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OXYCELLULOSE – MATERIAL FOR NEW APPLICATION AREAS

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Abstract: In this paper, the principles of the action of the selective ($NaIO_4$ and 2,2,6,6-tetramethylpiperidine-1-oxyl-TEMPO radical) and non-selective (H_2O_2 and $KMnO_4$) oxidation agents on cellulose are presented. Their importance in modifying the existing properties or giving new properties to cellulosic materials, as well as examples of their applications are also given. The oxidation product - oxycellulose presents the base for obtaining a wide range of materials for special applications. Particularly, the influence of TEMPO-mediated oxidation on natural and man-made cellulosic fibers is presented, with a detailed overview on the type and quantity of introduced functional groups, changes in structure, sorption and mechanical properties. Also, we described the use of TEMPO-mediated oxidation for the production of cellulosic nano-materials in the form of dispersions, particles and films, as well as the potential application of these nano-structural materials.

Keywords: Cellulose fibers, oxycellulose, TEMPO-mediated oxidation, new properties, nano-cellulose.

1. INTRODUCTION

Cellulose presents the most abundant organic compound available today on the Earth, generated in an annual rate of about 10^{12} tons. It is produced by nature like woods from the forest, soft plants, seed hairs of the cotton plant and bacterial cellulose. About 33% of all plant matter is cellulose (the cellulose content of cotton is about 90 % and that of wood is 40-50%) [1,2]. Cellulose was first isolated from plant material and its chemical composition was determined by the French chemist Anselme Payen in 1838 [3]. For millennia, cellulose has provided mankind with a functional, low cost and renewable raw material (in the form of intact wood and natural textile fibers, or in the form of paper and board) [4]. On the other hand, cellulose is a versatile starting material for subsequent chemical modification, aiming at the preparation of new type of cellulose based polymers, with advances in performance, so-called „biopolymers for the future", to be used in many areas of industry and domestic life [1]. One of the most interesting types of cellulose is nano-cellulose, due to its special properties and promising applications.

Among the numerous ways of chemical modifications, the oxidations of cellulose materials are commonly used procedures, because oxidation can improve existing properties or provide new, special properties to cellulose substrates. The oxidation product − oxycellulose presents the base for obtaining a wide range of materials for special applications [5].

This paper gives an overview of the principles of the action of the selective oxidation (with sodium-periodate and 2,2,6,6-tetramethylpiperidine-1-oxyl-TEMPO radical), as well as the non-selective oxidation (with hydrogen-peroxide and potassium-permanganate) agents on cellulose substrates. Importances of oxidative processes in modifying the existing properties or giving new properties to cellulosic materials, as well as examples of their applications are also given. Emphasis is placed on the influence of TEMPO-mediated oxidation on natural (cotton and hemp) and man-made cellulosic fibers (lyocell), with a detailed overview on the type and quantity of introduced aldehyde and carboxyl

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functional groups, changes in structure, sorption and mechanical properties. Also, we described the use of TEMPO-mediated oxidation for the production of cellulosic nano-materials in the form of dispersions, particles and films, as well as the potential application of these nano-structural materials.

2. OXIDATION OF CELLULOSE

It is known that cellulose is a linear, syndiotactic polymer and molecular structure of cellulose is made up of D-glucopyranose ring units linked together via β-(1,4) glycosidic bonds where two neighboring D-glucopyranose rings are rotated by 180 degrees with respect to each other to form cellobiose, which is the basic chemical unit of a cellulose molecule, in their lowest energy configuration. The pyranose rings are in the $^4C_1$ conformation, which means that the $–CH_2OH$ and $–OH$ groups as well as glycosidic bonds are all equatorial with respect to the mean planes of the rings (Figure 1). Cellulose fibers can be made up of about 10,000 anhydroglucose units (AGUs), depending on the origin of cellulose [6]. In cellulose polymers, the ends of each chain are chemically different; i.e. the hydroxyl groups at both ends of the cellulose chain show different behavior. One end is non-reducing with a pendant hydroxyl group, and the other has reducing properties, with a chemically reducing functionality [7,8].

In each anhydroglucose units within the cellulose chain, there are three hydroxyl groups: a primary group at C6, and two secondary groups at C2 and C3 which are located in the plane of the ring. As a result of the inductive effect of adjacent substituents, the acidity and tendency toward dissociation grow in the order: HO6 < HO3 < HO2 [9]. The interaction of these three hydroxyl groups and the ring-oxygen within the chain or between neighboring cellulose chains results in a vivid network of hydrogen bonds which has a significant effect on the properties and reactivity of cellulose [10]. The strong intra- and intermolecular hydrogen bonds network has a significant effect on the properties and reactivity of cellulose [10]. The three hydroxyl groups of the cellulose molecule can undergo chemical reactions common to all primary and secondary alcohol groups, such as esterification, nitration, eterification and oxidation [11]. Depending on which hydroxyl groups are affected by oxidizing agents, the oxidation processes are divided as non-selective and selective. The oxidation of cellulose presents a pivotal reaction in its functionalization and application providing more active sites on the cellulose chains and impart special properties to the cellulose fibers [12,13]. Oxidation is the only procedure that renders cellulose bioabsorbable in men [11].

2.1. Selective cellulose oxidation

Two methods that are nowadays frequently employed for the selective oxidation of cellulose substrates are TEMPO-(2,2,6,6-tetramethyl-piperidine-1-oxyl)-mediated oxidation [14] and periodate oxidation [15]. Although, both the TEMPO-mediated oxidation and periodate oxidation present selective forms of oxidation, they have different principles of the action and affect different hydroxyl groups in the glucose subunit (Figure 2).

