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Sorption properties of TEMPO-oxidized natural and man-made cellulose fibers

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ABSTRACT

Cotton and lyocell fibers were oxidized with sodium hypochlorite and catalytic amount of sodium bromide and 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO), under various conditions. Water-insoluble fractions, collected after TEMPO-mediated oxidation, were analyzed and characterized in terms of weight loss, aldehyde and carboxyl contents, and sorption properties. Aldehyde and carboxyl groups were introduced into the oxidized cotton up to 0.321 and 0.795 mmol/g, and into the oxidized lyocell up to 0.634 and 0.7 mmol/g, respectively, where weight loss was generally lower than 12% for cotton and 27% for lyocell. Oxidized cotton and lyocell were shown to exhibit 1.55 and 2.28 times higher moisture sorption than the original fibers, respectively, and water retention values up to about 85% for cotton and 335% for lyocell, while iodine sorption values of oxidized fibers were lower up to 35% for cotton and up to 18% for lyocell than the original fibers.

1. Introduction

The polysaccharides are the most abundant carbon-based polymers on the surface of the earth. For millennia, they have provided mankind with a functional, low cost and renewable raw material. By conservative estimates, well over 10^{12} tons of cellulose, starch and related biomaterials are generated on our planet each year due to natural processes (Hon, 1996; Schurz, 1999).

Chemical modifications of polysaccharides are interesting routes for preparing new type of polymers on the basis of cellulose, with advances in performance and application, so-called "biopolymers for the future" (Chang & Robyt, 1996; Hon, 1996; Schurz, 1999; Tahiri & Vignon, 2000). The three hydroxyl groups of the cellulose molecule responsible for sorption properties (moisture, water, dye sorption capabilities, etc.), can undergo chemical reactions common to all primary and secondary groups, such as esterification, nitration, etherification and oxidation. The oxidation of cellulosic material is a quite frequent procedure in cellulose chemistry, and the oxidation is the only process that renders cellulose bioabsorbable in man (Stilwell, Marks, Saferstein, & Wiseman, 1997). For specific applications of cellulose fibers in medical devices such as absorbable hemostatic agents and absorbable adhesion barriers, drug delivery matrix, scaffold in tissue engineering, sensors, etc., it is necessary to obtain cellulose fibers with improved sorption properties, while the rate of bioabsorption can be adjusted by the degree of oxidation (Hon, 1996; Stilwell et al., 1997).

In the recent decade, catalytic oxidation using water-soluble and stable nitroxyl radicals such as 2,2,6,6-tetramethylpyperidine-1-oxy radical (TEMPO) under aqueous conditions has become one of the interesting routes to introduce carboxyl functionalities into polysaccharides (Chang & Robyt, 1996; Dang, Zhang, & Ragauskas, 2007; de Nooy, Besemer, & van Bekkum, 1994; de Nooy, Besemer, & van Bekkum, 1995; Saito & Isogai, 2006; Saito, Shibata, Isogai, Suguri, & Sumikawa, 2005; Tahiri & Vignon, 2000). The TEMPO-mediated oxidation of cellulose was described to cause selective oxidation at C6 of the anhydroglucose units to carboxyl groups via the intermediate aldehyde stage. 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 (Chang & Robyt, 1996; Saito, Okita, Nge, Sugiyama, & Isogai, 2006). The advantages of TEMPO-mediated oxidation are: high reaction rate and yield; high selectivity; catalytic process, just modest degradation of polysaccharides through out the process, and only inexpensive NaClO and NaOH are consumed as the oxidation proceeds (Saito et al., 2006). On such way introduced functionalities can be either used directly because of their special properties, e.g. hydrophilization and improved sorption properties by introduction of carboxyl groups, or they can be used as reactive "chemical hooks" for further chemical modification.

According to the literature (Chang & Robyt, 1996; Dang et al., 2007; de Nooy et al., 1995; Saito & Isogai, 2005; Saito et al., 2005) TEMPO-mediated oxidation of cellulose pulp is widely investigated, while TEMPO-mediated oxidation of cellulose fibers has been investigated in considerable smaller scope (Saito & Isogai, 2006). In this paper, we chose cotton and lyocell fibers for

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obtaining information about influence of TEMPO-mediated oxidation on properties of natural and man-made cellulose fibers. After TEMPO-mediated oxidation of cellulose fibers under various conditions, collected water-insoluble fractions were analyzed and characterized in terms of weight loss values, aldehyde and carboxyl contents. The changes in sorption properties of cotton and lyocell fibers were evaluated by determination of moisture sorption, water retention power and iodine sorption value. On the bases of the results obtained in this study, an attempt has been made to explain the individual roles of introduced functionalities and changed fiber structure in the sorption properties of the oxidized cotton and lyocell fibers.

Table 1
Sample marks, oxidation conditions and weight loss of TEMPO-oxidized cellulose fibers (2.5 mg TEMPO/g of cellulose, RT, pH 10.5).

