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

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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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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

Table 1
Experimental conditions and results for batch oxidation experiments with use of buffered solution (tensile strength – TS, elongation – EL).

No	Mass (g)	T (°C)	pH	Time (min)	NaOCl (mmol/g)	WRV (g/g)	MC (g/g)	COOH (mmol/kg)	TS (cN)	EL (%)
1	–	–	Untreated	–	–	0.515 ± 0.004	0.091 ± 0.006	15.6 ± 1.0	501 ± 64	21 ± 2.4
2	3.58	23–25	10.51–10.45	60	2.64	0.573 ± 0.018	0.109 ± 0.006	226.3 ± 15.3	351 ± 54	16 ± 2.7
3	3.61	25–26	10.53–10.44	60	4.60	0.617 ± 0.011	0.111 ± 0.003	293.4 ± 3.8	362 ± 13	18 ± 1.3
4	3.57	25–26	10.67–10.53	60	9.96	0.653 ± 0.004	0.121 ± 0.001	364.8 ± 24.8	290 ± 42	17 ± 1.8
5	3.43	23–24	10.65–10.52	60	6.91	0.624 ± 0.005	0.112 ± 0.000	317.3 ± 0.3	346 ± 48	18 ± 2.2

(WRV) was calculated according to Eq. (1) (Zhang, Okubayashi & Bechtold, 2005).

$$\mathrm{WRV} = \frac{W_1 - W_2}{W_2} \quad (1)$$

where W_1 and W_2 are wet mass (g) and mass after drying (g), respectively. The values are given as mean of a double determination.

2.6. Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were recorded using a Bruker Vector 22 Spectrometer (Bruker Analytik, Vienna, Austria) attached with a diamond crystal ATR unit.

2.7. Tensile strength and elongation

Tensile strength and elongation to break of a single yarn extracted from the fabric (in weft direction) were determined according DIN EN ISO 2062:2006 using a Zwick/Roll universal tester (constant rate of extension, 110 mm/min, sample length at start 110 mm, pretension 0 N). The tests were performed with 10 repetitions.

2.8. Colour measurement

Colour coordinates of methylene blue treated samples were calculated from the diffuse reflectance using a KONICA MINOLTA spectrophotometer (CM 3610d, Konica, Japan; d/8 measurement geometry, sample diameter 8 mm, light source pulsed xenon lamp). CIELab colour coordinates were calculated for a 10° observer and D65 illumination. Colour coordinates represent lightness L^* (black = 0, white $L^* = 100$), the red(+)/green(−) axis a^* and the yellow(+)/blue(−) axis b^*. At a wavelength of 600 nm the Kubelka–Munk value K/S was calculated as a measurement which changes linearly with dyestuff concentration.

2.9. Ion exchange properties

A sample was surface oxidised by impregnation with 2 g/L NaBr and 0.3 g/L TEMPO in 0.1 M boric acid buffer solution (pH 10.5) and dried. Then a paste containing 25 g basis thickener (alginate 25 g/100 mL) and 10 mL NaOCl solution (see Section 2.3) was printed. The samples (2 g) then were shaken for 2 hrs at RT in water of different hardness (200 mL deionised water, 200 mL tap water approx 80 mg/L Ca^{2+}, mixture of 100 mL deionised water with 100 mL tap water). Then each sample was placed in 200 mL alkaline alizarin solution (0.1 g/L alizarin in 0.1 M NaOH) for 1 h at RT. The samples were rinsed 3 times in 100 mL Na_2CO_3 solution (0.1 g/L) and dried. Formation of the Ca^{2+}-alizarin complex on the fibre was observed by development of a violet colour (CIELab coordinates and K/S value 560 nm).

3. Results and discussion

3.1. Batch oxidation

During the cellulose oxidation with use of the TEMPO/NaBr/NaOCl a constant decrease in pH occurs, thus pH stabilisation by addition of NaOH is required. This makes the treatment rather complex. For a surface modification of cellulose fabric, e.g. by printing techniques stable pH conditions are necessary as the addition of alkali to stabilise the reaction conditions will not be possible. The continuous addition of alkali to the reaction volume was thus replaced by an inorganic buffer system designed to maintain the pH in solution during the TEMPO oxidation.

A series of batch oxidation experiments were performed to assess the chosen buffer system with regard to capacity and time stability. Also reference samples were obtained from the treatment with different amounts of oxidant. In the experiments 2–5 a 0.1 M borate buffer (pH 10.5) was used to stabilise the pH value of the solution between 10.6 and 10.4.

