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One-sided surface modification of cellulose fabric by printing a modified TEMPO-mediated oxidant

Christa Fitz-Binder, Thomas Bechtold*

Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Hoechsterstrasse 73, A-6850 Dornbirn, Austria[1]

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ABSTRACT

One-sided surface oxidation of lyocell type cellulose fabric can be achieved by use of a modified TEMPO-mediated oxidation system. A borate-based buffer was used to maintain stable pH conditions and screen printing was applied to achieve oxidation on the fabric surface only. To formulate an applicable procedure, the TEMPO/NaBr/NaOCl system was split into two treatment steps: firstly, the fabric was impregnated with a buffered TEMPO/NaBr solution and dried, then a thickened NaOCl paste was printed on the fabric. FTIR-ATR spectra and methylene blue sorption experiments demonstrated successful modification on the printed side of the fabric. Substantial increases in carboxylic group content and water retention value were observed. The higher concentration of carboxylic groups on the fabric surface also led to a localised increase in binding capacity for Ca^{2+}-ions. This new concept permits controlled oxidation of cellulose surfaces by printing techniques.

1. Introduction

For a wider technical use of cellulose as sustainable polymer, suitable methods are required for the physical and chemical modification of the material (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998a). Besides the selective functionalisation of the polymer in solution, the topochemical control of the reaction is also of interest to introduce local modifications at defined sites of a solid structure.

An important chemical strategy to introduce carboxylic groups at the C-6 of the cellulose polymer is TEMPO-mediated oxidation using the TEMPO/NaBr/NaOCl system (Saito & Isogai, 2004; Tahiri & Vignon, 2000). By TEMPO oxidation of fibrous material such as natural and man-made cellulose fibres or bacterial cellulose nanofibres, the modification of sorption properties can be achieved. The preparation of silver containing antibacterial fibres also has been described in the literature (Cao, Ding, Yu, & Al-Deyab, 2013; Ifuku, Tsuij, Morimoto, Saimoto, & Yano, 2009; Praskalo et al., 2009; Praskalo-Milanovic, Kostic, Dimitrijevic-Brankovic, & Skundric, 2010).

Oxidised cellulose nanofibres are of general interest as an environmentally friendly and biobased material (Isogai, Saitoa, & Fukuzumia, 2011; Okita, Saito, & Isogai, 2010).

TEMPO oxidation is often performed at pH 10.5. As the solution pH decreases during the course of the reaction, the shift in pH must be compensated by addition of a NaOH solution, which makes the procedure more laborious (Cao et al., 2013; Milanovic, Schiehser, Milanovic, Potthast, & Kostic, 2013). Different approaches in the use of a buffered solution to overcome the continuous addition of NaOH, and to add NaOCl dropwise have been reported in the literature (Li et al., 2013; Lin, Shuai, Zhenxiu, Hu, & Kuk, 2012; Xu, Dai, Sun, Wang, & Wu, 2012). Due to the insufficient capacity of the buffers used, a substantial decrease in pH to values near 10 or lower was observed (Xu et al., 2012).

The presence of carboxylic groups in the polymer chain modifies the swelling properties of the material and also the ability to bind cations through an ion-exchange mechanism involving COOH groups (Fitz-Binder & Bechtold, 2012; Lin et al., 2012). An increase in carboxylic group content thus leads to an increased metal ion binding capacity of the modified polymer (Emam, Manian, Siroka, & Bechtold, 2012; Gurgel, Junior, Gil, & Gil, 2008; Huang, Ou, Boving, Tyson, & Xing, 2009; Kongdee & Bechtold, 2004).

To transfer the TEMPO-mediated oxidation on a larger scale and also for the treatment of plane 2D-material such as fabric or nonwovens, both an efficient use of the chemicals applied and a robust technique of application are required. Continuous treatment processes are very efficient with regard to resources consumption and

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* Corresponding author. Tel.: +43 5572 28533; fax: +43 5572 28629.
E-mail address: Thomas.Bechtold@uibk.ac.at (T. Bechtold).

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productivity (Bechtold, Burtscher, & Hung, 2004). Different to batch techniques, continuous treatment requires the design of time stable reaction conditions as continuous addition of chemicals is not possible. As an advantage controlled one-side surface modification by TEMPO-mediated oxidation could be expected from a continuous printing process.

In this paper a modified TEMPO/NaBr/NaOCl oxidation technique suitable for printing is presented, which allows continuous surface oxidation of plane cellulose fabric. Selective oxidation of the lyocell type cellulose fibres can be achieved on one side of the fabric. FTIR-ATR, methylene blue sorption, determination of water retention value (WRV) and moisture content (MC) were used to characterise the surface modification. Sorption of Ca^{2+} ions was studied by alizarin staining and colour measurement.

2. Experimental

2.1. Materials and chemicals

Tempo oxidation experiments were performed with woven lyocell fabric provided by Lenzing AG, Lenzing Austria (100% lyocell type cellulose fibre 1.3 dtex, yarn count 50 m/g, plain weave, warp 37 yarn/cm, weft 27 yarn/cm, mass/area 1.309 g/dm^2, prewashed, ready to dye).

Purity of the chemicals used: KIO_3 (p.a., Merck, Darmstadt, Germany), KI and NaOH (p.a. Roth Karlsruhe, Germany), $Na_2S_2O_3$ (≥97%, Merck, Darmstadt, Germany), NaBr (>99%, Riedel-de Haen, Seelze, Germany), methylene blue (for microscopy, Merck, Darmstadt, Germany), boric acid (p.a., Zeller, Hohenems, Austria), ethanol (96%, Merck, Darmstadt, Germany, TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl, radical, 98%, Fluka, Buchs, Switzerland), NaOCl (technical grade, approx. 100 g/L active chlorine, Deuring, Hörbranz, Austria).