Sample mark		Oxidation conditions		Weight loss (%)	
Cotton	Lyocell	Conc. 13% NaClO (mmol/g cell)	τ (h)	Cotton	Lyocell
CI_1	LI_1	0.30	1:00	2.11	0.46
CI_2	LI_2		2:00	2.15	0.64
CI_3	LI_3		3:00	2.52	0.89
CI_4	LI_4		4:00	2.78	1.06
CII_1	LII_1	2.42	1:00	2.18	3.82
CII_2	LII_2		2:00	2.36	4.15
CII_3	LII_3		3:00	3.10	6.58
CII_4	LII_4		4:00	4.63	9.72
–	$LIII_{0.25}$	4.84	0:25	–	0.87
–	$LIII_{0.5}$		0:50	–	2.10
$CIII_1$	$LIII_1$		1:00	1.85	4.21
$CIII_2$	$LIII_2$		2:00	3.22	15.70
$CIII_3$	–		3:00	5.48	–
$CIII_4$	$LIII_4$		4:00	7.38	26.27
–	$LIV_{0.25}$	9.67	0:25	–	1.64
–	$LIV_{0.5}$		0:50	–	3.25
CIV_1	LIV_1		1:00	2.71	4.71
CIV_2	–		2:00	3.45	–
CIV_3	–		3:00	7.13	–
CIV_4	–		4:00	11.34	–
CO	LO	0	0:00	–	–

2. Materials and methods

2.1. Materials

Two cellulose samples, cotton as a natural fiber (Russian Co, I class 32/33 mm), and lyocell (Lenzing AG, Austria, fineness: 1.3 dtex, length: 38 mm; without spin finishing) as a man-made fiber, were used in this study. TEMPO, sodium bromide and 13% sodium hypochlorite solution, and other reagents and solvents obtained from commercial sources were p.a. grade, and used without further purification.

2.2. Preparation of TEMPO-oxidized cellulose fibers

The oxidation procedure was based on the literature methodology (Saito & Isogai, 2004; Saito & Isogai, 2005). In brief, cellulose fibers (10 g) was suspended in water (750 ml) containing TEMPO (0.025 g) and sodium bromide (0.25 g). Subsequently, a designed amount of NaClO solution containing 13% available chlorine, corresponding to 0; 0.30; 2.42; 4.84 and 9.67 mmol/g cellulose, was added to the cellulose slurry under continuous stirring. The pH of the slurry was maintained to be 10.5 ± 0.1 at room temperature by adding 0.5 M NaOH using pH meter MA 5740 (Iskra, Slovenia), for 0.25–4 h. Duration of oxidation was chosen according to the literature data (Saito & Isogai, 2004) suggesting that there is no clear increase in carboxylate content in the water-insoluble fractions during the oxidation longer than 4 h. After stirring for a designed time, the oxidation was quenched by adding ethanol (ca. 5 ml). The oxidized cellulose was washed thoroughly with water and then ethanol on a filter paper set in a Büchner funnel. The water-insoluble fractions thus obtained were then dried at room temperature for 48 h. Sample marks and TEMPO-mediated oxidation conditions are shown in Table 1.

2.3. Determination of weight loss

Loss in weight, as result of chemical treatment, was determined by the direct gravimetric method (Koblyakov, 1989).

2.4. Determination of carboxyl and aldehyde groups in the TEMPO-oxidized cellulose fibers

2.4.1. Carboxyl (COOH) groups

The carboxyl groups of the oxidized cellulose react with the salts of weaker acids such as calcium acetate, forming a salt of the oxidized cellulose and releasing an equivalent amount of the weaker acid. On this basis as well as by the modification of published calcium-acetate method (Kumar & Yang, 2002; Yackel & Kenyon, 1942), for determination of carboxyl content in oxidized cellulose fibers, the following method was developed. The cellulose should be obtained in the acidic form by replacement of its cations by hydrogen ions by the treatment of cellulose samples (0.5 g) with 0.01 M HCl for 1 h, followed by washing with distilled water. In the next step to the oxidized cellulose 50 ml of distilled water and 30 ml 0.25 M of calcium-acetate solution were added. After standing during 2 h with frequent shaking, to facilitate completion of the interchange, 30 ml portions of the liquid were titrated with 0.01 M sodium hydroxide, using phenolphthalein indicator. The carboxyl contents are calculated as follows:

$$\mathrm{COOH} = \frac{\frac{80}{30}\cdot 0.01\ \mathrm{M}\cdot V(\mathrm{NaOH})}{m(1-\frac{w}{100})}\ (\mathrm{mmol/g}), \qquad (1)$$

where 0.01 M is concentration of NaOH, V(NaOH) is volume (ml) of NaOH solution used for titration, *m* is weight of treated fibers (g), and *w* is moisture content (%).

2.4.2. Aldehyde (CHO) groups

The aldehyde content in water-insoluble fractions was measured according to the method described in literature (Parks & Hebert, 1972; Saito & Isogai, 2004). The water-insoluble fractions were further oxidized with sodium chlorite at pH 4–5 for selective conversion of the aldehyde groups in the samples to carboxyl ones, and carboxyl content was determined by above mentioned calcium-acetate method. Cellulose slurry with 10% consistency was prepared beforehand, and then this slurry (20 g) was added to a mixture containing $NaClO_2$ (1.81 g), 5 M CH_3COOH (20 g), and water (57 ml). Oxidation was carried out by stirring the mixture at room temperature for 48 h, followed by washing thoroughly with water by filtration. The carboxyl groups formed by the $NaClO_2$ oxidation were regarded as aldehyde groups present in the original water-insoluble fractions.