Conditions of TEMPO-mediated treatment and results are summarised in Table 1. The treated samples were characterised by determination of moisture regain, water retention value (WRV), carboxylic group number (COOH) and FTIR-ATR.

Fig. 1 shows the increase of the WRV, MC and COOH content with an increased amount of oxidant. The determination of the carboxylic group content is based on the selective sorption of the cationic dye methylene blue at the negatively charged carboxylate groups. Thus the sorption follows a Langmuir type isotherm. Particularly at a higher number of carboxylic groups sorption enters in the non-linear part of the isotherm and an underestimation of the carboxylic group content can occur. Thus given values of carboxyl group content indicate the minimum of actual formed carboxylic groups. The oxidation leads to a significant decrease in the tensile strength (Supplementary material Fig. S1). Independent of the amount of oxidant used the decrease in tensile strength (TS) stabilises between 280 and 360 cN which corresponds to a loss between 44 and 28% compared to original strength.

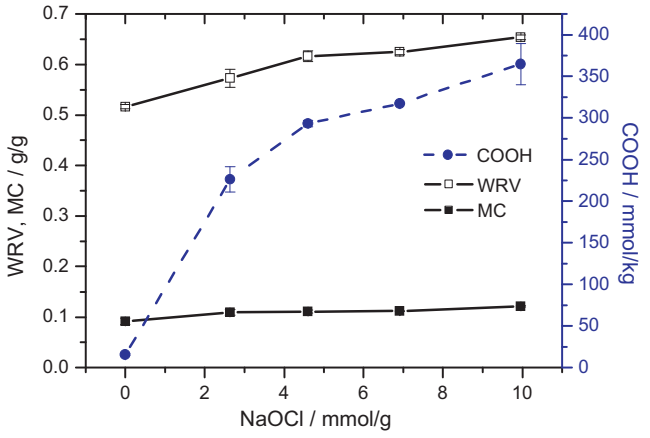

Fig. 1. Increase of the WRV (□), MC (■) and COOH (●) with amount of oxidant (samples 1–5).

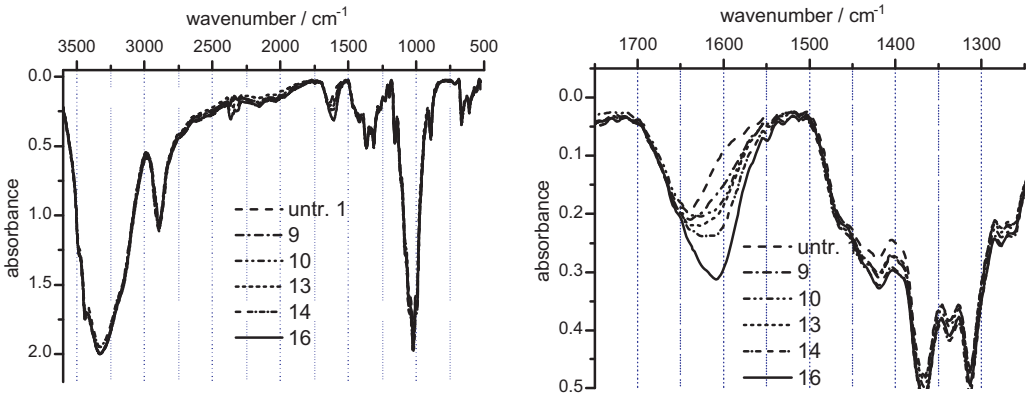

Fig. 2. FTIR-ATR spectra of selected NaOCl printed samples. Left: full spectrum. Right: magnified interval between 1250 and 1750 cm^{-1}.

In the FTIR spectra of the treated samples the characteristic bands for COOH groups appear at 1600 cm^{-1} (Supplementary material Fig. S2).

The pH values given in Table 1 indicate that the buffer capacity of the 0.1 M boric acid/NaOH buffer is sufficient to maintain a pH around 10.5 ± 0.1. This allows for the use of such a concept in applications where pH adjustment is not possible.

3.2. Oxidant printing experiments

Printing of a NaOCl containing paste on the lyocell fabric was investigated to study possible surface modification of the fabric without modification of the yarn core inside the fabric.

