

# On the relationship between fibre composition and material properties following periodate oxidation and borohydride reduction of lignocellulosic fibres

Verónica López Durán  · Per A. Larsson · Lars Wågberg

Received: 14 March 2016 / Accepted: 30 August 2016 / Published online: 2 September 2016  
© The Author(s) 2016. This article is published with open access at Springerlink.com

**Abstract** Periodate oxidation followed by borohydride reduction was performed on four structurally different pulp fibres to clarify the effect of chemical composition on the structural and mechanical properties of sheets made from these fibres. The main purpose was to explore the possibility of extending the use of lignocellulose fibres in novel applications. The degree of oxidation, morphological changes, chemical and physical structure of the fibres, the supramolecular ordering of the cellulose and the mechanical performance of handsheets made from the fibres were studied. The results showed that both periodate oxidation and borohydride reduction are more reactive towards the carbohydrates of the fibres and as a result,

there is an improvement in the tensile properties of the sheets. If the carbohydrates of the fibres are only periodate oxidised to produce dialdehydes, inter- and intra-fibre crosslinks can be formed, leading to paper with increase strength and higher stiffness. The borohydride reduction results in fibres and papers with a greater strength and ductility. It was also found that the characteristic ductility of these modified papers, emanating from the dialcohol cellulose produced, is limited with lignin-rich fibres.

**Keywords** Lignocellulose fibres · Periodate oxidation · Borohydride reduction · Dialdehyde cellulose · Dialcohol cellulose · Tensile strength · Strain-at-break

**Electronic supplementary material** The online version of this article (doi:[10.1007/s10570-016-1061-4](https://doi.org/10.1007/s10570-016-1061-4)) contains supplementary material, which is available to authorized users.

V. López Durán (✉) · P. A. Larsson (✉) · L. Wågberg  
Fibre and Polymer Technology, KTH Royal Institute of Technology, 10044 Stockholm, Sweden  
e-mail: vld@kth.se

P. A. Larsson  
e-mail: perl5@kth.se

V. López Durán · P. A. Larsson · L. Wågberg  
BiMaC Innovation, KTH Royal Institute of Technology, 10044 Stockholm, Sweden

L. Wågberg  
Wallenberg Wood Science Center, KTH Royal Institute of Technology, 10044 Stockholm, Sweden

## Introduction

In the search for novel bio-based materials as a replacement for non-renewable and non-biodegradable materials, cellulose, one of the main components of trees, is a potent candidate. Its advantages include good mechanical strength, high stiffness, low cost and good biodegradability (Wågberg and Annergren 1997; Bledzki and Gassan 1999; Kalia et al. 2011; Qiu and Hu 2013; Vuoti et al. 2013). However, cellulose is sensitive to moisture, limiting its application in environments with varying humidity, and it is non-thermoplastic and cannot therefore easily go through processes such as injection moulding, extrusion or

pressing operations into complex-shaped structures, and this limits its use in applications with advanced material demands (Klemm et al. 2011; Sehaqui et al. 2011; Vishtal and Retulainen 2014).

However, chemical modification of the cellulose makes it possible to develop new materials, and therefore new applications. Among the different chemical modifications that can be carried out on cellulose, periodate oxidation is able to selectively cleave the C2–C3 bond in the glucopyranose backbone of cellulose, in which OH groups are converted to aldehydes (Jackson and Hudson 1937). Efforts have been made to improve the reaction conditions and efficiency of periodate oxidation. Sirviö et al. (2011b) showed that the periodate reactivity can be improved by performing the reaction at elevated temperature. Reactivity can be further increased by the simultaneous use of salts, elevated temperature and cellulose pulp micronization (Sirviö et al. 2011c; Alam et al. 2012). Ultrasound treatment can also be used to increase the accessibility and reactivity (Aimin et al. 2005). However, since sodium periodate is fairly expensive and can be harmful to the environment, its recyclability is therefore also of major importance (Mehltretter 1955; Lister and Rosenblum 1961; Liimatainen et al. 2013; Koprivica et al. 2016).

The interest in periodate-based modification of cellulose is based on the introduction of aldehydes, which enables further conversion into, or reaction with, functional groups such as carboxylic acids (Crescenzi et al. 1984; Maekawa and Koshijima 1984, 1990), and primary (Maekawa and Koshijima 1991) and quaternary amines (Sirviö et al. 2011a). These modifications can provide green materials with potential applications such as superabsorbents (Zhang et al. 2008), biofloculants (Liimatainen et al. 2012), or packaging applications (Larsson et al. 2014a). The introduction of aldehydes reduces the moisture sorption and increases the dimensional stability of papers made of these fibres (Larsson et al. 2008; Gimåker et al. 2009). If the dialdehyde cellulose is further reduced to dialcohol cellulose, the material shows high ductility and formability (Zeronian et al. 1964; Larsson et al. 2014a, b). In fact, the consolidation and formability of these fibres are so high that oxygen barriers can be created by a conventional papermaking procedure (Larsson and Wågberg 2016). Typically, both periodate oxidation and borohydride reduction have been

applied to bleached chemical fibres and bacterial cellulose (Kim et al. 2000; Sirviö et al. 2011a, b).

To the best knowledge of the authors, there are no studies concerning the influence of the chemical composition of lignocellulosic fibres on the periodate oxidation and borohydride reduction. The main objective of this study is therefore to understand whether, and how, the two reactions, and ultimately the materials properties, are affected by the presence of non-cellulosic components. It is important to gain an understanding not only of the structural changes that take place when chemical modifications are performed, but also the influence of the chemical composition of the fibres on the performance of the materials produced and the potential use of lignin-rich fibres in new applications.

In the present work, a bleached chemical pulp and a dissolving grade pulp were used as cellulose-rich fibres and comparisons were made with an unbleached kraft pulp and a chemothermomechanical pulp (CTMP) rich in hemicelluloses and lignin. All the fibres were subjected to both periodate oxidation and borohydride reduction to compare the influence of the presence of lignin and hemicelluloses on the materials produced. Total charge density determinations, carbohydrate analysis, FT-IR, X-ray analysis, microscopy and mechanical testing of sheets made from the fibres were carried out.

## Materials and methods

### Materials

The four different types of fibres used in this study are listed in Table 1.

Sodium metaperiodate was purchased from Alfa Aesar. Hydroxylamine hydrochloride, 2-propanol, sodium borohydride, sodium monobasic phosphate, carbohydrate standards (arabinose, galactose, glucose, xylose and mannose) were all obtained from Sigma Aldrich and were used without further modification or purification.

### Methods

#### *Chemical modification of fibres*

Prior to modification, all the fibres were washed and transferred to their sodium form according to an earlier

**Table 1** Fibre characteristics

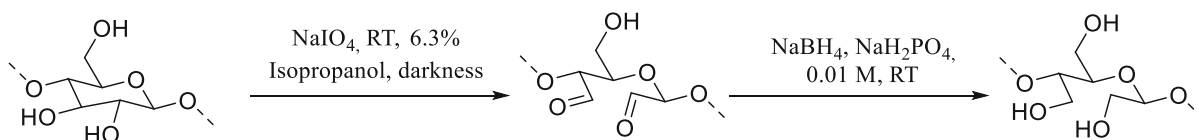
Fibres	Characteristics	Supplier
Bleached chemical	Dried unbeaten virgin softwood kraft pulp, fully bleached according to a (OO)Q(OP)(ZQ)(PO)-sequence, i.e. a Totally Chlorine Free-sequence O = oxygen (alkaline); Q = quelating stage; P = hydrogen peroxide (alkaline); Z = ozone (acid). The parentheses indicate that no washing was carried out between the two stages	SCA Forest Products (Östrand pulp mill, Timrå, Sweden)
Unbleached chemical	Never dried, unbleached and unbeaten softwood pulp from pure spruce with kappa number 101	
CTMP	Peroxide bleached, Norway spruce high-temperature chemothermomechanical pulp	
Dissolving grade	Acid-sulphite pulp cooked from a softwood mixture (60 % Norway spruce and 40 % Scots pine)	Domsjö Aditya Birla AB, Sweden

described protocol (Wågberg and Hägglund 2001). Fines were removed from the CTMP with a Dynamic Drainage Jar number 18 fitted with a 125 P screen, containing etched holes with a diameter of 76  $\mu\text{m}$ . Periodate oxidation and subsequent reduction with sodium borohydride (Fig. 1) were then carried out according to a previously described protocol known to maintain a high degree of polymerization (Larsson et al. 2014b). In brief, a fibre suspension of 4 g/L was allowed to react with 5.4 g  $\text{NaIO}_4/\text{g}$  fibre in the presence of 6.3 % of 2-propanol, at room temperature and in the dark, during 6 and 12 h. In addition, the less cellulose-rich CMTP was oxidised also for 24 h. The oxidation reaction was terminated by filtering the fibres and thorough washing with deionised water. Immediately after the washing step, the fibres were re-suspended in water to a concentration of 4 g/L. To this suspension, sodium phosphate with a final concentration of 0.01 M and 0.5 g of  $\text{NaBH}_4/\text{g}$  fibre were added. The mixture was allowed to react for 1 h. In all cases, the reaction was stopped by filtration and washing with deionised water until a conductivity  $<5 \mu\text{S}/\text{cm}$  was reached. For hemicelluloses, reactions similar to those with cellulose are anticipated, and it is well

known that periodate will react with lignin to cause for example a rapid demethylation (Adler and Hernestam 1955) and  $\text{NaBH}_4$  will also react with lignin causing an increase in the OH/CO ratio of the lignin (Marton and Adler 1961).