2.5. Determination of moisture sorption

Moisture sorption of oxidized cellulose fibers was determined according to standards (ASTM D, 2654-76, 1976). Fibers were exposed to standard atmosphere: 20 ± 2 °C, 65 ± 2% relative humidity, for 24 h (ASTM D, 1776-74, 1974). Moisture sorption was calculated as weight percentage of absolute dry material. Reported values are the mean values of three separate determinations. Variation between analyses was less than 8% in all cases.

2.6. Determination of water retention value

Water retention of cellulose fibers was determined in triplicate by standard centrifuge method (ASTM D, 2402-78, 1978). The variation coefficients were at the level of 10%.

2.7. Determination of iodine sorption value

The Schwertassek method was used for evaluation of the sorption properties of the cellulose fibers (Nelson, Rousselle, Cangemi, & Trouard, 1970; Siroka, Noisternig, Griesser, & Bechtold, 2008; Stankovič Elesini, Pavko Čuden, & Richards, 2002). Cellulose fibers (0.3 g) were treated with 2 ml of iodine solution KI_3 (5 g I_2 + 40 g KI + 50 ml H_2O) for 3 min, 100 ml saturated sodium sulphate (200 g/l) was then added and shaken for 1 h. The iodine concentration of the sample and blank was determined by titration with sodium thiosulphate (0.02 mol/g). The iodine sorption values (ISV) in mg I_2 per g of sample was calculated as follows:

$$\mathrm{ISV} = \frac{(b-t)\cdot(M\cdot 102)\cdot(M\cdot 126.91)}{m_a} = \frac{(b-t)\cdot 2.04\cdot 2.54}{m_a}\ (\mathrm{mg/g}), \tag{2}$$

where b is volume (ml) of $Na_2S_2O_3$ solution for blank titration, t is volume (ml) of $Na_2S_2O_3$ solution for the titration of sample solution, M is the molarity of the sodium thiosulphate (mol/g), 102 is a total volume (ml) of the solution, and m_a is the weight of absolute dry cellulose fibers (g).

According to Schwertassek, the absorption takes place in the amorphous phase. A ratio of ISV (per 1 g cellulose) to 412 (mg iodine absorbed per 1 g of methyl cellulose) determines the amorphous fraction. The crystallinity index (CrI) was calculated using equation (Nelson et al., 1970):

$$\mathrm{CrI} = 100 - \left(\frac{\mathrm{ISV}}{412}\times 100\right)\ (\%), \tag{3}$$

3. Results and discussion

3.1. Weight loss of TEMPO-oxidized cellulose fibers

During the TEMPO-mediated oxidation, the C6 primary hydroxyl groups of cellulose are converted to carboxyl groups via C6 aldehyde groups. The severity of treatment is generally characterized by weight loss, which is result of water-solubility of oxidation products, i.e. highly oxidized cellulose molecules and/or some of low-molecular weight products obtained due to proceeding beta-elimination at the C6 aldehyde intermediate and/or depolymerization by some active species such as hydroxyl radicals formed in situ as side reactions. TEMPO oxidation is usually carried out around pH 10–11 (in our experiments 10.5) since at lower pH hypochlorite becomes an overly aggressive and non-selective oxidant, and also TEMPO reactivity is decreased (Dang et al., 2007; de Nooy et al., 1995). Under the prevailing alkaline pH conditions the hydroxyl radicals formed from NaBrO and TEMPO rather than the beta-elimination are likely to participate in the depolymerization mechanism, resulting in remarkable decrease of the molecular weight (Saito & Isogai, 2004; Shibata & Isogai, 2003; Tamura, Wada, & Isogai, 2009). Also, in the case of cotton fibers the weight loss is a result of decomposition of impurities and natural pigments in cotton fibers (Fakin, Golob, Kleinschek, & Marechal, 2006; Stana-Kleinschek, Strnad, & Ribitsch, 1999), while for lyocell fibers weight loss can be additionally increased by strong fibrillation typical for wet treatments of lyocell fibers.

Generally higher weight loss is obtained for modified lyocell fibers, in comparison with modified cotton fibers (data are given in Table 1, and some of data are presented in Figs. 3 and 6); that is predicted result, due to the fact that lyocell fibers have lower degree of polymerization (550–600) compared to cotton fibers (2–3000); lower crystallinity index, i.e. 0.44 versus 0.80 for cotton, as well as due to more complex fine and micro structure of cotton than lyocell fibers (Albrecht, Reintjes, & Wulfhorst, 1997; Gamble, 2005; Kreze, Jeler, & Strnad, 2005; White, 2001).

The highest weight lost for lyocell fiber (26.27%) is determined for the sample oxidized with 4.84 mmol NaClO/g cellulose, in the TEMPO-mediated system, during 4 h (sample $LIII_4$), while for cotton fibers treated under the same conditions (sample $CIII_4$), the value of weight loss is 3.56 times lower (7.38%) (Table 1). The lyocell fibers oxidized under severe conditions (i.e. 4.84 mmol NaClO/g cellulose, during 2 and 4 h) suffered from a so deep structural damage that their complete characterization was impossible. The highest weight loss for cotton fiber (11.34%) is determinated for the sample treated in the TEMPO-mediated system, with 9.67 mmol NaClO/g cellulose for 4 h (sample CIV_4). This can be explained by the fact that, according to the literature (Saito & Isogai, 2004; Tahiri & Vignon, 2000), in the case of the TEMPO-mediated oxidation of native celluloses, the most of oxidized products are not soluble in water even after extended oxidation time, because the oxidation takes place in accessible or disordered regions in cellulose and the most of the C6 primary hydroxyl groups in native celluloses remain as they are in the oxidized products.

