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REVIEW - CHEMICAL FUNCTIONALIZATION OF COTTON FABRICS BY SELECTIVE OXIDATION

BY

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Abstract. This documentary study presents the possibilities of selective oxidation by sodium or potassium periodate and/or 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) of cotton textiles, the reaction mechanisms, the assessment and the analytical and instrumental determination of the degree of oxidation of the hydroxyl groups in the C2, C3 and C6 positions of the anhydroglucosidic unit (AGU), with aldehyde/carboxylic groups. The effects of selective oxidation on the molecular and morphological structure of cellulose are also briefly presented, since oxidation depending on the reaction conditions can significantly affect both the amorphous and crystalline areas of cellulose, at the microfibril level, which leads to a decrease in mechanical resistance, which is undesirable in the case of textiles with long-term use or even single-use. Selective oxidation in this case is a compromise between functionality (expressed by the content of aldehyde/carboxylic groups) and moderate degradation of the molecular and morphological structure of cotton cellulose.

Keywords: oxidized cellulose, sodium or potassium periodate, TEMPO, aldehyde and carboxyl groups, degree of oxidation.

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1. Introduction

The interest in functionalization and in particular in the selective oxidation of cellulose is in the attention of many researchers, as evidenced by the increase in the last 10-15 years in the number of scientific publications and patents reported.

The oxidation of cellulosic materials is a reaction widely used in the wood industry, but also in the bleaching of cellulosic textiles. In the chemical finishing of textile materials, oxidative bleaching is essential to decolorize the natural pigments found in the morphological structure of the cotton fibre, resulting in a material with a significant degree of whiteness, so necessary to dye the material in any colour. Conventional oxidizing agents (NaClO, H_2O_2, $HClO_4$, etc.) used for bleaching are non-selective, acting chemically on the chemical structure by the formation of aldehydic and carboxylic groups, but also on the morphological structure of the cellulosic fibres, action strongly dependent on the intensity of the applied treatments (Knill *et al*., 2003).

A number of biomedical uses of selectively oxidized cellulose are reported in the literature, as oxidized cellulose is biodegradable (Hao *et al*., 2018), readily bioresorbable (Patel *et al*., 2017), has hemostatic, wound healing properties due to its increased adhesion to the skin, (Pinho and Soares, 2018; Shaohua *et al*., 2020; Wang *et al*., 2021), has antibacterial effect (Jiang *et al*., 2022; Ghosh *et al.,* 2019), has the ability to sorb and retain polyamine compounds responsible for the odor of chronic wounds (Wen *et al*., 2023).

A number of studies and applications of selectively oxidized cellulose are also reported in the pharmaceutical field as a carrier for a number of active ingredients (Sharma *et al*., 2021), food (Singh *et al*., 2020) as well as in the field of water purification as adsorbent membranes with excellent retention properties of some heavy metals, organic compounds (Khan *et al*., 2018), and in the greening of the dyeing operation of cellulosic fibres by reducing the pollutant load of dye baths (Wu *et al*., 2023).

The selective oxidation leads to a number of structural changes, affects the intra- and inter-molecular bonds in the cotton fibre, leads to some degradation of the fibres by dislocation of amorphous zones and to a small extent also acts on the crystallinity of the oxidized fibres, but the latter action is dependent on the parameters of the oxidation reaction which is also reflected in the newly acquired properties such as tensile strength, elongation, high temperature resistance, moisture sorption capacity (Liu *et al*., 2018), increased reactivity and affinity towards chemical compounds (Zhang *et al*., 2020, Zhang *et al*., 2017). All these properties are largely due to the chemical and morphological structure of cellulose, briefly described below, but also to the reaction parameters (concentration of oxidizing agents, pH and temperature of the reaction medium, oxidation time) that control the degree of oxidation, and the evolution of the degree of polymerization, often decreasing due to the damage of the cellulosic structures (Coseri, 2017; Potthast *et al*., 2007).

The aim of this review is to present the current state of knowledge related to the selective oxidation of cotton textile materials, the analytical and instrumental methods used to quantify the functional groups obtained after oxidation, as well as the morphological structure changes that it undergoes during the selective oxidation reaction. The cellulosic structures to which reference will be made are selectively oxidized cotton yarns, knits and fabrics, and only in the part of the analysis of the chemical and morphological structure, where the methods of analysis applied for characterization are comparable, are those applied to the cellulosic forms of wood.

2. Cotton, cellulosic fibre

Cotton cellulose is a highly valuable natural biopolymer of polysaccharide nature is a major component of plant walls and is one of the most abundant resources for biomaterials due to its biocompatibility and plant origin (Klemm *et al*., 2005; Chen *et al*., 2015; Luo and Zhang, 2010). The cellulose molecule is an insoluble linear homopolymer formed of β (1 → 4)-D-glucopyranosidic β (1→4)-glucosyl units, the glucosidic bond is formed between the carbons in positions 1 and 4, as shown in Fig. 1a, called anhydroglucosidic anhydroglucosidic unit (AGU).

The authors (Blackwell, 1982; Atalla *et al*., 1984) consider the repeating structural unit of cellulose, kelobiose, which actually consists of 2 AGU units adjacent to, but rotated by 180° around the main catenary axis of cellulose, as shown in Fig. 1b. The ends of the chain contain a free hemiacetal group or free aldehydic group at the C1 position, with a reducing role, and at the other end at the C4 position, it contains a non-reducing group, a free hydroxyl group (Credou and Berthelot, 2014; Wohlert *et al*., 2022), as shown in Fig. 2.

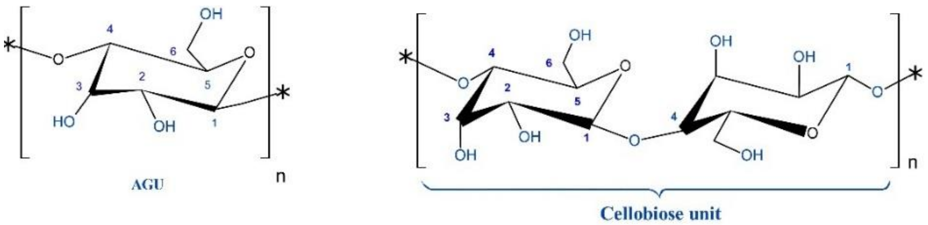

Fig. 1 – Schematic representation of a cellulose chain
(a) Repeating unit of cellulose molecular structure (AGU) (b) Cellobiose repeating unit.
The figures have been drawn by the authors with ChemSketch.

The three hydroxyl groups, primary at the C6 position and secondary at the C2 and C3 positions of the AGU are positioned in the ring plane (Tonozuka *et al.*, 2014), as shown in Fig. 1a and Fig. 2

The excellent properties of cotton cellulose (hydrophilicity, increased adsorption, flexibility, mechanical strength, etc.) described by (Marjory, 1986; Gupta, 2013; Liu *et al.*, 2018; Wohlert *et al.*, 2022) are due to the composition, chemical and morphological structure of cellulose.

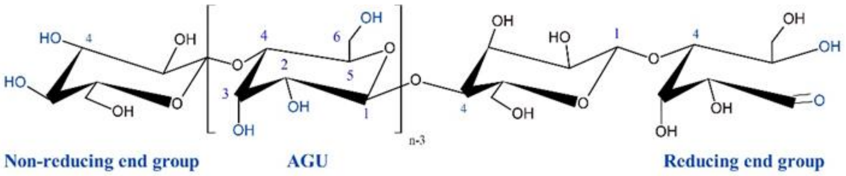

Fig. 2 – Schematic representation of the cellulose chain, on the right the reducing end (free aldehyde group) and on the left the non-reducing end (free hydroxyl group). The figures have been drawn by the authors with ChemSketch.

Figure 3 illustrates the chemical composition and morphological structure of cotton fibre (Gallo and Almirall, 2009). As can be seen cotton fibre has a hierarchical structure (Krakhmalev and Paiziev, 2006; Madhushree *et al.*, 2024) consisting on the outside of the cuticle, which is a thin protective layer, consisting predominantly of non-cellulosic components, proteins (1.0-2.1%), waxes (0.4-1.7%), pectins (0.4-1.9%), inorganic substances (0.7-1.8%) and other substances such as resins, pigments, hemicelluloses (1.5-2.5%). This chemical composition is the general composition of raw cotton fibres but it may vary depending on the type, origin, fibre maturity, geographical area and agricultural conditions during the cultivation of the cotton plant (Stathakos *et al.*, 2006; *** *Cotton Morphology and Chemistry*).

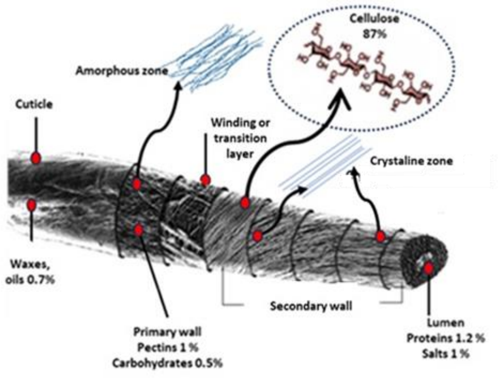

Fig. 3 – Morphological structure and chemical composition of cotton fibre. (Image adapted from Dochia *et al.*, 2012).

The primary wall is a thin layer of randomly oriented, disordered cellulosic fibrils (amorphous zone) with less than 30% cellulose content, explains the high flexibility, adsorption capacity and high reactivity of cotton fibre. The secondary wall is the main layer, which contains 87 - 90% cellulose of the weight of the fibres, it is thick, consisting of fibrils arranged in concentric layers in which are distinguished the crystalline areas ordered, dense, responsible for the mechanical strength of the fibre. In the central part is the lumen, which occupies about one-third of the thickness of the fibre and is responsible for storing and transporting nutrients to the cell nucleus and protoplasm (Broadbent, 2001).