#### Carbonyl content

The degree of oxidation after periodate oxidation was determined by reaction with hydroxylamine hydrochloride (Zhao and Heindel 1991; Larsson et al. 2008). The same method was also used after the borohydride reduction to control that all aldehydes had been converted to primary alcohols. Before the reaction, both the hydroxylamine hydrochloride and the fibre suspensions were set to pH 4. Then, 25 mL of 0.25 M hydroxylamine was allowed to react with 0.10–0.15 g of fibres for 2 h followed by filtration using a pre-weighted filter. The filtrate was kept for titration and the fibres were washed with water to get rid of excess of hydroxylamine and dried in an oven at 105  $^\circ\text{C}$  overnight for determination of the fibre mass. Titrations were performed by titrating the filtrate back to pH 4 with 0.1 M sodium hydroxide. Three separate

**Fig. 1** Chemical modification of cellulose by periodate oxidation and borohydride reduction

reactions with hydroxylamine were carried out for each sample.

### Sheet preparation

Paper sheets with a target grammage of 100 g/m<sup>2</sup> were prepared in a Rapid Köthen sheet former (Paper Testing Instruments, Austria). Sheets were dried between 400 mesh woven metal wires (The Mesh Company Ltd, Warrington, UK) attached to regular sheet-former carrier boards for 15 min at 93 °C, and at a reduced pressure of 95 kPa. Sheets were stored under controlled conditions, 23 °C and 50 % relative humidity, until further testing.

### Brightness

The brightness of the sheets was determined in accordance with ISO 2470:1999 with a Shimadzu UV–Vis equipment with an integrating sphere to measure the spectral reflectance. Sheets were folded three times to reach an approximate grammage of 800 g/m<sup>2</sup> to create an opaque sample. The samples were placed in the spectrometer and the brightness was measured with a broad-band filter with an effective wavelength of 457 nm. Nine measurements were made for each paper grade.

### Klason lignin and carbohydrate analysis

The carbohydrate and lignin composition of the samples was determined according to SCAN-CM 71:09, where hydrolysates were filtered and the insoluble fractions were dried and quantified as Klason lignin. Monosugars were analysed using a high-performance anion exchange chromatograph (Dionex, Sunnyvale, USA) equipped with a pulsed amperometric detector and a CarboPac PA-1 column. MilliQ water was used as eluent at a flow rate of 1 mL/min. The column was cleaned with water containing 200 mM sodium hydroxide and 170 mM sodium acetate. The injection volume was 10 µL. Anhydro correction factors for monosaccharides corresponding to 0.88 for xylose and arabinose and 0.9 for glucose, mannose and galactose were used to compensate for hydrogen and hydroxyl groups introduced during carbohydrate hydrolysis. Arabinose, galactose, glucose, xylose and mannose were used as calibration standards.

### Charge density determination

The total charge density was determined by conductometric titration according to SCAN-CM 65:02. Prior to titration, the fibre suspensions were set to pH 2, and kept at this pH for 30 min, followed by washing with deionised water until the conductivity was <5 µS/cm. Conductometric titrations were performed using a Metrohm 702SM Titrino titrator. About 0.2 g of fibres were placed in a glass container with 10 mL of 0.1 M NaCl, 5 mL of 0.01 M hydrochloric acid and water to a total volume of 500 mL, and 0.10 M NaOH was then added to the stirred suspension at a rate of 0.04 mL/min until pH 11 was reached. The total charge was then normalised with respect to the mass of fibres used in the analysis.

### Fourier transform infrared spectrometry (FTIR)

Spectra of sheets were obtained using a Perkin-Elmer Spectrum 2000 FTIR with an attenuated total reflectance crystal accessory (Golden Gate). Individual scans at 4.0 cm<sup>-1</sup> resolution were used in the 4000–600 cm<sup>-1</sup> interval and, 32 scans were made per sample. Each spectrum was normalised with respect to the maximum absorbance peak.

### X-ray diffraction

The molecular structure of the samples was studied using an X'Pert PRO XRD (PANalytica, The Netherlands). Diffraction patterns were obtained in reflexion in the angular range between 5° and 30° (2θ) with a step size of 0.020°, using CuKα radiation (1.5418 Å). The amount of crystalline material was determined by the height of the highest diffraction peak, and the amount of amorphous material was determined by the height of the minimum intensity between the major peaks. The crystallinity index was calculated by the difference between these two intensities, divided by the intensity of the highest peak. (Segal et al. 1959; French and Santiago Cintrón 2013), and the crystallite width was estimated using the Scherrer equation (Patterson 1939).

### Scanning electron microscopy

Sheet and fibre morphology were studied with a Hitachi S-4800 field emission scanning electron

microscope (SEM). To suppress specimen charging, the samples were first sputtered with a  $\sim 10$  nm Pt–PD coating in a 208 HR Cressinton sputter coater.

### *Mechanical testing*

The structural thickness of the sheets was evaluated according to SCAN-P 88:01. The tensile testing was performed using an Instron 5944 with a 500 N load cell. Strips with a width of 15 mm were clamped with a free span of 100 mm and strained at a constant rate of 100 mm/min. A total of 10 specimens from two sheets were tested and the results were reported for those which did not fail immediately in the jaw face. Stress–strain curves were recorded, and the Young's modulus was determined from the slope of initial linear strain region. Dry zero- and short-span (0.4 mm) tensile tests were performed on a Pulmac Z-span 3000. For each sample, eight test pieces were evaluated.

For unbleached kraft fibres, a short-span compression test (SCT) was performed with a L&W Compressive Strength Tester STFI (ABB Lorentzen and Wettre). The paper strip was placed between two clamps with a 0.7 mm free clamping length. Ten measurements were made per sample. All samples were conditioned and tested at 23 °C and 50 % relative humidity.

### *Samples name*

The first and the second numerals represent hours of oxidation and reduction respectively, e.g. 6 + 1 means 6 h of periodate oxidation and 1 h of borohydride reduction.

## **Results**

### Chemical characterization of chemically modified fibres

It is well documented that periodate oxidation results in the opening of the anhydroglucose ring of cellulose at the C2–C3 position (Jackson and Hudson 1937). To determine carbonyl formation after periodate oxidation, hydroxylamine titrations were carried out and the results are shown in Table 2. Differences in the chemical composition of the fibres resulted in different amount of aldehyde formation. Bleached chemical

fibres showed the greatest reactivity towards the periodate oxidation, since 1.9 and 2.5 mmol/g of carbonyls were formed after 6 and 12 h respectively.

Periodate-oxidized fibres were subsequently subjected to reduction with sodium borohydride to produce dialcohol cellulose as shown in Fig. 1. No carbonyls could be detected after borohydride reduction of the fibres. Compositions of sugars and lignin in the reference fibres and in the fibres after oxidation and reduction are listed in Table 3.

The total amount of detectable sugars decreased with increasing degree of modification for the bleached chemical, dissolving grade and unbleached chemical fibres, while the relative lignin content stayed almost constant. In the case of the CTMP, the relative lignin content was even higher after modification, i.e. the chemicals react mainly with carbohydrates. It should be noted that the sugar composition in Table 3 only include: arabinose, galactose, xylose and mannose, and that the analysis method is not sensitive to derivatised sugars.

The total fibre charge was measured both after oxidation and after sequential oxidation and reduction. The bleached chemical fibres and dissolving grade fibres showed a decrease in charge density, indicating that no oxidation to carboxyl groups had taken place (Table 4). On the other hand, CTMP and unbleached chemical fibres showed an increase in charge density after periodate oxidation. When the reduction step was carried out, a decrease in charge was observed in most of the samples, but, an increased charge density was observed after the reduction of the CTMP fibres.

When the periodate oxidation was performed on fibres having a high content of lignin, a change in colour towards a darker colour was observed, indicating the formation of conjugated structures. This effect was quantified by measuring the brightness of the sheets. CTMP sheets in particular showed a brightness decrease, in the interval of 6–12 h, from 75 to 25 % (Fig. 2) after the oxidation, whereas the other grades showed a much smaller decrease in brightness. On the other hand, after the borohydride reduction, the brightness of the CTMP sheets increased: from 25 % (for all oxidation times) to 38, 32 and 29 % after 6 + 1, 12 + 1 and 24 + 1 h respectively.

