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MILD OXIDATION OF CELLULOSE FIBERS USING DIOXYGEN AS ULTIMATE OXIDIZING AGENT

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Two types of regenerate cellulose fibres were oxidized under mild conditions, by using *N*-hydroxyphthalimide as catalyst and molecular oxygen as ultimate oxidizing agent. The amounts of negatively charged groups introduced were determined by means of potentiometric titration. The degree of polymerization and molar mass of the oxidized fibres determined viscosimetrically, has been found to be almost unaffected during oxidation.

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1. Introduction

Generally, the conventional regenerated cellulose fibers are prepared either by the indirect viscose process (viscose fibers) or using a modification of the basic procedure. The fiber production processes are based on the derivatisation of cellulose using carbon disulfide [1]. The fabrication of ultrathin fibers is achieved successfully by using electrospinning technique [2]. The chemical and physical properties of regenerated fibers can be improved by pretreatment processes, like alkaline washing, slack-mercerization and bleaching. The surface modification of regenerated fibers, by using either chemical or physical methods, is one of the most important process which lead to an increased adsorption and surface charge density, as a consequence of the higher amount of accessible negative fiber groups. One method to achieve this desire is oxidation on the surface fibers. Nitroxides, NO_2 and N_2O_4 have been used for the selective oxidation of primary hydroxyl group of cellulose [3]. $NaNO_2$ and $NaNO_3$ are other selective reagents for oxidation of OH group bonded at C_6. In this case, the reaction takes place homogeneously in 85% H_3PO_4 solution [4]. A mixture of $NaBrO_3$, $NaClO_3$ or $NaClO_2$ in 85% H_3PO_4 solution was reported to be efficient to modify primary hydroxyl group [5]. Very recently, a mild and an efficient method for oxidation of primary OH groups in alcohols in ionic liquid media have been reported [6]. At present, the most studied oxidation system for primary OH group oxidation of wide range of polysaccharides is 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) / NaBr / NaOCl [7]. In this oxidizing system, the actual oxidizing species is the nitrosonium ion [7], the oxidized form of TEMPO, Scheme 1. The generation of nitrosonium ion takes place *in situ*, through the reaction of TEMPO with hypobromide ions, which in turn are produced from bromide salt and NaOCl. Recently, the use of non persistent phthalimide-*N*-oxy (PINO) radical generate *in situ* from *N*-hydroxyphthalimide (NHPI) [8-10] has been reported for the oxidation of cellulose fibers, at room temperature, pH=10.5 in the presence of NaBr / NaOCl [11]. A general problem of the

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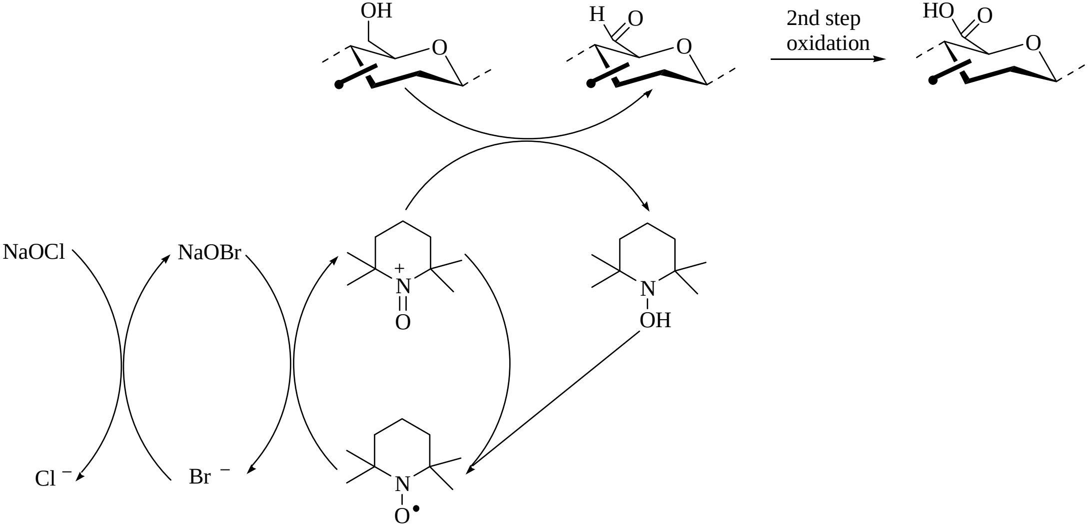
aforementioned oxidants (except TEMPO and NHPI) is that they are highly toxic, and the oxidation is accompanied by side reactions which eventually lead to depolymerization. Moreover, TEMPO/NaBr/NaOCl oxidation method is not waste free: at least one equivalent of sodium chloride is produced per one OH group oxidized. Other shortcomings are the use of sodium bromide as a cocatalyst, the price of TEMPO which is rather high, which means that efficient recycling is an important issue. Thus, it was of interest to study the oxidation of two types of cellulose fibers, i.e. viscose and modal, employed under mild conditions, at neutral pH, without any bromide or hypochlorite, using only molecular oxygen as ultimate oxidizing agent. Directly using oxygen (air) as an oxidant would therefore not only reduce the cost, it would also eliminate many environmental problems.