Fibrils are made of microfibrils, which in turn consist of long chains of cellulose molecules with a degree of polymerization in the case of cotton between 9000 - 15,000 and a crystallinity index of about 73% (Blackwell, 1982).

Degree of polymerization (DP) represents the number of glucose units in a polymer chain as defined by (Credou *et al.*, 2014) and the degree of crystallinity, degree of polymerization, moisture content of the fibre is dependent on the intermolecular hydrogen bonds between the cellulose chains and influences the physico-mechanical and chemical properties of cotton fibre, it is an important aspect when the textile is designed for long or single use, regardless of the area of its applicability.

3. Selective oxidation functionalization of cellulose cotton fibres

Cotton oxidation, traditionally applied after conventional pre-treatment processes, such as scouring to remove the tacking agent, alkaline or enzymatic cleaning is an essential operation that completely removes the cuticle, fatty substances, proteins and other non-cellulosic components, contributes to the increase of hydrophilicity of textile materials (Stanescu *et al.*, 2010). Bleaching removes the natural pigments from the cellulose fibres, it is carried out immediately after cleaning, in alkaline conditions and in the presence of oxidizing agents, most often hydrogen peroxide is used. The study developed by (Nassif, 2019) states that all pre-treatment operations depending on the aggressiveness of chemical processes affect in the sense of decreasing air permeability, breaking strength, and according to the authors the influence of cleaning operation is more pronounced than bleaching. A considerable increase in elongation at break is observed with cleaning followed by bleaching.

Selective oxidation of cellulosic fibres is an important method for the functionalization of cotton textile materials such as yarns, gauze, nonwovens and fabrics. Depending on the oxidizing agent used, carboxylic and/or aldehydic groups are generated by substituting the hydroxyl groups in the 6-position of the carbon of the pyranose ring with carboxylic groups when using the oxidizing agent 2,2,6,6,6-tetramethylpiperidin-N-oxyl (TEMPO), or a selective cleavage of the vicinal diols in the C2 and C3 positions of the AGU takes place, generating reactive aldehydic groups. The combination of periodate oxidation with the oxoammonium cations formed during TEMPO oxidation results in tricarboxylic celluloses (Sulaeva *et al*., 2015a; Coseri *et al*., 2013; Strnad *et al*., 2008; Diankova and Doneva, 2009). The positions of the three hydroxyl groups, primary position C6 and secondary positions C2 and C3 of the AGU unit are shown in Fig. 1a.

3.1. Periodate and TEMPO selective oxidation of cellulosic textile materials

3.1.1. Mechanism of periodate oxidation

The oxidation of cellulose in aqueous medium with sodium or potassium periodate (NaIO4 or KIO4), the Malaprade reaction, is a commonly used procedure for the modification of cellulosic textile materials, is a highly selective oxidation method, occurs through a specific reaction on vicinal diols (C2-C3), following which bond cleavage at C2-C3 positions occurs and consists in the substitution of hydroxyl groups at C2-C3 positions in AGU by aldehydic and/or ketone groups (Kim *et al.*, 2000). This chemical functionalization significantly contributes to improve some functional properties of cellulosic textile materials, and moreover, further allows various chemical modifications of post-oxidation, sulfonation or reductive amination, an additional functionalization for applications requiring increased hydrophilicity or hydrophobicity, high adsorption and sorption capacity, antimicrobial, hemostatic effect (Matsumura *et al*., 2000; Sulaeva *et al*., 2015a; Sun and Feng, 2024).

The reaction mechanism consists in the formation of a cyclic intermediate between periodate and diol, the periodate reacts with the hydroxyl groups at the C2 and C3 positions, forming a cyclic periodate-cellulose complex intermediate, initiated by nucleophilic attack of the periodate (Sun and Feng, 2024), then followed by cleavage of the C2-C3 bond and release of the iodide. The selective oxidation reaction with periodate is shown in Fig. 4, the two aldehyde groups are formed at the C2 and C3 positions, and the cellulose thus oxidized is referred to in most studies as dialdehyde cellulose, generally denoted DAC, aldehyde functionalized cellulose (AFC) or oxycellulose (OC).

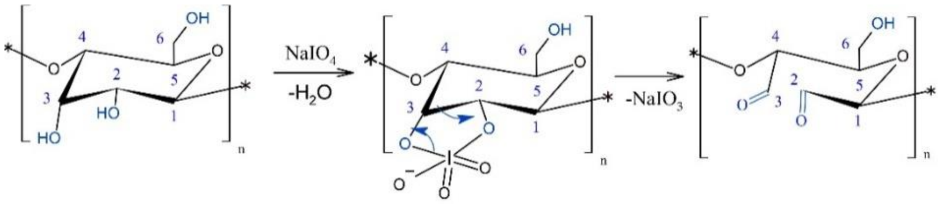

Fig. 4 – The main selective oxidation reaction of cotton cellulose with sodium periodate.
The figures have been drawn by the authors with ChemSketch.

Only in the case of cellulose solubilization design, with a high degree of oxidation, close to 100 %, it can be considered that each AGU of the oxidized cellulose contains two aldehyde groups instead of the initial hydroxyl groups in the C2 and C3 positions.

The aldehyde groups generated are reactive and can be found depending on the parameters of the oxidation reaction in various masked forms, which often makes it difficult to quantitatively estimate the amount of aldehyde groups by analytical and instrumental methods.

Along with the oxidized forms with free carbonyl groups, hydrated aldehyde structures can be formed, hemialdal between C2/C3 and inter and intramolecular hemiacetal between C2/C6 and C3/C6 structures are possible within the glycosidic units, as shown in Fig. 5 (Nypelö *et al.*, 2021; Sulaeva *et al.*, 2015b).

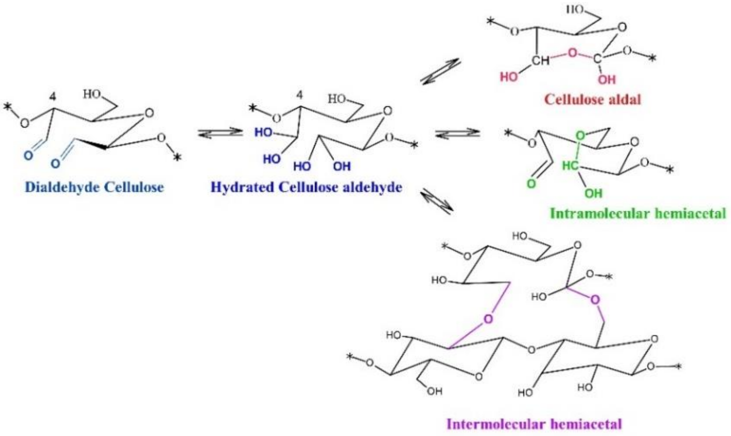

Fig. 5 – Formation of intermediate structures (hydrated cellulose, inter- and intramolecular hemiacetal, hemialdal).
The figures have been drawn by the authors with ChemSketch.

The recent study by Brault (Brault *et al.*, 2005), shows that the effect of side reactions, which may develop during oxidation under mild reaction conditions, numerous side reactions may occur due to the limited stability of the active form of the periodate molecule, which is dependent on the pH, concentration and temperature values used. The authors emphasize the effects of light and temperature on the instability of the hypervalent sodium periodate IO4- (+VII), which can be decomposed into different reduced forms: iodate IO_3^- (+V), iodide IO_2^- (+III), iodide I^- (-I), or molecular iodine I_2 (0). Side reactions of the metaperiodate may also occur with cellulose, in particular by oxidation of more than two vicinal hydroxyl groups in the AGU units at the chain end. These so-called non Malaprade reactions lead to the formation of soluble oxidized by-products such as formic acid and formaldehyde.

Simon and co-workers in the paper (Simon *et al.*, 2021; Simon *et al.*, 2023) recommend in the case of periodate oxidation to avoid any contamination with other compounds, a simple water wash to remove unreacted periodate. They specify that oxidation with periodate in aqueous solution often leads to hydrated, hemialdal, hemiacetal cellulose structures in equilibrium (Fig. 5) and only a small amount of the generated adehyde groups at the C2 and C3 positions are found in free form, which is why instrumental spectroscopic techniques (FTIR, NMR, Raman) do not detect aldehyde content, unlike analytical titration techniques (Amer *et al.*, 2016; Kim *et al.*, 2000; Simon *et al.*, 2022).

3.1.2. Mechanism of nitroxyl radical oxidation (2,2,2,6,6-tetramethylpiperidin-N-oxyl or TEMPO)

Selective oxidation with TEMPO is a method, which utilizes nitroxyl radicals, is a reaction taking place at the primary hydroxyl groups in the C6 position of the AGU unit with formation of carboxyl groups. In the case of cellulosic textile materials selective oxidation with TEMPO in the presence or absence of NaBr is reported in the scientific work by Toshikj (Toshikj *et al.*, 2019; Isogai *et al.*, 2011).

The reaction mechanism consists in the in-situ generation of the nitrozonium cation in the first step of the process, then in the presence of oxidizing agents such as sodium hypochlorite and bromide salts, hypobromide anions are produced, which further oxidize the nitrozonium cation to N-hydroxy-2,2,6,6-tetramethylpiperidine. The reaction medium has a pH of around to 10-10.5, provided by the presence of NaOH, which also neutralizes the carboxyl groups formed by oxidation. The reaction mechanism is shown in Fig. 6, according to Duceac (Duceac *et al.*, 2022).