3.2. Aldehyde and carboxyl contents in the TEMPO-oxidized cellulose fibers

Fig. 1 shows the effect of oxidation time and amount of added NaClO on aldehyde group content in the water-insoluble fractions of TEMPO-oxidized cotton and lyocell fibers. The aldehyde groups formed in the water-insoluble fractions are mostly due to C6 aldehydes present as the intermediate structure during the TEMPO-mediated oxidation and reducing ends formed from glycoside bonds by β-elimination at pH 10.5 and other depolymerization reactions during the oxidation (Saito & Isogai, 2004; Shibata & Isogai, 2003), as it was mentioned earlier.

The aldehyde group content in cotton fibers oxidized by different amount of the primary oxidant (NaClO) reached the maximum value after the 1 h of oxidation, and decreased slowly with increasing oxidation time (Fig. 1a). In the case of lyocell fibers and for the lowest concentration of oxidative agent (0.30 mmol NaClO/g cellulose), aldehyde group content in oxidized fibers increased with oxidation time, while for the higher concentration of NaClO aldehyde group content increased with oxidation time up to 2 h, depending on concentration NaClO, and then longer modification results in decrease of aldehyde content (Fig. 1b). Also, these results indicate that during the TEMPO-mediated oxidation, the aldehyde group content in cotton and lyocell fibers increased in a similar manner by the addition of NaClO up to 4.84 mmol per gram cellulose, and then decreased by the excess NaClO addition. Observed decrease of aldehyde group content can be explained by conversion of CHO groups into COOH groups due to the further oxidation process. The maximum aldehyde content for cotton fibers is 0.321 mmol/g cellulose (sample $CIII_1$, 1 h oxidation, 4.84 mmol NaClO/g cellulose), and for lyocell fibers 0.634 mmol/g cellulose (sample $LIII_{0.25}$, 15 min oxidation, 4.84 mmol NaClO/g cellulose), that is 12.5 and 15 times higher than corresponding values for unmodified cotton (0.0257 mmol/g cellulose,) and lyocell fibers (0.0421 mmol/g cellulose). Significant amounts of aldehyde groups present in all oxidized fibers, even after the 4 h oxidation, can be explained according to Saito and Isogai (2004) and Saito and Isogai (2006) by formation of intra- and inter-molecular hemiacetals with

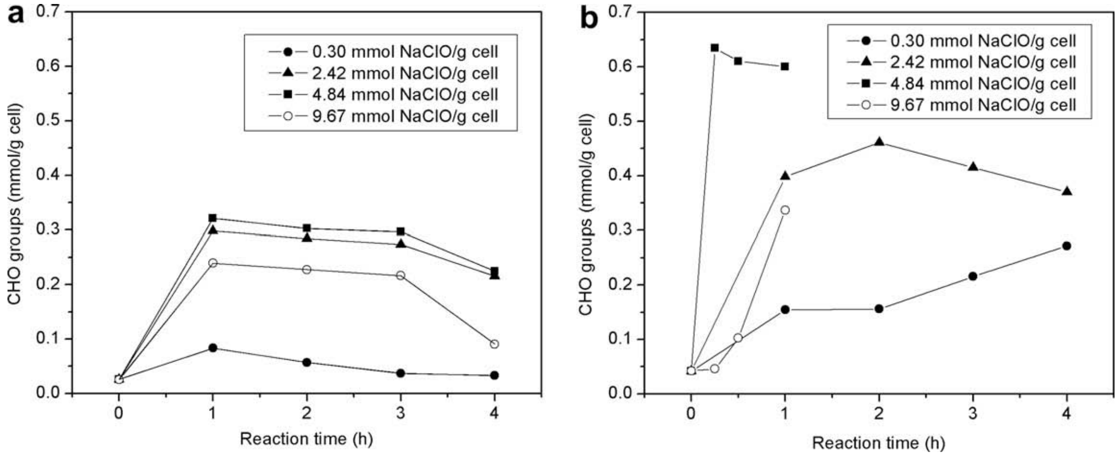

Fig. 1. Relationships between oxidation time and aldehyde group content in the water-insoluble fractions of TEMPO-oxidized (a) cotton and (b) lyocell fibers, where 0.30; 2.42; 4.84 and 9.67 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, at room temperature and pH 10.5.

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.

Fig. 2 shows the effect of oxidation time and amount of added NaClO on carboxyl group content in the water-insoluble fractions of TEMPO-oxidized cotton and lyocell fibers. The carboxyl group content in unmodified cotton and lyocell are 0.097 and 0.061 mmol/g cellulose, respectively. During the TEMPO-mediated oxidation of cotton fibers the carboxyl contents in oxidized fibers increased in all cases by the addition of oxidation agent (NaClO) and with increasing oxidation time (Fig. 2a). The carboxyl content in the water-insoluble fractions was within the range of 0.123–0.795 mmol/g cellulose. The maximum increase of carboxyl content in oxidized cotton fibers of 8.16 times ($COOH_{modified}$/$COOH_{unmodified}$) is obtained for the sample oxidized in the presence of 9.67 mmol NaClO/g cellulose during 4 h (sample CIV_4).

