Carbohydrate Polymers 98 (2013) 444–450

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Molecular weight distribution and functional group profiles of TEMPO-oxidized lyocell fibers

Jovana Milanovic[a], Sonja Schiehser[b], Predrag Milanovic[c], Antje Potthast[b], Mirjana Kostic[a,*]

[a] Department of Textile Engineering, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia
[b] Department of Chemistry, University of Natural Resources and Life Sciences, Muthgasse 18, A-1190 Vienna, Austria
[c] Department of Construction Materials, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 28 January 2013
Received in revised form 28 May 2013
Accepted 18 June 2013
Available online 26 June 2013

Keywords:
TEMPO-mediated oxidation
Lyocell fibers
Gel permeation chromatography (GPC)
Molecular weight distribution (MWD)
Fluorescence labeling
Functional group profiles

ABSTRACT

The effects of TEMPO-mediated oxidation, performed with NaClO, a catalytic amount of NaBr, and 2,2′,6,6′-tetramethylpiperidine-1-oxy radical (TEMPO), were studied on lyocell fibers by means of GPC using multiple detection and group-selective fluorescence labeling according to the CCOA and FDAM methodology. The applied method determines functional group content as a sum parameter, as well as functional group profiles in relation to the molecular weight of the cellulose fibers. Both the CHO and COOH profiles, as well as molecular weight alterations, were analyzed. A significant decrease in the average molecular weight was obtained during the first hour of TEMPO-mediated oxidation, but prolonged oxidation time resulted in no strong additional chain scission. Significant amounts of COOH groups were introduced in the high molecular weight fractions by the oxidation with higher concentrations of NaClO (2.42–9.67 mmol NaClO/g fiber) after modification times of 1 h or longer.

1. Introduction

The introduction of functionalities into cellulose fibers represents one of the prime factors determining the macroscopic properties and chemical behavior of modified fibers, such as water retention, wettability, strength, surface charge, cross-linking, aging, yellowing, etc. Due to their special properties (e.g., hydrophilization or improved sorption properties by introduction of carboxyl groups), the introduced functionalities can be use directly, or they can be use for further chemical modification (Potthast, Rosenau, & Kosma, 2006).

Oxidation is quite frequently used in cellulose chemistry for introducing functional groups into cellulose samples. Among oxidative procedures, TEMPO-mediated oxidation has become very common in recent years, as it is an interesting and promising method for introduction of carboxyl groups, via the intermediate aldehyde stage, at C6 positions of the anhydroglucose units (AGUs) of polysaccharides. The nitroxyl radical affects the oxidation from the alcohol to the aldehyde oxidation state, while the hypobromite generated in situ from hypochlorite and bromide performs further oxidation of the aldehyde to the carboxylic acid (Chang & Robyt, 1996; Saito & Isogai, 2006). The advantages of TEMPO-mediated oxidation are its high reaction rate and yield, high selectivity, catalytic process, and requirement only for inexpensive NaClO and NaOH, which are consumed as the oxidation proceeds. However, the method has some shortcomings, such as remarkable depolymerization, mainly due to a β-elimination side reaction, and cost issues (Saito, Okita, Nge, Sugiyama, & Isogai, 2006; Shinoda, Saito, Okita, & Isogai, 2012).

According to the literature (Isogai, Saito, & Fukuzumi, 2011; Okita, Saito, & Isogai, 2010; Saito, Hirota, Tamura, & Isogai, 2010; Saito, Shibata, Isogai, Suguri, & Sumikawa, 2005), the amount of introduced functional groups in TEMPO-oxidized cellulose samples have been widely determined by different conventional analytical and instrumental techniques, which provided an estimate of the overall content, that is a sum parameter. In contrast, a group profile in relation to the molecular weight of the oxidized cellulose has only been investigated in considerable smaller scope (Potthast, Kostic, & Schiehser, 2007).

In the present paper, some deeper insight was obtained into the influence of TEMPO-mediated oxidation on distribution of introduced aldehyde and carboxyl functional groups by analyzing the unmodified and oxidized lyocell fibers by means of gel permeation chromatography (GPC) using multiple detection and group-selective fluorescence labeling. Fluorescence labeling with carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide

* Corresponding author. Tel.: +381 11 3303 628; fax: +381 11 3370 387.
E-mail address: kostic@tmf.bg.ac.rs (M. Kostic).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.06.033

(CCOA) has been used for determination of aldehyde groups, while carboxyl content in lyocell fibers has been determined by fluorescence labeling with 9*H*-fluoren-2-yl-diazomethane (FDAM). Incorporation of fluorescence labeling for the determination of functional groups into GPC measurement of cellulose provides the functional group content as a sum parameter but also adds a group profile in relation to the molecular weight distribution, plus the average molecular parameters of the cellulose fibers (Mw, Mn). The applied method is highly sensitive and allows the determination of even very small amounts of oxidative structures, and very little sample material is needed (Röhrling, Potthast, Rosenau, Lange, Borgards, et al., 2002; Röhrling, Potthast, Rosenau, Lange, Ebner et al., 2002).

Lyocell fibers were chosen because changes in distribution of introduced functional groups can be measured without having effects originating from accompanying components, such as hemicelluloses, residual lignin, and other impurities that are present in natural cellulose fibers. Furthermore, the environment-friendly, relatively simple, and highly flexible technology for lyocell fibers, together with its unique properties (very high strength in comparison with other man-made cellulose fibers, high crystallinity, specific luster, and handle) have placed lyocell fibers in the center of attention in the textiles field since they were developed in the mid 1970s (El-Wakil & Hassan, 2008; Zhang, Zhang, Tong, Shao, & Hu, 2008).