Changes in chemical structure by periodate oxidation and borohydride reduction were examined by FTIR. Characteristic bands indicative of dialdehyde cellulose appeared at  $1740\text{ cm}^{-1}$ , while the intensity

**Table 2** Carbonyl content of the different fibres after periodate oxidation

Fibres	0 h (mmol/g)	6 h (mmol/g)	12 h (mmol/g)	24 h (mmol/g)
Bleached chemical	0.03 ± 0.01	1.9 ± 0.1 (16 %)	2.5 ± 0.1 (21 %)	–
Dissolving grade	0.03 ± 0.02	1.09 ± 0.04 (9 %)	1.48 ± 0.01 (12 %)	–
Unbleached chemical	0.4 ± 0.1	1.2 ± 0.1 (10 %)	1.77 ± 0.02 (15 %)	–
CTMP	0.32 ± 0.03	1.22 ± 0.01 (10 %)	1.45 ± 0.01 (12 %)	2.5 ± 0.2 (21 %)

The numbers in parentheses show the degree of oxidation

**Table 3** Neutral sugar composition and lignin content of chemically modified fibres

Fibres	Oxidation time + reduction timers	Arabinose (%)	Galactose (%)	Glucose (%)	Xylose (%)	Mannose (%)	Lignin (%)
Bleached chemical	0	0.7	n.d. <sup>a</sup>	78	8	8	<0.5
	6	0.1	n.d. <sup>a</sup>	52	2	2	<0.5
	6 + 1	0.1	n.d. <sup>a</sup>	45	1	2	<0.5
	12	0.1	n.d. <sup>a</sup>	56	2	1	<0.5
	12 + 1	0.1	n.d. <sup>a</sup>	54	1	1	<0.5
Dissolving grade	0	<0.1	<0.1	87	2	2	<0.3
	6	<0.1	n.d.	68	0.6	0.5	<0.2
	6 + 1	<0.1	n.d.	64	0.5	0.5	<0.2
	12	<0.1	n.d.	61	0.5	0.6	<0.1
	12 + 1	<0.1	n.d.	62	0.4	0.3	<0.1
Unbleached chemical	0	1	2	48	6	13	21
	6	0.2	0.2	47	4	2	17
	6 + 1	0.2	0.3	44	4	2	16
	12	n.d. <sup>a</sup>	0.2	37	3	1	19
	12 + 1	n.d. <sup>a</sup>	n.d. <sup>a</sup>	31	1	2	18
CTMP	0	0.9	2	48	6	13	28
	6	0.3	0.3	38	3	4	33
	6 + 1	0.4	0.4	34	3	4	34
	12	0.2	0.3	34	3	3	34
	12 + 1	0.1	0.2	23	2	2	32
	24	0.1	0.2	25	2	2	37
	24 + 1	0.1	0.2	19	1	2	34

<sup>a</sup> Below the detection limit of the instrument

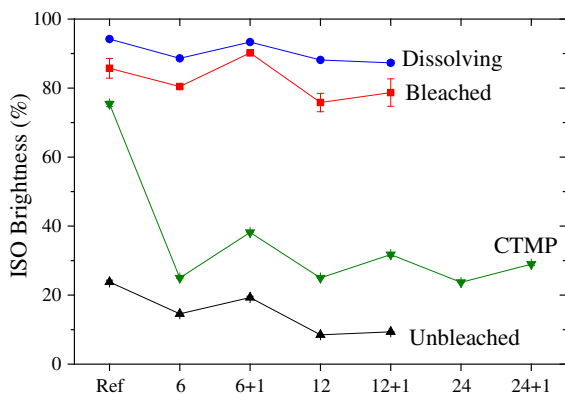
of the band at 880 cm<sup>-1</sup> increased (Kim et al. 2000; Sirviö et al. 2011c). For all the samples the characteristic peaks increased with increasing degree of oxidation (Fig. 3). The band at 1740 cm<sup>-1</sup> is characteristic of carbonyl groups, while the peak at 880 cm<sup>-1</sup> has been assigned to hemiacetals (Kim et al. 2000). CTMP sheets and sheets from unbleached

fibres also showed a characteristic band at 1660 cm<sup>-1</sup> which was earlier assigned to conjugated quinoid groups (Gosselink et al. 2011). The glucomannan peak at 810 cm<sup>-1</sup> disappeared after the oxidation treatment, which agrees with the results of the carbohydrate analysis; since both galactose and mannose were removed and/or oxidised by the treatment (Table 3).



**Table 4** Charge density after periodate oxidation and borohydride reduction

Fibres	0 h ( $\mu\text{eq/g}$ )	6 h ( $\mu\text{eq/g}$ )	6 + 1 h ( $\mu\text{eq/g}$ )	12 h ( $\mu\text{eq/g}$ )	12 + 1 h ( $\mu\text{eq/g}$ )	24 h ( $\mu\text{eq/g}$ )	24 + 1 h ( $\mu\text{eq/g}$ )
Bleached chemical	$58 \pm 3$	$31 \pm 5$	$31 \pm 4$	$32 \pm 3$	$20 \pm 2$	–	–
Dissolving grade	$32 \pm 1$	$28 \pm 1$	$28 \pm 1$	$22 \pm 3$	$19 \pm 4$	–	–
Unbleached chemical	$182 \pm 3$	$243 \pm 2$	$196 \pm 1$	$217 \pm 3$	$198 \pm 6$	–	–
CTMP	$196 \pm 7$	$268 \pm 3$	$222 \pm 10$	$240 \pm 1$	$255 \pm 11$	$182 \pm 18$	$250 \pm 1$

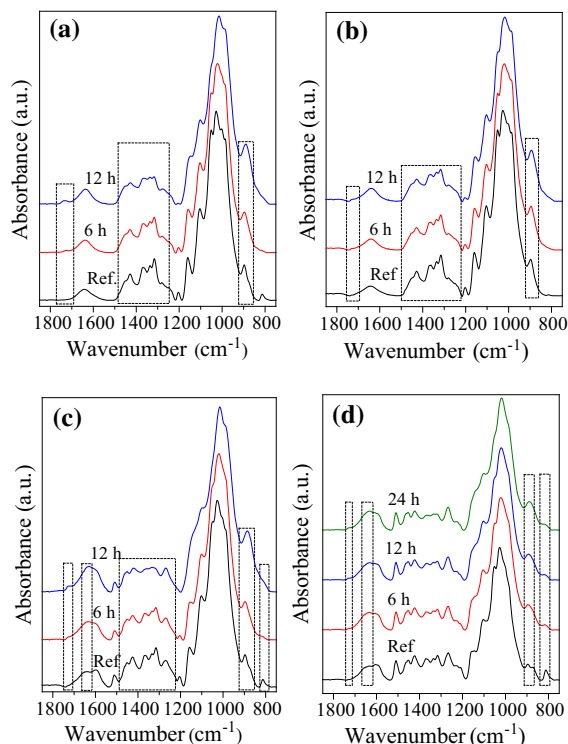
**Fig. 2** ISO Brightness of hand-sheets made of modified fibres

The region around  $1300\text{ cm}^{-1}$  is strongly affected by the crystallinity of cellulose, with bands at  $1315\text{ cm}^{-1}$  corresponding to  $\text{CH}_2$  vibrations,  $1335\text{ cm}^{-1}$  to  $-\text{OH}$  in-plane bending and  $1430\text{ cm}^{-1}$  to  $\text{CH}_2$  scissoring (Åkerholm and Salmén 2001).

Figure 4 shows that, as the degree of oxidation increased, the absorption at  $1075\text{ cm}^{-1}$  due to primary alcohols increased while the band from secondary alcohols at  $1100\text{ cm}^{-1}$  decreased (Langkilde and Svantesson 1995). Furthermore, peaks corresponding to carbonyls at  $1790\text{ cm}^{-1}$  were not detected after the reduction step and the absorbance around  $880\text{ cm}^{-1}$  was lower.

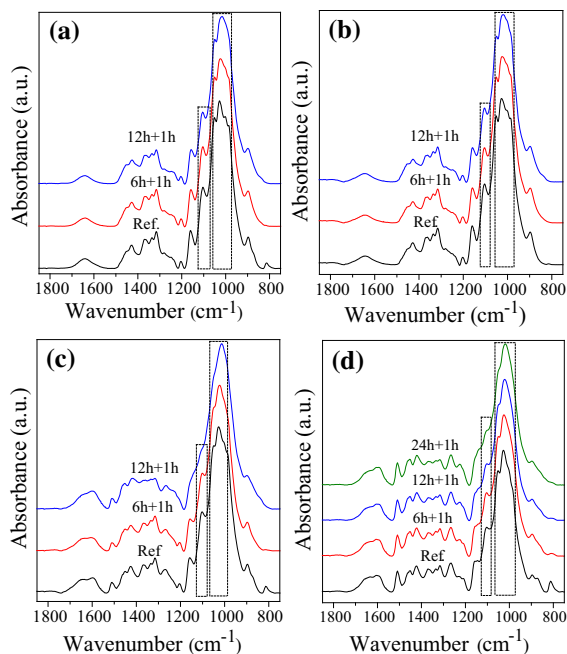
#### Crystallinity of the cellulose and morphology of the modified fibres

X-ray diffractograms of the chemically modified fibres are shown in Fig. 5. In general, the data show a decrease in the crystallinity with increasing degree of oxidation. Using the Scherrer formula to calculate the crystallite width, the bleached fibres showed a decrease from 4.1 to 3.6 and 3.0 nm after 6 and 12 h of oxidation, respectively. When the CTMP was oxidised to the same degree as the bleached fibres

**Fig. 3** FTIR spectra of fibres subjected to periodate oxidation for different times: **a** bleached chemical fibres, **b** dissolving grade fibres, **c** unbleached chemical fibres, and **d** CTMP fibres. The dashed boxes indicate characteristic regions for carbonyls at  $1740\text{ cm}^{-1}$ , crystalline cellulose around  $1300\text{ cm}^{-1}$  and hemiacetals at  $880\text{ cm}^{-1}$ . For unbleached and CTMP fibres, the region at  $1660\text{ cm}^{-1}$  shows *quinoid structures*

(Table 2), the crystallite width decreased to 2.8 nm, i.e. similar width to that of the unbleached material. Oxidation of the dissolving grade fibres for 12 h only reduced the width of the crystallites from 4.2 to 3.6 nm (data is showed in the supporting information), indicating a lower degree of oxidation on the cellulose in these fibres.