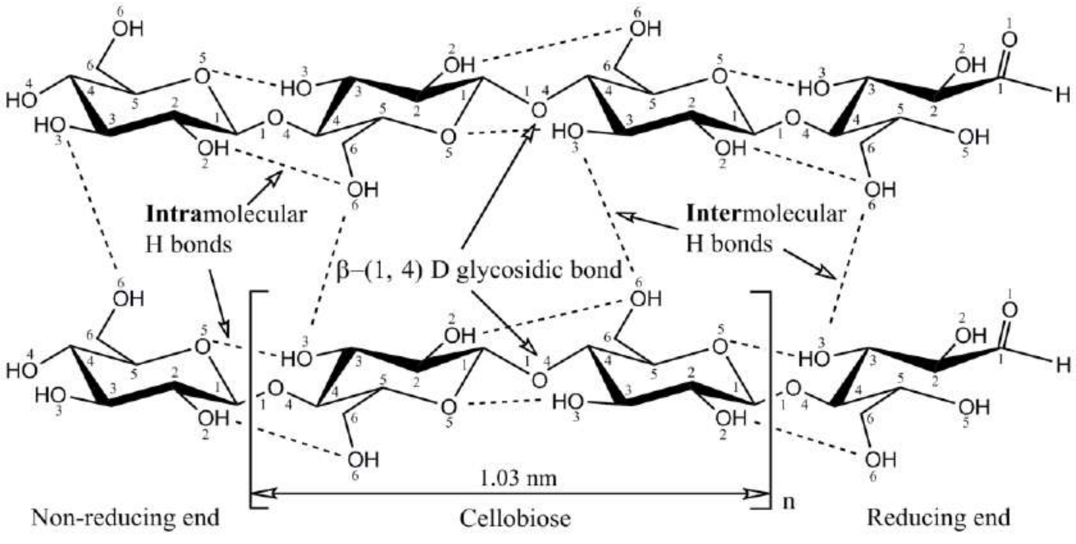


Figure 1. Molecular structure of cellulose and inter- and intra- molecular hydrogen bond formation in cellulose. Figure modified from the literature [8]

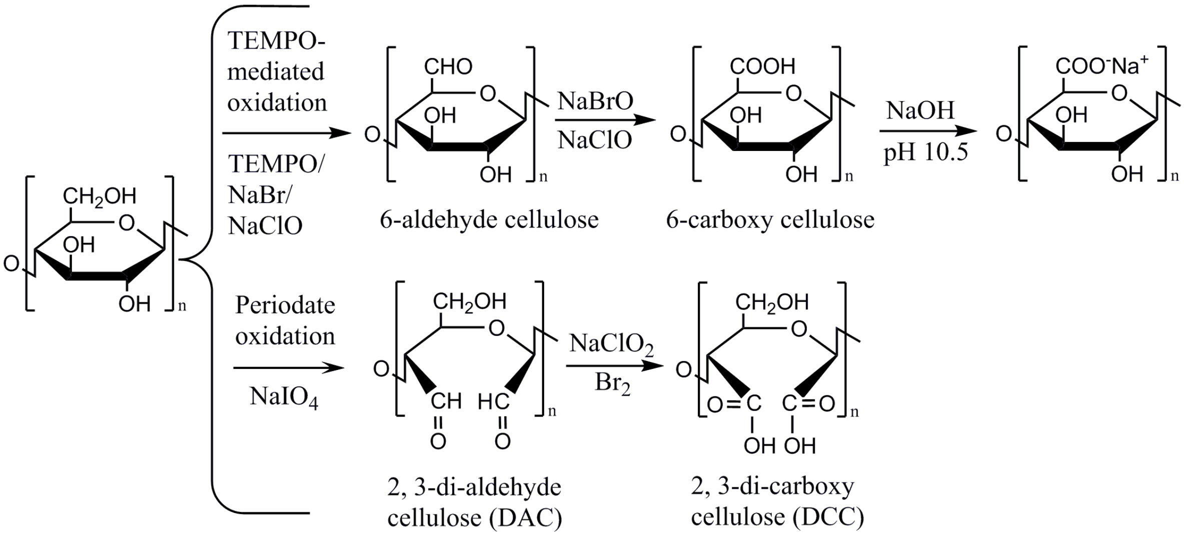


Figure 2. Scheme of selective TEMPO-mediated and periodate oxidation of cellulose. Figure modified from the literature [16]

TEMPO-mediated oxidation (shortly TEMPO oxidation) is the established name for the catalytic and selective oxidation of primary hydroxyl groups at C6 of carbohydrates, using stable 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), NaBr and NaClO, by which aldehyde and carboxyl functional groups can be introduced into solid polysaccharides [14, 17-20]. The nitroxyl radical affects the oxidation from the alcohol to the aldehyde oxidation state, while the hypobromide generated *in situ* from hypochloride and bromide performs the further oxidation of the aldehyde to the carboxylic acid [17-19]. The traditional method for the introduction of carboxyl groups at the C6 atom of anhydroglucopyranose units of cellulose by nitrogen dioxide [21], has been now completely replaced by the TEMPO-oxidation, due to numerous advantages such as: high reaction rate and yield; high selectivity; catalytic process, just modest degradation of polysaccharides throughout the process, and only inexpensive NaClO and NaOH are consumed as the oxidation proceeds [19, 22].

Various TEMPO oxidation systems and conditions have been applied to cellulose substrate in terms of region-selectivity at the C6 primary hydroxyls, oxidation efficiency and utilization of non-chlorine primary oxidants [14]. Saito and Isogai published a series of paper about the TEMPO-oxidation of cellulose under alkali conditions [18−20], and it was shown that efficient conversion of primary hydroxyl groups to carboxyl groups, via aldehydes groups, occurred by the TEMPO/NaBr/NaClO system at pH 10.5. Scheme of the selective TEMPO-oxidation at pH 10.5 is shown in Figure 2. In the case of oxidation of native cellulose, even under harsh oxidation conditions, almost no or only small amounts of water-soluble products were obtained, while oxidation of regenerated celluloses leads to water-soluble oxidized products, because regenerated celluloses are much more reactive toward TEMPO oxidation, mainly due to higher accessibility of cellulose II crystal structure (regenerated and mercerized cellulose) as compared to cellulose I (native cellulose) [14, 23, 24]. At alkaline pH, together with the oxidative process, depolymerization mechanism, i.e. β-elimination of glycoside bonds at the C6 aldehyde groups formed as intermediate structures, also occurred [14, 17, 25]. In order to avoid β-elimination reaction and protect low molecular weight compounds during TEMPO oxidation, Isogai and Hirota have been proposed TEMPO/NaClO/$NaClO_2$ oxidation systems as an alternative, where catalytic amounts of TEMPO and NaClO are combined with $NaClO_2$ as the primary oxidant, under aqueous conditions at pH 3.5–6.8 [26]. Even though times required for the oxidation are longer than those with the TEMPO/NaBr/NaClO system, the corresponding carboxyl compounds can be obtained in higher yields by the TEMPO-mediated oxidation under neutral conditions. The same oxidation system under neutral conditions was applied on cellulose fabric in order to enhance its ability to bind Cu^{2+} ions [27].