2. Materials and methods

2.1. Materials

A man-made cellulose fiber – lyocell (Lenzing AG, Austria, fineness: 1.3 dtex, length: 38 mm; without spin finishing), with a starting aldehyde content of 8.67 mmol/kg and carboxyl content of 16.46 mmol/kg, was used in this study. All chemicals were obtained from commercial sources and were p.a. grade.

2.2. Preparation of TEMPO-oxidized lyocell fibers

The oxidation procedure was based on the literature methodology (Saito & Isogai, 2004; Saito, Shibata, et al., 2005). Lyocell fibers (10 g) were suspended in water (750 cm^3) containing TEMPO (0.025 g) and sodium bromide (0.25 g). Subsequently, the designed amount of NaClO solution, containing 13% available chlorine, was added to the cellulose slurry corresponding to 0; 0.30; 2.42; 4.84 and 9.67 mmol/g fibers under continuous stirring. The pH of the slurry was maintained at 10.5 at room temperature by adding 0.5 M NaOH for 0.25–4 h. Duration of oxidation was chosen according to the literature data (Saito & Isogai, 2004), which indicated that no significant increase in carboxyl content occurred in the modified fibers during oxidations longer than 4 h. After stirring for a designed time, the oxidation was quenched by adding ethanol (ca. 5 ml). The oxidized lyocell fibers were washed thoroughly with water and then ethanol, on a filter paper set in a Büchner funnel. The oxidized samples were then dried at room temperature for 48 h.

2.3. Determination of aldehyde and carboxyl groups in the TEMPO-oxidized lyocell fibers

2.3.1. Labeling

Carbazole-9-carbonyloxyamine (CCOA) labeling of aldehyde groups was performed as described by Röhrling, Potthast, Rosenau, Lange, Borgards, et al. (2002), Röhrling, Potthast, Rosenau, Lange, Ebner et al. (2002) and Potthast et al. (2003). Fluorenyl diazomethane (FDAM) labeling of carboxyl groups followed the protocol of Bohrn et al. (2006).

2.3.2. General analytical methods

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; auto sampler, HP 1100 column oven, Gynkotek STH 585, fluorescence detector TSP FL2000 (CCOA) and Shimadzu RF535 (FDAM); multiple-angle laser light scattering (MALLS) detector, Wyatt Dawn DSP with argon ion laser (λ_0 = 488 nm); refractive index (RI) detector, Shodex RI-71. Data evaluation was performed with standard Chromeleon, Astra, and GRAMS/32 software.

2.3.3. GPC method

The following parameters were used in the GPC measurements: flow, 1.00 mL/min; columns, four PLgel mixed-A LS, 20 μm, 7.5 mm × 300 mm (Polymer Laboratories); fluorescence detection, λ_{ex} = 290 nm, λ_{em} = 340 nm (CCOA), λ_{ex} = 280 nm, λ_{em} = 312 nm (FDAM); injection volume, 100 μL; run time, 45 min. The mobile phase was N,N-dimethylacetamide/lithium chloride (0.9% w/v), filtered through a 0.02 mm filter.

GPC measurement in solvent system N,N-dimethylacetamide (DMAc/LiCl) is appropriate and efficient for studies of TEMPO-mediated oxidation of cellulose fibers, since no degradation whatsoever occurred during dissolution and measurement.

3. Results and discussion

3.1. Influence of TEMPO-mediated oxidation on the molecular weight distribution of modified lyocell fibers

The effect of the TEMPO-mediated oxidation on lyocell fibers can be generally characterized as a change in the average molecular weight (Mw) of the lyocell samples. The weight average molecular weight of unmodified lyocell fibers was 127.9 kg/mol, while for oxidized fibers the average molecular weight decreased under all oxidation conditions (Fig. 1). The significant decrease in Mw occurs during the first hour of oxidation (up to 6.5 times). According to the literature (Isogai et al., 2011; Potthast, Kostic, Schiehser, Kosma, & Rosenau, 2007; Shibata & Isogai, 2003; Tamura, Wada, & Isogai, 2009), the cellulose chain is not shortened by oxidation, but has suffered from a modification that eases further attacks on the molecule, mostly due to preceding β-elimination at the C6

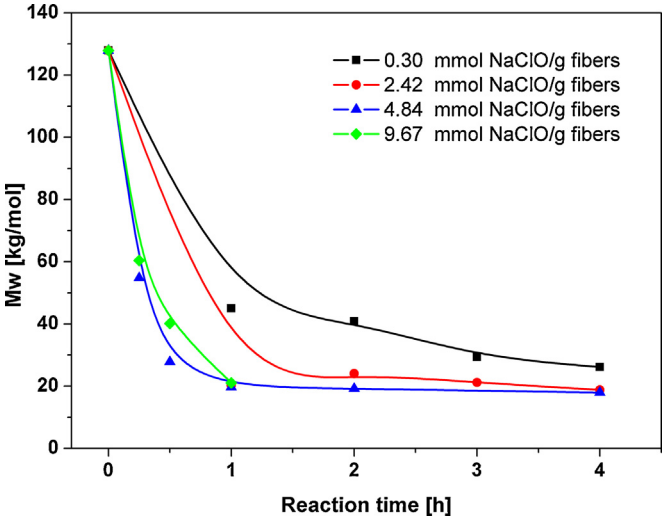

Fig. 1. Relationship between oxidation time and Mw of the TEMPO-oxidized lyocell fibers, where 0.30; 2.42; 4.84 and 9.67 mmol NaClO/g fiber was applied to the cellulose slurry, at RT and pH 10.5.

