Chlorine-Free Method for the Oxidation of Residual Aldehydes on TEMPO-Oxidized Cellulose

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With the advent of surface modification procedures for the production of fibrillated cellulose, it has become evident that some procedures have a limited negative impact on the cellulose surface chemistry. In the case of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl)-mediated oxidation, this is evident from the residual aldehyde groups present on the surface and the impact on the colour stability of the resulting material under conditions of high temperature drying. In this paper, an alternative is presented for the common procedure for the oxidation of aldehydes on TEMPO oxidized cellulose using an acidified solution of sodium chlorite. By using potassium peroxymonosulfate, residual aldehyde groups were converted to carboxylic groups, and the colour stability of the modified cellulose fibers was increased. The post-oxidation procedure takes place under mildly alkaline conditions, which preserves the surface charge on the TEMPO modified cellulose fibers, and this in turn helps with fibrillation of the material into a nanofibrillar form.

Keywords: TEMPO cellulose; Nanocellulose; Potassium peroxymonosulfate; Oxone®; Oxidation

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INTRODUCTION

Cellulose, a common and naturally occurring homopolymer of glucose, linked with $\beta-(1 \rightarrow 4)$ glycosidic bonds (Habibi 2014), offers a valuable source for a wide range of different materials, including woven fabrics, esters, ethers, and nanocellulosic materials (Edgar *et al.* 2001). The term nanocellulose commonly describes a group of materials that differ in their morphology, with the three distinct types being nanofibrillated cellulose, cellulose nanocrystals, and bacterial nanocellulose (Klemm *et al.* 2011). There are several methods for producing cellulose nanoparticles, but in practice only a handful of methods are viable for pilot scale. High-pressure homogenization was the first process used to produce cellulose nanoparticles, namely nanofibrillated cellulose (Turbak *et al.* 1983). Initially, this process was costly; however, with recent advancements in pretreatment steps, such as enzymatic hydrolysis (Henriksson *et al.* 2007), TEMPO-mediated oxidation (Isogai *et al.* 2011), and carboxymethylation (Wågberg *et al.* 2008; Chinga-Carrasco and Syverud 2014), production costs of nanofibrillated cellulose have been significantly reduced. Alternatively, cellulose nanocrystals are produced with acid hydrolysis of cellulose. The acid hydrolyses for the amorphous regions in the cellulose structure leave only the crystalline regions intact (Voronova *et al.* 2013). The most common acid used today is sulfuric acid, which also introduces a negative surface charge to the nanocrystal surface that eases its dispersion in water (Eyley and Thielemans 2014).

TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl)-oxidation of cellulose is a pretreatment process that imparts a negative charge on the surface of cellulose chains, making fibrillation easier and at the same time introducing a new functional group that can be exploited for a number of chemical reactions. De Nooy *et al.* (1995) were the first to employ TEMPO-mediated oxidation for the conversion of primary hydroxyl groups to carboxyls on water-soluble glucans. Recently, this procedure has been used on cellulose fibers to greatly effect TEMPO-mediated oxidation by selectively oxidizing the primary alcohol groups on the cellulose chain to carboxyl groups *via* an aldehyde intermediate (Saito and Isogai 2004). While this method yields carboxyl groups, inevitably there are aldehyde groups present as a consequence of the TEMPO oxidation reaction and the incomplete conversion of the aldehyde groups into the desired carboxyl form (Mishra *et al.* 2012). It is estimated that roughly 0.1 to 0.3 mmol/g of aldehyde groups are present in cellulose fibers after TEMPO-mediated oxidation in an ordinary laboratory oxidation setup (Saito and Isogai 2004; Jaušovec *et al.* 2015). Residual aldehydes present a potential problem as they cause discoloration during high temperature drying due to their ability to cleave the $\beta - (1 \rightarrow 4)$ bonds between the glucose molecules (Isogai *et al.* 2011). This could prove to be problematic during the manufacture of films based on the TEMPO oxidized nanofibrillated cellulose or for further functionalization. Residual aldehydes also present a potential source of carboxylic groups. Conversion of these groups to their carboxylic form increases the functional potential of the material.

Mishra *et al.* (2012) have done fieldwork related to the post-oxidation of TEMPO cellulose with the aim of increasing the carboxyl group content on TEMPO oxidized cellulose. The research focus was on post-oxidation of the aldehyde groups in an acidified sodium chlorite ($NaClO_2$) system. However, the consumption of chlorous acid is large, at 3 moles per mole of aldehyde (Mishra *et al.* 2012). Potentially, alternatives exist for the oxidation of aldehydes, namely Tollens' reagent and Cr(VI) compounds under acidic conditions, of the two, one being a laboratory procedure based on silver, the other, an environmentally hazardous procedure due to the presence of highly carcinogenic and acutely toxic chromium compounds.

This paper proposes a procedure for the post-oxidation of TEMPO cellulose based on potassium peroxymonosulfate (Oxone$^{®}$) in a bicarbonate buffer. The advantages of this system are the lack of chlorine compounds, low cost reagents, and low oxidant concentrations while maintaining the correct aldehyde conversion degree. With the use of a potassium peroxymonosulfate-based post-oxidation system, the total amount of free chlorine or chlorine dioxide in the wastewaters is close to zero, as the sodium hypochlorite is consumed in the TEMPO oxidation. The remainder of the sodium hypochlorite is then consumed in the oxidation of a small amount of primary alcohol, which is added at the end of the reaction in order to terminate it completely by reacting with the residual hypochlorite. The oxidation of aldehydes using potassium peroxymonosulfate has been described by Webb and Ruzskay (1998), where organic aldehydes were successfully oxidized to carboxyl equivalents in a water/acetone medium, with good yields. In conjunction with acetone, potassium peroxymonosulfate forms a reactive peroxide called dimethyl dioxirane (an acetone peroxide monomer). Dimethyl dioxirane is a very powerful yet unstable oxidizer that is used for the oxidation of various aldehydes. Overall, potassium peroxymonosulfate has proven itself in the oxidation of various aromatic aldehydes (Gandhari *et al.* 2007) and simpler aliphatic ones to their carboxyl derivatives and esters (Travis *et al.* 2003). A procedure based on aqueous acetone or a modified procedure using potassium peroxymonosulfate could be successfully employed on TEMPO oxidized cellulose to convert the residual aldehydes to carboxylic acids (Fig. 1).