Scheme 1. Oxidation scheme of primary hydroxyl groups of cellulose in the presence of TEMPO/BrNa/NaClO system

2. Experimental

2.1. Materials

The regenerated cellulose fibers, i.e. viscose (CV), and modal (CMD) were produced by Lenzing AG Lenzing, Austria. Table 1 presents the specifications and some of the most important fiber structure characteristic of investigated cellulose fibers.

Table 1. Specifications and structure characteristics of regenerated cellulose fibers [11].

Fibre type	Standard / Method	CV	CML
Linear density, T_t [dtex]	DIN 53812	1.88 ± 0.15	1.78 ± 0.23
Fiber length, l [mm]	DIN 53808	39.9 ± 0.51	40.1 ± 0.33
Fiber diameter, d [μm]	DIN 53811	14.3 ± 1.39	14.2 ± 1.10
Density, ρ [g/cm^3]	DIN 53479	1.5045	1.5141
Degree of polymerization, DP	DIN 54270	308 ± 2.49	488 ± 6.95
Molecular mass, M	DIN 54270	49957 ± 402	79045 ± 1126
Crystallinity index, CrI	X-ray wide angle diffraction	0.25	0.37
Orientation factor, $f_{\Delta n}$	Birefringence	0.58 ± 0.07	0.69 ± 0.08
Void volume, V_p [cm^3/g]	Size Exclusion Chromatography (SEC)	0.68	0.49

Chemicals used in reaction, NHPI, anthraquinone, were of laboratory grade and used without further purification.

2.2. PINO-mediated oxidation of cellulose fibers.

The oxidation of viscose and modal fibres to result oxidized viscose (OCV) and oxidized modal fibres (OCMD) respectively has been carried under following condition: 16 g of fibres (CV or CMD) were placed in a 3 L two-necked flask, containing 1.4 L deionised water:acetonitrile (6:1 vol), equipped with a balloon filled with O_2. NHPI together with anthraquinone (3.2 mmol of each) were added, and the resulted suspension was kept at room temperature under stirring for 5 days. The reaction was quenched by adding 100 mL ethanol, and the oxidized fibres were filtered off. The recovered fibres were washed with acetone and deionised water.

2.3. Potentiometric titration

The viscose fibres were added into a aqueous solution containing 0,1 M potassium chloride and 0,1 M hydrochloric acid. The fibre suspension was then stirred with a magnetic stirrer for about a half an hour.

The pH potentiometric titration of the fibre suspension was carried out with a Mettler Toledo T70 titrator, using a 10 mL burette in an inert atmosphere (N_2 bubbling). The solution was titrated from the initial pH = 2,5 to the preset pH = 11, with 0,1 M KOH. The potential of the solution was measured in pH, using a Mettler Toledo DG-117 pH glass electrode. The same solution was also titrated without the fibres sample as a blank acid – base titration for data evaluation purpose. The amount of negatively charged groups was calculated, by subtracting the blank titration from the sample titration. All presented values are the mean values of 3 parallel measurements, the standard deviation of measurements being within 4%.

2.4. Fourier transform infrared spectroscopy/attenuated total internal reflection spectroscopy (FT-IR/ATR)

FT-IR/ATR experiments were carried out on silicon single-crystal parallelepiped internal reflexion elements (IRE) (55 mm x 5 mm x 2 mm, 45^o incident angle), using a Bruker Vertex 70 instrument. All the spectra were the results of 256 co-added scans at a resolution of 4 cm^{-1}.