SEM images of the different fibres were also collected to study the effect of the chemical



**Fig. 4** FTIR spectra of oxidised and reduced fibres: **a** bleached chemical fibres, **b** dissolving grade fibres, **c** unbleached chemical fibres, and **d** CTMP fibres. The *dashed boxes* at  $1075\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  indicate characteristic regions for primary alcohols and secondary alcohols respectively

modification on the fibre morphology. After oxidation the fibres appear to have a similar length to that of the reference but they appear thinner and straighter. In all cases, the sheets formed after oxidation and reduction appear to have a denser and more consolidated structure (Fig. 6). Figures showing treated fibres for 6 and 6 + 1 h, and 12 and 12 + 1 h for CTMP are available in the supporting information.

### Mechanical characterization

The mechanical properties of paper are highly dependent on the density of the paper (Seth 1990) and it is hence important to determine how much the modification alters the consolidation of the fibres during sheet preparation. Figure 7a shows that the density did not significantly change after the periodate oxidation, but there was a considerable increase in density after the borohydride reduction. This increase is probably due to a softening of the fibres following the borohydride reduction. Sheets from bleached chemical fibres, dissolving grade fibres and unbleached chemical fibres showed a high ductility after partial modification to

dialcohol cellulose, but this change was not as significant in the CTMP sheets.

Tensile strength and strain-at-break are presented in Fig. 7c, d, respectively. There was a steady increase in tensile strength with increasing degree of oxidation in the range of oxidation studied, and after borohydride reduction the sheets became even stronger. The greatest increase in strength was observed for the sheets made from dissolving grade fibres, in which the tensile strength increased from 4 to 54 MPa. The enhancement in mechanical properties, seems, nevertheless to be dependent on the composition of the fibres. The strain-at-break, on the other hand, generally decreased after periodate oxidation and increased after borohydride reduction; which is well in agreement with earlier findings (Zeronian et al. 1964; Larsson et al. 2008, 2014b).

Due to the differences in tensile properties observed in sheets made from different fibres, and as an attempt to fully understand the mechanical properties of sheets made of different fibres, the properties of individual fibres were estimated using zero-span testing. The results are shown in Table 5. After the periodate modification, the strain-at-break of the fibre decreased with increasing degree of oxidation, but the strain-at-break increased significantly after the subsequent reduction with sodium borohydride. This effect was, however, highly dependent on the types of fibre used.

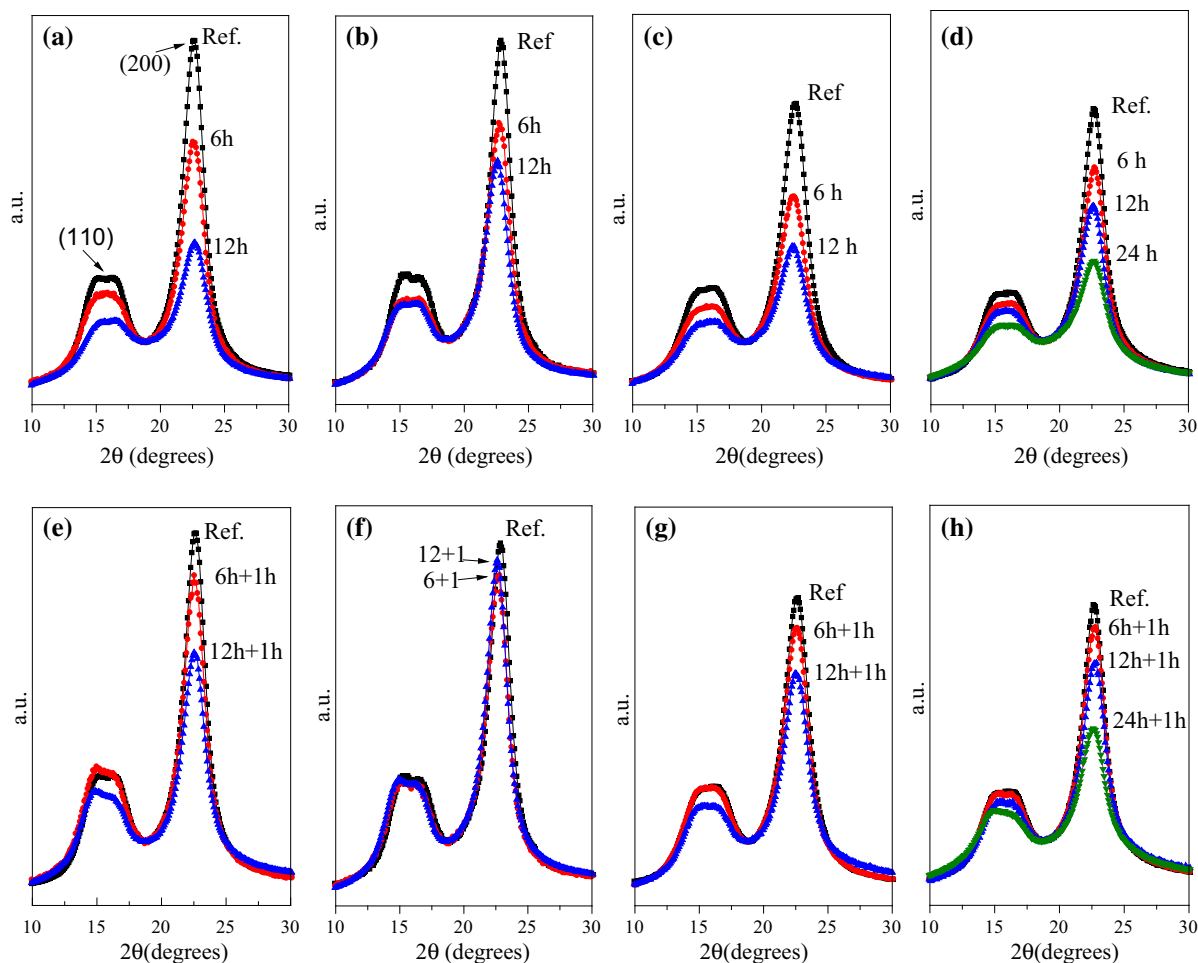
Figure 8 shows the results of the short-span compression test on the unbleached kraft fibres. A large improvement from 27 to 45 kNm/kg was observed after the modification. This improvement was independent from the modification time or the type of modification performed on the fibres.

### Discussion

#### Chemical composition of modified fibres

Four different lignocellulosic fibres were oxidised with sodium metaperiodate to produce 2,3-dialdehyde cellulose, followed by a reduction with borohydride to produce dialcohol cellulose. To compare the efficiency of the periodate oxidation on the different fibres, the carbonyl content was measured before and after defined modification times (Table 2). One component contributing to the total carbonyl content of non-modified unbleached and CTMP fibres, i.e. their





**Fig. 5** X-ray diffraction patterns of chemically modified fibres. The *upper diffractograms* show the patterns after periodate oxidation of: **a** bleached chemical fibres, **b** dissolving grade fibres, **c** unbleached chemical fibres and **d** CTMP fibres, and the