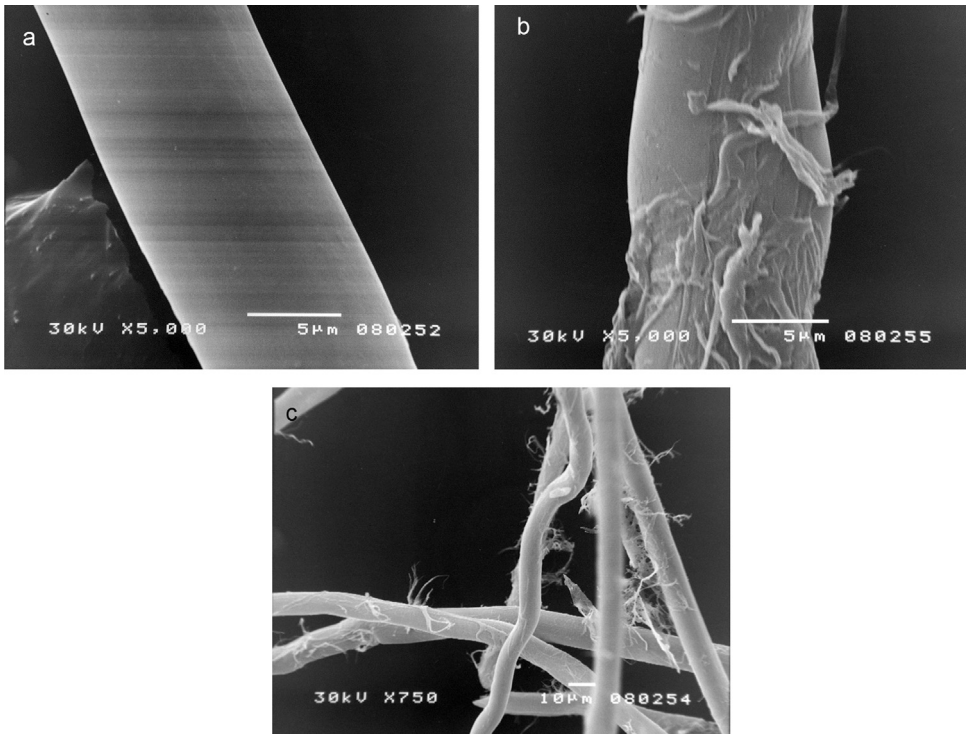

Fig. 2. SEM images of (a) unmodified, (b) and (c) lyocell fibers modified with 0.30 mmol NaClO/g fibers for 4 h, at RT and pH 10.5.

aldehyde intermediate. The strong fibrillation of lyocell fibers (Fig. 2) that occurred during the oxidation, especially under severe conditions, makes fibers more accessible to the reactive species, thereby allowing additional decreases in the average molecular weight of TEMPO-oxidized fibers. With prolonged oxidation time, no strong additional chain scission occurred; i.e., only a slight decrease in the weight average molecular weight was obtained.

In addition to changes in the weight average molecular weight (Mw), TEMPO-mediated oxidation also influenced the molecular weight distribution (MWD). The shifting of the MWD curves (Fig. 3) indicates that the MWD is changed due to degradation during TEMPO-mediated oxidation.

In the case of modification with the lowest concentration of NaClO (0.30 mmol NaClO/g fibers), the difference between the molecular weight distribution of untreated and oxidized lyocell fibers is apparent for all oxidation times. For oxidized fibers, only a minor difference is noted between molecular weight distributions with prolonged oxidation time (Fig. 3a). For that group of samples, modified with 0.30 mmol NaClO/g fibers, the polydispersity index (PDI) ranged from 2 to 2.2 for 1–4 h. Similar results were obtained for samples modified with 2.42 mmol NaClO/g fibers (data not shown). Modification with 4.84 mmol NaClO/g fibers causes a shift in the MWD curve to the lower molecular weights. The molecular weight distribution remains quite stable with prolonged oxidation time and a broad curve of molecular weight distribution was obtained for the modified fibers, especially for samples modified for 2 and 4 h. The calculated PDI values of these samples are 7.8 and even 9.4, respectively. The broadening of the MWD at higher degrees of oxidation may be explained as a superposition of degradation (broadening "in the direction of lower Mw") and inter-chain cross-linking, due to introduction of aldehyde groups (broadening "in the direction of increased Mw").

Too severe conditions (i.e., TEMPO-mediated oxidation with 9.67 mmol NaClO/g fibers, longer than 1 h) result in destruction of the fiber structure (Praskalo et al., 2009) and complete characterization was not possible for those modified lyocell fibers.

Additional information on the shape of the molecules in solution is provided by the MALLS data. The angular dependence of the scattered light can be used to determine the radius of gyration (Rg), and a double-logarithmic plot of Rg vs. Mw (conformation plot) can be used to determine the shape factor ν, which characterizes polymer coil expansion. Values for ν may range from 0.3 for compact spheres to 0.5 for quasi-ideal unexpanded θ-coils to 1.0 for completely expanded coils (Pfefferkorn, Beister, Hild, Thielking, & Kulicke, 2003; Thielking & Kulicke, 1998).