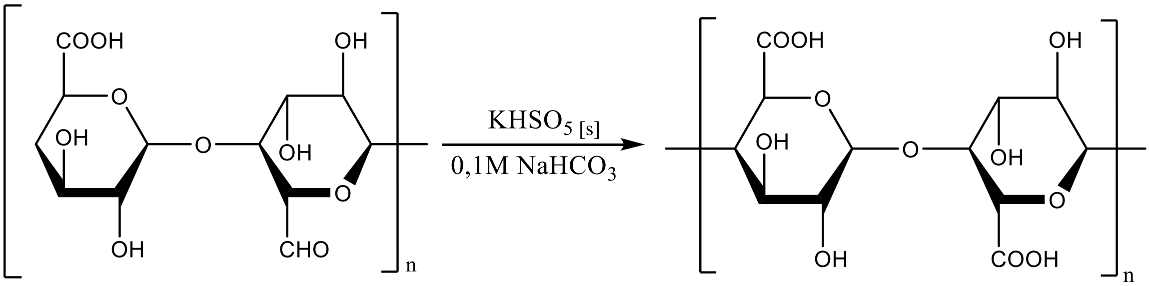

Fig. 1. Proposed reaction schematic for the post-oxidation of aldehydes on TEMPO modified cellulose

EXPERIMENTAL

Materials

A never-dried cellulose dissolving pulp was used for all experiments. The pulp contained only traces of lignin, roughly 8% hemicelluloses, and over 92% cellulose. Potassium peroxymonosulfate (Oxone®), sodium bicarbonate, EDTA (ethylenediamine-tetraacetic acid), and sodium hypochlorite were purchased from Acros Organics (Geel, Belgium). TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl), sodium bromide, sodium hydroxide, and hydrochloric acid were obtained from Sigma Aldrich (Darmstadt, Germany). All reagents were used as received and without any additional purification.

Methods

TEMPO oxidation

TEMPO oxidation was carried out as previously described (Isogai *et al.* 2011; Levanič 2015). The amounts of reagents used were adjusted to accommodate a larger quantity of cellulose. Briefly, 50 g of never-dried cellulose pulp (dry equivalent) was suspended in 4 L of distilled water, and a corresponding amount of TEMPO and sodium bromide were added to the suspension. A calculated amount of 13% sodium hypochlorite solution was added once the sodium bromide and TEMPO were dissolved. The pH was adjusted to 10 with 0.5 M hydrochloric acid and maintained between 10 and 10.2 with 0.5 M sodium hydroxide. The reaction was stopped with the addition of 250 mL of ethanol. The TEMPO oxidized cellulose fibers were separated from the reaction medium using a 20 mesh PE-HD screen and rinsed several times with warm distilled water. After rinsing, the fibers were dewatered using vacuum filtration until a solids content of roughly 25% was reached. This was the base material for the post-oxidation procedure.

Post-oxidation with potassium peroxymonosulfate

Initially, a screening experiment was done with the procedure proposed by Webb and Ruzskay (1998) in a 78/22 ratio mixture of water/acetone with added sodium bicarbonate (amount equating to a final 0.1 M solution) and EDTA. Next, 1 g of TEMPO oxidized cellulose fiber was suspended in 100 mL of the prepared acetone medium, and potassium peroxymonosulfate was added in the form of a dry powder (100, 200, or 300 mg). The mixture was left to react for 2 h and then filtered and rinsed several times with distilled water.

After the initial aqueous acetone experiment, a modified procedure using only potassium peroxymonosulfate in a bicarbonate buffer at elevated temperature was tested to see if a simplified version could be viable for the post-oxidation. The procedure was conducted at three different temperatures (22, 40, and 70 ºC), four different reaction times (2, 4, 6 or 8 h), and three different potassium peroxymonosulfate loadings (100, 200 and 300 mg/g). Briefly, 1 g of dry weight equivalent TEMPO cellulose fiber was transferred into an Erlenmeyer flask, to which 100 mL of sodium bicarbonate buffer (pH 8) was added. The flask was transferred into a temperature controlled oil bath (40 or 70 ºC) or left in an outside environment (air conditioned at 22 ºC) to represent room temperature conditions. After 5 min of stirring under reaction conditions, the potassium peroxymonosulfate was added as a dry powder and the reaction mixture was left to react for a predetermined amount of time (2, 4, 6, or 8 h). After post-oxidation, the samples were protonated using 0.1 M hydrochloric acid, rinsed several times with distilled water, flash frozen in liquid nitrogen, and freeze dried. To compare the efficacy of the potassium peroxymonosulfate post-oxidation procedure, a sample of TEMPO oxidized cellulose fiber was also oxidized in an acidified sodium chlorite solution according to Mishra *et al.* (2012) with a sodium chlorite loading of 340 mg per gram of cellulose. The sodium chlorite procedure is considered to have a 100% conversion rate for residual aldehydes and is, as such, used as a reference for comparison of the potassium peroxymonosulfate procedure.

Additionally, the sodium chlorite and 300 mg/g potassium peroxymonosulfate procedures were performed on neat dissolving pulp to see if it was possible to directly oxidize the hydroxyl groups on the cellulose under specific conditions.