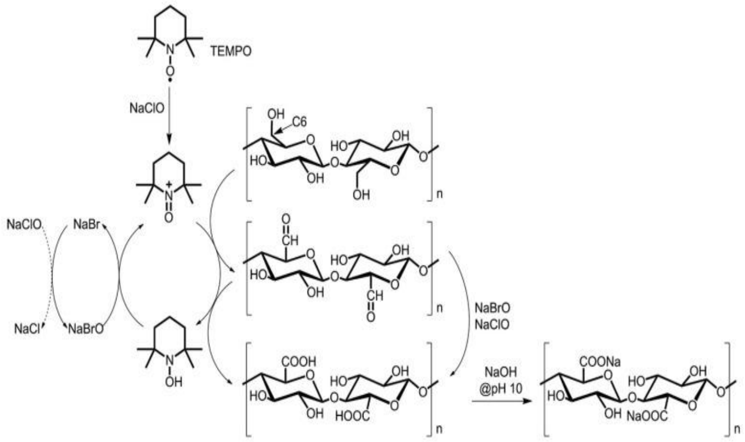

Fig. 6 – Selective oxidation mechanism of cellulose in the presence of TEMPO, NaClO and NaBr (Duceac *et al.*, 2022).

As shown in Fig. 6 the intermediate species that are formed during the oxidation process are: N-hydroxy-2,2,6,6,6-tetramethylpiperidine (the reduced TEMPO form); the nitrotium radical (the oxidized form of TEMPO); the nitrotium cation (the active oxidizing species in cellulose); and the sodium salt of aldehyde hydrate.

In the first stages of oxidation, the primary hydroxyl groups, C6 position are oxidized, aldehyde groups are formed, but as in the case of periodate oxidation there is the possibility of formation of hemiacetal compounds, by intra- and intermolecular reactions between hydroxyl groups and aldehyde groups, but also hydrated forms (Kato *et al.*, 2003; Duceac *et al.*, 2022). In the final stage the aldehyde hydrates and/or hemiacetal hydrate forms are oxidized by oxoammonium cations, resulting in sodium salts of carboxylic acid fragments and the intermediate, reduced form of TEMPO.

The authors De Nooy and Isogai (De Nooy *et al.*, 1994; Isogai *et al.*, 2011) show that in TEMPO/NaBr/NaClO oxidation of native cellulose with type I cellulose crystal structure no change in morphological structure, especially on the crystalline zone, is observed, even when using large amounts of reagents. The authors note only the attack on the microfibrillar surface, which leads to low oxidation degrees, an objective often pursued in the case of cellulosic textile materials with long use (Bragd *et al.*, 2000).

3.1.3. Kinetics of selective oxidation reactions

Sultana N. (Sultana *et al.*, 2024) reviews the kinetics of periodate oxidation and provides important insights related to the optimization of the oxidation process. They consider that, the reaction parameters, temperature and pH, as well as high concentrations of periodate IO4 - (above 1 mol/L), considerably influence the obtaining of DAC, but also of the hydrated intermediate forms, hemiacetal and aldal. The authors show that the formation of DAC follows the pseudo-first order kinetic pattern, and that driving the oxidation reaction at high temperatures and high periodate concentrations leads to a significant growth and rapid formation of the DAC form, but also to a significant degradation of the cellulose structure in the crystalline zone. They show schematically the three reactions with rate constants for DAC formation (k1), cellulose degradation (k2) and DAC degradation (k3) as shown in Fig. 7. The kinetic model developed by the authors shows that increasing the temperature has a more pronounced effect on k1 than increasing the periodate concentration, and also any increase in temperature by 10°C leads to an increase of about 5% in DAC formation, but also to an increase of about 15% in degradation of the cellulosic structure.

Sun and co-workers confirm in the study undertaken (Sun *et al.*, 2015) that, temperature plays a significant role in the formation of DAC, but the increase in temperature is detrimental to the accelerated degradation of the cellulosic structure, in agreement with (Sultana *et al*., 2024; Liu *et al*., 2012). The authors refer to the existence of three reactions, which occur during oxidation. In the first reaction, initially, the attack is rapid and cleavage of the bond between C2 and C3 of the AGU unit and the formation of DAC occurs, with only the amorphous region being affected. The second reaction, the β - glycosidic bond cleavage reaction, which leads to the degradation of DAC, is slow, taking place on the microfibril surface. The last reaction, that of acid hydrolysis of glycosidic bonds, leads to cellulosic fragments and affects the crystalline core. These findings, consistent with the mechanisms depicted in Fig. 6, 7 and 8, explain the influence of reaction parameters on the morphological structure of cellulose.

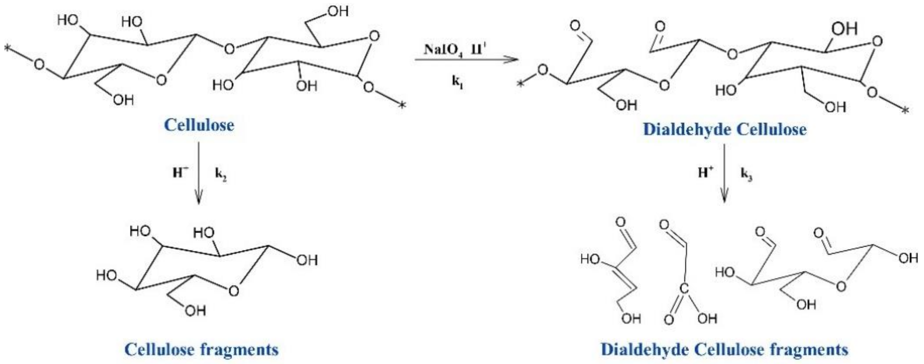

Fig.7 – Schematic of periodate-mediated oxidation of cellulose and degradation reactions.
The figures have been drawn by the authors with ChemSketch.

Thus, oxidation under mild conditions leads only to a slight damage of the amorphous zone and will not significantly affect the crystalline region, but as the intensity of the reaction conditions increases, the degree of oxidation increases and the crystallinity of the cellulose will be significantly affected, in the sense of decreasing the zone, which affects the mechanical strengths of the textile materials.

The kinetics of periodate oxidation of flax and cotton cellulose is also studied by Calvini (Calvini *et al.*, 2006) under mild reaction conditions at room temperature, at oxidation times ranging from one hour to 120 hours. They follow the oxidation progress, by determining the degree of polymerization, by the method of measuring the intrinsic viscosity of the cellulose solutions, also using a pseudo-first order kinetic model. The obtained results show that in the early cellulose, oxidation occurs only on isolated domains by dislocation, as stated by Nypelö (Nypelö *et al.*, 2021) illustrated in Fig. 8, followed by the attack on crystalline zones propagating with increasing periodate concentration, temperature or in case of long oxidation durations.

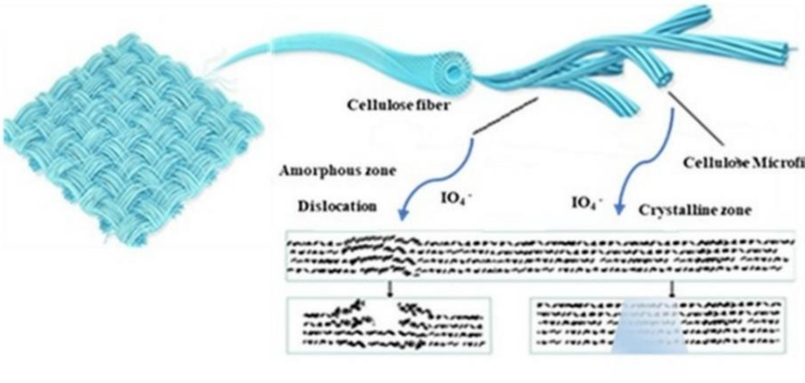

Fig.8 – Schematic representation of oxidative reaction mechanisms on the morphological structure of cotton fibre under mild reaction conditions.
The figures have been drawn by the authors with Canva.

In the case of oxidation of cellulosic textile materials, only a moderate attack on the amorphous zone and not affecting the crystalline region is preferable, the latter being responsible for the high mechanical strengths of the textile material, as confirmed by (Hao *et al*., 2018; Pejic *et al*., 2015; Praskalo *et al.*, 2009).

3.2. Parameters of selective oxidation reactions

Most studies related to selective oxidation have been reported using cotton yarns, probably due to the easy microstructure and increased accessibility of selective oxidizing agents to cellulosic fibres.

Scientific studies reported in the last 10-15 years are reviewed, reaction parameters are presented: oxidizing agent concentration, pH of the reaction medium, temperature and oxidation time.

Fras and co-workers (Fras *et al*., 2004) compare selective oxidation with KIO_4 with non-selective oxidation with $HClO_4$ on cotton yarns, previously alkaline cleaned and bleached with hydrogen peroxide. The samples are placed in 0.01 M KIO_4 solution at 20°C for 6 and 24 hours and in 0.1 M $HClO_4$ solution at 20°C for 24 and 48 hours, respectively. After selective oxidation the samples are treated with sodium chlorite 0.2 M solution at 20°C for 24 hours at pH = 6.0 for chemical conversion of aldehyde groups to carboxyl groups.

Toshikj et al. (Toshikj *et al.*, 2017), report the influence of cleaning and mercerization operation of cotton yarns carried out under traditional conditions, i.e. alkaline compared to the use of alkaline and acid pectinases on potassium periodate oxidation under the reaction conditions- 1g/L KIO_4, at 60°C, for 1 hour. Alkaline-scouring cotton yarns, in all pretreatment sequences, showed the lowest number of aldehydic groups, whereas cotton yarns cleaned and mercerized with alkaline pectinase and acid pectinase and oxidized with alkaline pectinase and acid pectinase showed an increased content of aldehydic groups.