The corresponding conformation plots for TEMPO-oxidized lyocell fibers are shown in Fig. 4. Conformation analysis demonstrated that increasing degrees of oxidation decreased the radius of the molecules for the same molecular weight, indicating that the molecules became more compact. This can be explained by the introduction of aldehyde groups, which are available for different types of hemiacetal linkages (i.e., inter-residue hemiacetal linkages (between different AGUs of a chain) and chain-to-chain hemiacetals) (Potthast, Kostic, Schiehser, et al., 2007). The MALLS data (Fig. 4) support the presence of predominant intra-chain-type linkages in TEMPO-oxidized lyocell fibers because the Mw did not change significantly with increasing compactness. The obtained results are in agreement with the literature (Saito, Yanagisawa, & Isogai, 2005), which confirmed the absence of chain-to-chain hemiacetal linkages between cellulose molecules in solution. So, if we consider the results for the MWD and MALLS investigations, it can be concluded that, depending on oxidative conditions, both degradation and intra-chain cross-linking occurs during the TEMPO-mediated oxidation of modified lyocell fibers.

Since the TEMPO-mediated oxidation does not end by introducing aldehyde groups, but leads to their conversion to the COOH groups and to other changes in the structure of the modified fibers (Praskalo et al., 2009), we also have analyzed the effect of oxidation conditions on the shape factor ν (Fig. 5).

Increasing the concentration of NaClO decreased the value of the shape factor. The smallest changes in shape factor occurred when the oxidation was done with the lowest concentration of

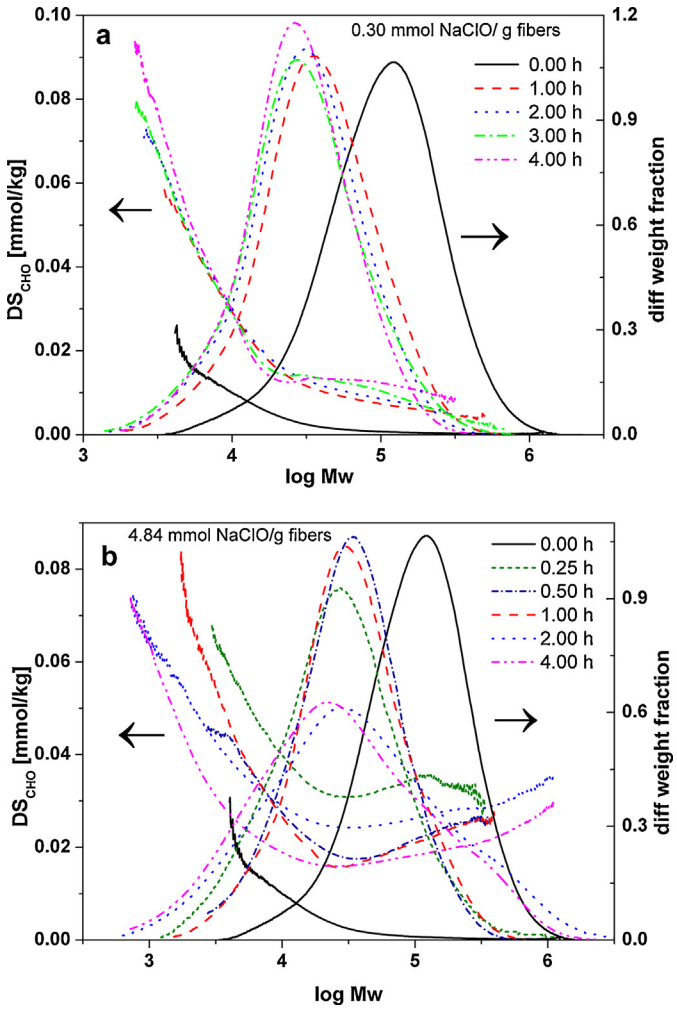

Fig. 3. The molecular weight distribution (MWD) and aldehyde profile (DS_{CHO}) for unmodified and TEMPO-oxidized lyocell fibers, where (a) 0.30 and (b) 4.84 mmol NaClO/g fiber was applied to the cellulose slurry, during 0.25–4 h, at RT and pH 10.5.

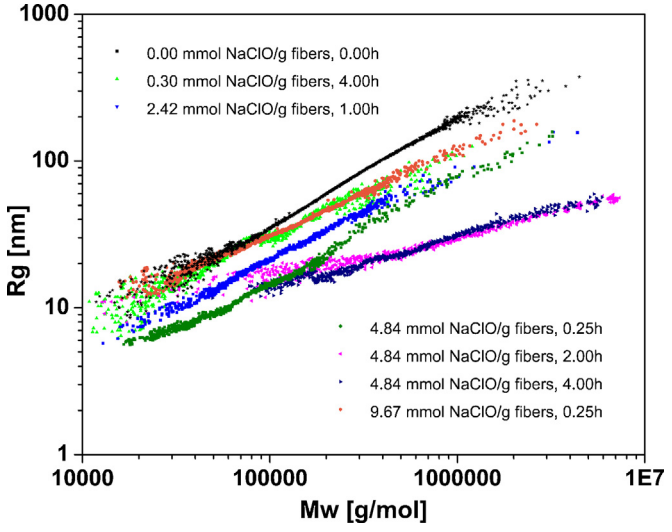

Fig. 4. Conformation analysis (i.e., double logarithmic plot of Mw vs. radius of gyration (Rg)) for TEMPO-oxidized lyocell fibers.