In the case of oxidized lyocell fibers there is no clear correlation between NaClO concentration, oxidation time and introduced carboxyl groups (Fig. 2b). Lyocell fibers oxidized in the presence of the lowest amount of NaClO (0.30 NaClO mmol/g cellulose) showed the same behaviour as oxidized cotton fibers, i.e. the carboxyl group content increased with prolonged oxidation time. In the case of lyocell oxidation in the presence of higher amount of oxidative agent, i.e. 2.42 and 4.84 mmol NaClO/g cellulose, carboxyl group content 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 content in oxidized lyocell fibers can be explained by dissolution of highly oxidized cellulose fractions, as it can be seen from the Fig. 3. In the case of regenerated cellulose, when the carboxyl content in average is more than about 0.7 mmol/g, the oxidized products turn to have higher water-solubility and thus are removed to the filtrates during the washing process. Applying severe conditions (9.67 mmol NaClO/g cellulose) in the case of TEMPO-mediated oxidation of lyocell fibers, results in loosing fibrous structure and for textile applications only oxidation under mild conditions should be used.

Obtained results show that regenerated cellulose fibers (lyocell), are much more reactive toward TEMPO oxidation mainly due to the lower crystallinity index and less complex fine and micro structure than cotton fibers, as well as higher accessibility of cellulose II crystal structure (regenerated and mercerized cellulose) as compared with cellulose I (native cellulose), which is in agreement with literature data (Isogai & Kato, 1998; Saito & Isogai, 2004; Tahiri & Vignon, 2000).

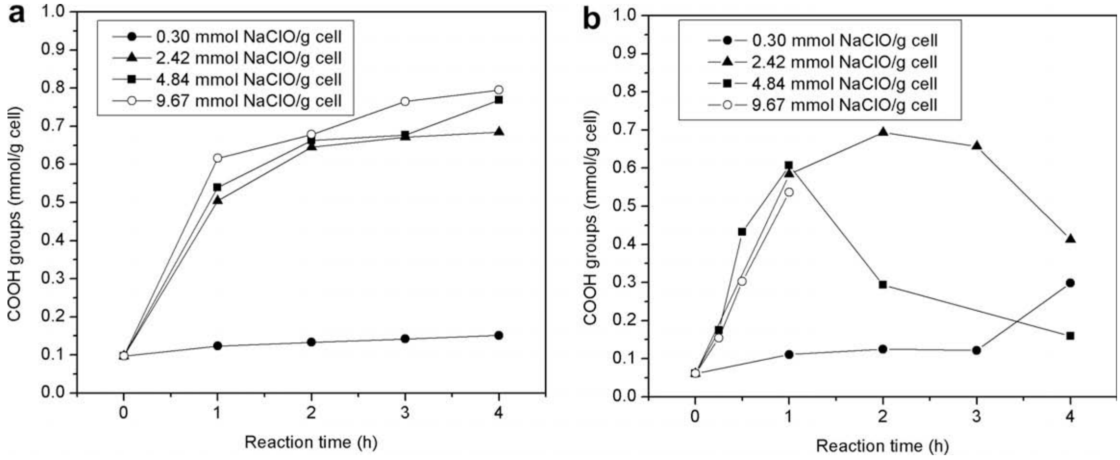

Fig. 2. Relationships between oxidation time and carboxyl content in the water-insoluble fractions of TEMPO-oxidized (a) cotton fibers and (b) lyocell, where 0.30; 2.42; 4.84 and 9.67 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, at room temperature and pH 10.5.

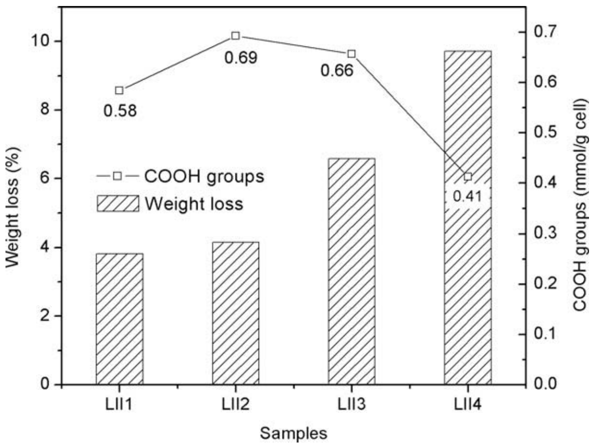

Fig. 3. Carboxyl group content in the water-insoluble fraction and weight loss of TEMPO-oxidized lyocell fibers modified with 2.42 mmol NaClO (per gram of cellulose), during 1–4 h, at room temperature and pH 10.5.

3.3. Moisture sorption and water retention value of TEMPO-oxidized cellulose fibers

As it has been reported earlier (Dang et al., 2007; Saito & Isogai, 2004) that together with the introduction of aldehyde and carboxyl groups into cellulose by the TEMPO-mediated oxidation, the fibrous morphology of cellulose fibers has been changed, depending on the oxidation conditions. Changes in cellulose chemical composition, crystallinity and pore structure during the TEMPO oxidation affect the sorption properties which have been evaluated by determination of moisture sorption (MS), water retention value (WRP) and iodine sorption value (ISV).