In another study by Toshikj (Toshikj *et al.*, 2019), an oxidation system mediated by potassium periodate with different concentrations (0.5; 1.0; 2.0; 4.0 and 10 g KIO_4/g cellulose) for 30 min at 60°C and TEMPO/NaBr/NaClO (0.0025 g TEMPO/g cellulose, 0.025 g NaBr and 4.84 mmol NaClO/g cellulose) with different times (15, 30, 45, 60 and 120 min) to obtain aldehydic, respectively carboxylic oxy-cellulose with different oxidation levels. The oxidized celluloses were further treated with sodium chlorite to convert the aldehyde groups formed by oxidation to carboxylic groups, yielding a tricarboxylic oxycellulose. The degree of oxidation was assessed by evaluating the amount of aldehyde and carboxyl groups formed by analytical methods and FTIR-ATR spectrometry. For a short treatment time, a higher oxidation level could be achieved by potassium periodate oxidation and sodium bromide (NaBr), TEMPO oxidation, whereas a longer oxidation time was required to reach the same oxidation level using the bromide-free TEMPO system. The type and level of oxidation of the oxycellulose obtained influenced the mechanical properties, degree of polymerization, alkaline stability and whiteness.

Wang (Wang *et al.*, 2024) comparatively study the selective oxidation of cotton fibre pulp with $NaIO_4$ at pH=4.0 and 0.4 g $NaIO_4$/g cellulose, followed by post-oxidation with $NaClO_2$ at room temperature, 12 h, with combined oxidation of TEMPO/NaBr/NaClO (0.025 g/ 0.25 g) at pH=10.0 at room temperature, duration for 60 min and sodium periodate (4 g), pH=4.0, at 60°C for 30 min. In both cases, 10 grams of cotton cellulose pulp were oxidized. After oxidation, the fibres were washed with distilled water and freeze-dried for 24 hours.

In the studies (Nikolic *et al.*, 2010; Nikolic *et al.*, 2011) the authors subject cotton yarns to oxidation with sodium periodate, at concentrations of 0.2% and 0.4% (w/v) in 50 mL acetate buffer solution (pH=4.0), at room temperature, in the absence of light, for different durations from 30 minutes to 6 hours. After oxidation, the samples were washed with cold distilled water, filtered and dried at room temperature for 72 hours. The determination of aldehyde groups was based on the quantification of carboxyl groups after oxidation with $NaClO_2$.

Pejic and collaborators (Pejic *et al.*, 2015) modified the functionality of cotton yarns with 0.2% and 0.4% (w/v), i.e. concentrations of 2.0 mg/mL and 4.0 mg/mL sodium periodate solutions in 0.1 M acetate buffer solution (ratio 1:50, w/v) at pH = .4, for different periods of time from 15 minutes to 360 min, followed by a post-oxidation with sodium chlorite. The oxidation reactions were performed at room temperature, in the absence of light.

The study by Hao (Hao *et al.*, 2018) describes the selective oxidation of cotton and viscose knitwear with sodium periodate, using two concentrations of 0.03 mol/L and 0.06 mol/L of sodium periodate, the oxidation time of 6 hours in closed vessels and at room temperature, under stirring at a speed of 60 revolutions/min. A float ratio of 1:50 (50 mL solution/g cellulosic material) was established. After the oxidation was completed, the cotton samples were soaked in 0.1 M glycerol solutions for 30 minutes to remove the unreacted oxidant and then rinsed with cold distilled water and air-dried.

Diankova and co-authors (Diankova *et al.*, 2009) study the influence of oxidizing agents such as hydrogen peroxide, sodium hypochlorite and sodium periodate for different types of textiles (including cotton gauze, cotton knit bandage and viscose/polyester, non-woven fabric) alkaline scoured with 14% NaOH. Selective oxidation was performed with 0.5% sodium periodate solution, at pH=3.0, at 20°C, for 24 and 42 hours. The oxidation reaction proceeded best on gauze, then on knitwear and finally on nonwoven viscose/polyester blend, independent of the oxidation variant, which also demonstrates the influence of the nature, structure and chemical composition of the textile material, but also of characteristics such as e.g. density, thickness and specific gravity. Depending on the nature of the oxidizing agent and the content of aldehyde groups generated, the decreasing order is sodium periodate, followed by sodium hypochlorite and hydrogen peroxide. Sodium periodate also leads to the greatest decrease in the degree of polymerization (DP).

In the work developed by (Wu *et al.*, 2023) the authors selectively oxidize cotton fabric with TEMPO with and in the absence of NaBr. The best results to obtain an optimal grafting of the amine groups of guanidine were obtained at a dosage of 1.67 mg/L TEMPO and 3 g/L NaClO, without NaBr, Liquor ratio (LR): 1:75, pH=10.5, 20°C, 30 minutes.

The results obtained regarding the content of aldehyde and carboxyl groups, as well as the analytical methods used for their determination, are included in Table 1, sub-point 4.2.6. The content of aldehyde and carboxyl groups is usually expressed in mmol/g, μmol/g, μmol/100 g, mmol/kg, describing the millimolar content of aldehydes or carboxyl groups per gram, 100 grams or kg of oxidized product.

4. Analytical and instrumental methods, for determining chemical, structural and morphological changes

The determination of aldehyde groups and/or newly formed carboxylic groups following oxidation with periodate at the C2 and C3 positions or mediated by TEMPO at the C6 position of the AGU monomer unit is particularly important to evaluate the chemical functionality and degree of oxidation of cellulosic textile materials.

The degree of oxidation (DO) is an extremely important indicator in evaluating the performance of the cellulose oxidation process with periodate and/or TEMPO and can be quantified based on the number of oxidized AGU units denoted by x out of the total anhydroglucosidic units (n), y represents the number of unoxidized AGU units, shown in Fig. 9.

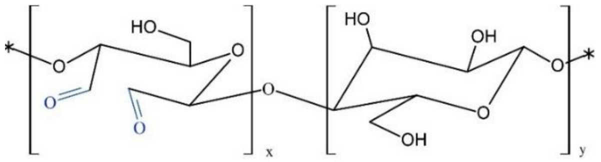

Fig.9 – Schematic representation of the number of Oxidized AGU units and the number of unoxidized AGU units.
The figures have been drawn by the authors with ChemSketch.

To calculate the degree of oxidation taking into account the reasoning developed by (Brandén *et al.*, 2017) it can be stated that following oxidation the mass of the oxidized product free of moisture (m) is composed of two parts, an oxidized part ($m_{oxidized}$) and a non-oxidized part ($m_{unoxidized}$), as shown in eq. (1):

$$m = m_{oxidized} + m_{unoxidized} \tag{1}$$

or by eq. (2) as it all shows (Brandén *et al.*, 2017):

$$m = Mw_{OAGU} * x + M_{wAGU} * y \tag{2}$$

where: m is the dry weight of the product; Mw_{OAGU} is the molar mass of the oxidized AGU unit, Mw_{OAGU}= 192.124 g/mol; Mw_{AGU} is the molar mass of the unoxidized AGU unit, Mw_{AGU}=162.14 g/mol; x is the number of moles of aldehyde groups and is determined by an analytical method, expressed in mmol/g or µmol/g; y - the number of moles of unoxidized AGU units.

The number of moles of unoxidized units is calculated according to the eq. (3):

$$y = \frac{m - M_{wOAGU} * x}{M_{wAGU}} \tag{3}$$

Finally, the degree of oxidation (DO) is calculated according to eq. (4):

$$DO\ \% = \frac{x}{x+y} * 100 \tag{4}$$

The specialized literature presents several analytical and instrumental methods for the quantification of aldehyde and carboxyl groups and it is considered that the number of oxidized AGU units is associated with the content of aldehyde or carboxyl groups (Potthast *et al.*, 2006).

4.1. Quantification of aldehyde groups

4.1.1. Hydroxylamine hydrochloride method (with oxime)

In the case of this method, the number of oxidized AGU units is associated with the content of aldehyde groups determined by the reaction between hydroxylamine hydrochloride and aldehyde groups, Fig. 10. The reaction proceeds with the release of two moles of hydrochloric acid, which is then titrated with a base, sodium hydroxide. The amount of dialdehyde formed by the oxidation of cellulose is related to the consumption of the base and is equal to half a mole of sodium hydroxide, Brandén states (Brandén *et al.*, 2017; Madivoli *et al.*, 2019; Zhao and Heindel, 1991; Ding *et al.*, 2017).

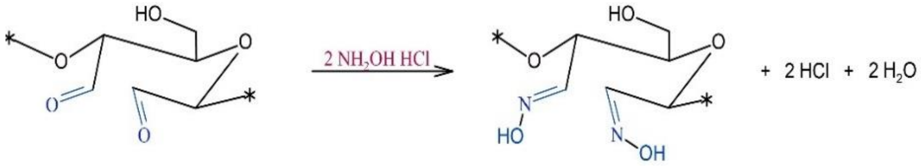

Fig. 10 – The reaction pathway between dialdehyde cellulose and hydroxylamine hydrochloride.
The figures have been drawn by the authors with ChemSketch.

4.1.2. Iodometric method (I)

The iodometric method (I) is a traditional method for determining the content of aldehyde groups, by indirect titration, the excess iodine is titrated, the iodine not consumed by the aldehyde groups by titration with sodium thiosulfate, in the presence of starch, according to the reactions given in eq.(5) and eq. (6).

$$\mathrm{R-CHO+\ I_2+H_2O\rightarrow R-COOH+2I^-+2H^+} \tag{5}$$

$$\mathrm{I_2+2S_2O_3^{2-}\rightarrow 2I^-\ +\ S_4\,O_6^{2-}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

As can be seen, stoichiometrically for 1 mole of I_2, 2 moles of $Na_2S_2O_3$ are consumed.