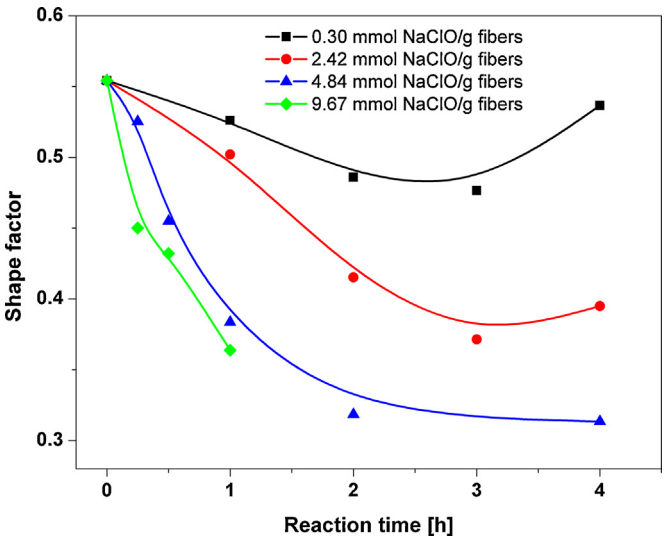

Fig. 5. Relationship between oxidation time and shape factor ν for the TEMPO-oxidized lyocell fibers, where 0.30; 2.42; 4.84 and 9.67 mmol NaClO/g fibers was applied to the cellulose slurry, during 0.25–4 h, at RT and pH 10.5.

NaClO, and the largest when the oxidation was carried out with the highest concentration of NaClO. Fig. 5a clearly shows that the oxidation time also affects the change in shape factor. Increasing the modification time up to 3 h decreases the shape factor value, most likely due to intra-chain cross-linking of introduced CHO groups. However, prolonging the oxidation process for more than 3 h increases the shape factor value. The reason for this lies in the conversion of CHO groups into the COOH groups, which is more pronounced under more severe oxidation conditions. Introduced carboxyl groups have anionic charges that cause electrostatic repulsions that can result in expansion of cellulose molecules and in an increase of the shape factor.

Since the content of introduced functional groups depends on the conditions of TEMPO-mediated oxidation, their influence on the amount and distribution of introduced functional groups will be further discussed in detail.

3.2. *Influence of TEMPO-mediated oxidation on the distribution of aldehyde and carboxyl groups*

During TEMPO-mediated oxidation, the C6 primary hydroxyl groups of cellulose are converted to carboxyl groups via the intermediate C6-aldehyde groups (Chang & Robyt, 1996; Saito & Isogai, 2006; Saito, Shibata, et al., 2005). The effect of oxidation time and amount of added NaClO on aldehyde and carboxyl group content in oxidized lyocell fibers, i.e., the water-insoluble fractions in the oxidized lyocells, is shown in Fig. 6.

In this study, weight ratios of the water-soluble fractions in the oxidized lyocells, which were lost during washing process, were thought to be ignorable, because the degrees of oxidation were sufficiently low (see Fig. 6a and b).

3.2.1. *The aldehyde group content*

The aldehyde group content in lyocell fibers oxidized by the lowest concentration of oxidant (0.30 mmol NaClO/g fibers) increased with increasing oxidation time, while higher concentrations of NaClO first increased the aldehyde content with oxidation time up to 1 h (i.e., 2 h), depending on NaClO concentration, and then prolonged oxidation resulted in a decrease in aldehyde content (Fig. 6a). During the further oxidation process, CHO groups are converted into COOH groups, and this conversion is the reason for decrease in the numbers of CHO groups. The maximum aldehyde