Conductometric titration

Conductometric titration of all samples was conducted on the freeze-dried and protonated material. First, 50 mL of distilled water was added to 100 mg of freeze-dried material in a titration cup. The material was dispersed overnight using a magnetic stirrer. A T50 automatic titration system (Mettler Toledo, Griefensee, Switzerland) was used; after 2.5 mL of 0.1 M hydrochloric acid was pre-dispensed into the titration cup containing the sample, 0.1 M sodium hydroxide solution was titrated in 50 µL increments. The titration values were plotted in statistical software, and the consumption of sodium hydroxide was determined graphically. The total carboxyl group content was calculated from the sodium hydroxide consumption according to Eq. 1,

$$C_{COOH} = \frac{V_2 - V_1}{m_1} * C_{NaOH} \tag{1}$$

where V_1 and V_2 are the initial and final sodium hydroxide consumption values, respectively, as determined graphically from the plotted data, m_1 is the mass of the sample in grams, and C_{NaOH} is the concentration of the sodium hydroxide solution. The result is given in mmols of carboxyl groups per gram of dry sample.

Colour stability evaluation using CIE Lab system

After titration, the cellulose sample was recovered and rinsed several times with distilled water to remove the titration reagents, especially the residual sodium hydroxide. The rinsed fibers were deposited on filter paper and oven-dried at 105 ºC for 24 h. High temperature drying is used to evaluate colour changes before and after post-oxidation.

The color evaluation was performed according to the CIE $L^*a^*b^*$ system using an X-Rite SP62 spectrophotometer (X-Rite GmbH - OPTRONIK™, Berlin, Germany). The L^*, a^*, and b^* colour parameters were recorded for the base material, sodium chlorite oxidized control sample (procedure by (Mishra *et al.* 2012)), and finally for the potassium peroxymonosulfate treated samples. Total colour change was calculated for all the samples according to the CIE76 formula for evaluation of colour differences, as shown in Eq. 2,

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1) + (a^*_2 - a^*_1) + (b^*_2 - b^*_1)} \qquad (2)$$

where L_2*, a_2*, and b_2* are the L^*, a^*, and b^* values for the TEMPO cellulose sample (significant discoloration) and L_1*, a_1*, and b_1* are the values for the sample in question. Finally, the relative efficiency of the procedure was evaluated by calculating the percentage of total colour change of the post-oxidation samples in relation to the sodium chlorite control sample. The calculations were made according to Eq. 3,

$$Y = \frac{\Delta E_{sample}}{\Delta E_{control}} * 100 \qquad (3)$$

where the total colour change of the potassium peroxymonosulfate treated samples ($\Delta E_{\mathrm{sample}}$) is presented as a percentage of the colour change for the sodium chlorite treated sample ($\Delta E_{\mathrm{control}}$), which is considered the optimal procedure with a predicted 100% aldehyde conversion rate and minimal colour change after a 24 h exposure to 105 ºC.

FT-IR measurements

The standard sample and post-oxidized samples of interest were analyzed on a Spectrum Two UATR FTIR device (Perkin Elmer, Waltham, MA, USA) equipped with a monolithic diamond single reflection ATR unit according to Barsberg *et al.* (2013). For the background, 16 scans were acquired, and each sample spectrum was obtained from 16 scans at a resolution of 4 cm^{-1}. These spectra are presented in arbitrary A_N units.

SEM imaging

Structural analysis was conducted on a Quanta 250 SEM (FEI, Thermo Fisher, Waltham, MA, USA). Scanning electron microscopy (SEM) samples were prepared by dispersing 50 mg of freeze-dried sample in 50 mL of distilled water (0.1% fiber suspension). The fiber suspension was shaken, and a small drop was placed on a gold-plated polycarbonate membrane. The fibers were deposited on the membrane by vacuum filtration. The fibers themselves were not coated in a conducting material to preserve any minute morphological differences.

Fibrillation analysis by centrifugation

Post-oxidation samples were subject to high-pressure homogenization on a Panda PLUS 2000 device (GEA Niro Soavi, Parma, Italy), according to an in-lab procedure for producing nanofibrillated cellulose from surface charged cellulose fibers. A separate batch of TEMPO cellulose fiber was prepared according to the aforementioned procedure. Samples were subject to post-oxidation with sodium chlorite and a single potassium peroxymonosulfate loading, which was considered optimal· After each pass through the homogenizer, two samples were centrifuged for 15 min at 5000 rcf, and their phases were separated and dried. The total solids content for the two phases and their respective percentages were calculated.

RESULTS AND DISCUSSION

Carboxylic Group Content in Modified Fibers

Titration data for TEMPO cellulose fiber samples treated with the modified potassium peroxymonosulfate procedure showed an increase in carboxyl content across the board compared to the base material (Fig 2). The initial content of carboxyl groups in original TEMPO cellulose was marked on the graph with a red line and represents the value at 1.43 mmol/g. The upper value of 1.70 mmol/g was marked on the graph with a blue dotted line and represented the total possible value of carboxyl groups as determined by the post-oxidation with sodium chlorite in an acidified buffer solution as described by Mishra *et al.* (2012). The values on the graph represent the averages and deviations of 3 samples. Titration data (Fig. 2) shows that the reaction temperature played a significant role in the efficacy of the proposed post-oxidation procedure. Interestingly, even at room temperatures, it was observed that there was an increase in carboxyl content, however, the data was significantly more scattered indicating poor reaction conditions. A similar carboxyl content can be observed in all samples oxidized at 70 ºC.