Aware of the importance of environmental protection, a lot of effort has been invested in finding the TEMPO-oxidation system without using harmful reagents. For this purpose an interesting approach is the use of enzymes, e.g. oxidase and peroxidase, using oxygen and hydrogen peroxide, respectively, as primary oxidizing agents. This technology is used for polysaccharide oxidation. Viikari et. al. [28] have published the results of oxidation of starch and cellulose with the TEMPO/laccase/oxygen system. The efficiency of laccase-TEMPO treatment on the sisal cellulose fibers was also investigated [29].

Periodate oxidation is one of the rare examples of highly selective reaction for cellulose modification [30]. This reaction cleaves the C2-C3 bond in the glucopyranoside ring and the adjacent hydroxyl groups at these positions are converted to aldehydes producing dialdehyde cellulose. The resulting aldehyde compound 2,3-di-aldehyde cellulose (DAC) can be further converted to 2,3-di-carboxyl cellulose (DCC) [15, 30], or imines (Schiff bases) with primary amines, which can serve as useful intermediates for cellulose-based specialty materials, such as an adsorbent of heavy metal enzyme [31], amino polysaccharides or dye [32], which broadens the range of applications of oxidized cellulose [15]. The significant advantages of periodates over other oxidizing agents is that they minimize degradation and retain the mechanical and morphological properties of the starting material, as well as the conversion of 1,2-dihydroxyl (glycol) groups to paired aldehyde groups occurs without significant side reactions [15, 32].

2.2. Non-selective oxidation of cellulose

Hydrogen peroxide and potassium permanganate are well known nonselective oxidizing agents for cellulose substrates. These non-selective oxidative agents affect all three hydroxyl groups present on C2, C3 and C6 atoms in the glucopyranoside ring and the hydroxyl groups at these positions can be converted to aldehyde or carboxyl groups [33]. Additionally, hydrogen peroxide and potassium permanganate are capable of oxidizing low molecular impurities on natural cellulose fiber surfaces that are particularly important in the case of bast cellulose fibers, thus obtaining not only greater whiteness, but also eventual surface cleaning and removing of lignin and hemicelluloses, and oxidation of available functional groups of fibers. By changing the parameters of the oxidation (concentration of oxidizing agents, pH, reaction time and temperature) it is possible to obtain cellulose fibers with a different amount of introduced aldehyde and carboxylic groups. Although non-selective oxidations are more difficult to control, they still have a wide application in the field of cellulose modification, because they are significantly cheaper than selective oxidations and they are more easily performed [33,34].

3. PROPERTIES AND APPLICATIONS OF TEMPO OXIDIZED NATURAL AND MAN-MADE CELLULOSE FIBERS

Over the past 10 years, growing interest over the modification of cellulose fibers has led researchers to focus on enriching the functional group amount of cellulose fibers by chemical oxidation. Oxidative functionalities are one of the prime factors which determine macroscopic properties and chemical behavior of cellulose materials. The carbonyl and carboxyl groups have effect on numerous macroscopic properties of cellulose, such as: surface charge density, strength properties, metal ion retention, water retention and wettability, yellowing, aging, cross-linking, brightness reversion, acidification, instability towards alkali, etc. [25]. Functional groups, introduced in cellulose substrate by oxidative processes, can be used directly because of their special properties or they can be used as reactive “chemical hooks” for further chemical modification.

3.1. TEMPO-mediated oxidized natural and man-made cellulose fibers

In the case of native cellulose (cellulose I); cellulose pulp from wood and plants, cotton linters and holocellulose from spruce, were widely investigated as a substrate in TEMPO oxidation [18-20, 35-38], while TEMPO oxidation of cellulose fibers, such as cotton, lyocell, hemp, sisal, jute and ramie, has been investigated in smaller scope [39-43]. As we mentioned previously, Saito and Isogai have been publishing papers about application of TEMPO oxidation on native cellulose and concluded that introduced functional groups must be present on crystal surfaces and in disordered regions with quite high densities [18-20]. Moreover, solid-state 13C-NMR and X-ray diffraction analyses revealed that the carboxyl and aldehyde groups introduced into the TEMPO-oxidized celluloses were mostly present at the C6 position of only the surfaces of cellulose I crystallites or surfaces of cellulose microfibrils without any oxidation at the C6 primary hydroxyl groups of inside cellulose I crystallites of cotton linters [44]. When regenerated and mercerized, celluloses (cellulose II) are used as a substrate in TEMPO oxidation, water-soluble β-1,4-linked polyglucuronic acid sodium salt (cellouronic acid) having the homogeneous chemical structure that can be obtained quantitatively as the oxidized products [45]. TEMPO-mediated oxidation was also applied on cellulose III samples, and it was concluded that TEMPO oxidation was highly selective for primary hydroxyl groups, whereas secondary hydroxyl groups were in most cases insensitive toward oxidation [46].

In this paper, cotton and hemp fibers, as natural cellulose fibers, and lyocell fibers, as a man-made cellulose fiber, were chosen for discussing the influence of TEMPO-mediated oxidation on properties of natural and man-made cellulose fibers.