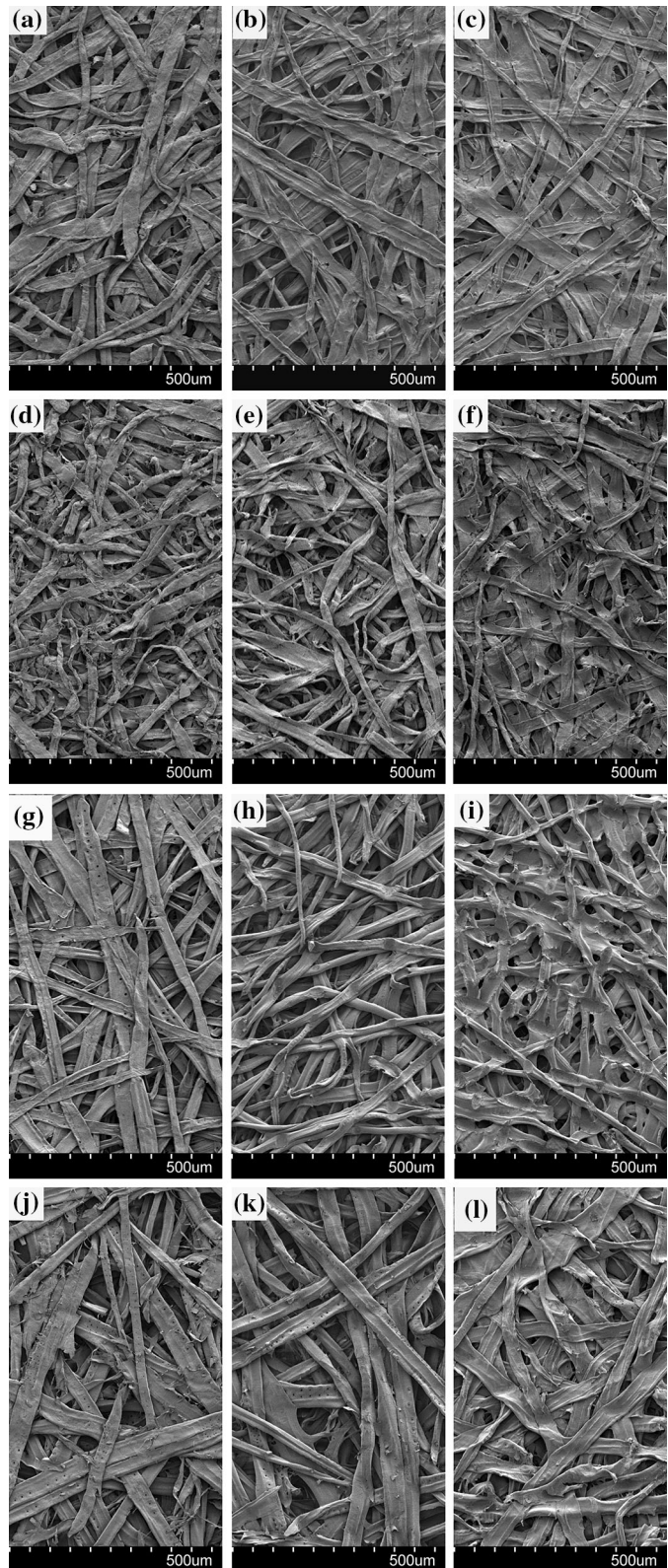
*lower diffractograms* show data after further reduction with borohydride; **e** bleached fibres, **f** dissolving grade, **g** unbleached chemical, and **h** CTMP

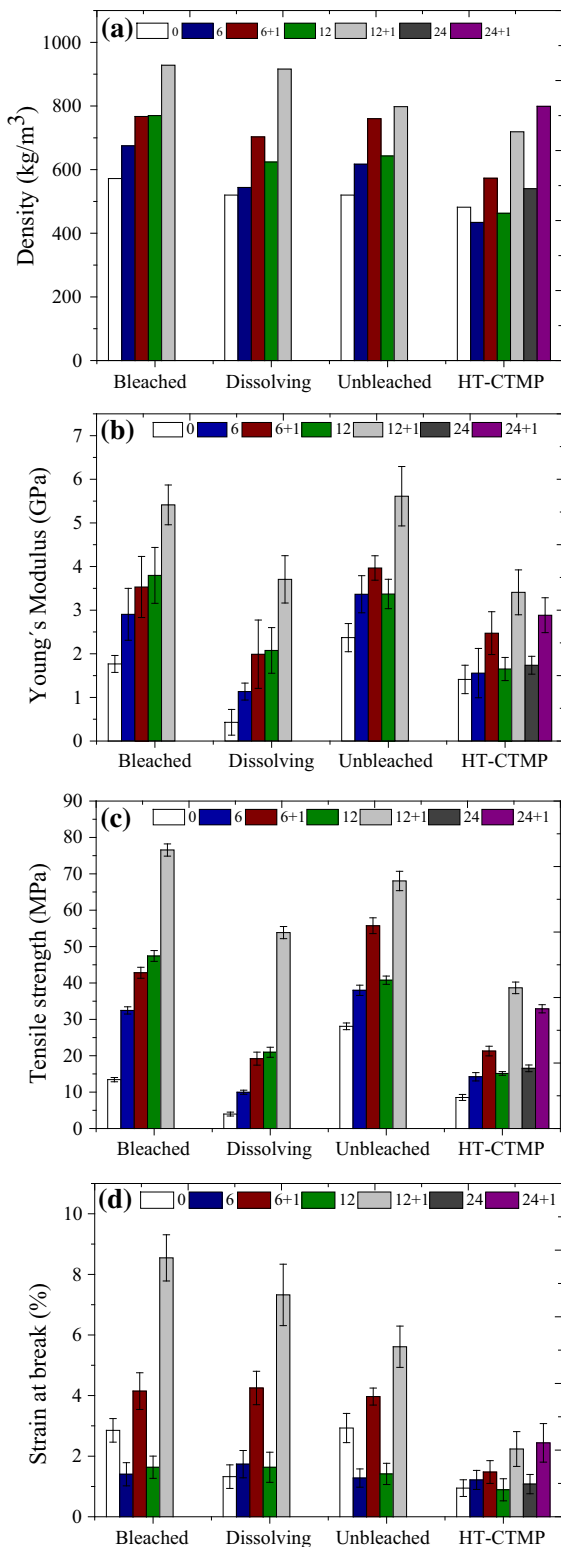
ability to react with hydroxylamine hydrochloride, is coniferaldehyde (Argyropoulos et al. 1995) and this must be corrected when evaluating the carbonyl content of the unbleached chemical and CTMP fibres. It was found that the different types of fibres had different carbonyl contents both before and after the same time of oxidation. The differences can be attributed to the followings factors: (1) different contents and availability of vicinal diols in the different types of fibres (Table 3), which naturally limits the formation of aldehydes, i.e. carbonyls that can be detected by reaction with hydroxylamine hydrochloride, (2) the periodate reacts with hemicelluloses which may be later dissolved and lost before the analysis (Larsson et al. 2014b, for example,

showed that low-DP materials are removed), (3) reactions between periodate and lignin yielding compounds that can react with hydroxylamine, e.g. phenolic guaiacyl.

Interestingly, despite the high content of cellulose in the dissolving grade fibres, the carbonyl content after 12 h oxidation was about half of that found in the bleached chemical fibres. For the viscose process of dissolving grade fibres the presence of hemicelluloses is undesirable since they can cause problems during the later alkalization (Christov and Prior 1993). Duchesne et al. (2001) showed that removal of hemicelluloses increased the fibre wall compactness by allowing the microfibrils to associate into larger fibril aggregates. Furthermore, Palme et al. (2016)

**Fig. 6** SEM images of (*first row*) **a–c** bleached chemical fibres, (*second row*) **d–f** dissolving grade fibres (*third row*) **g–i** unbleached chemical fibres and (*fourth row*) **j–l** CTMP fibres. The *first column* shows unmodified fibres; the *second column* shows fibres 12 h after periodate oxidation (24 h in the CTMP case) and the *third column* shows fibres after reduction with borohydride





**Fig. 7** Mechanical properties of sheets from chemically modified fibres: **a** density, **b** Young's modulus, **c** tensile strength and, **d** strain-at-break

showed that dissolving grade fibres have a lower water retention value compared with bleached kraft fibres, and hence a lower availability of the cellulose for the oxidation.

Periodate oxidation is highly selective towards vicinal alcohols, but many other chemical reactions can take place between sodium periodate and wood-based fibres, one being the reaction with phenolic guaiacyl compounds. During this reaction, ortho-quinone structures are formed from the phenolic hydroxyl group (Lai et al. 1990; Fig. 9). The formation of quinones during the periodate oxidation was supported by the decrease in brightness of the sheets (Fig. 2) and by the conjugated quinoid groups that appeared at about  $1660\text{ cm}^{-1}$  in the IR spectra. A further treatment with borohydride not only reduce the dialdehydes formed, but also reduce conjugated carbonyls to their corresponding alcohols (Chaikin and Brown 1949).