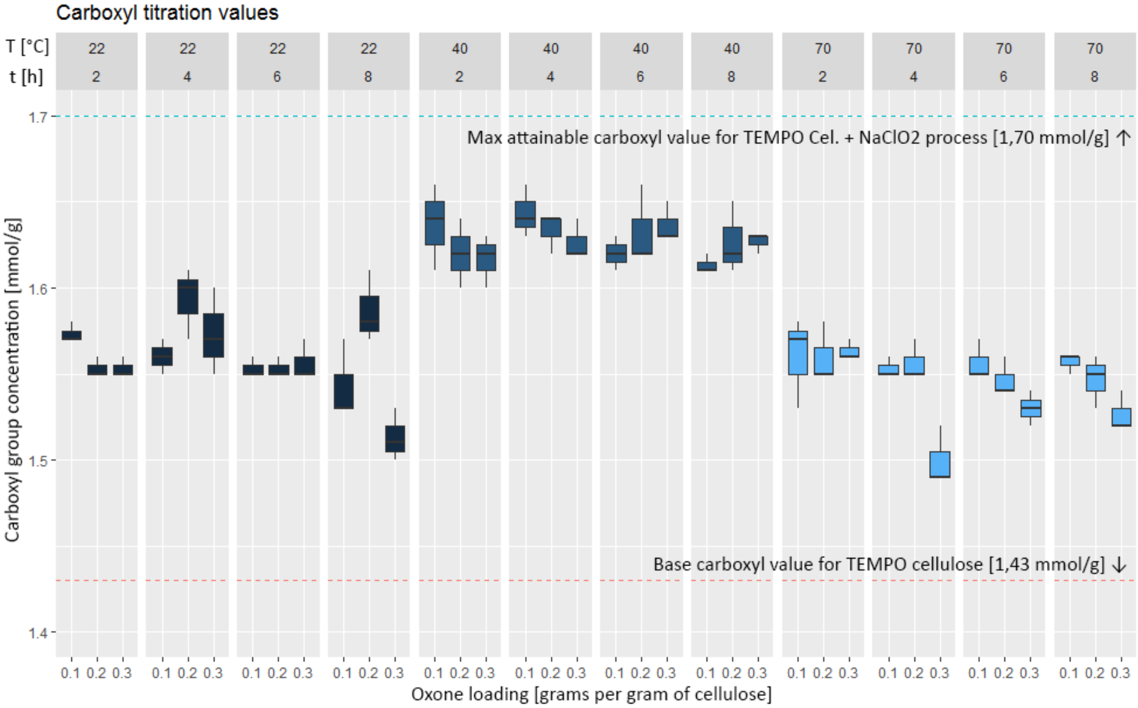

Fig. 2. Carboxyl group contents in different grades of post-oxidized TEMPO modified cellulose fibers.

An intermediate temperature of 40 ºC was optimal out of the tested temperatures. There was a statistically significant difference only for temperature values, whereas the potassium peroxymonosulfate concentration and duration did not have a great impact on the reaction. This may be due to the low number of aldehydes present (0.27 mmol/g), because even at the lowest concentration over 4 h resulted in the conversion of a large percentage of the aldehydes. The lowest temperature was expected to be the least efficient because reaction rates, in general, are slow at room temperature. This is also a noted problem for potassium peroxymonosulfate-based oxidation (Webb and Ruzskay 1998).

The higher temperature reaction was as effective as its room temperature counterpart and less effective than the 40 ºC regime. Currently, no viable explanation for this behavior is known. However, it is speculated that the thermal stability of the bicarbonate buffer and potassium peroxymonosulfate in the solution at these temperatures may be compromised to a degree where the amount of reagent decreases due to thermal decomposition after which point there is an insufficient oxidizer present to complete the reaction to a degree that can be observed at intermediate temperatures (40 ºC).

The initial titration of the samples post-oxidized in a water/acetone medium showed no increase in carboxyl content compared with the control TEMPO cellulose. A similar result was found for neat pulp treated with the original or modified aqueous procedure. Thus, the process using water/acetone was deemed not suitable for the post-oxidation of TEMPO cellulose. No further analyses and tests were conducted on these samples.

Colour Stability

Colour stability was evaluated with the CIE *L*a*b** system, and the total colour change was calculated for each sample. Table 1 presents the results of the colour stability measurements. First, a comparison was made between the base material (TEMPO cellulose) and the sodium chlorite control sample. The sodium chlorite was considered the optimal sample and the total colour change (ΔE) towards the TEMPO cellulose sample was considered the optimal outcome of the post-oxidation procedure, *i.e.*, maximum possible colour difference).