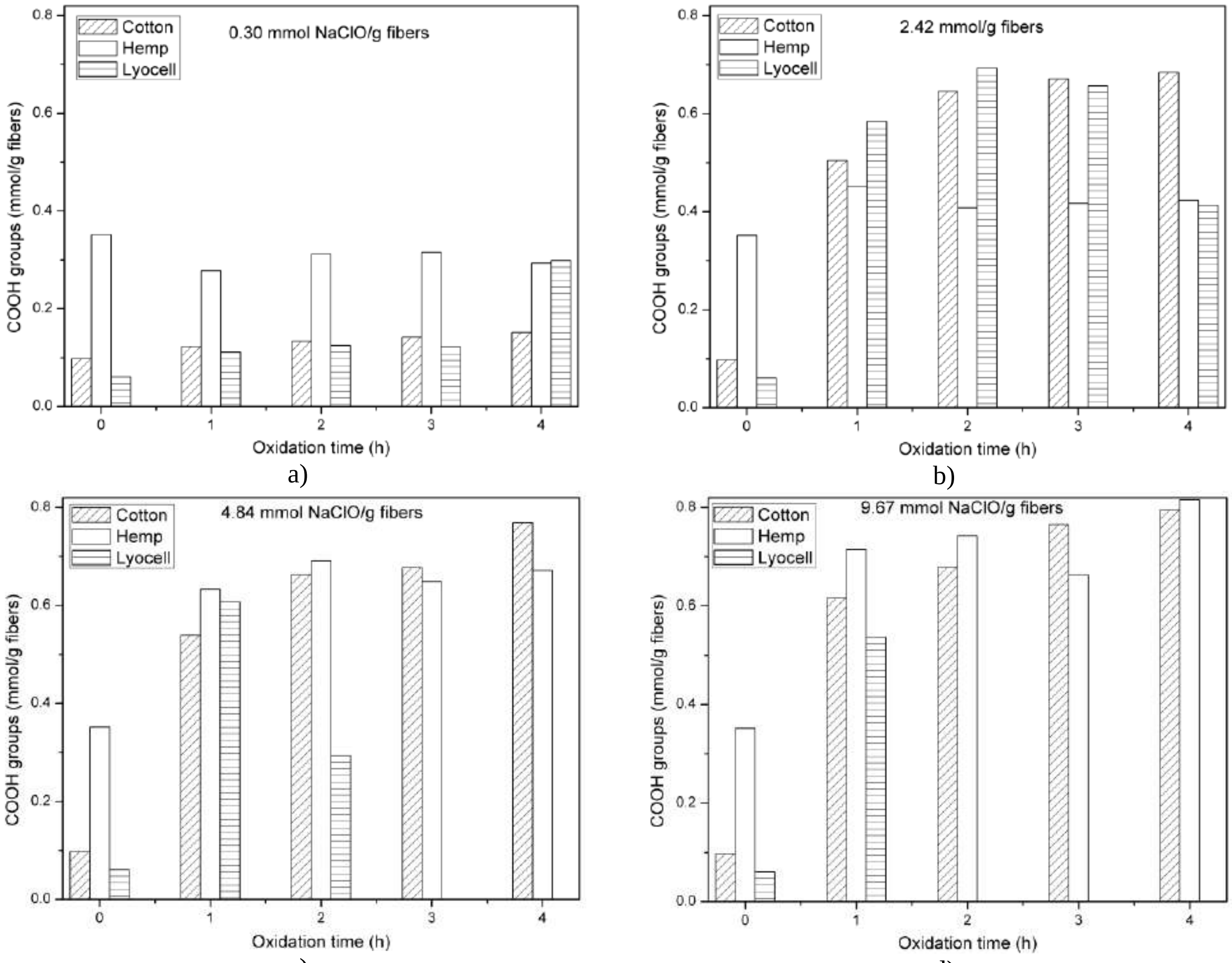
By changing the oxidative conditions (0; 0.30; 2.42; 4.84 and 9.67 mmol of NaClO/g cellulose, 0.25–4 h, pH 10.5), significant amounts of aldehyde and carboxyl groups can be introduced into cellulose fibers. The amount of introduced aldehyde groups in cotton and hemp fibers was increased by factor 12.5 and by factor 6.4, respectively, while for the lyocell fibers this increase was 15, depending of oxidative conditions (factor = $CHO_{max}/CHO_{unmodified}$ fibers) [39, 41]. The formation of new aldehyde groups in oxidized cellulose fibers is due to alcohol conversion to the aldehyde oxidation state that is affected by the nitroxyl radical, as well as due to reducing ends formed from glycoside bonds by β-elimination at pH 10.5 and other depolymerization reactions during the oxidation [14, 24, 44]. Significant amounts of aldehyde groups present in all oxidized fibers, even after the 4 h oxidation, can be explained according to Saito and Isogai [19, 39] by formation of intra- and inter-molecular hemiacetals with cellulose hydroxyls in the solid water-insoluble fractions, which are likely to have high resistance to the next TEMPO-mediated oxidation step (i.e. converting to carboxyl groups) by steric hindrance.

The amount of introduced carboxyl groups in cotton, hemp and lyocell fibers is presented in Figure 3. TEMPO-mediated oxidation, applied under various conditions on cellulose fibers, leads to increase of carboxyl groups amount, due to the further oxidation process, i.e. the CHO groups conversion into COOH groups, that is determined by the amount of NaClO.

The carboxyl group amounts in oxidized cotton fibers increased for all oxidative conditions, in the range from 0.123 to 0.795 mmol/g cellulose, compared to COOH group amount in unmodified cotton fibers (0.097 mmol/g fibers). The maximum carboxyl group amount (0.795 mmol/g cotton) was obtained for the cotton fibers oxidized with 9.67 mmol NaClO/g cellulose during 4 h [39].

In the case of TEMPO-mediated oxidation of hemp fibers, the results obtained for carboxyl groups amount show decrease in COOH groups amount, for two lower concentrations of primary oxidant (Figure 3a and 3b), mainly due to the fact that a part of NaClO was consumed in oxidation and degradation of noncellulosic components in hemp fibers, while remaining oxidant was not sufficient for significant conversion of aldehyde to carboxyl groups. Oxidization with higher concentrations of NaClO/g fibers (Figure 3c and 3d), leads to increase of carboxyl groups amount during oxidation time up to 1 and 2 h, respectively, and later with prolonged oxidation time, decreased slightly to the lower value. The highest value of carboxyl group amount in oxidized hemp fibers is obtained for the sample oxidized during 4 h with 9.67 mmol NaClO/g fiber (0.815 mmol/g fibers), probably because of the more “opened and accessible structure” of hemp fibers to the oxidant after removal of a significant amount of non-cellulosic components [41].

Lyocell fibers, as a regenerated cellulose fibers, are much more reactive toward TEMPO-mediated oxidation, compared to natural cellulose fibers [39, 47], due to the lower crystallinity index and less complex fine and micro structure than natural cellulose fibers, as well as higher accessibility of cellulose II crystal structure (regenerated and mercerized cellulose) as compared to the cellulose I (native cellulose) [14, 24, 44]. When oxidation of lyocell fibers is applied in the presence of the lowest amount of NaClO (Figure 3a), the carboxyl group amount increased with prolonged oxidation time. In the case of lyocell oxidation in the presence of higher amount of oxidative agent (Figure 3b and 3c), carboxyl group amount increased with prolonged oxidation up to 2 and 1 h, respectively, and after reaching the maximum decreased slightly in the case of oxidation with 2.42 mmol NaClO/g cellulose, and very sharply in the presence of 4.84 mmol NaClO/g cellulose. That decrease in carboxyl amount in oxidized lyocell fibers can be explained by dissolution of highly oxidized cellulose fractions. In the case when oxidized lyocell fibers should have textile application, the oxidation should not be applied under severe conditions ((Figure 3d)) because of loosing fibrous structure of oxidized lyocell fibers. The highest value of carboxyl amount in oxidized lyocell fibers (0.693 mmol/g fibers) was obtained for the sample oxidized with 2.42 mmol NaClO/g fiber, during 4 h.



a) b)

c) d)

Figure 3. Carboxyl groups amount in oxidized cotton, hemp and lyocell fibers were a) 0.30, b) 2.42, c) 4.84 and 9.67 mmol of NaClO/g fibers was applied to the cellulose slurry, during 1−4 h, at room temperature and pH 10.5

Functional groups amount in different TEMPO oxidized cellulose substrates is shown in Table 1. The oxidative conditions are available in literature given in Table 1.