To avoid oxidative decomposition of the printing paste the stability of the TEMPO/NaBr/NaOCl system in thickened printing pastes was investigated. Iodometric titration of oxidant containing pastes indicate sufficient stability of all tested thickeners (polyvinylalcohol, carboxymethylcellulose, esterified starch, carboxymethyl starch, alginate) in presence of 0.5 g/L NaBr and 0.075 g/L TEMPO. A substantial decrease in oxidant concentration to less than 30% of the initial value was observed for the major part of thickeners when 5 g/L NaBr and 0.75 g/L TEMPO were present in the paste. In the case of alginate thickener nearly 50% of the oxidant remained active after a period of 60 min, thus alginate was used as thickening system for printing experiments and pastes were used immediately after preparation without further storage.

To achieve stable process conditions the reactive oxidant system was split into two parts which were applied consecutively.

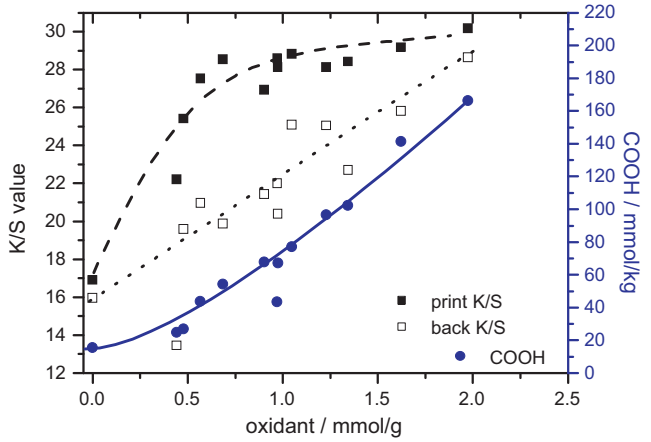

Fig. 3. Colour depth (K/S) of samples 1 and 6–17 at printed side (■) and reverse side (□) after methylene blue dyeing, and COOH content (●) in mmol/kg as function of mmol oxidant printed per g cellulose.

Firstly the fabric samples were impregnated with a solution of TEMPO, NaBr and buffer (pH 10.5) and dried, then a paste containing NaOCl and alginate thickener was printed on the fabric by screen printing. Such a procedure restricts the reaction of the TEMPO/NaBr/NaOCl system on the surface area of the fabric, where the TEMPO/NaBr/buffer comes into contact with printed NaOCl oxidant.

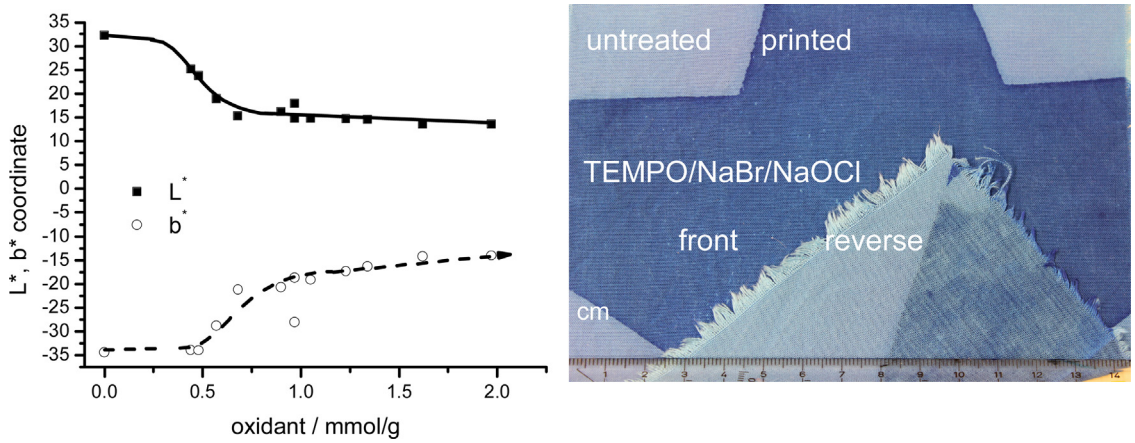

Fig. 4. Colour coordinates L^* (lightness) (■) and b^* (yellow–blue) (○) of printed samples 1 and 6–17 on printed side after methylene blue dyeing as function of mmol oxidant applied per g cellulose and photograph of a printed and methylene blue dyed sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Surface oxidation of lyocell fabric by printing. Conditions and results: experiment number, volume of NaOCl added to 5 g of basis paste, oxidant printed per g of fabric mmol/g, colour coordinates and K/S value (600 nm), moisture content (MC), water retention value (WRV), carboxylic group content (COOH) mmol/kg.