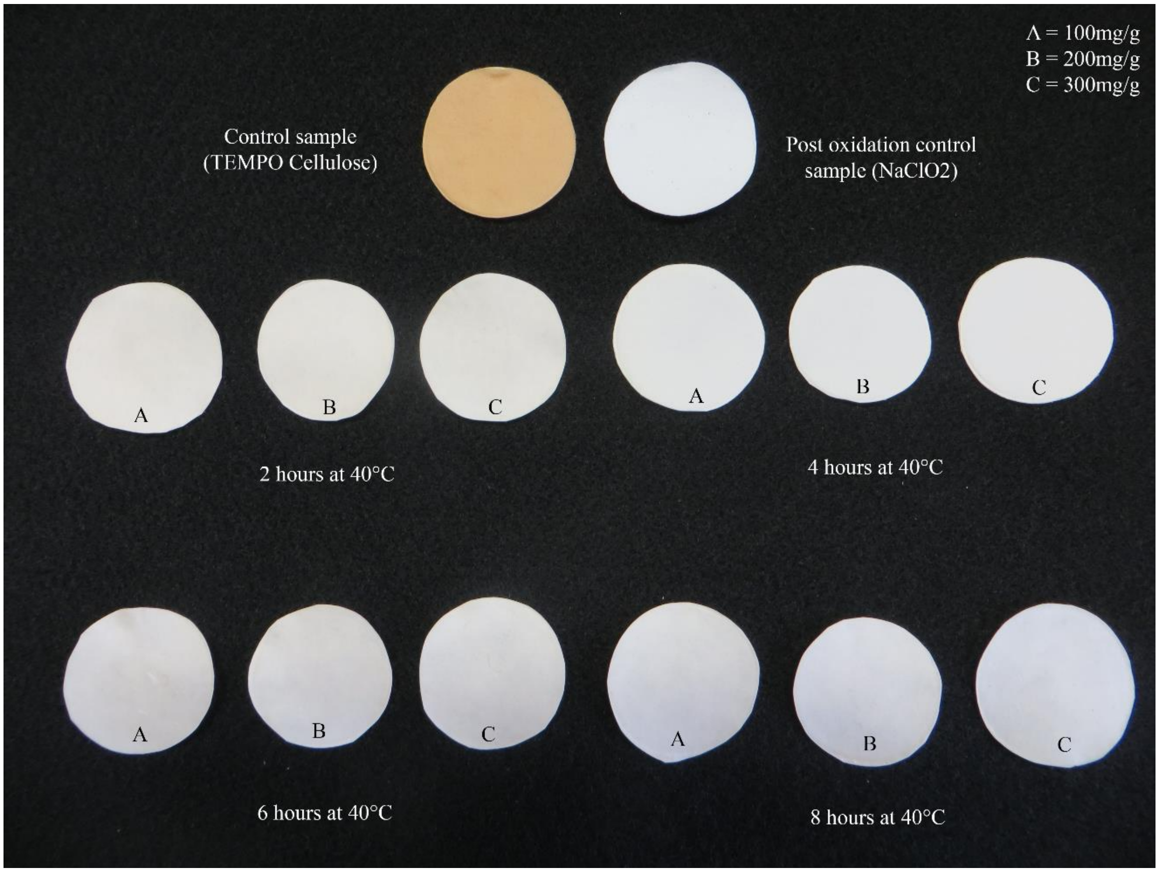

Fig. 3. Discoloration of post-oxidized samples compared with the control TEMPO cellulose

Table 1. CIE *L*a*b** Parameters for Cellulose Samples after 24 h at 105 °C

Sample ID	*L**	*a**	*b**	Δ*L**	Δ*a**	Δ*b**	Δ*E*	Relative yield (%)
TEMPO Cellulose	74.54	8.04	28.92	/	/	/	/	/
$NaClO_2$ Control	96.22	-0.27	1.56	-21.68	8.31	27.36	35.88	100
22/2/0.1	91.04	-0.41	6.32	-16.50	8.45	22.60	29.23	81
22/2/0.2	88.23	-0.22	8.17	-13.69	8.26	20.75	26.20	73
22/2/0.3	87.48	-0.41	7.55	-12.94	8.45	21.37	26.37	73
22/4/0.1	87.92	-0.56	8.21	-13.38	8.60	20.71	26.11	73
22/4/0.2	87.42	-0.11	7.52	-12.88	8.15	21.40	26.27	73
22/4/0.3	87.44	-0.44	7.03	-12.90	8.48	21.89	26.79	75
22/6/0.1	87.72	-0.35	6.48	-13.18	8.39	22.44	27.34	76
22/6/0.2	88.32	-0.15	4.94	-13.78	8.19	23.98	28.84	80
22/6/0.3	87.13	0.12	4.93	-12.59	7.92	23.99	28.23	79
22/8/0.1	85.74	1.12	7.74	-11.20	6.92	21.18	24.94	69
22/8/0.2	86.22	1.25	8.17	-11.68	6.79	20.75	24.76	69
22/8/0.3	85.62	1.15	8.17	-11.08	6.89	20.75	24.51	68
40/2/0.1	89.51	-0.74	3.96	-14.97	8.78	24.96	30.40	85
40/2/0.2	91.34	-0.78	3.62	-16.80	8.82	25.30	31.62	88
40/2/0.3	90.00	-0.73	3.44	-15.46	8.77	25.48	31.07	87
40/4/0.1	93.45	-0.24	1.45	-18.91	8.28	27.47	34.36	**96**
40/4/0.2	93.74	-0.18	1.18	-19.20	8.22	27.74	34.72	**97**
40/4/0.3	94.58	-0.29	1.64	-20.04	8.33	27.28	34.86	**97**
40/6/0.1	89.60	-0.72	3.85	-15.06	8.76	25.07	30.53	85
40/6/0.2	89.55	-0.76	3.54	-15.01	8.80	25.38	30.77	86
40/6/0.3	89.48	-0.69	3.93	-14.94	8.73	24.99	30.40	85
40/8/0.1	89.79	-0.49	2.78	-15.25	8.53	26.14	31.44	88
40/8/0.2	87.98	-0.59	3.30	-13.44	8.63	25.62	30.19	84
40/8/0.3	89.02	-0.48	3.00	-14.48	8.52	25.92	30.89	86
70/2/0.1	89.52	-0.92	4.33	-14.98	8.96	24.59	30.16	84
70/2/0.2	89.73	-0.88	3.45	-15.19	8.92	25.47	30.97	86
70/2/0.3	89.62	-0.90	3.87	-15.08	8.94	25.05	30.58	85
70/4/0.1	89.07	-0.78	3.84	-14.53	8.82	25.08	30.30	84
70/4/0.2	89.67	-0.63	3.36	-15.13	8.67	25.56	30.94	86
70/4/0.3	89.72	-0.61	3.38	-15.18	8.65	25.54	30.94	86
70/6/0.1	87.17	-0.73	4.82	-12.63	8.77	24.10	28.59	80
70/6/0.2	89.00	-0.90	5.72	-14.46	8.94	23.20	28.76	80
70/6/0.3	88.82	-0.57	3.65	-14.28	8.61	25.27	30.28	84
70/8/0.1	88.39	-0.37	2.38	-13.85	8.41	26.54	31.10	87
70/8/0.2	88.77	-0.50	2.91	-14.23	8.54	26.01	30.85	86
70/8/0.3	88.51	-0.11	1.47	-13.97	8.15	27.45	31.86	89

* The *x*/*y*/*z* parameters in the initial column are equal to temperature (°C). duration (h), and potassium peroxymonosulfate loading (in grams per gram of oxidized cellulose), respectively. The final column is the calculated relative yield or efficiency as compared to the reference procedure (higher numbers means a weaker discoloration)

The potassium peroxymonosulfate treated samples, were compared to the sodium chlorite control sample and a relative efficacy of the procedure was calculated based on the total colour change of the potassium peroxymonosulfate sample compared to the sodium chlorite sample.