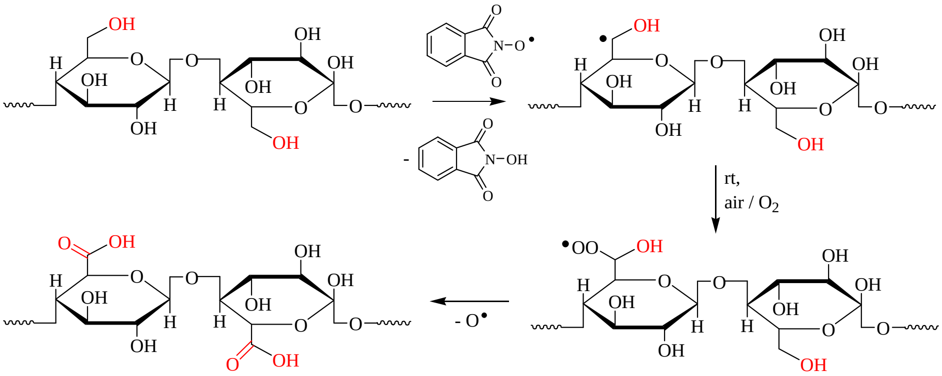
2.5. Molecular mass and degree of polymerization

The molecular mass and the degree of polymerization were determined viscosimetrically after dissolving the cellulose samples in solvent EWNN (FeTNa sodium salt of ferric tartaric acid) according to standard DIN 54 270. The viscosity measurements were performed in a modified Ubbelohde viscometer (capillary length 78 mm, capillary bore width 0.75 mm, volume of the bulb between the marks 7 cm^3).

3. Results and discussion

3.1. PINO-mediated oxidation of cellulose fibers.

NHPI promotes the oxidation of a wide range of organic compounds with dioxygen in the presence of cocatalyst, able to abstract a hydrogen atom [8, 13]. In this oxidation, the PINO radical generated *in situ* is able to abstract a hydrogen atom from substrate, to form a carbon centred radical, which eventually is trapped by dioxygen to for the oxygenated products, Scheme 2. NHPI is cheap, non-toxic, easily prepared from phthalic anhydride and hydroxylamine. Due to the two fold screw axis structure [14] of the cellulose chain, only half of the hydroxymethyl groups are available for reaction, the other being buried inside the crystallite.



Scheme 2. The oxidation scheme of cellulose performed by NHPI and O_2

The potency of PINO to oxidize cellulose primary OH group is linked with the bond dissociation value (BDE) value of the N-OH precursor, that is, NHPI, which has 88 kcal mol^{-1}, much higher than TEMPO, in which the NO-H bond of the hydroxylamine group it is only 69 kcal mol^{-1} [15]. Thus the catalytic effect of NHPI on free radical autoxidations has two origins: a higher rate of propagation, and a lower rate of termination due to extremely efficient scavenging of alkylperoxy radicals by NHPI [16].

The amount of negatively charged groups on cellulose fibres as determined by potentiometric titration is shown in Table 2.

Table 2. Amount of negatively charged groups (n) on oxidized viscose fibres

Sample	n [mmol/kg]
CV	0
CMD	0
OCV	37,5
OCMD	19,0

Fig. 1 presents the charge isotherms of oxidized OCV and OCMD in comparison with non oxidized CV sample.