Introduction of functional groups into cellulose fibers by the TEMPO-mediated oxidation, has considerable influence on the fibrous morphology, sorption and mechanical properties of cellulose fibers and therefore, on their reactivity, quality and usage. Additionally, in the case of oxidation of bast cellulose fiber, a significant simultaneous removal of lignin and hemicelluloses can be achieved. For TEMPO-oxidized hemp fibers, the removal of lignin was up to 77.09%, and hemicelluloses removal was up to 62.61%. Hemp fibers with a reduced content of lignin and hemicelluloses were also finer and with improved water uptake behavior, characterized by moisture sorption and water retention value. The maximum value of 8.45% (ratio $w_{mod}/w_0 = 1.16$) is obtained for hemp fibers with introduced maximum carboxyl group amount [41]. The results are in agreement with those obtained for TEMPO-oxidized cotton fiber (a maximum value of 8.97%, ratio $w_{mod}/w_0 = 1.55$) that is expected result, as both oxidized fibers belong to the group of natural cellulose fibers [39]. Moisture sorption of oxidized lyocell fibers is in the range from 9.59% to 20.58% [47].

Important properties of cellulose fibers are their interactions with liquid water which results in swelling of fibers, mainly due to the wide expansion of amorphous regions [39, 48]. The water retention value (WRV) of the TEMPO-oxidized cotton and hemp fibers increased with increasing NaClO charge and oxidation times approaching a maximum value of 85.4% and 125.41%, respectively, for both fibers oxidized under the most severe conditions, with introduced maximum carboxyl group amount. Water retention values of the TEMPO-oxidized lyocell fibers changed from 34.1% to even about 335%, depending of oxidation conditions. The maximal increase of WRV (335.3%) is due to significant morphological changes from fibrous forms to short fragments and losing the fibrous structure of lyocell under severe conditions of TEMPO-mediated oxidation [39,41,47].

As a result of dissolving accessible cellulose fractions and the changes in fibrous morphology during the oxidative treatment of cellulose, TEMPO-oxidized cotton, hemp and lyocell fibers have lower accessibility compared to unmodified fibers, as it was confirmed by determination of the iodine sorption value [39,41,47].

The application of too severe conditions of TEMPO-mediated oxidation results in loss of fibrous forms. In the case when preservation of fibrous structure of oxidized cellulose fibers is also important, oxidation should be conducted at milder conditions.

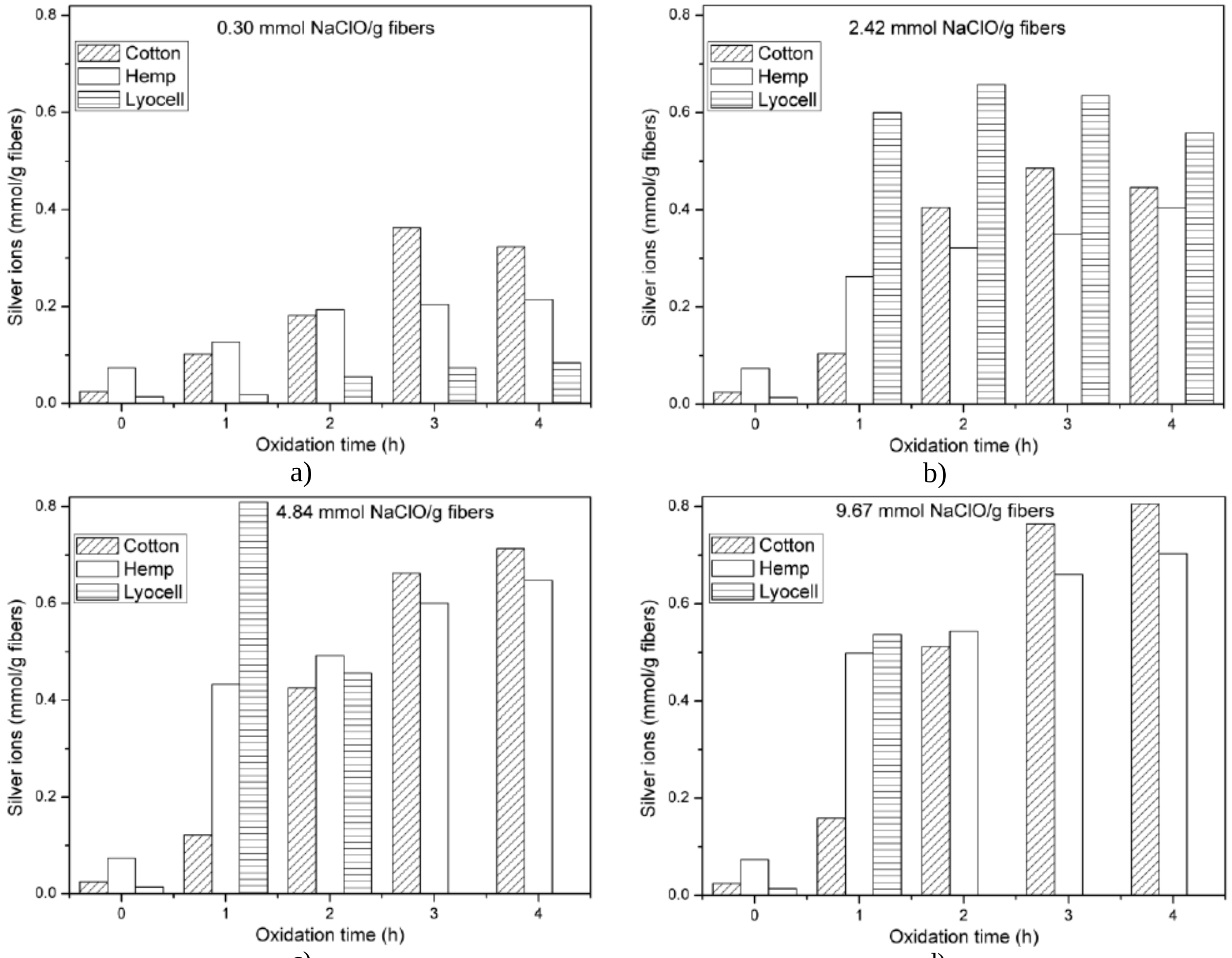
Table 1. Functional groups amount in different TEMPO oxidized cellulose substrates. Applied oxidation conditions are available in the literature