No	NaOCl (ml/5 g basis)	Oxidant (mmol/g)	Colour coordinates				MC (g/g)	WRV (g/g)	COOH (mmol/kg)
			L^*	a^*	b^*	K/S			
1 Untreated	0	0	32.28	0.51	−34.38	16.91	0.091	0.527	15.6
1 Untreated			31.30	0.81	−33.41	15.95			
6 Front	0.5	0.44	25.16	6.64	−33.90	22.20	0.112	0.512	24.9
6 Back			31.54	1.61	−31.14	13.46			
7 Front	0.5	0.48	23.80	6.94	−33.95	25.42	0.112	0.605	26.9
7 Back			29.01	1.86	−33.70	19.59			
8 Front	1.0	0.57	18.87	10.03	−28.84	27.54	0.108	0.553	43.6
8 Back			27.25	2.72	−32.53	20.97			
9 Front	1.0	0.97	17.92	10.56	−28.03	28.59	0.108	0.563	43.4
9 Back			27.12	2.78	−33.09	22.01			
10 Front	1.5	0.90	16.16	9.31	−20.71	26.94	0.101	0.559	67.6
10 Back			26.06	3.29	−31.41	21.43			
11 Front	1.5	0.68	15.36	10.41	−21.15	28.54	0.113	0.530	54.4
11 Back			28.49	1.27	−32.26	19.87			
12 Front	2.0	0.97	14.77	9.61	−18.65	28.13	0.109	0.547	67.1
12 Back			28.24	1.16	−32.08	20.38			
13 Front	2.0	1.05	14.86	9.50	−19.11	28.83	0.109	0.600	77.2
13 Back			22.45	6.02	−30.00	25.10			
14 Front	3.0	1.23	14.73	8.82	−17.32	28.13	0.114	0.577	96.6
14 Back			22.81	5.69	−29.40	25.05			
15 Front	3.0	1.34	14.58	8.15	−16.32	28.42	0.107	0.586	102.3
15 Back			24.96	3.57	−30.41	22.71			
16 Front	4.0	1.97	13.64	7.42	−14.02	30.19	0.119	0.647	166.1
16 Back			15.03	9.00	−18.92	28.65			
17 Front	4.0	1.62	13.62	8.24	−14.23	29.19	0.115	0.593	141.4
17 Back			19.38	5.44	−22.93	25.82			

From the printed area and the concentration of the NaOCl added to the paste, the oxidant applied per g of fabric could be calculated (Table 2). To characterise the achieved surface oxidation, FTIR-ATR spectra were recorded. As the formation of carboxyl groups can be observed at 1640–1610 cm^{-1}. In Fig. 2, the FTIR spectra of selected samples are shown. The increase of the absorption at 1610 cm^{-1} with the amount of oxidant printed per g of fabric demonstrates the more intensified surface oxidation.

The printed samples were stained with methylene blue to mark the carboxylic groups in the oxidised area (0.1 g, 25 mL MB, 25 mL buffer). Colour measurement was used to characterise the surface modification. Dyestuff absorption is given in CIELab coordinates and in terms of K/S measured at 600 nm (Figs. 3 and 4). The colour coordinates clearly indicate the achieved difference between the printed surface and the reverse side of the fabric (Fig. 3). As the printed samples were tested by methylene blue sorption, the change in absorbance of the staining solution represents an average value including the treated and untreated side of a sample. In a similar way, the methylene blue dye gets darker (L^*) and intense (b^*) with an increasing amount of oxidant printed on the surface (Fig. 4).

The changes in L^* and b^* with the amount of oxidant applied indicate a threshold value of 0.5 mmol/g oxidant which has to be exceeded to achieve a substantial impact on the carboxylic group content.

The change in carboxylic group content also influences the WRV of the samples (Fig. 5). As the oxidative effect is concentrated on the surface of the fabric, the measured WRV represents an average value throughout the fabric and thus appears smaller compared to batch treatments (Praskalo et al., 2009).

The ion-exchange properties of the surface treated material can be demonstrated by the Ca^{2+}-uptake from diluted aqueous solution (tap water 80 mg/L Ca^{2+}, total hardness 14° dH). After a period of 2 h in Ca^{2+}-containing solution, Ca^{2+} is bound to the carboxylic groups of the oxidised surface and can be visualised by formation of the coloured Ca^{2+}–alizarin complex.