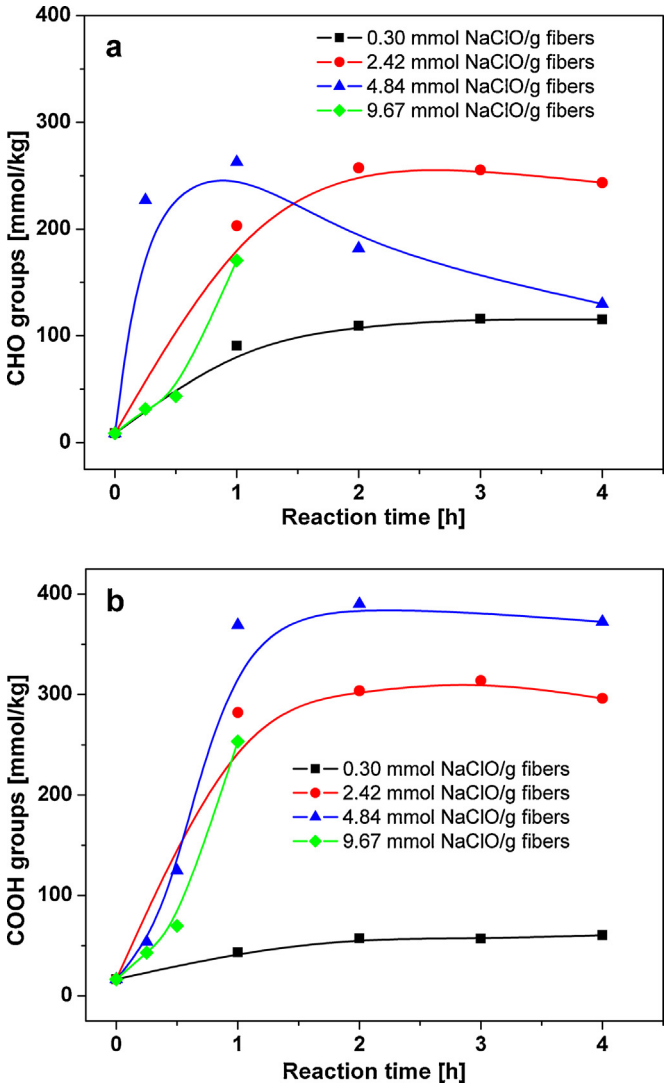

Fig. 6. Relationship between oxidation time and (a) aldehyde and (b) carboxyl group content in the TEMPO-oxidized lyocell fibers, where 0.30; 2.42; 4.84 and 9.67 mmol NaClO/g fibers was applied to the cellulose slurry, during 0.25–4 h, at RT and pH 10.5.

content for lyocell fibers of 262.76 mmol/kg fibers was obtained for a sample modified with 4.84 mmol NaClO/g fibers for 1 h; this was 30 times higher than the corresponding values for unmodified lyocell fibers (8.67 mmol/kg fibers). According to Saito and Isogai (2004) and Saito and Isogai (2006), the presence of significant numbers of aldehyde groups in oxidized lyocell fibers can be explained by formation of intra- and inter-molecular hemiacetals with cellulose hydroxyls in the solid water-insoluble fractions, which are likely to have a higher resistance to the subsequent oxidation by steric hindrance.

A detailed consideration of the influence of TEMPO-mediated oxidation on the lyocell fibers, in addition to determination of aldehyde groups as a sum parameter, requires the determination of a functional group profile in relation to the molecular weight of the cellulose fibers. The aldehyde group profile (DS_{CHO}) and molecular weight distribution (MWD) for unmodified and TEMPO-oxidized lyocell fibers with 0.30 mmol NaClO/g fibers and 4.84 mmol NaClO/g, were previously shown in Fig. 3a and b. In the case of modification with the lowest concentration of NaClO, the increase in the aldehyde group content is obtained for oxidized samples and pronounced introduction of aldehyde group content is detected in the low molecular weight region. The prolonged oxidation time has a slight influence on aldehyde content. When the oxidation is carried out with 4.84 mmol NaClO/g fibers, a significant number of aldehyde groups were observed in both, low (DP < 200) and high (200 < DP < 2000) molecular weight fractions. When the aldehyde groups should be introduced into high molecular weight fraction, a better effect can be achieved by increasing the concentration of NaClO than by prolonging the oxidation time.

3.2.2. The carboxyl group content

The carboxyl group content in unmodified lyocell fibers, as determined by the FDAM protocol, was 16.46 mmol/kg fibers. In contrast, for oxidized lyocell fibers, the carboxyl group content increased within the range of 42.97–390.07 mmol/kg fibers, depending on oxidative conditions (Fig. 6b). The increase in carboxyl group content can be explained by conversion of CHO groups into COOH groups due to further oxidation processes. Carboxyl group content in lyocell fibers oxidized in the presence of the lowest amount of NaClO (0.30 NaClO mmol/g fibers) showed similar behavior to aldehyde groups (i.e., the carboxyl group content slightly 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 fibers), the carboxyl group content increased with prolonged oxidation up to 3 and 2 h, respectively, and after reaching the maximum, decreased slightly in both cases. The maximum increase in carboxyl content in oxidized lyocell fibers of 23.7 times ($COOH_{mod}/COOH_{unmod}$) was obtained for the sample oxidized in the presence of 4.84 μmol NaClO/g fibers for 2 h. As we mentioned previously (Praskalo et al., 2009), too severe conditions (9.67 mmol NaClO/g fibers), in the case of TEMPO-mediated oxidation of lyocell fibers, result in loosening of the fibrous structure and for these modified fibers did not undergo complete characterization.

Deeper insight into the influence of TEMPO-mediated oxidation on distribution of introduced COOH groups was obtained by analyzing the COOH group profile in relation to the molecular weight distribution (MWD) (Fig. 7).

During the modification with the lowest concentration of NaClO (0.30 mmol/g fibers), the prolongation of modification time resulted in a gradual increase in the low molecular weight fractions, and the most COOH groups were introduced into these specific fractions (Fig. 7a). Similar to the situation noted for the CHO groups, the COOH groups were also introduced primarily into the short chains, which means that the conversion of CHO into COOH groups took place in molecular weight fractions with a low degree of polymerization (DP < 100).

Modification in the presence of 2.42 mmol NaClO/g fibers also caused a significant increase in the low molecular weight fractions. The comparison of COOH group distribution in the samples treated with 2.42 mmol NaClO/g fibers and with 0.30 mmol NaClO/g fibers shows that far greater amounts of COOH groups were introduced into the chains with the low degree of polymerization (100 < DP < 200), but also in the chains with the high degree of polymerization (200 < DP < 2000), due to the oxidation process running in these fractions as well (Fig. 7b).