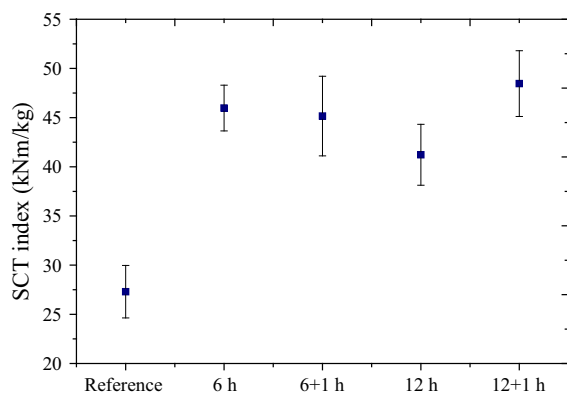
The chemical composition of the fibres given in Table 3 shows that the relative content of lignin in CTMP is higher after periodate oxidation than before the reaction. Possibly, hemicelluloses, and some amorphous parts of the cellulose, could be solubilised and further removed during washing, which will result in an increase in the lignin content of the remaining material. Okita et al. (2009) used TEMPO-mediated oxidation on softwood thermomechanical fibres and found that their system can be used to oxidise and remove both lignin and hemicelluloses. Despite the reaction with phenolic groups of lignin, periodate was not able to delignify the fibres, which suggests a greater selectivity towards cellulose and hemicelluloses. By comparing the bleached fibres and the fibres from CTMP, it is evident how the different components of the fibres affect the oxidation reaction, since it takes twice the time for CTMP fibres to reach the same carbonyl content as the bleached chemical fibres (Table 2).

A considerable decrease in the concentration of glucose in the fibres was also noted (Table 3). It is, however, difficult to establish whether the lost material has the same composition as the remaining material. Furthermore, after periodate oxidation the

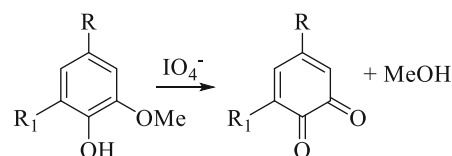
**Table 5** Mechanical properties at the fibre level by zero- and short-span measurements

Fibres	Oxidation time + reduction time	Zero-span tensile strength (MPa)	Short-span tensile strength (MPa)	Estimated single-fibre strain-at-break (%) <sup>a</sup>
Bleached chemical	0	59 ± 3	33 ± 7	14
	6	32 ± 11	34 ± 4	1
	6 + 1	83 ± 11	74 ± 6	9
	12	50 ± 10	51 ± 7	0.1
	12 + 1	126 ± 7	119 ± 13	34
Dissolving grade	0	37 ± 5	15 ± 3	16
	6	20 ± 7	13 ± 4	5
	6 + 1	49 ± 4	35 ± 2	10
	12	31 ± 2	26 ± 6	2
	12 + 1	85 ± 2	70 ± 30	23
Unbleached chemical	0	101 ± 9	95 ± 8	5
	6	38 ± 6	37 ± 7	1
	6 + 1	80 ± 6	83 ± 6	3
	12	38 ± 4	37 ± 5	1
	12 + 1	101 ± 4	111 ± 3	8
CTMP	0	44 ± 5	38 ± 4	6
	6	15 ± 2	14 ± 2	1
	6 + 1	41 ± 3	36 ± 4	5
	12	13 ± 6	10 ± 9	2
	12 + 1	54 ± 8	53 ± 8	6
	24	16 ± 2	13 ± 1	2
	24 + 1	59 ± 2	52 ± 4	7

<sup>a</sup> Batchelor and Westerlind (2003)

**Fig. 8** Compression strength of unbleached kraft fibres

chemical structure of cellulose is altered, which also results in the introduction of “new” monosugars upon hydrolysis. An example of the reactions that can take place during the hydrolysis is that partially oxidised



Where:  
R= lignin side chain  
R<sub>1</sub>= H, OCH<sub>3</sub> or lignin unit

**Fig. 9** Formation of o-quinone compounds during periodate oxidation (Lai et al. 1990)

cellulose can be further converted to erythritol (Vee-laert et al. 1994). The carbohydrate analysis (Table 3) also shows how hemicelluloses are removed both by periodate oxidation and by borohydride reduction. In the case of borohydride reduction, the material losses may be due to an increased solubility in water of dialcohol cellulose.

Native cellulose has no charged moieties apart from a very small charge due to oxidised end-groups of cellulose and it is therefore probable that the removal of hemicelluloses as water-soluble compounds seen in Table 3 affects the charge density of the modified fibres. A decrease in charge density was indeed seen in the bleached chemical fibres and the in dissolving grade fibres (Table 4). Larsson et al. (2014b) showed that by adding isopropanol and performing the periodate oxidation in the dark the degree of polymerization of the fibres was not significantly affected. However, the molecular mass distribution of treated samples became narrower and the peak corresponding to 110 kDa disappeared, indicating a removal of hemicelluloses. The IR-spectra after both periodate oxidation and borohydride reduction showed no peaks corresponding to carboxylate groups, supporting the general idea that periodate oxidation only oxidises vicinal alcohols to aldehydes which agrees well with other studies on cellulose, e.g. Sirviö et al. (2011b). Both CTMP and unbleached chemical fibres showed the same trend upon periodate oxidation. The charge density increased with short oxidation times and reached a maximum before starting to decrease after extended periodate oxidation. One possible explanation can be found in Adler and Hernestam (1955), who proposed that the guaiacol moiety of lignin reacts with the periodate to form a mesomeric radical that can react with a hydroxyl radical and form a hemiacetal. The hemiacetal can then release methanol to form an o-quinone which finally undergoes periodate oxidation to muconic acid. Alternatively, the charges present are not removed by the modifications but, since non-charged material is removed the charge density of the remaining fibres increases. The fact that the charge density goes up and then down indicates that there is probably a combination of both these effects.

Changes in the chemical structure after both modifications were examined by FT-IR. In this study, the earlier assigned peaks from carbonyls and hemiacetals were detected as small shoulders. As reported by Kim et al. (2000), distinct peaks of dialdehyde cellulose were only seen when the degree of oxidation was at least of 12 %. This explains why the carbonyl peak intensity is weak after 6 h of oxidation. Recent studies also suggest that after oxidation the carbonyls immediately form hemiacetals and cannot therefore be detected (Guigo et al. 2014).

A decrease in crystallinity (Kim et al. 2000; Chavan et al. 2002; Larsson et al. 2013) has been found after periodate oxidation of bleached chemical fibres. In this study, the fraction of non-ordered cellulose increased with increasing degree of oxidation, as shown by the decrease in height of the crystalline peak in the IR spectra (Fig. 3) as well as in the X-ray diffractograms (Fig. 5). On the other hand somewhat surprisingly, the crystallinity index of samples after borohydride reduction was slightly higher than before reduction. This can probably be explained by the removal of water-soluble compounds such as hemicelluloses and dialcohol cellulose during the reduction step.

#### Effect of fibre composition on the mechanical properties of sheets made of modified fibres

Figure 7 shows that the tensile strength and Young's modulus increased after periodate oxidation, and that the effect was significantly different depending on the type of fibre used. The effects can be explained by the formation of covalent intra- and inter-fibre crosslinks between the aldehydes formed and neighbouring primary alcohols (Zeronian et al. 1964; Weatherwax and Caulfield 1978; Larsson et al. 2008, 2013). As the oxidation time increases, and consequently the degree of oxidation increases, more carbonyl groups are available to form covalent bonds, resulting in even stronger and stiffer sheets. The effect of the formation of intra-fibre bonds was also studied by measuring the mechanical properties of individual fibres (Table 5). The results showed significant changes in properties after modification by periodate oxidation and borohydride reduction when bleached kraft fibres, dissolving fibres and unbleached fibres were used as a starting material whereas the effect on CTMP fibres was not as pronounced. Zhang et al. (2013) showed that the removal of lignin leads to an increase in the tensile strength of single fibres. Furthermore, lignin can also prevent the interaction between the modified cellulose and native cellulose.

Larsson et al. (2014b) described the formation of an amorphous shell of dialcohol cellulose enveloping the crystalline fibril core of cellulose. According to their study, this shell facilitates high flexibility and molecular mobility, which leads to a closer contact between the fibres and gives a highly consolidated sheet. In this work, both SEM images and zero and short-span measurements support this hypothesis. In Fig. 6, the

sheets made of bleached chemical and dissolving grade fibres show more collapsed fibres and larger dense areas in the sheet after borohydride reduction. Less densification was observed in the case of the CTMP sheets, and, as already mentioned, the presence of lignin reduced or at least inhibited the molecular mobility of the modified cellulose in these fibres. Furthermore, the estimated single-fibre strain-at-break of bleached chemical and dissolving grade fibres resulted in 34 and 23 %, respectively, after 12 h periodate oxidation, whereas it was limited to a few per cent for the CTMP.

The short-span tensile strength of the unbleached kraft fibres decreased from 95 to 37 MPa after 6 and 12 h respectively. Presumably, the degree of oxidation and, therefore, the degree of crosslinking within the individual fibres was high, making them brittle. The effect of crosslinking, and thereby molecular mobility, on individual fibre strength has also been reported by Hosseinpourpia et al. (2015) who studied the effect of two amino resins, N-methylol melamine and 1,3-dimethylol-4,5-dihydroxyethylenurea, on the zero-span strength. A decrease in zero-span tensile strength was observed when the cellulosic fibres were treated with these resins, which was explained by an increase in the stiffness and a brittleness of the fibres as a consequence of embedding the fibres in a rigid matrix and by crosslinking. Crosslinks prevent slippage between fibrils and thereby reduce the flexibility of single microfibrils which is necessary to effectively distribute the applied stress (Zeronian et al. 1989).