Oxidized cellulose substrate	COOH and CHO, mmol/g cell	Comments	Ref.
Softwood	1.65 and 0.07	Aldehyde amounts of the all oxidized celluloses in this study ranged from 0.0 to 0.07 mmol/g; more than 90% of the oxidized groups were carboxyl.	[38]
Hardwood	1.69 and 0/00	In this study, the TEMPO-mediated oxidation treatment with excess NaClO continued up to 5 h for all the samples.	[38]
Sulfite pulp	0.92 and 0.29	A significant increase in water retention value has been observed for sample oxidized to carboxyl amounts above 0.7 mmol/g; TEMPO oxidation clearly helps the cellulose disintegration process, by electrostatic repulsions between microfibrils, where significant amounts of carboxyl groups were introduced.	[37]
Spruce holocell	1.16 and 0.09	Neither crystallinity nor crystal size of cellulose I of the original native celluloses was changed under the conditions adopted in this study.	[35]
Cellulose III	DO=0.39	Oxidation of cell III samples is highly selective for primary OH, whereas secondary OH groups were in most cases insensitive toward oxidation. The carboxyl groups amount is given as degree of oxidation (DO) Cellulose III was obtained from rayon.	[44]
Cotton linters	0.7 and 0.3	Selective oxidation occurred on crystal surfaces and in disordered regions of cellulose; Water retention values increase from 60% to 280%.	[18]
Cotton fibers	1.36 and 0/00	Aldehyde groups in the TEMPO-oxidized celluloses were mostly converted to carboxyl groups under the conditions used in this study.	[38]
Cotton yarn	0.667 and 0.124	Samples with this amount of functional groups exhibited the highest immobilized trypsin content of 6.5 mg/g of dried cotton yarn and activity of 5.03 U/g, i.e., 30.6% of the total initial activity of trypsin in solution, corresponding to 94% activity retention.	[40]
Cotton fabric	0.76 and 0.33	For samples with this amount of functional groups, total amount of subsequently deposited Cu after reduction was 225 μmol/g.	[27]
Sisal	108 and -; (meq/g)	The laccase–TEMPO treated pulp exhibited the highest yield in carboxyl groups (a 30% increase relative to the control pulp).	[42]
Hemp	0.815 and 0.415	By TEMPO oxidation of hemp fibers, a significant removal of lignin (up to 77.09%) and hemicelluloses (up to 62.61%) from hemp fibers was achieved.	[41]
Jute	/	The introduced COOH groups were used to prepare cellulose–silver nano-composites using silver nitrate and TEMPO oxidized jute fibers without any reducing reagents by microwave heating.	[43]
Ramie	0.94 and 0.25	TEM observations confirmed that the microfibrillar nature as well as the original fibrous forms of the native celluloses was mostly maintained, even though significant amounts of functional groups (carboxyl and aldehyde groups) were introduced by the TEMPO-mediated oxidation.	[35]
Lyocell	0.7 and 0.634	Moisture sorption of oxidized lyocell fibers was in the range from 9.59% to 20.58%. The water retention value of the TEMPO-oxidized lyocell fibers changed from 34.1% to even about 335%, depending on oxidation conditions.	[39] [47]

3.2. Antimicrobial fibers based on TEMPO-oxidized cellulose fibers

Textile fibers with antimicrobial properties should protect customers and disable the growth or directly destroy many pathogens that cause numerous diseases and infections in hospital environments as well as in daily life [49]. On the TEMPO-oxidized cotton, hemp and lyocell fibers with improved sorption properties, the antimicrobial properties can be accomplished by different metal ions sorption (silver, copper, zinc ions, etc.) [27,47,49]. Due to special characteristic of silver ions, such as possessing of both antibacterial and antifungal activity, and the fact that bacteria are not able to develop their resistance to the silver, as in the case of antibiotics, the silver ions have been established as the most commonly applied agent in today's antimicrobial application areas [49].

Figure 4 shows the result obtained for silver ions sorption on TEMPO-oxidized cotton, hemp and lyocell fibers. The unmodified cellulose fibers sorbed the lowest amount of silver (0.024 mmol/g cotton fibers; 0.074 mmol/g hemp fibers and 0.014 mmol/g lyocell fibers), compared to oxidized cellulose fibers [47,50,51]. Changes in fiber morphology, together with introduced hydrophilic carboxyl groups, cause improvement in sorption properties (water retention and moisture sorption) of TEMPO-oxidized cellulose fibers that positively affect subsequent silver sorption by TEMPO-oxidized cellulose fibers. In all cases, where TEMPO-mediated oxidation was applied, the increase in the silver sorption by oxidized cellulose fibers was obtained, ranging for cotton fibers from 0.102 to 0.806 mmol/g fibers; for hemp fibers: from 0.127 to 0.703 mmol/g fibers; and for lyocell fibers: from 0.018 to 0.809 mmol/g fibers. The obtained results show that silver sorption by modified cellulose fibers generally increased with increasing either primary oxidant concentration or the duration of oxidation. The effect of reaction time on the silver content is more pronounced than the effect of the concentration of primary oxidant, especially in the case of higher NaClO concentrations (4.84 and 9.67 mmol NaClO/g fibers) [47,50,51].



a) b) c) d)

Figure 4. Silver ions amount in oxidized cotton, hemp and lyocell fibers were a) 0.30, b) 2.42, c) 4.84 and 9.67 mmol of NaClO/g fibers was applied to the cellulose slurry, during 1−4 h, at room temperature and pH 10.5.

The antimicrobial activity of the silver loaded TEMPO-oxidized cotton, hemp and lyocell fibers was confirmed against different pathogens: *C. albicans* (ATCC 24433), *S. aureus* (ATCC 25923) and *E. coli* (ATCC 25922), among them the Gram-positive bacterium *S. aureus* is the most sensitive to all silver-loaded TEMPO-oxidized cellulose fibers (Table 2). Although, there is no clear dose dependant antimicrobial activity, the quantity of bonded silver ions, in all cases, is enough to develop desirable antimicrobial activity in the silver-loaded TEMPO-oxidized cellulose fibers [47,50,51].