The TEMPO-mediated oxidation using 4.84 mmol NaClO/g fibers introduced the highest amount of carboxyl groups, up to 24 times more than in the unmodified lyocell fibers. However, the distribution curves of the COOH groups were grouped into two areas, depending on the oxidation time (Fig. 7c). Apparently, if the modification time is longer than 30 min, significant amounts of COOH groups occur in both the low molecular fractions and in those with a higher degree of polymerization.

For lyocell fibers modified by the highest concentrations of NaClO (9.67 mmol/g fibers), significant increases in COOH groups are obtained by oxidation times up to 1 h (Fig. 7d).

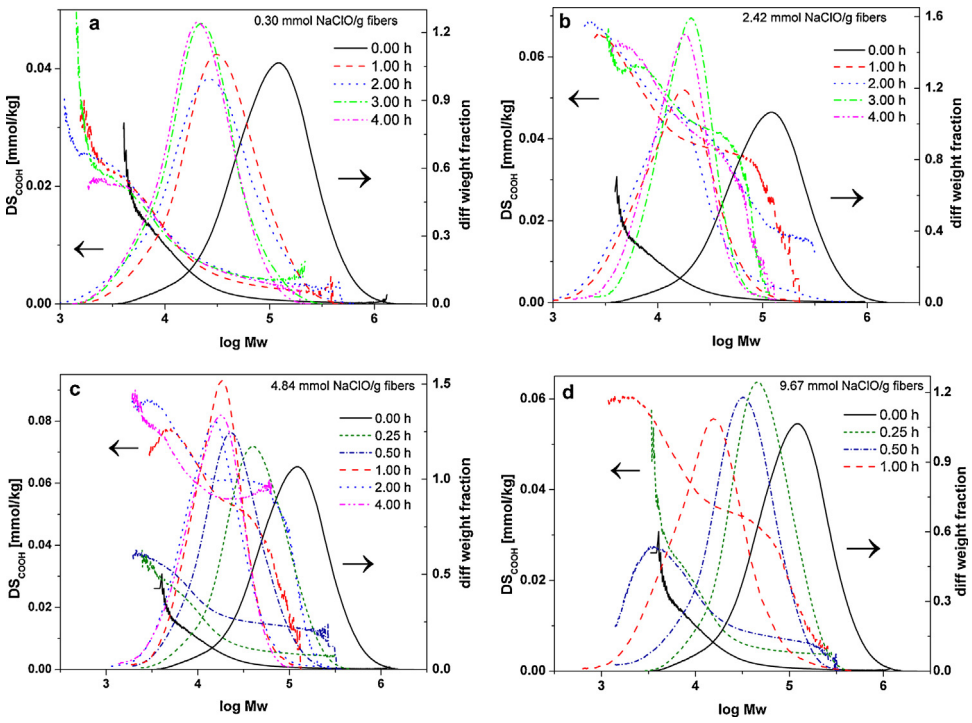

Fig. 7. Carboxyl profiles (DS_{COOH}) and molecular weight distribution (MWD) for unmodified and TEMPO-oxidized lyocell fibers where (a) 0.30; (b) 2.42; (c) 4.84; and (d) 9.67 mmol NaClO/g fibers was applied to the cellulose slurry, during 0.25–4 h, at RT and pH 10.5.

Application of the TEMPO-mediated oxidation for a modification time of up to 1 h, for all concentrations of NaClO (0.30–9.67 mmol NaClO/g fibers), resulted in COOH groups that are mostly present in low molecular weight fraction. Nevertheless, significant amounts of COOH groups can be introduced into the high molecular weight fractions by performing the oxidation using higher concentrations of NaClO (2.42–9.67 mmol NaClO/g fibers) during the modification times up to 1 h and longer.

Some differences between the MWD of oxidized lyocell fibers obtained after CCOA and FDAM labeling (e.g., Figs. 3b and 7c) can be explained by the difference in the labeling protocols, that are only differ in one pre-labeling step. For the CCOA method the samples are directly placed in buffer pH 4.5 for the labeling reaction. This pH is not sufficient to open all hemi-acetals formed, hence, in some cases some high-Mw material appears due to hemi-acetal cross-linking (see Fig. 3b). As we explained earlier, the tendency of hemi-acetal formation increases with increasing degree of oxidation. In the case of carboxyl group labeling the carboxyl groups need to be protonated before reacting them with the FDAM label. Hence a brief (1–2 min) acid treatment at pH 1 is performed. For the highly oxidized fibers, e.g., Figs. 3b and 7c, the hemi-acetals are opened at this low pH (acetals are sensitive to very low pH, the above mentioned buffer pH 4.5 is not sufficient), hence the cross-linked material is not present at the COOH-labeled material.

4. Conclusions

TEMPO-mediated oxidation is a very efficient procedure for the introduction of significant numbers of aldehyde and carboxyl groups into cellulose fibers, and the amount of these functional groups can be controlled by selecting appropriate oxidative conditions. The maximum increase in aldehyde and carboxyl content in TEMPO-oxidized lyocell fibers was obtained for sample modified with 4.84 mmol NaClO/g fibers for 1 and 2 h, respectively. The method applied for the determination of functional groups by fluorescence labeling provided the functional group content as a sum parameter but also generated a group profile in relation to the molecular weight of the cellulose fibers. When introduction of aldehyde groups is desired in a high molecular weight fraction, a better effect can be achieved by increasing the concentration of NaClO, rather than prolonging the oxidation time. Introduction of significant numbers of COOH groups in the high molecular weight fractions can be achieved by performing the oxidation with higher concentrations of NaClO (2.42–9.67 mmol NaClO/g fiber) at a modification time of 1 h or longer.