The standard post-oxidation procedure with a 100% aldehyde conversion rate was the best option when colour stability and optimal carboxyl yield is desired (Table 1).

Samples that underwent the potassium peroxymonosulfate procedure achieved a lower value of colour difference (Δ*E*) compared to the sodium chlorite process (Fig. 4). This can be explained by the titration data as well. It is evident that there were still small amounts of aldehydes present that caused discoloration *via* beta linkage cleaving. The colour change between the 40 and 70 ºC samples was minimal, whereas the 22 ºC samples showed significantly more yellowing than the higher temperature samples. Significant yellowing in the low-temperature samples was in accordance with the titration data that showed lower carboxyl group values and, in turn, a higher aldehyde content. In the case of the 40 °C and 70 ºC samples, the colour differences were less pronounced, but some discoloration was present. The levels of discoloration however were not fully in accordance with the titration data, since a stronger discoloration would be expected in the 70 ºC samples due to their higher aldehyde content. The exception in this case being the 4 h/40 ºC sample, which showed minimal discoloration, comparable to the control sodium chlorite sample (Fig. 3).

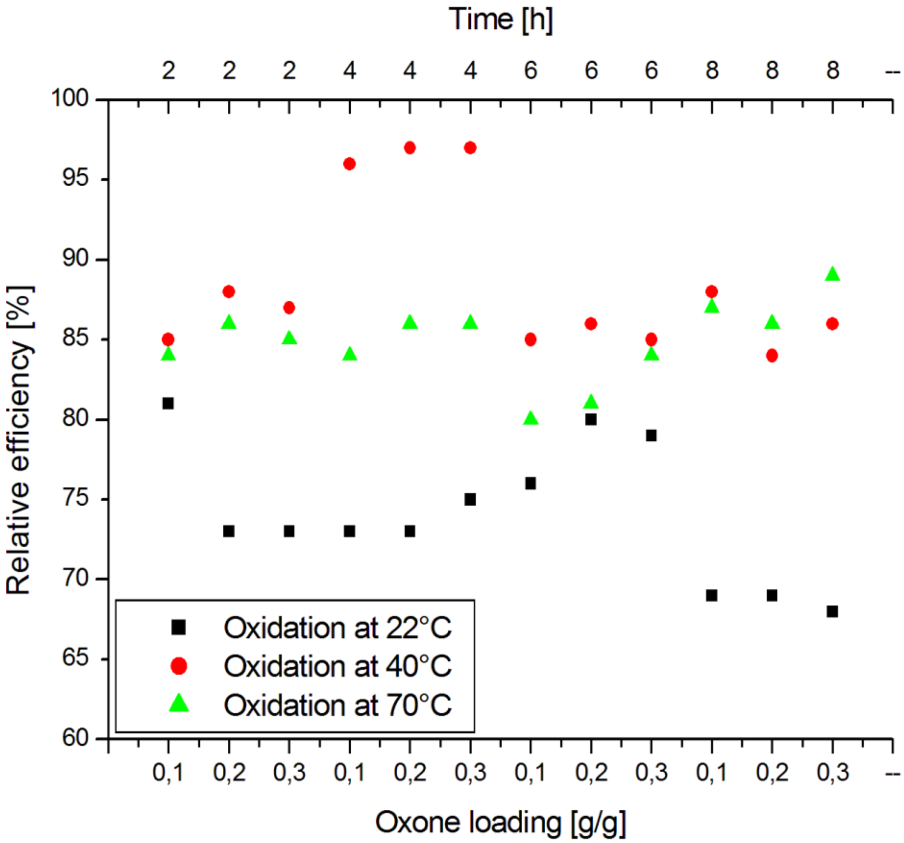

Fig. 4. Graph representation of colour change as a dependence on potassium peroxymonosulfate loading, temperature, and time

FT-IR Measurements

TEMPO-oxidized cellulose and several other samples from the post-oxidation procedures were analyzed using FT-IR. All samples had characteristic cellulose bands. Bands at 3600 to 3100 cm^{-1} corresponded to O-H stretching. The C-H stretching band was located at 2900 cm^{-1}. The band around 1430 cm^{-1} was assigned to $–CH_2–$ and is known as the crystallinity band, whereas the band at 900 cm^{-1} corresponds to the C-O-C stretching present in β-(1→4) glyosidic links and are known as the amorphous band (Ciolacu *et al.*

2011). Additionally, all samples have a carboxyl group band present at 1725 cm^{-1} and a weak water artifact band at 1640 cm^{-1}, indicating adsorbed water in the samples. All spectra were very similar to each other (Fig. 5). No cellulose II was indicated (missing band at 3500 cm^{-1}). This usually appears when cellulose is subject to alkaline conditions. In this case, however, the alkalinity at pH = 8 was weak enough not to cause any changes in the crystal structure of the cellulose. Normalized carboxyl band intensity does not seem to differ between the samples, even though the conductometric titration data showed an increase in carboxyl content values for the post-oxidized samples. The IR spectra differences at 1725 cm^{-1} seemed miniscule at best. Hence, this method is not suitable for the relative determination of carboxyl group concentration. The authors suspect this is due to the measurable but minor difference in the amount of carboxylic groups, where the small increase in –COO$^-$ groups simply does not give a large enough response that would be measurable by FT-IR. The most suitable method for the determination is conductometric titration, which was used extensively.