Moisture sorption values yield information on the extent of areas accessible to water vapor within a fiber. Moisture sorption values for unmodified and modified cotton and lyocell fibers are presented in Fig. 4a and b. Moisture sorption values for unmodified cotton and lyocell used in this experiment, are 5.77% and 9.04%, respectively. The obtained data showed that the moisture sorption value of oxidized cotton increased with increasing NaClO charge and oxidation times approaching a maximum value of 8.97% (ratio $w_{mod}/w_0 = 1.55$), obtained for sample oxidized under the most severe conditions (4 h, 9.67 mmol NaClO/g cellulose – sample CIV_4).

Lyocell fibers oxidized in the presence of the lowest amount of NaClO (Fig. 4b) showed a slight increase of moisture sorption (9.59–9.69%) during 3 h of modification, and then a strong jump (20.58%) with further oxidation (sample LI_4). Under severe conditions, i.e. higher concentration of NaClO/g cellulose, results gave an increase in moisture sorption, followed by a strong decrease with prolonged oxidation, which can be connected with similar changes in hydrophilic carboxyl group content, which is ilustrated in Fig. 2b. Moisture sorption of oxidized lyocell fibers is in the range from 9.59% to 20.58%. The highest increase of moisture sorption (i.e. ratio $w_{mod}/w_0 = 2.28$), in comparison with unmodified lyocell fiber, is obtained for the sample oxidized for 4 h with 0.30 mmol NaClO/g cellulose (sample LI_4).

The obtained results become clearer if we correlate the content of introduced COOH groups in TEMPO-oxidized cellulose fibers and their moisture sorption values (Fig. 5). The moisture sorption values increase roughly linearly with increasing the carboxylate content of the water-insoluble fraction of both cotton and lyocell. Exception was observed only in the case of lyocell fibers oxidized with 0.30 mmol NaClO/g cellulose for 4 h, which had the highest moisture sorption value. The above mentioned correlation can be explained by the fact that free hydroxyl and carboxyl groups at the cellulose fibers amorphous regions and at the crystallites' surface are responsible for the moisture sorption (Pejic, Kostic, Skundric, & Praskalo, 2008; Siroka et al., 2008), and the carboxyl groups introduced by TEMPO oxidation are present on the crystal surfaces and in disordered regions of celluloses, without any introduction into the inside of the cellulose crystallites (Saito & Isogai, 2004; Saito & Isogai, 2006).

Other important properties of cellulose fibers are their interactions with liquid water which result in swelling of fibers, mainly due to the wide expansion of amorphous regions. When cellulose fibers are immersed in water they swell and imbibe considerably more water, than they are capable of holding. The total water holding capacity of a fiber can be estimated by determining water retention value. All water absorbing and holding surfaces, cracks, and cavities are included with the water retention measurement. Fig. 4c and d depicts water retention values of the water-insoluble fractions of the TEMPO-oxidized cotton and lyocell fibers oxidized under different condition (i.e. oxidation times and NaClO charge). The WRVs of the TEMPO-oxidized cotton fibers increased with increasing NaClO charge and oxidation times approaching a maximum value of 85.4%, obtained for sample oxidized under the most severe conditions (4 h, 9.67 mmol NaClO/g cellulose – sample CIV_4). The increases are due to the introduction of hydrophilic carboxyl groups and morphological changes (from fibrous forms to short fragments) and effectively eliminated hydrophobic impurities from the surface of the fibers. Oxidative treatment under alkaline conditions would be expected to remove most of the remaining noncellulosic components thus enabled water molecules to penetrate into the cotton fibers (Fakin et al., 2006; Obendorf & Borsa, 2001; Stana-Kleinschek et al., 1999).

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.

The WRVs of oxidized lyocell fibers are mostly higher than WRVs of oxidized cotton fibers. This result indicates that the fiber structure of oxidized lyocell is less stable than that of cotton and water can more easily invade the structure which can be explained by the lower crystallinity, large pore volume and inner surface area of lyocell compare to the cotton fiber, as well as strong fibrillation of the long fibers that is typical for oxidized lyocell fibers.

3.4. Iodine sorption value

The iodine sorption test is generally conceded to be an essentially empirical measure of cellulose accessibility to aqueous solutions in the fiber amorphous areas and it is inversely proportional to the fiber crystalline phase, expressed by the crystallinity index (CrI), therefore iodine takes place only in less ordered amorphous regions of cellulose (Fakin et al., 2006; Kreze et al., 2005).

The mechanism of iodine sorption differs from water sorption at the partially-positive hydrogen atoms of the cellulose polar hydroxyl group because three-iodide ions (built up when an iodide ion is added to an iodine molecule) are preferentially adsorbed in a monomolecular layer, whereas additional water molecules are bound to the water monomolecular layer by hydrogen bounds. Therefore, water sorption and retention power are a measure of swelling ability and the accessibility of fibers to aqueous baths during wet finishing processes whereas iodine sorption is a measure of the accessibility of fibers and the crystallinity index (Fakin et al., 2006).