Table 2. The antimicrobial activity of silver-loaded TEMPO-oxidized cotton, hemp and lyocell fibers [47, 50, 51]

Samples	COOH group, mmol/g fibers	Silver, mmol/g fibers	Width of the inhibition zone after 24 h (mm)		
			S. aureus	*E. coli*	*C. albicans*
Unmodified Cotton fibers + silver	0.097	0.024	In contact	In contact	In contact
Unmodified Hemp fibers+ silver	0.352	0.074	1 – 1.5	1 - 1,5	1 – 1.5
Unmodified Lyocell fibers+ silver	0.061	0.014	2.0 – 2.5	1.5	2.5
Oxidized Cotton* + silver	0.768	0.714	2	2	1
Oxidized Hemp** + silver	0.671	0.648	4	1.5 - 2	3 – 3.5
Oxidized Lyocell*** + silver	0.584	0.600	3.5 – 4.0	2.5	3.0

* Cotton fibers oxidized with 4.84 mmol NaClO/g fibers, during 4h
** Hemp fibers oxidized with 4.84 mmol NaClO/g fibers, during 4h
*** Lyocell fibers oxidized with 2.42 mmol NaClO/g fibers, during 1h

Another example of TEMPO-oxidized cellulose application for obtaining antimicrobial cellulose materials is *in situ* synthesis of Cu/Cu_2O nanoparticles. In this case, TEMPO/NaClO/$NaClO_2$ system was applied under neutral conditions for selective oxidation of cotton fabric to enhance its ability to bind Cu^{2+} ions and formation Cu/Cu_2O nanoparticles after Cu^{2+} ions reduction [27].

In order to preserve the structure of cellulose fibers i.e. their mechanical strength, authors of this study was focused on much shorter oxidation times compare to oxidation conditions applied by Errokh et al. (2016) [52]. The influence of functional aldehyde and carboxyl groups generated by TEMPO-mediated oxidation at cotton fabrics on the amount, activity and stability of *in situ* synthesized Cu/Cu_2O nanoparticles, was investigated. Table 3. shows relation between oxidation time and either carboxyl or aldehyde group amount in the oxidized fabrics as well as total amount of Cu after Cu^{2+}-ions reduction. The extension of TEMPO-mediated oxidation time led to an increase of carboxyl group amount. Consequently, larger amounts of Cu/Cu_2O nanoparticles were synthesized. However, all fabricated textile nano-composites independently of the chemical composition provided maximum reduction of *E. coli* and *S. aureus* bacteria colonies (reduction 99.9%), while antifungal activity was acceptable (reduction over 87.5 %). It was also shown that cotton fabrics impregnated with Cu/Cu2O nanoparticles ensured a controlled release of Cu^{2+} ions in physiological solution which is an imperative for infection prevention [27].

Table 3. Relation between oxidation time, carboxyl and aldehyde group amount in the oxidized fabrics, and total amount of Cu after Cu^{2+}-ions reduction [27]

Sample	Duration of oxidation (min)	Aldehyde amount (µmol/g)	Carboxyl amount (µmol/g)	Total amount of Cu after reduction (µmol/g)
1	15	169.9 ± 25.9	462.0 ± 9.2	175±17
2	45	230.4 ± 35.2	562.5 ± 49.2	219±22
3	180	334.6 ± 53.4	761.3 ± 48.8	225±22

3.3. TEMPO-oxidized cellulose fibers for tripsin immobilization

Immobilization of an enzyme could add new functionalities to a cellulose substrate. At the same time, it could solve significant problems regarding the use of native enzymes, such as their low stability. Cellulose materials, being nontoxic, non-carcinogenic, and biocompatible, are frequently used as carriers for immobilization of enzymes intended for therapeutic purposes such as proteases [53]. Among proteases, which are widely used for wound treatment, trypsin is a known wound cleanser which can be used to remove dead tissue from wounds, burns and ulcers [54].

Taking into account necrolytic, anti-inflammatory and drainage properties of trypsin, i.e., its ability to speed up growth of new tissue and skin grafts and to inhibit growth of some microorganisms, the obtained enzyme-active cellulose fibers could be used as bandages and dressings in wound treatment. Cellulose materials activated by periodate oxidation are the most frequently employed for trypsin immobilization [55-59]. A literature survey revealed a lack of information concerning the uses of TEMPO-oxidized cellulose as carrier for trypsin immobilization. Generally, the application of TEMPO-oxidized polysaccharide substrate for immobilization of an enzyme is investigated in a considerably small scope. TEMPO-oxidized cellulose fibers and microcrystalline cellulose were used as supports for the immobilization of horseradish peroxidase [60] and lipase [61], respectively, by adsorption. Covalent immobilization of trypsin was achieved on Sepharose bearing mainly aldehyde groups introduced by oxidation with a laccase-TEMPO system [62].

Nikolic and coworkers [40] used TEMPO-oxidized cotton fibers containing different amounts of carboxyl groups as well as fibers containing both carboxyl and aldehyde groups for trypsin immobilization through the ionic interaction or together with the Schiff's base formation, respectively. The higher activity of the immobilized trypsin and the higher stability were obtained with fibers containing both functional group types (Table 4). In particular, the cotton sample containing 0.1236 mmol/g CHO and 0.6671 mmol/g COOH groups (oxidized with 4.84 mmol/g NaClO during 180 min) exhibited the highest immobilized protein content of 6.5 mg/g of dried cotton yarn (32.5% of the initial protein content in trypsin solution) and activity of 5.03 U/g, i.e., 30.6% of the total initial activity of trypsin in solution, corresponding to 94% activity retention. According to the presented results, the immobilized activity determined for these fibers originated mostly from the covalently bound trypsin, which was supported by the results obtained for trypsin immobilization on periodate oxidized cotton fibers [63]. It was also shown that the amount and activity of trypsin immobilized on TEMPO-oxidized cotton was dependent not only on fibers' functional group type and content, but also on their accessibility, charge density, and functional group profiles in relation to the molecular weight distribution of the cotton fibers [40].