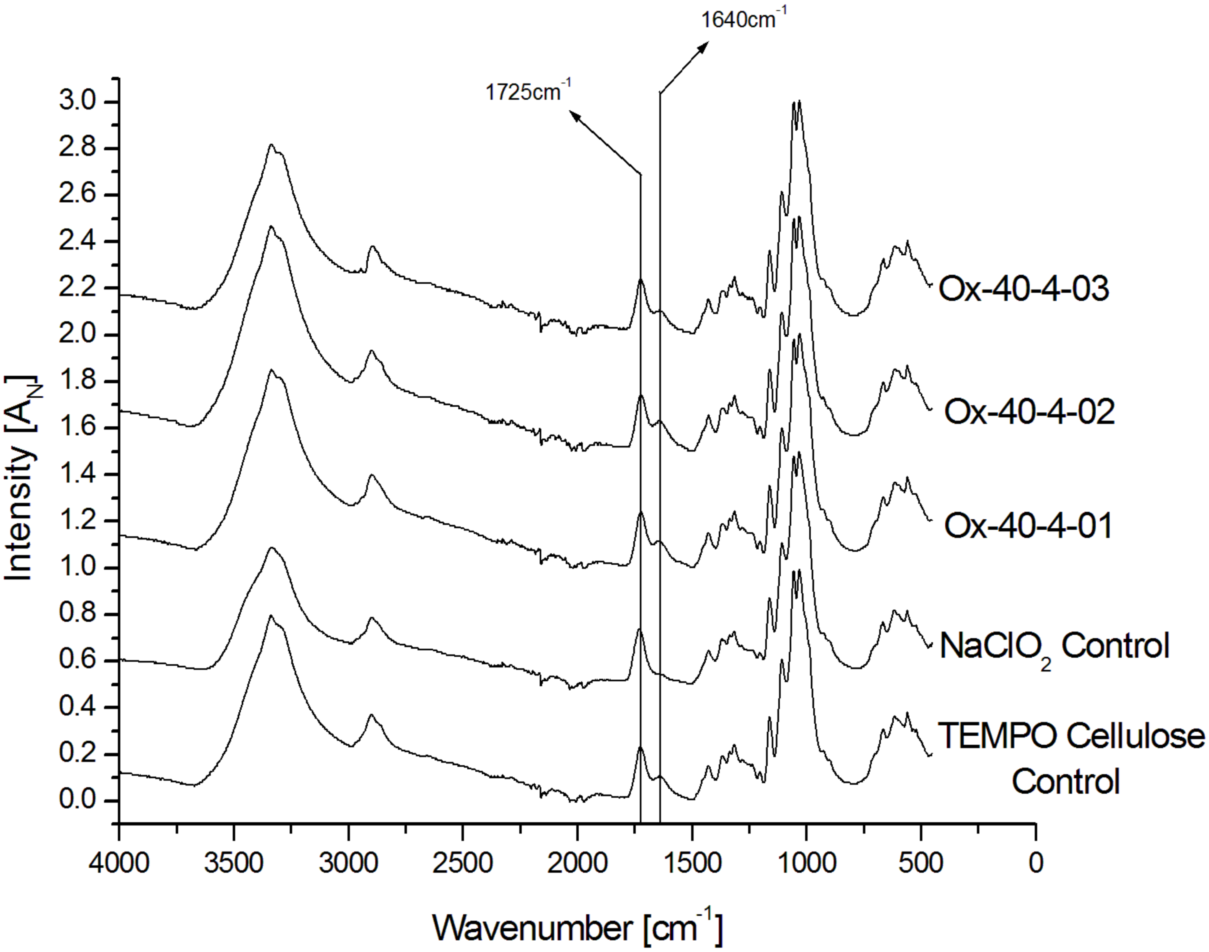

Fig. 5. IR Spectra of selected post-oxidation samples

Morphology of Untreated and Treated Cellulose Fibers

According to SEM imaging (Fig. 6), the main differences between the different grades of treated cellulose fibers lie in the surface morphology of the fibers and the presence of fiber fines. The untreated cellulose fibers had a rough surface structure with small fibrils clearly visible between fibers as well as a network of individualized fibrils on the fiber surface (Fig. 6a).

After TEMPO-mediated oxidation, significant structural damage can be observed on the fibers, indicating that a relatively strong chemical treatment took place (Fig. 6b). TEMPO-oxidized cellulose fibers were flattened by the treatment and the smaller fibrils on the untreated fibers disappeared. Both were presumed to be a consequence of a partial fibrillation of the material that took place during the chemical treatment, since the whole reaction was carried out under mild agitation. Even such mild mechanical agitation seemed to be enough to disintegrate the already small individualized fibril bundles.

Additional chemical treatment of the TEMPO oxidized fibers to eliminate residual aldehydes had a small effect on the fiber surface morphology (Figs. 6c and d). Treating the TEMPO oxidized fibers with an acidified sodium chlorite solution removed residual aldehydes but seemed to close the fiber surface, as it appeared much smoother than in the case of the pure cellulose fibers or TEMPO-oxidized fibers. These were the expected results of treating the fibers with an acidified medium. Protonation of the carboxylate anions took place, which effectively neutralized the surface charge that was present. The lack of electrostatic repulsion forces in between the fibers or fibrils allowed them to consolidate into a compact structure where close acting attraction forces took over (hydrogen and Van der Waals bonds).