4.1.3. Method with 2,3,5-Triphenyltetrazolium chloride (Tetrazolium - TTC)

The tetrazolium method is a sensitive and relatively simple spectrophotometric method for the determination of aldehyde groups (Fras Zemljić *et al.*, 2009; Afzal and Wang, 2019). The tetrazolium salt 2,3,5-Triphenyltetrazolium chloride (TTC) or Nitroblue Tetrazolium (NBT), reacts with aldehyde groups, forming a coloured formazan compound -

triphenyltetrazolium formazan (TTF), insoluble in water, red in colour, according to the reaction in Fig. 11 (Ahmad, 2021). After separation of the formazan and its solubilization in dimethylsulfoxide (DMSO) or absolute ethyl alcohol, the absorbance of the samples is measured spectrophotometrically. The content of aldehyde groups can be quantified based on a calibration curve drawn for known concentrations of aldehydes such as glyoxal. The method has been validated on compounds with known aldehyde content, such as formaldehyde, acetaldehyde and glutaraldehyde by Marjamaa (Marjamaa *et al*., 2024).

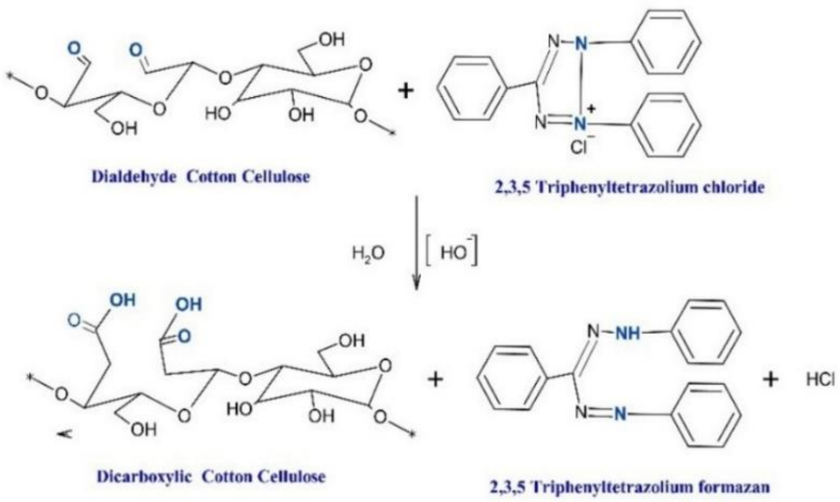

Fig. 11 – Reaction mechanism of 2,3,5, triphenyltetrazolium chloride (TTC) with DAC and formation triphenyltetrazolium formazan (TTF).
The figures have been drawn by the authors with ChemSketch.

The study (Fras Zemljič *et al*., 2009) describes the method for determining aldehyde groups with TTC according to Szabolcs (Szabolcs *et al*., 1961), which suspends approximately 0.6-4.6 g of dry cellulose fibre in a 0.1% TTC solution and a 0.2 M KOH solution, at 100º, for 10 minutes, during which the coloured product, formazan, is formed. The content of reduced aldehyde groups under these conditions is determined spectrophotocolorimetrically at 546 nm, based on the determination of the formazan formed (Fras Zemljič *et al*., 2009) or at 482 nm as shown (Ahmad *et al*., 2021), determination at the UV-VIS spectrometer of the reacted TTC.

The study developed by (Toshikj *et al*., 2017), comparatively analyses the 2 methods, the iodometric and the TTC method, and states that the TTC method allows for a more sensitive detection of aldehyde groups after oxidation of cotton yarns with periodate, and has a higher accuracy than the iodometric method.

4.1.4. Elemental analysis

The previously listed analytical methods applied for the quantification of functional groups can be a challenge most of the time in the case of yarns, cellulose fibres as stated (Vicini *et al*., 2004). They offer a simpler alternative for determination, namely elemental analysis, which can be applied in the case of the hydroxylamine hydrochloride method to determine, for example, the nitrogen content of oxime-modified aldehydes. Elemental analysis is also reported by (Fras Zemljič *et al*., 2009) in the case of oxidation of cotton yarns with 0.01 M KIO_4, at 20°C for 12 hours, by determination e.g. by XPS. The recorded spectra show for the unoxidized samples an elemental composition of (% O - 39.8; % C – 60.3; % N -0; % Si- 0.6), and for the samples oxidized with KIO_4 (% O - 36.7; % C – 62.5; % N -0.2; % Si- 0.4).

4.1.5. Method for determining the cupric index

The content of aldehyde groups can also be determined spectrophotometrically by the cupric number (cooper number), which is defined according to TAPPI T430 (TAPPI Official Test Method T430, 1994), and by (Diankova *et al*., 2009), as the number of grams of metallic copper, Cu_2O, that can be reduced from a solution of copper (II) sulfate by 100 grams of cellulose fibre. The principle of the method is based on the reaction of aldehyde groups with copper ions (Cu^{2+}). The authors state that, in the case of oxidation of cotton cellulose materials (gauze, knitwear, nonwovens) with sodium periodate under conditions of pH=3.0, temperature of 20°C, for 20 hours, high values of copper number show the formation of aldehyde groups in the C2 and C3 positions of the AGU monomer, in contrast to oxidation in the presence of H_2O_2 and NaClO, at pH=9.0-9.5 where low values of copper number confirm the formation of ketone groups to the detriment of aldehyde and carboxyl groups. These non-selective oxidizing agents produce ketocelluloses (Diankova *et al*., 2009).

4.1.6. UV-VIS spectrophotometric method

Another method is based on UV-VIS spectrophotometric determination of the residual (unreacted) periodate concentration. It is an indirect method for determining the carbonyl groups formed. The periodate consumption is monitored using UV-VIS spectroscopy by measuring the absorbance of periodate at 222 nm, a method applied by (Han *et al*., 2010; Simon *et al*., 2022) or at 290 nm by (Wen *et al*., 2023). The concentration of aldehyde groups is quantified by the difference between the initial periodate concentration and the residual concentration. The periodate concentration is calculated from the recorded absorbance, based on a calibration curve for known periodate concentrations.

4.1.7. FTIR-ATR spectroscopic method (Fourier transform infrared spectrometry using attenuated total reflectance)

Identification of aldehyde groups in oxidized cellulose species using infrared (IR) analysis is often used, even though it is often not conclusive. In the case of cotton textiles, FTIR-ATR was used to analyse the changes in the chemical structure following oxidation with sodium periodate. The typical band of aldehyde groups appears at wavelengths of 1730-1740 cm^{-1} (Sun *et al.*, 2015; Kim *et al.*, 2000; Durán *et al.*, 2018) and two absorption bands are assigned at wavelengths of 1740 cm^{-1} and 880 cm^{-1} for the carbonyl group, respectively for the hemiacetal form or for the hydrated aldehyde forms.

Kim (Kim *et al.*, 2000) shows that only at an oxidation degree of around 12% is the well-defined peak at 1740 cm^{-1} recorded, and for the hemiacetal form a diffuse peak appears only at oxidation degrees exceeding 20%.

Identifying changes in chemical structure by selective oxidation with acceptable accuracy may only be possible at relatively high degrees of oxidation. In the case of oxidation of textile materials, in order to obtain quantifiable data, most of the time FTIR-ATR analysis is correlated with analytical methods for determining new functional groups or by correlation with near infrared spectroscopy (NIR (Simon *et al.*, 2022).

The authors (Toshikj *et al.*, 2019) in agreement with (Sivakova *et al.*, 2008) confirm that, in the case of cotton oxycelluloses, the identification of aldehyde groups is difficult, due to the coexistence of fully hydrated or hemiacetal forms, which is why broad regions between 1720 -1780 cm^{-1} are identified in the FTIR-ATR spectra.

Oh and co-authors (Oh *et al.*, 2005) calculate the relative absorbance ratio ($A_{4000–2995}/A_{993}$), as a criterion for assessing the decrease in hydrogen bond intensity by decreasing absorbance. They also mention the absorbance at 1430 cm^{-1} and 987–893 cm^{-1}, calculate the ratio (A_{1430}/A_{900}), which is attributed to the adsorption of the crystalline area and used to calculate the crystallinity index of the cellulose I structure.

4.2. Quantification of carboxyl groups

An advantage of the periodate oxidation method is the possibility of subsequently oxidizing the aldehyde groups to carboxylic groups in the presence of e.g. $NaClO_2$ shown in the reaction in Fig. 12. The content of aldehyde groups is calculated by the difference between the carboxyl groups before and after post-oxidation, especially when textile materials previously bleached by a non-selective oxidation procedure, such as e.g. with NaClO, H_2O_2 or $HClO_4$, are subjected to selective oxidation with periodate and/or TEMPO, processes by which already before oxidation with periodate or TEMPO certain primary and/or secondary hydroxyl groups in AGU are oxidized to ketone, carbonyl or carboxyl groups as shown (Diankova and Doneva, 2009).

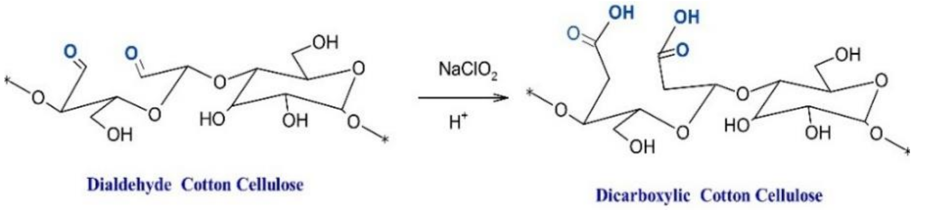

Fig. 12 – Oxidation of DAC with sodium chlorite.
The figures have been drawn by the authors with ChemSketch.