The TEMPO-mediated oxidation is accompanied by degradation effects (β-elimination from aldehydes at pH 10.5), which results in a decrease in the weight average molecular weight. A significant decrease in Mw is obtained during the 1 h of oxidation, while prolonged oxidation times result in no strong additional chain scission (i.e., the decrease in the weight average molecular weight reaches an almost constant level).

Acknowledgments

This study has been supported by the Ministry of Education and Science and Technological Development of the Republic of Serbia (Project OI 172029) and COST Action FP 0901.

References

Bohrn, R., Potthast, A., Schiehser, S., Rosenau, T., Sixta, H., & Kosma, P. (2006). The FDAM method: Determination of carboxyl profiles in cellulosic materials by combining group-selective fluorescence labelling with GPC. *Biomacromolecules*, *7*, 1743–1750.

Chang, P. S., & Robyt, J. F. (1996). Oxidation of primary alcohol groups of naturally occurring polysaccharides with 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion. *Journal of Carbohydrate Chemistry*, *15*, 819–830.

El-Wakil, N. A., & Hassan, M. L. (2008). Structural changes of regenerated cellulose dissolved in FeTNa, NaOH/thiourea, and NMMO systems. *Journal of Applied Polymer Science*, *109*, 2862–2871.

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

Okita, Y., Saito, T., & Isogai, A. (2010). Entire surface oxidation of various cellulose microfibrils by TEMPO-mediated oxidation. *Biomacromolecules*, *11*, 1696–1700.

Pfefferkorn, P., Beister, J., Hild, A., Thielking, H., & Kulicke, W. M. (2003). Detremination of the molar mass and the radius of gyration, together with their distributions for methyl-hydroxy-ethyl-celluloses. *Cellulose*, *10*, 27–36.

Potthast, A., Kostic, M., & Schiehser, S. (2007). Studies on oxidative modifications of cellulose by the tempo and periodate oxidation system. In *Italic 4, Science and technology of biomass: advances and challenges* 8–10 May.

Potthast, A., Kostic, M., Schiehser, S., Kosma, P., & Rosenau, T. (2007). Studies on oxidative modification of cellulose in the periodate system: Molecular weight distribution and carbonyl group profiles. *Holzforschung*, *61*(6), 662–667.

Potthast, A., Rohrling, J., Rosenau, T., Borgards, A., Sixta, H., & Kosma, P. (2003). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 3. Monitoring oxidative processes. *Biomacromolecules*, *4*, 743–749.

Potthast, A., Rosenau, T., & Kosma, P. (2006). Analysis of oxidized functionalities in cellulose. *Advances in Polymer Science*, *205*, 1–48.

Praskalo, J., Kostic, M., Potthast, A., Popov, G., Pejic, B., & Skundric, P. (2009). Sorption properties of TEMPO-oxidized natural and man made cellulose fibers. *Carbohydrate Polymers*, *77*, 791–798.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Borgards, A., Sixta, H., et al. (2002). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 2. Validation and application. *Biomacromolecules*, *3*, 969–975.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Ebner, G., Sixta, H., et al. (2002). A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 1. Method development. *Biomacromolecules*, *3*, 959–968.

Saito, T., Hirota, M., Tamura, N., & Isogai, A. (2010). Oxidation of bleached wood pulp by TEMPO/NaClO/$NaClO_2$ system: Effect of the oxidation conditions on carboxylate content and degree of polymerization. *Journal of Wood Science*, *56*, 227–232.

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

Saito, T., & Isogai, A. (2006). Introduction of aldehyde groups on surfaces of native cellulose fibers by TEMPO-mediated oxidation. *Colloids and Surfaces*, *289*, 219–225.

Saito, T., Okita, Y., Nge, T. T., Sugiyama, J., & Isogai, A. (2006). TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidized products. *Carbohydrate Polymers*, *65*, 435–440.

Saito, T., Shibata, I., Isogai, A., Suguri, N., & Sumikawa, N. (2005). Distribution of carboxylate groups introduced into cotton linters by the TEMPO-mediated oxidation. *Carbohydrate Polymers*, *61*, 414–419.

Saito, T., Yanagisawa, M., & Isogai, A. (2005). TEMPO-mediated oxidation of native cellulose: SEC-MALLS analysis of water-soluble and-insoluble fractions in the oxidized products. *Cellulose*, *12*, 305–315.

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

Shinoda, R., Saito, T., Okita, Y., & Isogai, A. (2012). Relationship between length and degree of polymerization of TEMPO-oxidized cellulose nanofibrils. *Biomacromolecules*, *13*, 842–849.

Tamura, N., Wada, M., & Isogai, A. (2009). TEMPO-mediated oxidation of (1-3)-b-D-glucans. *Carbohydrate Polymers*, *77*, 300–305.

Thielking, H., & Kulicke, W.-M. (1998). Determination of the structural parameters of aqueous polymer solutions in the molecular, partially aggregated, and particulate states by means of FFFF/MALLS. *Journal of Microcolumn Separations*, *10*(1), 51–56.

Zhang, H., Zhang, H., Tong, M., Shao, H., & Hu, X. (2008). Comparison of the structures and properties of lyocell fibers from high hemicellulose pulp and high α-cellulose pulp. *Journal of Applied Polymer Science*, *107*, 636–641.