Table 4. Performances of trypsin immobilized on TEMPO and periodate oxidized cellulose fibers

Oxidation	TEMPO oxidation [40]		Periodate oxidation [63, 64]	
Carrier-group type	Cotton-CHO+COOH	Cotton-COOH	Cotton-CHO	Viscose-CHO (BSA)
Functional group content, mmol/g	0.1236+0.6671	0.7907	0.067	0.6446
Protein content, mg/g	6.5	6.7	6.1	7.6
Activity, U/g (R[a], %)	5.03 (94.15)	1.87 (34.03)	1.22 (46.03)	0.78 (22.32)
Activity retention,%	50.4	45.4[b*]	90.0	97.3

[a] R stands for "Retention of specific activity"
[b] Activity retention after storage at 4 °C for 60 days; [b*] for 30 days

3.4. TEMPO-oxidized cellulose fibers for obtaining nano-cellulose materials

A powerful TEMPO-mediated oxidation nowadays is applied, as the first step on the way to obtain both cellulose nano-fibrils (CNF) and cellulose nano-crystals (CNC) [14,65−68]. Cellulose particles with at least one dimension in nano-scale (1–100 nm) are referred to as nano-cellulose [14,69]. The obtaining of cellulose nano-fibrils from cellulose substrates can be achieved by three types of treatments: mechanical (e.g. homogenization, grinding, and milling); chemical (e.g. TEMPO-mediated oxidation); and by combination of mechanical and chemical treatments [70]. Although production of nano-fibrillated cellulose using only mechanical disintegration requires high energetic costs [71], researchers have applied chemical treatments as pre-treatments for obtaining nano-fibrillated cellulose. In order to decrease energy needed for cellulose fibrillation, the TEMPO-mediated oxidation is one of the most promising chemical pre-treatments. During the mechanical treatment, as a result of regioselective conversion of the primary hydroxyl groups via aldehydes to carboxyl, the nanofibrils within the fibers separate from each other more easily due to the repulsive forces between the ionized carboxyl which overwhelm the hydrogen bonds holding them together [14]. Depending on the type of mechanical and chemical disintegration techniques used, a large variety of CNF grades can be obtained.

In our laboratory, methods for the disintegration of TEMPO-oxidized cellulose fibers and production of nano-cellulose dispersions and nano-films were investigated (Figure 5).

Figure 5. Nano-cellulose dispersion and nano-cellulose film obtained from TEMPO-oxidized cellulose

One of the first applications of the obtained cellulose nano-materials was the reinforcement of paper and the restoration of artwork on paper, where promising results were obtained related to the application of nano-cellulose in this field (unpublished results). Our result confirms literature data, that the mechanical properties (high strength and stiffness) and the surface reactivity (with numerous hydroxyl groups), the specific organization, as well as the small dimensions of nano-cellulose well impart useful properties to materials reinforced with nano-cellulose fibers [72]. Nano-fibrillated cellulose, inheriting the properties of cellulose, can offer new excellent properties due to nano-scale effects, including high specific surface area, porosity, biodegradation, biocompatibility, unique optical properties, etc. [12,73], thereof nano-cellulose materials can be applied in so many different fields and some examples of their applications are:

- Water/wastewater treatment processes [74]
- Scaffolds [75]
- Packing [66, 76]
- Papermaking industry [77-80]
- For conservation of cultural heritages [81]
- Anti-microbial compounds[82]
- Nano-composite materials [83, 84]
- „Green” electronics [85]
- Colloid, solid films, emulsions, foams and aero gels [86].

The different types of products obtained from CNF are available in the form of: suspensions, powders, films, hydrogels, aerogels, nano-papers or films [69].

The quantitative characterization of the obtained material during conversion of microscopic fibers to CNF is a current issue for both scientific community and industry. Although some products based on nano-cellulose materials are available on the market [69], and even though a numerous papers with the topic of nano-cellulose as a promising material are available in scientific literature, there are still many challenges remaining to be overcome. Aimed to industrial applications of nano-cellulose materials, some progress should need to take place in the terms of controlling production of cellulose nano-materials and in order to become practicable, the procedures should be adapted to industrial conditions.

4. CONCLUSIONS

Cellulose is one of the most fascinating, renewable natural polymers produced by photosynthesis. Besides of providing mankind with a functional, low cost and renewable raw material (in the form of intact wood and natural textile fibers, or in the form of paper and board), the cellulose substrate presents versatile starting material for subsequent chemical modification, aiming at the preparation of new type of cellulose based polymers, with advances in performance, so-called ‘‘biopolymers for the future”. Among the numerous ways of chemical modifications, the oxidations of cellulose materials are quite frequent procedures, since they allow the cellulose substrate to be improved by existing ones or give new, special properties to cellulose substrates. A powerful TEMPO-mediated oxidation is nowadays frequently used oxidative procedure for selective introduction of new functional groups to cellulose substrates. The introduced functional groups can be used directly, because of their special properties or they can be used as a reactive „chemical hooks" for further chemical modification, while the oxidative product – *oxycellulose,* presents the base for obtaining a wide range of materials for special applications. A selective TEMPO-mediated oxidation serve as successful chemical treatment applied for obtaining one of the most interesting types of cellulose - nano-cellulose, material with the special properties and promising applications. Nano-cellulose materials have huge potential in many applications, from wastewater treatment processes, flexible optoelectronics and „Green" electronics, papers and packing products, nano-composites and colloid to scaffolds for tissue regeneration. Still, there are many challenges that remain to be overcome before industrial applications of nano-cellulose materials.

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ОКСИЦЕЛУЛОЗА – МАТЕРИЈАЛ ЗА НОВА ПОДРУЧЈА ПРИМЕНЕ

Сажетак: У овом раду представљени су принципи дејства селективних ($NaIO_4$ и 2,2,6,6-тетраметилпиперидин-1-оксил - ТЕМПО радикал) и неселективних (H_2O_2 и $KMnO_4$) оксидационих средстава на целулозу, њихов значај у модификовању постојећих или давању нових, специјалних својстава целулозним материјалима, као и примери њихове примене. Производ оксидације – оксицелулоза, представља полазну основу за добијање широког спектра материјала специјалне намене. Посебно је представљен утицај ТЕМПО-оксидације на природна и хемијска целулозна влакна, са детаљним освртом на тип и количину уведених функционалних група, променама у структури, сорпционим и механичким својствима. Описана је и примена ТЕМПО-оксидације за добијање целулозних наноматеријала у облику дисперзија, честица и филмова, као и потенцијал примене ових наноструктурних материјала.

Кључне речи: целулозна влакна, оксицелулоза, ТЕМПО-оксидација, нова својства, наноцелулоза.

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