The same principle is applied in several studies (Fras *et al.*, 2004; Liimatainen *et al.*, 2012; Toshikj *et al.,* 2019, Kumar and Yang, 2002) for the determination of new functional groups. The determination of the content of aldehyde groups is carried out by analysing the group content of the carboxylic acid derivatives of the dialdehyde polysaccharide before and after oxidation with sodium chlorite.

A recent study by (Brault *et al.*, 2005) considers that both oxidative steps, Fig. 12, are known to be particularly slow and can lead to several secondary reactions, which are responsible for the discrepancies systematically observed in the determination of the DO. The methods for titrating carboxylic groups in DCC before and after oxidation with sodium chlorite are not conclusive, significant differences are obtained in the values obtained for quantifying aldehyde groups compared to the values obtained by established analytical methods for determining aldehyde groups (e.g. titration with hydroxylamine hydrochloride, iodometric or with TTC), most likely due to the consumption of chlorite only at a single aldehyde group and not at both groups, and this probably occurs due to the intramolecular formation of hemiacetal-type structures.

The most used determination methods in this case are the Ca-acetate method, followed by titration with sodium hydroxide (NaOH), or complexometrically by titrating with ethylenediaminetetraacetic acid (EDTA) in the presence of murexide or Eriochrome Black T.

4.2.1. Ca-acetate and sodium hydroxide method (Ca-acetate-NaOH)

The authors (Toshikj *et al.*, 2016) describe this method as simple, very easy to conduct for the determination of carboxyl groups, consisting of treating oxidized cellulose fibres with a Ca-acetate solution, which is maintained at room temperature under stirring for 12 hours to facilitate ion exchange, then filtered and titrated with NaOH solution, in the presence of phenolphthalein.

4.2.2. Complexometric method Ca-acetate and ethylenediaminetetraacetic acid (Ca-acetate - EDTA)

This method has a greater applicability than the Ca-acetate - NaOH method, ensuring greater reproducibility and sensitivity as stated (Fras *et al.*, 2004; Toshikj *et al.*, 2017). The method consists of immersing cotton fibres in distilled water and Ca-acetate solution at a pH=10.0, provided by the ammonia buffer solution under frequent stirring for 12 hours, then filtering, and the filtrate is titrated with EDTA solution in the presence of the Eriochrome Black T indicator.

4.2.3. Methylene blue (MB) method

In order to determine the carboxyl groups, the UV-VIS spectrophotometric method can be applied at a wavelength between 600 and 660 nm, in the case of determining the carboxyl groups by the method of staining the oxidized samples with methylene blue (MB), a cationic dye, which binds to the carboxyl groups of the oxidized cellulose (Ewa *et al.*, 2001; Chen, 2002). This method is based on the principle of light absorption by a coloured compound, in this case unabsorbed, unreacted MB. It is a relatively simple and efficient technique for quantifying carboxylic groups by measuring the absorption of electromagnetic radiation.

The authors (Fras *et al.*, 2004) studied the selective oxidation of cotton yarns with periodate and the non-selective oxidation with perchloric acid and concluded that both methods, the MB staining method and the Ca-acetate EDTA complexometric titration methods, are in excellent correlation. They state that complexometric titration induces smaller systematic errors and higher accuracy than the methylene blue spectrophotometric method, which is recommended only as a reference method to confirm any trend in the results obtained by the complexometric method.

4.2.4. Conductometric method

The study developed by (Fras *et al.*, 2005; Toshikj *et al.*, 2019) refers to the conductometric determination of carboxylic groups, according to the method described by (Saito and Isogai, 2004), in which oxidized cellulose samples are transformed into protonated forms by treatment with hydrochloric acid (pH=2.5), a step that is followed by immersing the samples in a sodium chloride solution, necessary to control the ionic strength of the solution, then titrated with a NaOH solution to a pH = 11.

4.2.5. FTIR-ATR spectroscopy

FTIR-ATR spectroscopy also provides information on the formation of carboxyl groups. The peaks recorded at 1750 cm^{-1} and 1650 cm^{-1} correspond to the stretching of the C=O bonds in the carboxylic group in the protonated form, respectively to the vibrational stretching of the C=O bonds in the carbonyl groups of the carboxylate ions, as shown (Wang *et al*., 2024). Also, an intact structure of the cellulose macromolecule is confirmed by the presence of characteristic peaks at 3460 cm^{-1} (stretching vibration of O-H bonds), 2900 cm^{-1} stretching of the C-H bond and 1050 cm^{-1} stretching of the C-O-C bonds in the cellulose skeleton, values confirmed by (Wang *et al*., 2024; Calvini *et al*., 2006; Liu *et al*., 2018).

4.2.6. Values of the content of functional groups (aldehyde and/or carboxyl) of selectively oxidized textile materials

Values of the content of functional groups (aldehyde and/or carboxylic) of selectively oxidized textile materials depending on the reaction parameters and the analytical determination method are listed in Table 1. The reaction conditions, the oxidizing agents used were described in subsection 3.2.

Table 1

Content of functional groups (aldehyde and/or carboxylic) of selectively oxidized cotton textiles depending on the nature of the textile material and the analytical determination method

Fabric type	Method	Functional groups mmol/kg		Reference
		Aldehyde	**Carboxylic**	
Cotton yarn Alkaline scouring H_2O_2 bleaching HCl demineralization KIO_4 oxidation	MB	-	48.25 - 50.44	Fras *et al.*, 2004
	Ca acetate-EDTA	-	21.36 - 26.91	
Cotton yarn without pretreatment	Hydroxylamine hydrochloride	75 -100		Pejic *et al.,* 2015
Raw cotton yarn without pretreatment Oxidation with $NaIO_4$ 0.2% -0.4% (w/v)	Ca acetat -NaOH	-	50 - 99.2	Nikolic *et al.*, 2011
Cotton pulp (alkaline treatment) Oxidation with $NaIO_4$ 0.4 g/g cellulose or 8 g/L	Conductometric titration	-	714.9	Wang *et al.*, 2024

Cotton pulp (alkaline treatment) TEMPO/NaBr/ NaClO	Conductometric titration		700.7	
Cotton yarn Alkaline scouring and mercerization	TTC	216.5	-	Toshikj *et al.*, 2017
	I	90.3	-	
	MB	-	11.5	
	Ca acetate-EDTA	-	25	
	Ca acetate-NaOH	-	53.6	
Cotton yarn Alkaline scouring, bleaching with H_2O_2	TTC	99	-	Fras Zemljič *et al.*, 2009
Cotton yarn Alkaline scouring, bleaching with H_2O_2 KIO_4 oxidation +TEMPO/NaBr/ NaClO	Conductometric titration	88	793	Toshikj *et al.*, 2019
	Ca acetate -NaOH	101	747	
Cotton yarn Alkaline scouring, bleaching with H_2O_2 KIO4 oxidation + TEMPO/ NaClO	Conductometric titration	134	684	
	Ca acetate -NaOH	179	640	
Cotton knitwear	Hydroxylamine hydrochloride	113.3-187.4	-	Hao *et al.*, 2018
Viscose knitwear		1284	-	
Raw Cellulose Fibre Oxidation TEMPO/NaBr/ NaClO	Ca-acetate-NaOH	80 - 321	123 - 795	Praskalo *et al.*, 2009
Lyocell Oxidation TEMPO/NaBr/ NaClO		40 - 634	180 - 700	
Gauze, cotton knit Viscose/PES nonwoven Alkaline scouring	Cupric index Gauze - 24.74 g I_2/100g Knit - 23.84 g I_2/100g Nonwoven - 1.7 g I_2/100g		-	Diankova and Doneva, 2009
	I	Gauze - 513.1 Knit – 491.7 Nonwoven – 23.4	-	

4.3. Degradation analysis of the morphological structure of the oxidized cellulose macromolecule

4.3.1. Loss of cellulose substance

Cellulose loss is determined directly gravimetrically on cellulosic samples dried at constant pond, before and after oxidation. Aggressive oxidative attack on cellulosic materials can lead to significant cellulosic loss (Nikolic *et al.*, 2011; Praskalo *et al.*, 2009).

Nikolic and co-authors (Nikolic *et al.*, 2011) show that for raw cotton yarns oxidized with 0.2% and 0.4% (w/v) sodium periodate, the loss of cellulose is 2.5% and occurs in the first 30 minutes, after which it remains constant and is independent of increasing oxidizing agent concentration or oxidation time.

Praskalo (Praskalo *et al.*, 2009) reports in the case of oxidation of cotton yarns with TEMPO/NaBr/NaClO at the lowest concentration used of 0.3 mmol/g after 4 hours of oxidation a loss of cellulose of 2.78%, and at the maximum concentration of 9.67 mmol/g the same duration, a loss of 11.34%.

4.3.2. Determination of the degree of polymerization by intrinsic viscosity measurement

The degree of polymerization (DP) of oxidized cellulose decreases with increasing degree of oxidation and is due to DAC depolymerization. Also, the degree of polymerization decreases with increasing number of aldehydic or carboxyl groups. states (Hao *et al.*, 2018).

DP by viscometric method is determined according to ISO 5351-2010. DP evolution of cellulosic forms is followed by dissolving cotton textile fibres. The authors (Fras *et al.*, 2004; Toshikj *et al.*, 2017) dissolve the cellulosic fibre in the sodium salt of ferric tartaric acid (EWNN) and determine the intrinsic viscosity (ɳ) of the solutions by the modified Ubbelohde method (capillary length 78 mm, capillary diameter 0.75 mm, 0.7 cm^3). DP was calculated using the Kuhn, Mark, Houwink relation, eq. (7):

$$DP_{ɳ}^{\alpha} = \frac{1}{K_p} ɳ \tag{7}$$

where: Kp =33 10^{-3} [dL/g] and α =0.74.