Traditionally, unbleached kraft fibres are used to produce, for example, cardboard and corrugated boxes. In general, boxes are piled on top of each other and stored for long time, and a high SCT has been shown to improve the creep properties of these papers. The compression strength of unbleached kraft fibres showed a large improvement after the chemical modification. The results show that after 6 h of oxidation the compression strength index was improved from 27 to 46 kNm/kg. Interestingly, no further significant change was achieved by extended oxidation, or by reduction to dialcohol cellulose. This improvement could possibly be explained by the formation of inter- and intra-fibre crosslinks, presumably the covalent bonds or high consolidation for the oxidised and reduced fibres could prevent delamination of the fibre wall under compressive load. To put this improvement in context, Gärdlund et al. (2005)

absorbed polyelectrolyte complexes of polyallylamine hydrochloride and polyacrylic acid on unbleached kraft fibres with different yields. The best results observed in that study was an improvement in SCT index from 25 to 35 kNm/kg. Fibres with lower yields showed the greatest improvement in the compression strength, presumably due to an increase in internal bonding within the fibre wall. Moreover, high yield fibres showed an enhancement of the joint strength. No doubt this is a significant result that deserves further investigations.

## Conclusions

Four different types of wood fibres were chemically modified into partial derivatives of dialdehyde cellulose or dialcohol cellulose by periodate oxidation and subsequent borohydride reduction. The results show that bleached chemical fibres are more susceptible to this chemical modification than dissolving grade fibres, unbleached chemical fibres or CTMP fibres. Even though the periodate oxidation showed a high selectivity towards vicinal alcohols, the formation of quinone groups in the lignin was also observed. Due to the presence of these quinones, a decrease in brightness of the unbleached chemical and CTMP fibres was observed. Besides differences in reactivity, it can also be concluded that even at a similar degree of oxidation, the lignin- rich CTMP does not benefit as significantly in terms of strain-at-break after periodate oxidation and borohydride reduction. Even though no ductile materials could be developed from CTMP fibres, the mechanical strength of paper sheets made from these fibres increased as a result of both modifications. Chemically modified unbleached kraft fibres showed a great increase in the compressive strength.

**Acknowledgments** This study was supported by VINNOVA, the Swedish Governmental Agency for Innovation Systems, through BiMaC Innovation Excellence Centre. SCA R&D Centre is acknowledged for the zero- and short-span measurements. Lars Wågberg also acknowledges the financial support of the Wallenberg Wood Science Centre.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original



author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

- Adler E, Hernestam S (1955) Estimation of phenolic hydroxyl groups in Lignin. I. Periodate oxidation of guaiacol compounds. *Acta Chem Scand* 9:319–334. doi:[10.3891/acta.chem.scand.09-0319](https://doi.org/10.3891/acta.chem.scand.09-0319)
- Aimin T, Hongwei Z, Gang C et al (2005) Influence of ultrasound treatment on accessibility and regioselective oxidation reactivity of cellulose. *Ultrason Sonochem* 12:467–472. doi:[10.1016/j.ultsonch.2004.07.003](https://doi.org/10.1016/j.ultsonch.2004.07.003)
- Åkerholm M, Salmén L (2001) Interactions between wood polymers studied by dynamic FT-IR spectroscopy. *Polymer (Guildford)* 42:963–969. doi:[10.1016/S0032-3861\(00\)00434-1](https://doi.org/10.1016/S0032-3861(00)00434-1)
- Alam MN, Antal M, Tejado A, van de Ven TGM (2012) Salt-induced acceleration of chemical reactions in cellulose nanopores. *Cellulose* 19:517–522. doi:[10.1007/s10570-011-9649-1](https://doi.org/10.1007/s10570-011-9649-1)
- Argyropoulos DS, Heitner C, Schmidt JA (1995) Observation of quinonoid groups during the light-induced yellowing of softwood mechanical pulp. *Res Chem Intermed* 21:263–274. doi:[10.1007/BF03052257](https://doi.org/10.1007/BF03052257)
- Batchelor WJ, Westerlind BS (2003) Measurement of short span stress–strain curves of paper. *Nord Pulp Pap Res J* 18:44–50. doi:[10.3183/NPPRJ-2003-18-01-p044-050](https://doi.org/10.3183/NPPRJ-2003-18-01-p044-050)
- Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. *Prog Polym Sci* 24:221–274. doi:[10.1016/S0079-6700\(98\)00018-5](https://doi.org/10.1016/S0079-6700(98)00018-5)
- Chaikin SW, Brown WG (1949) Reduction of aldehydes, ketones and acid chlorides by sodium borohydride. *J Am Chem Soc* 71:122–125. doi:[10.1021/ja01169a033](https://doi.org/10.1021/ja01169a033)
- Chavan VB, Sarwade BD, Varma AJ (2002) Morphology of cellulose and oxidised cellulose in powder form. *Carbohydr Polym* 50:41–45. doi:[10.1016/S0144-8617\(01\)00367-8](https://doi.org/10.1016/S0144-8617(01)00367-8)
- Christov LP, Prior BA (1993) Xylan removal from dissolving pulp using enzymes of *Aureobasidium pullulans*. *Biotechnol Lett* 15:1269–1274
- Crescenzi V, Dentini M, Meoli C et al (1984) Dicarboxyamyllose and dicarboxycellulose, stereoregular polyelectrolytes: binding of calcium and magnesium ions. *Int J Biol Macromol* 6:142–144. doi:[10.1016/0141-8130\(84\)90055-2](https://doi.org/10.1016/0141-8130(84)90055-2)
- Duchesne I, Hult EL, Molin U et al (2001) The influence of hemicellulose on fibril aggregation of kraft pulp fibres as revealed by FE-SEM and CP/MAS <sup>13</sup>C-NMR. *Cellulose* 8:103–111. doi:[10.1023/A:1016645809958](https://doi.org/10.1023/A:1016645809958)
- French AD, Santiago Cintrón M (2013) Cellulose polymorphy, crystallite size, and the Segal crystallinity index. *Cellulose* 20:583–588. doi:[10.1007/s10570-012-9833-y](https://doi.org/10.1007/s10570-012-9833-y)
- Gärdlund L, Forsström J, Andreasson B, Wågberg L (2005) Influence of polyelectrolyte complexes on the strength properties of papers from unbleached kraft pulps with different yields. *Nord Pulp Pap Res J* 20:36–42
- Gimåker M, Olsson A-M, Salmén L, Wågberg L (2009) On the mechanisms of mechano-sorptive creep reduction by chemical cross-linking. In: *Advances in pulp and paper research*, 14th fundamental research symposium, Oxford, UK, pp 1001–1017
- Gosselink RJA, van Dam JEG, de Jong E et al (2011) Effect of periodate on lignin for wood adhesive application. *Holzforchung* 65:155–162. doi:[10.1515/HF.2011.025](https://doi.org/10.1515/HF.2011.025)
- Guigo N, Mazeau K, Putaux J-L, Heux L (2014) Surface modification of cellulose microfibrils by periodate oxidation and subsequent reductive amination with benzylamine: a topochemical study. *Cellulose* 21:4119–4133. doi:[10.1007/s10570-014-0459-0](https://doi.org/10.1007/s10570-014-0459-0)
- Hosseinpourpia R, Adamopoulos S, Mai C (2015) Tensile strength of handsheets from recovered fibers treated with *N*-methylol melamine and 1,3-dimethylol-4,5-dihydroxyethylurea. *J Appl Polym Sci* 132:41280. doi:[10.1002/app.41290](https://doi.org/10.1002/app.41290)
- Jackson EL, Hudson CS (1937) Application of the cleavage type of oxidation by periodic acid to starch and cellulose. *J Am Chem Soc* 59:2049–2050
- Kalia S, Dufresne A, Cherian BM et al (2011) Cellulose-based bio- and nanocomposites: a review. *Int J Polym Sci*. doi:[10.1155/2011/837875](https://doi.org/10.1155/2011/837875)
- Kim UJ, Kuga S, Wada M et al (2000) Periodate oxidation of crystalline cellulose. *Biomacromolecules* 1:488–492. doi:[10.1021/bm0000337](https://doi.org/10.1021/bm0000337)
- Klemm D, Kramer F, Moritz S et al (2011) Nanocelluloses: a new family of nature-based materials. *Angew Chem Int Ed* 50:5438–5466. doi:[10.1002/anie.201001273](https://doi.org/10.1002/anie.201001273)
- Koprivica S, Siller M, Hosoya T et al (2016) Regeneration of aqueous periodate solutions by ozone treatment: a sustainable approach for dialdehyde cellulose production. *ChemSusChem* 9:825–833. doi:[10.1002/cssc.201501639](https://doi.org/10.1002/cssc.201501639)
- Lai Y-Z, Guo X-P, Situ W (1990) Estimation of phenolic hydroxyl groups in wood by a periodate oxidation method. *J Wood Chem Technol* 10:365–377. doi:[10.1080/02773819008050245](https://doi.org/10.1080/02773819008050245)
- Langkilde FW, Svantesson A (1995) Identification of celluloses with Fourier-transform (FT) mid-infrared, FT-Raman and near-infrared spectrometry. *J Pharm Biomed Anal* 13:409–414. doi:[10.1016/0731-7085\(95\)01298-Y](https://doi.org/10.1016/0731-7085(95)01298-Y)
- Larsson PA, Wågberg L (2016) Towards natural-fibre-based thermoplastic films produced by conventional papermaking. *Green Chem* 18:3324–3333. doi:[10.1039/C5GC03068D](https://doi.org/10.1039/C5GC03068D)
- Larsson PA, Gimåker M, Wågberg L (2008) The influence of periodate oxidation on the moisture sorptivity and dimensional stability of paper. *Cellulose* 15:837–847. doi:[10.1007/s10570-008-9243-3](https://doi.org/10.1007/s10570-008-9243-3)
- Larsson PA, Kochumalayil JJ, Wågberg L (2013) Oxygen and water vapour barrier films with low moisture sensitivity fabricated from self-cross-linking fibrillated cellulose. In: *the pulp and paper research fundamental research society, 15th fundamental research symposium, Lancashire, UK*, pp 851–866
- Larsson PA, Berglund LA, Wågberg L (2014a) Ductile all-cellulose nanocomposite films fabricated from core–shell structured cellulose nanofibrils. *Biomacromolecules* 15:2218–2223. doi:[10.1021/bm500360c](https://doi.org/10.1021/bm500360c)
- Larsson PA, Berglund LA, Wågberg L (2014b) Highly ductile fibres and sheets by core–shell structuring of the cellulose nanofibrils. *Cellulose* 21:323–333. doi:[10.1007/s10570-013-0099-9](https://doi.org/10.1007/s10570-013-0099-9)