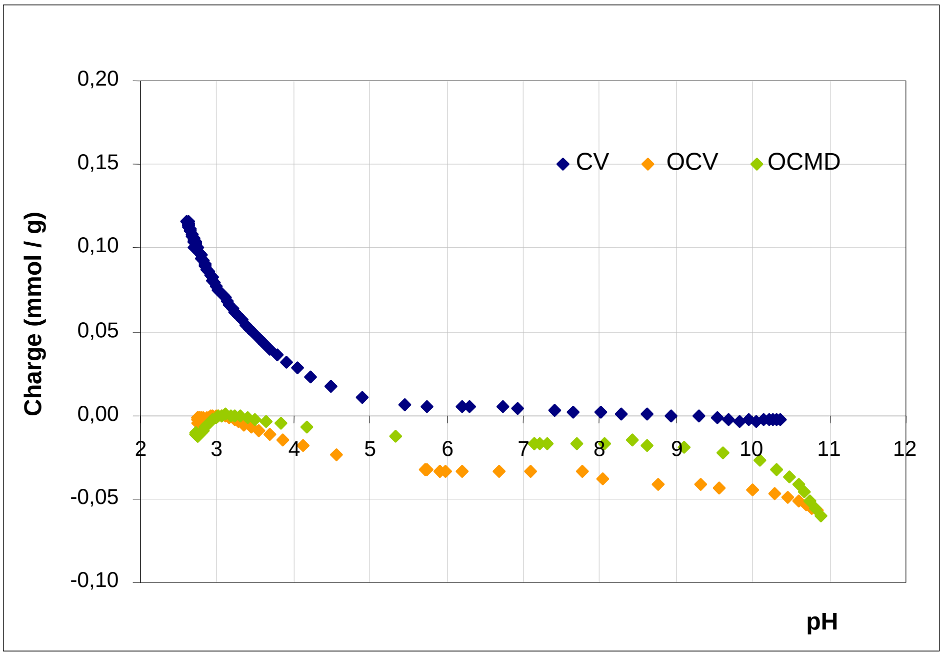


Fig. 1. Charge isotherms of CV , OCV and OCMD fiber samples per gram

From table 1 and Fig. 1 one can observe that sample OCMD (19 mmol/kg) exhibits 49% less negative charge than sample OCV (38 mmol/kg). These differences may reflect solid-state structures and/or distribution of disordered regions along one cellulose chain in the cellulose II samples.

The p*K* values of both OCMD and OCV samples were determined to be p*K* = 4, and were calculated, using the one-pK model, described by equation (1):

$$\mathrm{pH} = \mathrm{p}K - \log\left(\frac{\theta}{1-\theta}\right) \tag{1}$$

where θ represents the degree of protonation which was obtained from the plateau values $Q_{\max}V_{t,\max}$ and $Q_{\min}V_{t,\min}$ of the isotherms as, equation (2):

$$\theta = \frac{QV_t - Q_{\min}V_{t,\min}}{Q_{\max}V_{t,\max} - Q_{\min}V_{t,\min}} \tag{2}$$

while p*K* is the deprotonation equilibrium constant.

3.2. Fourier transform infrared spectroscopy/attenuated total internal reflection spectroscopy (FT-IR/ATR)

The results of FTIR analysis of the two original (CV and CMD) and oxidized (OCV and OCMD) fibers are shown in Figure 2. The spectra of CV and CMD shows similar chemical composition, with representative peaks located at around 4,000 – 2,995 cm^{-1} (hydrogen-bonded OH stretching), 2891 cm^{-1} (CH stretching mode). The band from 1646 cm^{-1} (0.35) is more intensive in modal fibers and shifted to higher value than for viscose 1641 cm^{-1} (0.15) and is attributed to OH bending mode due to bound water. The other two typical peaks for cellulose are present at 1430 cm^{-1} and 900 cm^{-1}. The first is known as a “crystalline” and the second as an “amorphous” adsorption band. The spectra of the oxidized (OCV and OCMD) fibers, due to the lower content of COOH groups are not very different than those of the original fibers, the main changes are barely visible in the 1640-1740 cm^{-1} range, especially for the modal samples. This is a clear indication that the ring structure of the cellulose is not substantially changed during oxidation. Moreover, the structure of the oxidized fibers must therefore have a strong relationship with the structure of the original samples.

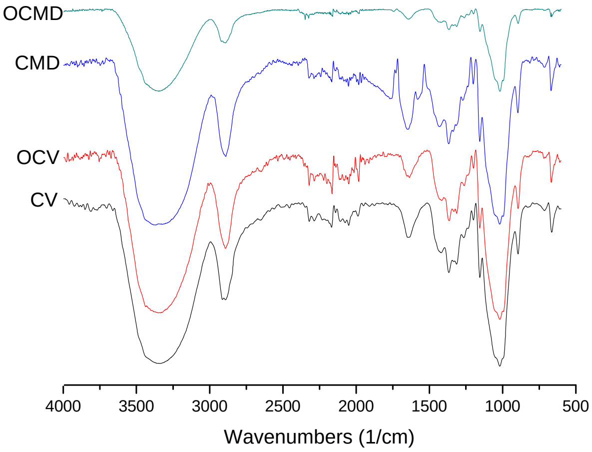


Fig. 2. ATR FT-IR spectra of starting (CV and CMD) and oxidized (OCV and OCMD) fibers (spectra were vertically shifted for bettr comparison).

3.3. Molecular mass and degree of polymerization

The intrinsic viscosity $[\eta]$ was calculated from the efflux time of cellulose solution (t), the blank EWNN solution (t_0), and from the concentration of cellulose in solution (c) according to the Schulz-Blaschke, equation (3):

$$[\eta] = \frac{(\eta_{\mathrm{rel}} - 1)/\mathrm{c}}{1 + \mathrm{k}_\eta \cdot (\eta_{\mathrm{rel}} - 1)} \tag{3}$$

where η_{rel} is the relative viscosity and k_η is the coefficient for a given polymer solvent system ($0.3 < \mathrm{k}_\eta > 0.4$). The molecular mass and degree of polymerization were calculated from the relationship between intrinsic viscosity $[\eta]$ and molecular mass, according with Kuhn-Mark-Houwink-Sakurada (KMHS) equation (4):

$$[\eta] = \mathrm{K} \cdot \mathrm{M}^{\alpha} \tag{4}$$

K is a constant value, depending on the solvent at a given temperature and α is the value which describes the flexibility of molecules ($0.5 < \alpha < 0.8$).