For unmodified cotton and lyocell fibers used in this experiment, the ISVs are 54.1 and 164.5, respectively. The ISVs for modified cotton and lyocell fibers are presented in Fig. 6. The different conditions of TEMPO-mediated oxidation differently influenced the accessibility of the oxidized cellulose fibers. Generally, the

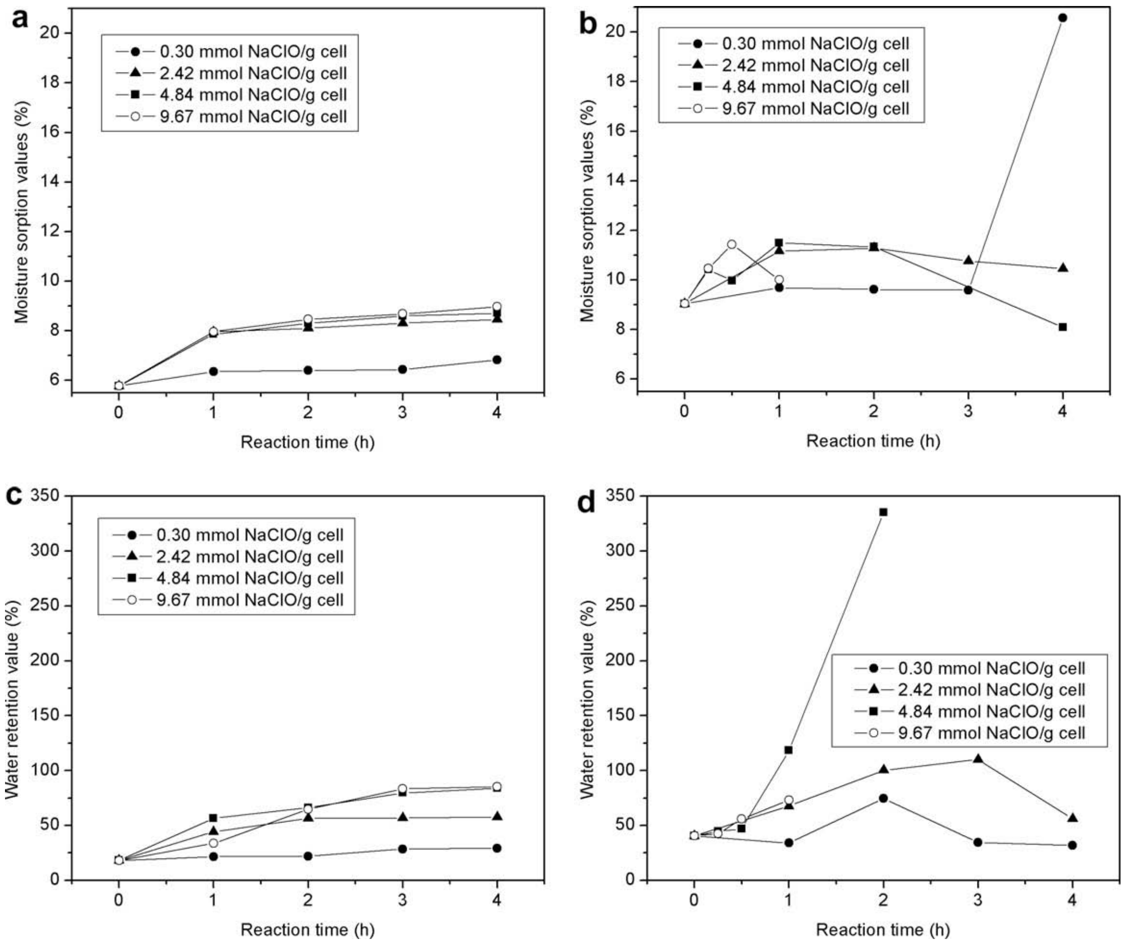

Fig. 4. Moisture sorption (MS) and water retention values (WRV) of the water-insoluble fractions of TEMPO-oxidized: (a and c) cotton and (b and d) lyocell fibers where 0.30; 2.42; 4.84 and 9.67 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, at room temperature and pH 10.5, for the different oxidation times (1–4 h).

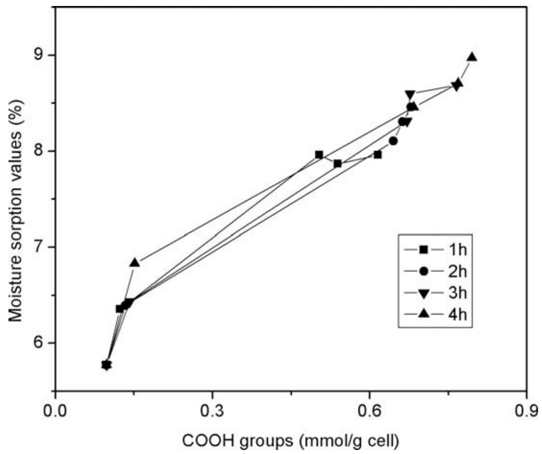

Fig. 5. Relationship between carboxyl content and moisture sorption values of the water-insoluble fraction of TEMPO-oxidized cotton fibers, modified with 0.30–9.67 mmol NaClO (per gram of cellulose) during 1–4 h, at room temperature and pH 10.5.

