TEMPO oxidized cotton occurs to the greatest extent due to an increase in the content of carboxyl groups as well as a decrease in the crystallinity index [8, 9].

From Table 2. it can be seen that the water retention value is 34.47% for Co1, 37.76% for Co2, 53.70% for Co3, 35.51 % for Co1_{aged}, 38.93 % for Co2_{aged} and 55.86 % for Co3_{aged}. Comparing the water retention values determined immediately after TEMPO oxidations and 10 years later, it is clear that 10 years aging increased the water retention values of TEMPO oxidized cotton yarns. Given that the crystallinity index remains unchanged, it is indicated that only the increase in the content of carboxyl groups contributed to the increase in the water retention value of TEMPO oxidized cotton yarns after 10 years aging (Table 2). By comparing the changes in the content of carboxyl groups and the water retention value of TEMPO oxidized cotton yarns that occurred



after 10 years aging (Table 2), it can be concluded that they are directly proportional. Namely, with increasing changes in the content of carboxyl groups of TEMPO oxidized cotton yarns that occurred after aging ($0.008 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{cotton yarn}$ for Co1 < $0.028 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{cotton yarn}$ for Co2 < $0.036 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{cotton yarn}$ for Co3) there is increasing changes in the water retention value of TEMPO oxidized cotton yarns that occurred after aging (1.04 % for Co1 < 1.17 % for Co2 < 2.16 % for Co3).

3. CONCLUSION

In this study, cotton yarns were TEMPO oxidized in time intervals of 30, 60 and 120 min. Investigation of the influence of long-term aging on the properties of TEMPO oxidized cotton yarns (content of carboxyl and aldehyde groups, crystallinity index and water retention value) showed that TEMPO oxidized cotton yarns have increased content of carboxyl groups (up to $0.036 \text{ mmol}\cdot\text{g}^{-1}$ cotton yarn for Co3_{aged}), decreased content of aldehyde groups (up to $0.052 \text{ mmol}\cdot\text{g}^{-1}$ cotton yarn for Co3_{aged}), unchanged crystallinity index and increased water retention value (up to 2.16 % for Co3_{aged}) after 10 years aging, confirming that TEMPO oxidized cotton is prone to aging processes.

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