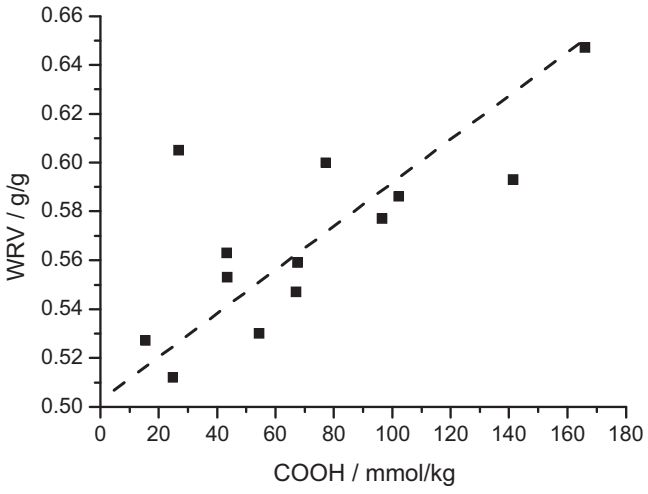

Fig. 5. Water retention value (■) as function of carboxylic group content (COOH).

The fixation of alizarin on the surface of the printed material increased with Ca^{2+} bound on the fibre which demonstrates the ability of the modified material to bind Ca^{2+}-ions from diluted solution (Table 3) (Fitz-Binder & Bechtold, 2012).

The CIELab coordinates and the K/S values of the untreated lyocell sample (18) and of the TEMPO/NaBr impregnated unprinted

Table 3
Formation of the Ca^{2+}–alizarin complex after surface oxidation – colour coordinates L^*, a^*, b^*, and K/S (560 nm).

	Sample	L^*	a^*	b^*	K/S
18	Untreated	45.3	13.87	−22.67	3.3
19	TEMPO/no print	45.90	14.96	−21.73	3.1
20	Deionised water	50.55	12.42	−17.49	2.2
21	50/50 deion/tap water	44.06	14.84	−19.57	3.4
22	Tap water	40.56	17.07	−21.90	4.5

sample (19) were similar, which demonstrated, that the effects of TEMPO/NaBr alone were negligible. During fabric preparation, the samples were in contact with tap water, thus the Ca^{2+}-binding sites in these samples already had been loaded with Ca^{2+}-ions and substantial binding of alizarin was observed with samples 18 and 19 (Fitz-Binder & Bechtold, 2012). The sample which had been treated in deionised water showed a lighter colour (20) compared to the others, as part of the Ca^{2+} had been removed during the treatment in deionised water. A constant increase in Ca^{2+}-binding was observed with increasing Ca^{2+}-content offered in solution, as can be seen by the gradual change in CIELab coordinates and with an increase of K/S value.

4. Conclusions

Printing techniques are suitable to achieve controlled surface modification of cellulose fabric by TEMPO mediated oxidation. By use of an appropriate buffering system, the pH shift in the TEMPO/NaBr/NaOCl can be controlled within a narrow range of ±0.1 pH units. This is a prerequisite to avoid continuous adjustment of pH by addition of NaOH to maintain the reaction pH near 10.5 and to apply such a system in a printing technique.

The TEMPO/NaBr/NaOCl system is highly reactive, thus separation of the chemicals was used to permit better control of conditions. Initially the fabric was impregnated with a buffered TEMPO/NaBr solution, subsequently the NaOCl containing paste was applied by screen printing.

Such a procedure allows controlled surface oxidation of the cellulose fabric, which then exhibits a high COOH concentration on one side of the fabric. Dependent on the amount of NaOCl printed per g of fabric, carboxylic group contents up to 160 mmol/kg were determined in the samples. As these values represent average values including both sides of the fabric, the effective surface concentration will be substantially higher.

FTIR spectra and methylene blue sorption experiments demonstrated that a local oxidation of the cellulose had been achieved. The increased COOH content also leadsto a higher binding capacity for Ca^{2+} through ion exchange reactions.

The presented results indicate a new technique to modify the surface of 2D-cellulose material (fabric, nonwovens, paper) by a printing technique. Using patterned screen or ink-jet techniques a local modification of surfaces can be achieved.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.02.025.

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