However, the potassium peroxymonosulfate post-oxidation process was carried out in an alkaline medium, which preserved the surface charge on the TEMPO oxidized fibers. The fibers that were treated with potassium peroxymonosulfate appeared to have significantly more structural damage (Fig. 6d). This resulted in an increased amount of fiber fragments and visualization of microfibrillar bundles on the fiber surface (Fig. 6d).

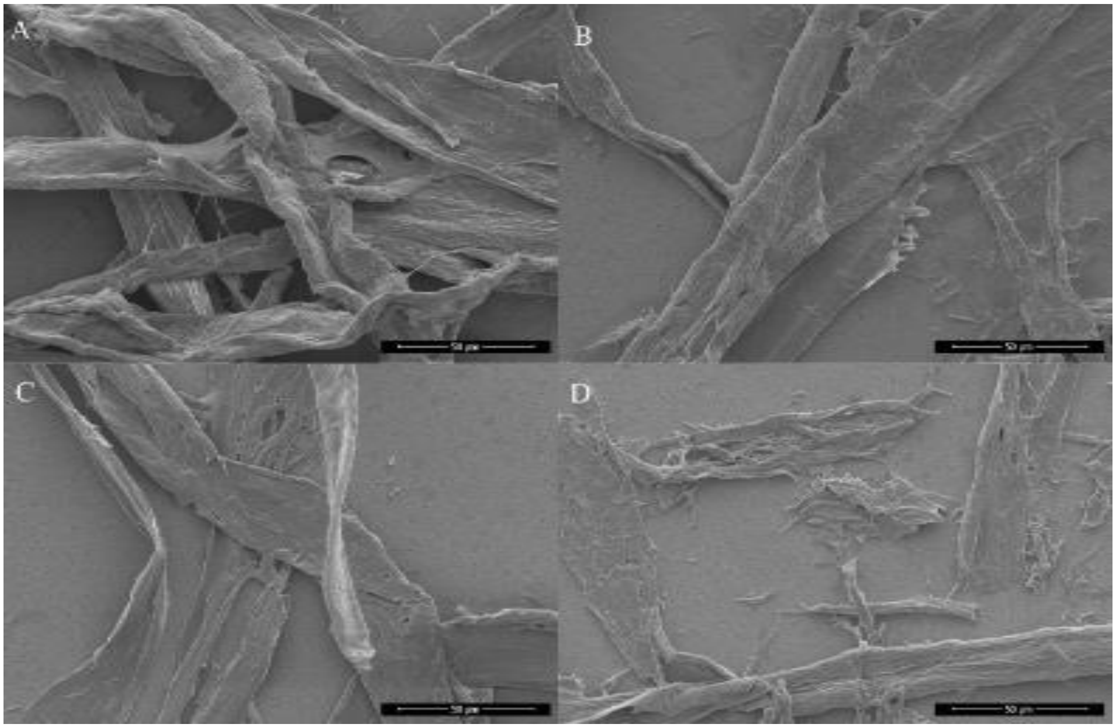

Fig. 6. SEM images of (A) raw unmodified cellulose fibers, (B) TEMPO modified fibers, (C) Sodium chlorite treated TEMPO modified fibers, and (D) potassium peroxymonosulfate-treated TEMPO modified fibers. Magnification bars indicate 50 µm.

Table 2. Fibrillation Yields as Determined by Centrifugation of Nanocellulose Dispersion (100% = No phase separation)

Material	Dissolving cellulose pulp (< 0.05 mmol/g)	TEMPO cellulose (1.35 mol/g)	potassium peroxy-monosulfate-treated TEMPO cellulose (1.42 mmol/g)	Sodium chlorite treated TEMPO cellulose (1.49 mmol/g)
Pass\Yield (%)				
1 (500 bar)	5.37% (+/- 0.21%)	38.78% (+/- 1.01%)	100%	18.21% (+/- 0.43%)
2 (1000 bar)	8.12% (+/- 1.01%)	100%	100%	100%
3 (1000 bar)	8.61% (+/- 1.03%)	100%	100%	100%

Fibrillation Yields

Fibrillation tests indicated that there was a difference between different grades of cellulose that were employed in the homogenization process (Table 2). Dissolving pulp fibers had a nanoparticle yield between 5 and 9% after the third pass through the homogenizer. TEMPO cellulose had a nanoparticle yield of 38.8% after the first pass. Subsequent samples could not be effectively separated into their fibrillated and unfibrillated fractions. The TEMPO modified and potassium peroxymonosulfate-treated sample could not get 2 fractions even after the first pass, and thus, this sample was considered fully fibrillated after a single pass through the homogenizer. Sodium chlorite treated TEMPO cellulose while still being fully fibrillated after the second and third homogenization steps, the yield after the first pass was only 18.2%, which was significantly lower than the normal TEMPO cellulose (Table 2). This was in accordance with the morphology of the treated cellulose fibers (Fig. 6).

CONCLUSIONS

1. Treatment of TEMPO-oxidized cellulose fibers with potassium peroxymonosulfate (Oxone®) in a modified process, which omits acetone, successfully oxidized part of the available aldehyde groups on the fiber surface as seen by increased carboxyl content and enhanced colour stability.
2. Different oxidant loading, temperature, and time regimes were investigated and it was determined that an intermediate temperature of 40 ºC and reaction time of 4 h was more successful at oxidizing the aldehyde groups and enhancing colour stability than at a higher or lower temperature. Oxidant loading had a minimal effect on the outcome of the reaction, due to the small number of aldehydes present.
3. Compared to a reference procedure, 80% efficiency could be achieved by the potassium peroxymonosulfate procedure.
4. Reaction conditions with the potassium peroxymonosulfate process were more favorable for TEMPO modified cellulose as it preserves the surface charge on the TEMPO modified fibers, which helps the fibrillation process, which was observed by the higher nanoparticle yield during centrifugation and significant fiber damage by the mild agitation that was used during chemical treatment.

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