Table 3, presents the results obtained for the both, original and oxidized samples. It can be observed that the oxidized samples (OCV and OCMD) have a comparable molecular mass and degree of polymerization with the original samples, the loss of molecular mass being only 8% in the case of viscose fibers and 5% for the modal fibers. These values demonstrates that depolymerization processes by β-elimination which occur in the case of using TEMPO/NaOCl/KBr system is almost negligible in the PINO/O_2 oxidation of cellulose fibers since it was reported for the former oxidizing system an enormous drop of the degree of polymerization from 380 to 49 (in the case of Tencel fibers) and from 680 to 38 (in the case of Bemliese fibers) [17].

Table 3. Specific viscosity η_{spec}, reduced viscosity η_{red}, intrinsic viscosity $[\eta]$, viscosity-average molecular mass $\overline{\mathrm{M}}_\eta$ and degree of polymerization $\overline{\mathrm{DP}}_\eta$ of regenerated cellulose and oxidized fibers.

Sample	η_{spec}	η_{red}	$[\eta]$ [ml/g]	$\overline{\mathrm{M}}_\eta$ [g/mol]	$\overline{\mathrm{DP}}_\eta$
CV	0.253	260.028	239.460	49.957 ± 402	308 ± 2,49
OCV	0.238	242.173	224.068	45.881 ± 1406	283 ± 8,68
CMD	0.378	386.340	342.504	79.045 ± 1126	488 ± 6,95
OCMD	0.359	367.896	327.936	74.760 ± 487	461 ± 3,01

4. Conclusions

NHPI and molecular oxygen can be successfully used for the mild and moderate oxidation of cellulose fibers of viscose and modal type. The oxidation reaction takes place at room temperature, at neutral pH, and converts moderately the primary OH groups from cellulose to carboxylic ones. Notably, the degree of polymerization and molecular mass of original materials are preserved during the oxidation reaction, only modest decreases of these parameters being observed.

Acknowledgements

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References

[1] G. Cook, in: Handbook of textile fibres, Man-Made Fibres, 5th ed., Merrow, Durham, pp. 47-64 (1984).
[2] D. Paneva, N. Manolova, I. Rashkov, H. Penchev, M. Mihai, E. S. Dragan, Digest Journal of Nanomaterials and Biostructures **5**(4), 811 (2010).
[3] D. S. Zimnitsky, T. L. Yurkshtovich, P. M. Bychkovsky, J. Polym. Sci., Part A: Polym. Chem. **42**, 4785 (2004).
[4] V. Kumar, T. Yang, Carbohydr. Polym. **48**, 403 (2002).
[5] M. Pagliaro, Carbohydr. Res. **308**, 311 (1998).
[6] J. Safaei-Ghomi, A. R. Hajipour, M. Esmaeili, Digest Journal of Nanomaterials and Biostructures **5**(3), 865 (2010).
[7] P. L. Bragd, H. Bekkum, A. C. Besemer, Top. Catal. **27**, 49 (2004).
[8] S. Coseri, Catal. Rev. **51**, 218 (2009).
[9] S. Coseri, Eur. J. Org. Chem. **2007**, 1725 (2007).
[10] S. Coseri, J. Phys. Org. Chem. **22**, 397 (2009).
[11] S. Coseri, G. Nistor, L. Fras, S. Strnad, V. Harabagiu, B. C. Simionescu, Biomacromolecules **10**, 2294 (2009).
[12] T. Kreze, S. Strnad, K. Stana-Kleinschek, V. Ribitsch, Mater. Res. Innovat. **4**, 107 (2001).
[13] S. Coseri, Mini-Rev. Org. Chem. **5**, 222 (2008).
[14] Y. Habibi, H. Chanzy, M. R. Vignon, Cellulose **13**, 679 (2006).
[15] P. Astolfi, P. Brandi, C. Galli, P. Gentili, M. F. Gerini, L. Greci, O. Lanzalunga, New J. Chem. **29**, 1308 (2005).
[16] R. A. Sheldon, I. W. C. E. Arends, Adv. Synth. Catal. **346**, 1051 (2004).
[17] T. Isogai, M. Yanagisawa, A. Isogai, Cellulose 16, 117 (2009).