- Liimatainen H, Sirviö J, Sundman O et al (2012) Use of nanoparticulate and soluble anionic celluloses in coagulation-flocculation treatment of kaolin suspension. *Water Res* 46:2159–2166. doi:[10.1016/j.watres.2012.01.035](https://doi.org/10.1016/j.watres.2012.01.035)
- Liimatainen H, Sirviö J, Pajari H et al (2013) Regeneration and recycling of aqueous periodate solution in dialdehyde cellulose production. *J Wood Chem Technol* 33:258–266. doi:[10.1080/02773813.2013.783076](https://doi.org/10.1080/02773813.2013.783076)
- Lister MW, Rosenblum P (1961) The oxidation of nitrite and iodate ions by hypochlorite ions. *Can J Chem* 39:1645–1651. doi:[10.1139/v61-211](https://doi.org/10.1139/v61-211)
- Maekawa E, Koshijima T (1984) Properties of 2,3-dicarboxy cellulose combined with various metallic ions. *J Appl Polym Sci* 29:2289–2297. doi:[10.1002/app.1984.070290705](https://doi.org/10.1002/app.1984.070290705)
- Maekawa E, Koshijima T (1990) Preparation and characterization of hydroxamic acid derivative and its metal complexes derived from cellulose. *J Appl Polym Sci* 40:1601–1613. doi:[10.1002/app.1990.070400916](https://doi.org/10.1002/app.1990.070400916)
- Maekawa E, Koshijima T (1991) Preparation and structural consideration of nitrogen-containing derivatives obtained from dialdehyde celluloses. *J Appl Polym Sci* 42:169–178. doi:[10.1002/app.1991.070420120](https://doi.org/10.1002/app.1991.070420120)
- Marton J, Adler E (1961) Carbonyl groups in lignin III. Mild catalytic hydrogenation of Björkman Lignin. *Acta Chem Scand* 15:370–383
- Mehlretter CL (1955) Electrochemical production of periodate oxypolysaccharides US 2713553A
- Okita Y, Saito T, Isogai A (2009) TEMPO-mediated oxidation of softwood thermomechanical pulp. *Holzforschung* 63:529–535. doi:[10.1515/HF.2009.096](https://doi.org/10.1515/HF.2009.096)
- Palme A, Theliander H, Brelid H (2016) Acid hydrolysis of cellulosic fibres: comparison of bleached kraft pulp, dissolving pulps and cotton textile cellulose. *Carbohydr Polym* 136:1281–1287. doi:[10.1016/j.carbpol.2015.10.015](https://doi.org/10.1016/j.carbpol.2015.10.015)
- Patterson AL (1939) The scherrer formula for X-ray particle size determination. *Phys Rev* 56:978–982. doi:[10.1103/PhysRev.56.978](https://doi.org/10.1103/PhysRev.56.978)
- Qiu X, Hu S (2013) ‘Smart’ materials based on cellulose: a review of the preparations, properties, and applications. *Materials (Basel)* 6:738–781. doi:[10.3390/ma6030738](https://doi.org/10.3390/ma6030738)
- Segal L, Creely JJ, Martin AE, Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Text Res J* 29:786–794. doi:[10.1177/004051755902901003](https://doi.org/10.1177/004051755902901003)
- Sehaqui H, Allais M, Zhou Q, Berglund LA (2011) Wood cellulose biocomposites with fibrous structures at micro- and nanoscale. *Compos Sci Technol* 71:382–387. doi:[10.1016/j.compscitech.2010.12.007](https://doi.org/10.1016/j.compscitech.2010.12.007)
- Seth RS (1990) Fibre quality factors in papermaking-I. The importance of fibre length and strength. *Mater Res Soc Symp Proc Mater Res Soc* 197:125–141
- Sirviö J, Honka A, Liimatainen H et al (2011a) Synthesis of highly cationic water-soluble cellulose derivative and its potential as novel biopolymeric flocculation agent. *Carbohydr Polym* 86:266–270. doi:[10.1016/j.carbpol.2011.04.046](https://doi.org/10.1016/j.carbpol.2011.04.046)
- Sirviö J, Hyvakkö U, Liimatainen H et al (2011b) Periodate oxidation of cellulose at elevated temperatures using metal salts as cellulose activators. *Carbohydr Polym* 83:1293–1297. doi:[10.1016/j.carbpol.2010.09.036](https://doi.org/10.1016/j.carbpol.2010.09.036)
- Sirviö J, Liimatainen H, Niinimäki J, Hormi O (2011c) Dialdehyde cellulose microfibrils generated from wood pulp by milling-induced periodate oxidation. *Carbohydr Polym* 86:260–265. doi:[10.1016/j.carbpol.2011.04.054](https://doi.org/10.1016/j.carbpol.2011.04.054)
- Veelaert S, de Wit D, Tournois H (1994) An improved kinetic model for the periodate oxidation of starch. *Polymer (Guildford)* 35:5091–5097. doi:[10.1016/0032-3861\(94\)90670-X](https://doi.org/10.1016/0032-3861(94)90670-X)
- Vishtal A, Retulainen E (2014) Boosting the extensibility potential of fibre networks: a review. *BioResources* 9:7933–7983
- Vuoti S, Laatikainen E, Heikkinen H et al (2013) Chemical modification of cellulosic fibers for better convertibility in packaging applications. *Carbohydr Polym* 96:549–559. doi:[10.1016/j.carbpol.2012.07.053](https://doi.org/10.1016/j.carbpol.2012.07.053)
- Wågberg L, Annergren G (1997) Physicochemical characterization of papermaking fibres. In: *The fundamentals of papermaking materials—11th fundamental research symposium*, vol 1, Fundamental Research Committee and Pira International, Leatherhead, pp 1–82
- Wågberg L, Hägglund R (2001) Kinetics of polyelectrolyte adsorption on cellulosic fibers. *Langmuir* 17:1096–1103. doi:[10.1021/la000629f](https://doi.org/10.1021/la000629f)
- Weatherwax RC, Caulfield DF (1978) The pore structure of papers wet stiffened by formaldehyde crosslinking. II. Results from nitrogen sorption. *J Colloid Interface Sci* 67:506–515. doi:[10.1016/0021-9797\(78\)90241-2](https://doi.org/10.1016/0021-9797(78)90241-2)
- Zeronian SH, Hudson FL, Peters RH (1964) The mechanical properties of paper made from periodate oxycellulose pulp and from the same pulp after reduction with borohydride. *Tappi* 47:557–564
- Zeronian SH, Bertoniere NR, Alger KW et al (1989) Effect of dimethyloldihydroxyethyleneurea on the properties of cellulosic fibers. *Text Res J* 59:484–492
- Zhang J, Jiang N, Dang Z et al (2008) Oxidation and sulfonation of cellulose. *Cellulose* 15:489–496. doi:[10.1007/s10570-007-9193-1](https://doi.org/10.1007/s10570-007-9193-1)
- Zhang S, Fei B, Yu Y et al (2013) Effect of the amount of lignin on tensile properties of single wood fibers. *For Sci Pract* 15:56–60. doi:[10.1007/s11632-013-0106-0](https://doi.org/10.1007/s11632-013-0106-0)
- Zhao H, Heindel ND (1991) Determination of degree of substitution of formyl groups in polyaldehyde dextran by the hydroxylamine hydrochloride method. *Pharm Res* 8:400–402