TEMPO-oxidized cellulose fibers have lower ISV value compared to unmodified fibers. Reduced ISVs for TEMPO-oxidized cotton fibers (in the range from 35.5 to 53.6), and for lyocell fibers (from 135.9 to 158.4), are consequence of the dissolution of highly accessible fractions, and the formation of carbonyl and carboxyl groups during the oxidative treatment of cellulose. Lower ISVs for oxidized cellulose fibers and above mentioned dissolution, show that the oxidation takes place in accessible and/or disordered regions in these TEMPO-oxidized cellulose samples, that is in agreement with the literature (Saito & Isogai, 2004). This can be confirm by the relationship between the ISVs and weight loss, for the set of TEMPO-oxidized cotton and lyocell fibers modified under the same condition, in the presence of 2.42 mmol NaClO/g cellulose (Fig. 6).

Exception that can be seen for TEMPO-oxidized lyocell fibers, in comparison to the cotton fibers oxidized under the same conditions, can be explained by strong fibrillation and the losing of fibrous form of lyocell fibers.

Weight loss also has influence on the crystallinity index of TEMPO-oxidized cotton and lyocell fibers, that is calculate on the basis of ISV. During the TEMPO-mediated oxidation, crystallinity was increased and changed in the range from 86.9 for unmodified cotton fibers to 87.0–91.9 for TEMPO-oxidized cotton fibers; and for lyocell fibers, crystallinity index slightly increased from 60.07 (unmodified fibers) to 61.5–67.0 for TEMPO-oxidized lyocell fibers (data not shown). The obtained increase in crystallinity for the TEMPO-oxidized cellulose sample is due to partial loss of the disordered regions during the washing process because of their increased water-solubility (Saito & Isogai, 2004).

4. Conclusions

This study demonstrates the potential of the selective TEMPO-mediated oxidization towards natural and man-made cellulose fibers (i.e. cotton and lyocell fibers). By the TEMPO-mediated

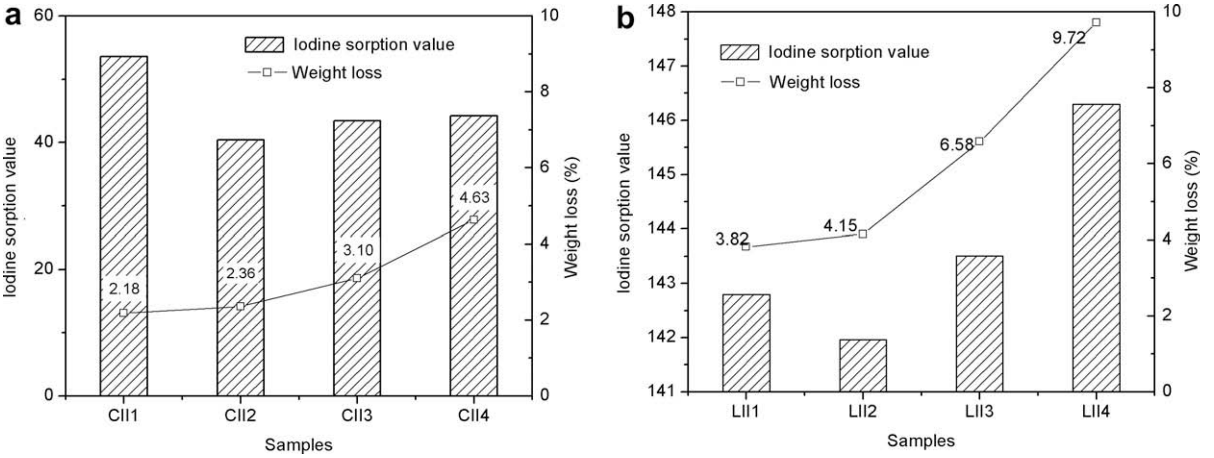

Fig. 6. Relationship between ISV value of the water-insoluble fraction and weight loss of TEMPO-oxidized (a) cotton and (b) lyocell fibers, modified with 2.42 mmol NaClO (per gram of cellulose), at room temperature and pH 10.5.

oxidation of cellulose fibers, significant amounts of aldehyde and carboxyl groups can be introduced into cellulose fibers (the maximum increase of aldehyde content is by factor 12.5 and carboxyl content by 8.2 for oxidized cotton fibers, while for oxidized lyocell fibers maximum increase is by factor 15 for aldehyde and 11.4 for carboxyl content), and the amounts of these functional groups are controllable by selecting the oxidation conditions. The amount of introduced acid groups has considerable influence on the sorption properties and the accessibility of TEMPO-oxidized cotton and lyocell fibers, and therefore, on their reactivity. The increase of moisture sorption and water retention values is obtained for both fibers and the TEMPO-mediated oxidation can be used to impart cotton and lyocell fibers with various moisture sorption and water retention values by controlling the oxidation conditions. Iodine sorption values of TEMPO-oxidized cellulose fibers are smaller (in the range from 35.5 to 53.6 for TEMPO-oxidized cotton fibers, and for lyocell fibers from 135.9 to 158.4) than iodine sorption values for unmodified cotton (54.1) and lyocell (164.5) fibers. The obtained results show that the water retention value exhibits the highest sensitivity to changes in the structure (mainly number, type and accessibility of sorption sites in the fiber) of TEMPO-oxidized cotton and lyocell fibers, followed by less sensitive iodine sorption value, while the moisture sorption exhibits the lowest sensitivity to changes in fiber structure.

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