The active chlorine content of the NaOCl solution was determined by iodometric titration using a titroprocessor 0.1 M $Na_2S_2O_3$ solution and starch indicator for end point determination. All molar amounts of oxidant presented in this work are calculated as equivalents, thus one molecule of NaOCl represents two equivalents of oxidant.

2.2. TEMPO/NaBr/NaOCl batch oxidation

A mass of 3.3–3.6 g lyocell fabric was placed on a cylindrical mount and pre-wetted in deionised water at RT for 1 h.

Boric acid (6.18 g, 0.1 M) was dissolved in 800 mL deionised water, adjusted to pH 10.5 by addition of NaOH (approx. 92 mL, 1 M) and filled to 1 L with water. 0.025 ± 0.001 g TEMPO was dissolved in 750 mL of the buffer solution, then 0.25 g NaBr was added and the pre-wetted fabric sample was placed on the cylindrical mount. Following the addition of NaOCl solution the oxidation was carried out for 1 h at RT (Table 1). Then the reaction was then stopped by addition of 5 mL ethanol and the mount with the fabric sample was removed and rinsed three times with a solution of 2 mL ethanol in 800 mL water. A small amount of ethanol was added to the rinse to assure full reaction stop. The fabric then was dried at ambient temperature.

2.3. Selection of thickener and oxidant printing

Commercial samples of polymers (polyvinylalcohol (Elvanol, DuPont; Vinarol, Clariant) carboxymethylcellulose (Tylose CR 700N Hoechst, Frankfurt a. M. Germany), esterified starch (Solamyl, Agrana, Gmuend, Austria), carboxymethyl starch (Amitrolit, Agrana, Gmünd, Austria) and alginate (aginate printing thickener, Jos. Otten, Hohenems, Austria) were dissolved at 80 °C in a buffer solution (1 M boric acid and NaOH to pH 10.5) to form a 10 g/L buffered solution. 1 g NaBr and 0.015 g or 0.15 g TEMPO was dissolved in 1 L of buffer solution (0.1 M boric acid, NaOH to pH 10.5). After cooling down of the thickener solution to RT, to 50 mL of the TEMPO solution was added to 50 mL of the thickener solution and mixed. Then 2.5 mL of ca. 1 M NaOCl solution was added.

Samples were analysed for the decrease in NaOCl concentration during a period of 2 h by iodometric titration with 0.1 M $Na_2S_2O_3$.

For printing experiments, firstly the fabric sample was impregnated with a solution of 2 g/L NaBr and 0.3 g/L TEMPO in 0.1 M boric acid buffer (pH 10.5) by means of a laboratory padder (3 m/min roller speed and 2 bar nip pressure, pick up 68%, padder HVF, Mathis, Niederhasli, Switzerland). The samples then were dried in a laboratory drier (Mathis Labdryer, Mathis, Niederhasli, Switzerland) at 60 °C for 5 min.

For the printing paste, a thickener basis was prepared by dissolution of 20 g/100 mL (basis I) or 25 g/100 mL (basis II) of alginate thickener by heating to the boil. To 5 g of basis (I) 0.5–3 mL NaOCl (3.53 M) were added, 4 mL NaOCl was added to basis (II). The mixtures were then stirred to obtain a homogenous paste. The formulation was then printed by screen printing (mono-filament, plain weave, filament diameter 80 μm, open area 130 μm × 130 μm) on a weighed NaBr/TEMPO/buffer containing lyocell fabric. From the printed area and the increase in weight, the added mass of oxidant was calculated. The prints were rested for 30 min covered by a PE-film, washed thoroughly with tap water and dried at ambient temperature.

2.4. Determination of moisture content and carboxyl group content

The carboxyl group content (COOH) was determined after the oxidation treatment of the cellulose samples (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998b). First 0.30 g methylene blue was dissolved in 750 mL deionised water. Then the pH was adjusted to 8.5 by addition of 4 M NaOH and the solution was filled to 1 L. Samples with a weight of 0.2–0.5 g were stored at 20 °C and 65% r.h. for at least 24 h to equilibrate the moisture content. The samples were weighed and then dried for 4 h at 105 °C. They were then cooled down in a desiccator and weighed in dry state to determine the moisture content. The values are given as the mean of a double determination.

For determination of the carboxylic group content 25 mL methylene blue solution and 25 mL buffer solution pH 8.5 were added to an exact sample weight, e.g. 0.05 g. The samples were shaken in the solution overnight at RT. A blank value was determined by analysing a solution without addition of cellulose sample. After equilibration, 2.5 mL of the solution was acidified with 5 mL of 0.1 M HCl and filled to 50 mL with water (double determination). The absorbance of the solution at 664.5 nm was then measured with a double beam spectrophotometer (Hitachi U-2000 Spectrophotometer, 10 mm cuvette). Borate buffer served as reference. The carboxyl group content was then calculated as mmol/kg cellulose material as mean of a double determination (Philipp, Rehder, & Lang, 1965).

2.5. Water retention value

An exact mass of 0.5 g fabric was placed in 40 mL of deionised water overnight to achieve complete swelling of the cellulose. At the end of the immersion step, fibres were centrifuged at 4000 × g for 10 min using 50 mL centrifuge tubes with a filter inlay to remove capillary water (Multifuge 1L, D-37520 Osterode, Germany). The samples were weighed and dried at 105° for 4 h, then placed in a dessicator to cool down and weighed again. Water retention value