In the study by Wang and co-authors (Wang *et al.*, 2024) cellulosic fibres are dissolved in cupric ethylenediamine (CED) and the intrinsic viscosity is determined on a viscometer. The relation he uses to calculate the DP is given by eq. (8):

$$DP^{0.905} = 0.75\ ɳ \tag{8}$$

According to (Wang *et al.*, 2024) the cotton fibres selectively oxidized with TEMPO/Na Br/NaClO (0.0025 g TEMPO/fibre) and sodium periodate (0.4 g $NaIO_4$/g cotton fibre) respectively have DP values of 101.86 and 731.77 respectively, compared to the non-oxidized cotton fibre, which has DP= 1872.82, showing a degradation of cellulosic fibres, periodate oxidation has a lower effect on depolymerization.

The study on periodate oxidation (1 g/L KIO_4, 60°C, 1 hour) of mercerized and alkaline-scoured cotton yarns (Toshikj *et al.*, 2017) obtained a DP for oxidized yarns of 206.28, compared to 1185.51 for non-oxidized fibres.

4.3.3. Differential Scanning Calorimetry (DSC) method

Differential Scanning Calorimetry (DSC) is an important method that measures the heat flux associated with amorphous or crystalline, transitioning structural changes of materials as a function of temperature and time in a controlled atmosphere. DSC provides quantitative and qualitative information about physical and chemical changes in endothermic or exothermic processes.

The authors of the paper (Xu and Du, 2011) subjected cotton fibres to periodate oxidation at different concentrations (0.1 - 1.0 mg/L) and durations (0 - 3 hours). As the authors state the DSC curves for the samples oxidized in the endothermic stages decomposed at a higher temperature than the non-oxidized samples up to 350°C, however, with increasing oxidation degree, the endothermic decomposition peak of oxidized cotton cellulose shifted rapidly, indicating the decrease in decomposition temperature.

4.3.4. Determination of mechanical resistance

Also, in order to assess the degree of degradation of the cellulosic matrix, mechanical strengths such as tensile strength, elongation at break (Nypelö *et al.*, 2021) are determined, which are performed according to the current standards EN ISO 2062: 2009. Related to the mechanical strength of oxidized cellulosic fibres (Toshikj *et al.*, 2017), reports in the case of periodate oxidation, a tensile strength and elongation at break lower by only 23% and 15.8%, respectively, compared to non-oxidized samples, which shows that, a moderate degradation of the cellulosic macromolecule occurs.

In the study also developed by Toshikj (Toshikj *et al.*, 2019) the selective oxidation with KIO_4 (0.1 - 1.0 g/g cellulose) and TEMPO of alkaline-cleaned cotton yarns bleached with hydrogen peroxide leads to a 65% decrease in breaking strength at the maximum concentration and 33% at the minimum concentration. In the case of TEMPO-mediated oxidation without NaBr, a 77.3% decrease is reported for 120 minutes under the same conditions, but in the presence of NaBr the decrease is 73.2%. The decrease in values is due to the presence of NaClO which accelerates the degradation, NaBr has an additional effect in favouring the degradation of the cellulose molecular chain.

4.3.5. FTIR-ATR spectroscopy

FTIR-ATR spectroscopy can also give information on the integrity of the cellulosic macromolecule and the degradation of the cellulosic macromolecule (Chinkap *et al.*, 2004; Youn *et al.*, 2005).

Wang and co-authors (Wang *et al.*, 2024) attribute the peaks recorded at 1750 cm^{-1} and 1650 cm^{-1} to the stretching of the C=O groups in the protonated form of the carboxylic groups, respectively, to the vibration of the C=O bond in the carbonyl groups in the carboxylated form. The peak corresponding to absorption at wavelength 1050 cm^{-1} indicates cleavage of the glycosidic bond in the cellulosic macromolecular skeleton. Simon in the study (Simon *et al.*, 2022), indicates the absorption bands at wavelengths 2900 cm^{-1} and 1030 cm^{-1} respectively indicate C-H bond stretching and C-O-C bond vibration in the pyranosidic ring. The absence of these peaks may confirm the intact structure of the cellulosic macromolecule, which is characterized by peaks at 3460 cm^{-1} (O-H bond stretching vibration), 2900 cm^{-1} C-H bond stretching) and 1050 cm^{-1} (C-O-C bond stretching in the cellulosic skeleton), values also attributed by (Wang *et al.*, 2024).

4.4. Analysis of the morphological structure of cellulose macromolecule and properties acquired after selective oxidation

4.4.1. X-ray diffraction (XRD)

X-ray diffraction is a frequently used method for evaluating structural changes in cellulose. The crystallinity index (CrI) is a valuable indicator, expressed in % and calculated by the area ratio method of the crystalline and amorphous peaks. Depending on the reaction conditions, periodate oxidation induces some rearrangement of the cellulose macromolecular chain, with a slight perturbation of the crystallinity of the fibre. In case of cotton fibres crystallinity index is an essential parameter to characterize the internal, fine structure of the fibres, it is calculated by the peak area ratio method as mentioned by (Xu and Du, 2011). They state that, in the case of cellulose, the most commonly chosen crystalline peak is the 002 reflection, which is present between 22-24° at 2θ, usually choosing the intensity at about 18° (the minimum between peaks).

Wang and co-authors (Wang *et al.*, 2024) report for TEMPO-oxidized cellulose and periodate the crystalline peak at 22.8^{o} at 2θ, while for the non-crystalline (amorphous) value, the values 14.9^{o} and 16.7^{o}, respectively. They state that, XRD is an empirical method, it can only provide relative values, because the measured spectrum always contains contributions from amorphous regions and in the position of crystalline peaks.

The relative CrI is calculated with eq. (9) according to (French, 2014; Wang *et al.*, 2024), which also indicates certain values for the intensity of the peaks in the crystalline and amorphous regions for both cellulose I (native) and cellulose II, which has undergone certain chemical modifications.

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \; x \; 100; \;\; [\%] \qquad (9)$$

where: I_{002} is the maximum diffraction intensity of crystalline from plane (002) at $2\theta = 22.5^o$ for cellulose I and $2\theta = 21.7^o$ for cellulose II, while I_{am} is the intensity of amorphous scatter at $2\theta = 18^o$ for cellulose I and $2\theta = 16^o$ for cellulose II.

In the study by Hao and co-workers (Hao *et al.*, 2018), samples of cotton fabric oxidized with very fine sodium periodate ground by X-ray diffraction at diffraction angles of 5^o and 40^o at a scan rate of 2^o/minute are analysed. The CrI is calculated after deconvolution. The authors show that the XRD spectra of the non-oxidized and sodium periodate-oxidized samples at concentrations of 0.03 and 0.06 mol/L show a slight change in crystalline structure, the calculated CrI of the oxidized cotton fabrics have values of 57.0% and 52.6% respectively at the two concentrations, the CrI decreased very little, compared to the non-oxidized samples 59.3%.

The slight loss of crystallinity of oxidized cotton samples has also been reported by other researchers (Kim *et al.*, 2000; Siller *et al.*, 2015) and is only due to the disruption of the order structure of cotton. In contrast, the authors (Xu and Huang, 2011) reported a slight increase in crystallinity after periodate oxidation due to partial dissolution of the oxidized cellulose fraction. Guigo and co-workers (Guigo *et al.*, 2014) showed that low OD cellulose microfibrils (carbonyl content 0.38-1.75 mmol/g) following periodate oxidation, the crystallinity and ultrastructure of the cellulose is preserved intact, as oxidation is only performed at the surface of the cellulose.

The CrI was also calculated according to the iodine sorption index (ISV) described in section 4.4.3. by (Nikolic *et al.*, 2011).

4.4.2. Cellulose fibre surface analysis by Electron Microscopy (SEM -Scanning Electron Microscopy)

SEM is a reflectance-based method of microstructural analysis, and the underlying principle of scanning electron microscopy is the analysis of secondary electrons, which are emitted from the surface of the sample to be analysed when it is bombarded by a beam of high-energy, primary electrons. SEM images allow clear images and provide information on the surface morphological structure of the fibre, in general on the primary cellulosic fibre wall. It can be observed in the case of oxidation with sodium periodate at a concentration of 0.06 mol/L (Hao *et* *al*., 2018), some breaks, longitudinal or transverse fragmentations due to the oxidative erosion activity of periodate, while in the case of TEMPO the fibre image reveals only some transverse cracks, states (Wang *et al*., 2024).

4.4.3. Iodine sorption index (ISV)

The iodine sorption index (ISV) is an empirical method and provides information on the sorption capacity of aqueous solutions by the cellulosic fibrous matrix, on the accessibility of the cellulosic fibres in the amorphous zone and is inversely proportional to the crystalline phase of the fibres. ISV is determined according to the Schwertassek method (Nelson *et al*., 1970; Haule, 2016), which states that adsorption occurs in the amorphous zone. Cellulose samples are immersed in KI_3 solution, then in a saturated sodium sulphate solution for one hour, (filtered), and the filtrate is titrated with sodium thiosulfate (Strnad *et al*., 2001).

Periodate oxidation has been reported by (Hao *et al*., 2018; Pejic *et al*., 2015; Praskalo *et al*., 2009) in the sense of increased accessibility of fibres to aqueous solutions. They obtained a sorption index ISV of 54.1 mg I_2/g product for non-oxidized cotton cellulosic fibres, while for those oxidized with TEMPO and NaClO at room temperature and pH 10.5 the sorption index decreases depending on the reaction conditions and varies between 35.5 - 53.6 mg I_2/g, indicating that the selective oxidation reaction occurs first in the amorphous, disordered zone of microfibrils, as illustrated in Fig. 8.

Nikolic and co-authors (Nikolic *et al*., 2011) in the oxidation variant with 0.4% $NaIO_4$ for 6 hours at room temperature obtained an ISV value of 57.9 mg I_2/g comparable to the non-oxidized sample, 61.4 mg I_2/g. The authors' interpretation is based on the interaction of iodate ions (IO_4^-) with the protons of the hydroxyl ions of the cellulose molecule via electrostatic interactions. Contrary to water adsorption, iodine does not adsorb in multimolecular layers, but it forms a monomolecular layer. Due to their high degree of crystallinity, these groups block the accessibility of water, which leads to lower ISV values. The CrI is 86.9% for oxidized cotton fibres compared to non-oxidized fibres, which have CrI = 86.5%, indicating that the crystalline region of the cellulosic fibres is not affected.

The values calculated with eq. (10), are in agreement with the Schwertassek method, (Nelson *et al*., 1970) and it is shown that, the adsorption rate of iodine per gram of methylcellulose is 412 mg I_2/g and determines the amorphous fraction.

$$CrI = 100 - \left(100\,\frac{ISV}{412}\right) \qquad (10)$$

4.4.4. Hydrophilicity (Moisture sorption capacity)

Moisture sorption capacity is determined according to ASTM D 2654-76, which consists of placing the cotton samples in a controlled atmosphere at 20°C and relative humidity of 65±2% for 24 hours (ASTM D 1776-74), expressed in % and calculated by the ratio of the mass of the conditioned dry sample to the mass of the original sample.

Nikolic (Nikolic *et al.*, 2011) reports in the case of oxidation with 0.4% NaIO4 for 6 hours a moisture sorption capacity of about 6.4%, a slight increase compared to non-oxidized cotton yarns, which have a water sorption capacity of ca. 6.25%. The authors also state that the crystalline, ordered region of microfibrils does not contribute significantly to the water sorption process.

4.4.5. Water retention value (WRV)

WRV may indicate the degree of swelling of cellulosic fibres, it is determined according to the SCAN-C 62:00(2000) method, which states that a certain amount of cellulosic fibre dried to constant weight (m_1) is weighed on an analytical balance, then immersed in distilled water for 30 minutes, vacuum filtered, centrifuged at 8000 rpm, weighed on an analytical balance (m_0), then calculated by eq. (11):

$$WRV = \frac{m_0 - m_1}{m_1}\, x\, 100;\ [\%] \tag{11}$$

where: m_0 is the sample mass after centrifugation (grams) and m_1 is the sample mass after drying (grams).

Wang and co-authors (Wang *et al.*, 2024) showed that cotton fibres selectively oxidized with TEMPO/NaBr/NaClO (0.0025 g TEMPO)/g fibre, respectively sodium periodate (0.4 g $NaIO_4$/g cotton fibre) achieve WRV values close to 298.76% and 296.75% compared to 159.10% of non-oxidized cotton fibre, in contrast (Nikolic *et al.*, 2011). They report in the case of sodium periodate oxidation a decrease in water retention, as early as the first 30 minutes of oxidation, the values decrease from the value of 30.6% (non-oxidized sample) to 22.7% and 22.4% at 0.2% and 0.4% $NaIO_4$ concentration, respectively. After 6 hours a water sorption capacity increases slightly by 21.3%. The authors explain this variation of water sorption on the basis of possible cross-linking reactions, on the basis of formation of intermediate structures, hemiacetal, aldal type.

4.4.6. Stability of whiteness, yellow index (Yellow index-YI)

The stability of the whiteness of oxycellulose shall be determined according to the Whiteness Index (WI_{CIE}) according to ISO 105-J02:1999, using a spectrophotometer. In the CIELab colour system, the b* value represents the blue-yellow colour coordinates, a negative value indicates a predominantly blue colour, a positive value a yellow colour.

Toshikj (Toshikj *et al.*, 2019) reports for samples oxidized with potassium periodate a decrease in the WI_{CIE} index as the value of b* increases, which increases with increasing periodate concentration. For samples oxidized with TEMPO in the presence of NaBr, the WI_{CIE} index decreases less significantly, and for TEMPO oxidation in the absence of NaBr, the WI_{CIE} decrease is even slightly smaller. The decrease in the WI_{CIE} index for TEMPO oxidation compared to periodate is due to the use of NaClO, which is a traditional oxidizing agent, but has a negative impact on the environment due to the use of halogenated reagents (NaOCl, NaBr, $NaClO_2$). In sodium chlorite post-treatment all samples showed increasing WI_{CIE} due to the bleaching ability of sodium chlorite and probably the increase in whiteness is also due to the conversion of aldehyde groups to carboxyl groups (Toshikj *et al.*, 2019).

Milanovic and co-workers (Milanovic *et al.*, 2020) studied the natural, five-year aging of cotton yarns selectively oxidized with TEMPO. They state that yarns with high degree of oxidation, low but stable average molecular weight, showed an increased yellow index, but the mechanical strengths were maintained at post-oxidation values regardless of the degree of oxidation acquired.

5. Conclusions

Today, cellulose is the most widely available biopolymer in the world, and cotton together with viscose is the most commonly used textile material in the textile industry, due to its excellent physico-chemical and mechanical properties. As a biomaterial, cotton cellulose can participate in a number of chemical, biochemical reactions that give it functional properties so much in demand in biomedical applications, such as antimicrobial, hemostatic, modulating dressings for healing and odor absorption of purulent wounds, surgical sutures, gauze, diapers, tampons, carrier matrix for controlled release of drugs, in tissue engineering. But last but not least, a functionalized form of cotton can contribute to the greening of dyeing operations and can give multiple functions to a textile material, it can allow dyeing with dyes from dye classes other than the established ones.

The present work describes one of the most important oxidation reactions frequently used in recent years, the selective oxidation reactions with periodate and TEMPO, which have an increased regioselectivity for the secondary, respectively primary hydroxyl groups in the AGU of cellulose. Depending on the oxidizing agent used, carboxylic and/or aldehydic groups are generated by substitution of the hydroxyl groups in the 6-position of the carbon of the pyranose ring by carboxylic groups when using oxidizing agent TEMPO, or a selective cleavage of the vicinal diols in the C2 and C3 positions of the AGU occurs, generating two reactive aldehydic groups on the AGU, forming DAC.

Combination of periodate oxidation with the oxoammonium cations formed during TEMPO oxidation results in TCC.

The reaction conditions strongly influence the course of oxidation reactions, so mild reaction conditions should be chosen to favour the formation of DAC and TCC, respectively, and to limit the development of side reactions. In terms of reaction parameters, the selective periodate oxidation of cotton fabric should be conducted in slightly acidic medium (pH=3-6), temperature ranges from room temperature, 20 - 25ºC, which is usually associated with longer reaction times (12, 24 hours) to 30ºC - 60ºC with reaction times ranging from 30 minutes - 6 hours. In the case of textile materials, the concentrations of periodate used vary between 0.02-0.09 mol/L. Any increase in periodate concentration above 0.1 mol/L leads to significant loss of cellulosic substance, degradation of the structure, affecting the crystallinity and mechanical strength of textile materials.

The paper focuses on the description of reaction mechanisms, kinetics of oxidation reactions, reaction conditions, and analytical and instrumental techniques used to determine the content of newly formed aldehyde and carboxyl groups in cellulose fibres oxidized with periodate and/or TEMPO, but also instrumental techniques giving information on the degradation of cellulose fibres (DP, XRD - crystallinity index, mechanical resistances, SEM electron microscopy) and on the effects obtained after oxidation (iodine sorption number, hydrophilicity, water retention and whiteness degree).

The analytical methods by volumetric titration (oximetric, iodometric, tetrazolium, cupric index, Ca-acetate-NaOH, Ca-acetate-EDTA, MB), conductometric titration provide an estimation of the content of aldehyde and carboxyl groups, they must necessarily be correlated with spectroscopic methods FTIR-ATR, UV-VIS spectrophotometric, X-ray diffraction (XRD), determination of the DP, etc., in order to be able to provide a conclusive overview of the progress and effects conferred to cellulosic cotton by selective oxidation reactions.

If at the molecular level the mechanisms and kinetics of oxidation reactions are well known, the same cannot be said about the influence of selective oxidation on the morphological structure of cotton cellulose, because there are controversies between the opinions on the effect of the amorphous and crystalline regions. The future of scientific research related to the selective oxidation of cellulose textile materials lies in the optimization of the oxidation process in the direction of minimal fibre crystallinity damage in order to obtain multifunctionalized textile materials with long-lasting or disposable use.

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REVIEW - FUNCȚIONALIZAREA CHIMICĂ A MATERIALELOR TEXTILE CELULOZICE DIN BUMBAC PRIN OXIDARE SELECTIVĂ

(Rezumat)

Acest studiu documentar prezintă posibilitățile de oxidare selective mediate de periodat de sodiu sau potasiu și/sau de 2,2,6,6-tetrametilpiperidin-1-oxil (TEMPO) ale materialelor textile din bumbac, mecanismele de reacție, aprecierea și modul de determinare analitică și instrumentală a gradului de oxidare ale grupărilor hidroxilice din pozițiile C2, C3 și C6 a unității AGU cu grupări aldehidice/carboxilice. Se prezintă efectele oxidării selective asupra structurii moleculare și morfologice ale celulozei, deoarece oxidarea în funcție de condițiile de reacție poate afecta semnificativ atât zona amorfă, cât și zona cristalină a celulozei, la nivel de microfibrile, ceea ce conduce la scăderea rezistențelor mecanice, fapt nedorit în cazul materielor textile cu utilizare îndelungată sau chiar de unică folosință. Oxidarea selectivă în acest caz este un compromis între funcționalitate (exprimat prin conținutul de grupări aldehidice/carboxilice) și degradarea moderată a structurii moleculare și morfologice a celulozei din bumbac.