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Bromide-free oxidizing system for carboxylic moiety formation in cellulose chain

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ABSTRACT

NHPI (*N*-hydroxyphthalimide) was used to mediate the oxidation of cellulose fibers in the absence of sodium bromide, as traditionally was used in this kind of transformations, solely using sodium hypochlorite (NaOCl) as the primary oxidant. Avoiding the use of NaBr is highly desired from both environmental and corrosion concerns. The non-persistent PINO (phthalimide-*N*-oxy) radical, the key species in the oxidation reaction, has been *in situ* generated from NHPI and copper (II) chloride. The reaction was performed at room temperature at pH = 10.5. The carboxylic moiety formation was evidenced by FTIR and X-ray photoelectronic spectroscopy (XPS) and the content of the negatively charged groups determined by potentiometric titration. The changes appeared in crystallinity were evidenced by X-ray diffraction technique.

1. Introduction

de Nooy, Besemer, and van Bekkum (1995) reported in 1995 for the first time, the oxidation of water-soluble polysaccharides using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), sodium bromide and sodium hypochloride at pH between 9 and 11. Since then, an impressive number of scientific reports on using this oxidizing system have been published, covering a wide range of polysaccharides, such as cellulose (Kitaoka & Isogai, 2000; Perez, Montanari, & Vignon, 2003; Saito & Isogai, 2004; Shibata, Yanagisawa, Saito, & Isogai, 2006), starch (de Nooy, Besemer, & van Bekkum, 1994), pullulan (de Nooy, Besemer, van Bekkum, van Dijk, & Smith, 1996), chitosan (Bordenave, Grelier, & Coma, 2008), chitin (Muzzarelli, Muzzarelli, Cosani, & Terbojevich, 1999), curdlan (Delattre et al., 2009), galactomannan (Sierakowski, Milas, Desbrières, & Rinaudo, 2000), and scleroglucan (de Nooy, Rori, Masci, Dentini, & Crescenzi, 2000a, 2000b). All these polysaccharides have been oxidized by using sodium hypochlorite/sodium bromide tandem as the regenerating system of nitrosonium ion (TEMPO$^+$) which is the actual oxidizing species (Fig. 1).

Generally, quite impressive amount (between 10 and 30%) of sodium bromide is required in order to restart the catalytic cycle. Clearly, from both, industrial and environmental points of view, a process without sodium bromide would be a better alternative to those existing today. Few reports on bromide-free oxidizing systems are published, and refers to carbohydrates like starch (Bragd, Besemer, & van Bekkum, 2000), methyl α-D-glucoside and sucrose (Brochette-Lemoine, Joannard, Descotes, Bouchu, & Queneau, 1999).

Taking into account that *N*-hydroxyphthalimide (NHPI) has become in the last two decades, one of the most promising catalyst for the oxidation of wide range of organic substrates (Biliuta, Fras, Harabagiu, & Coseri, 2011; Biliuta, Fras, Strnad, Harabagiu, & Coseri, 2010; Coseri, 2007, 2008, 2009a, 2009b; Coseri, Mendenhall, & Ingold, 2005) we were interested to test NHPI's impressive catalytic activity on cellulose oxidation in the absence of NaBr as traditionally this reaction was performed. We had previously reported its efficiency as an efficient mediator for cellulose oxidation in a "traditional" protocol, in the presence of NaBr (Coseri et al., 2009). For this purpose we tried to mimic natural oxidative processes in which enzymes are very effective. Copper enzymes are extensively used as "green methods" for converting OH groups to carbonyl compounds (Sheldon, Arends, & Dijksman, 2000). For example, galactose oxidase, a mononuclear copper enzyme, oxidize alcohols to aldehydes through an Cu(II)-phenoxyl radical species (Whittaker, Ekberg, & Peterson, 2000). Another copper-dependant oxydase, laccase, was shown to catalyze the aerobic oxidation of alcohols in combination with TEMPO (2,2,6,6-tetramethylpiperidinyloxy) (Fabbrini, Galli, & Gentili, 2002).

2. Experimental

2.1. Materials

The regenerated cellulose fibers, viscose type (CV) (fineness 1.9 dtex, average length 39 mm, fiber diameter 15 μm), were produced by Lenzing AG Lenzing, Austria.

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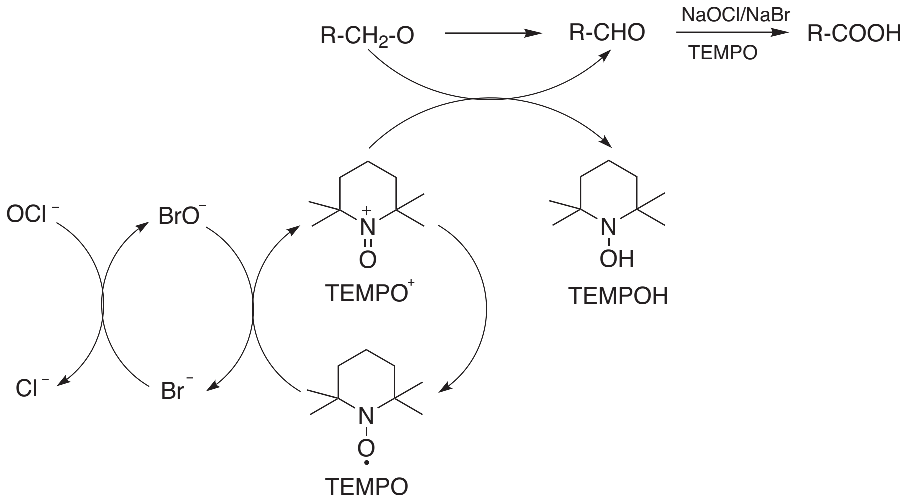

Fig. 1. TEMPO-mediated cycle for the oxidation of the primary OH groups in polysaccharides in the presence of NaOCl/NaBr tandem.

NHPI, copper(II) chloride, sodium hypochlorite (4% weight) were purchased from Aldrich and used without further purification.

2.2. Phthalimide N-oxyl (PINO)-mediated oxidation of cellulose fibers

The oxidation of viscose fibers to yield oxidized viscose (OCV) has been carried under following condition: 5 g of fibers were placed in a 1 L two-necked flask, containing 300 mL deionized water. NHPI and $CuCl_2$ (0.1 mmol of each/g cellulose) were then added. The pH was adjusted to 10.5 by addition of 0.4 mol L^{-1} NaOH solution, and then the sodium hypochlorite solution (5 mmol/g cellulose fibers) was added, the resulted suspension being kept at room temperature under stirring for 2 and 4 h, respectively. The reaction was quenched by adding 10 mL ethanol, and the oxidized fibers were filtered off. The recovered fibers were washed with acetone and deionized water.

2.3. Potentiometric titration

The oxidized viscose fibers were added into aqueous solution containing 0.1 M potassium chloride and 0.1 M hydrochloric acid. The pH potentiometric titration of the fiber suspension was carried out with a Mettler Toledo T70 titrator, using a 10 mL buret in an inert atmosphere (N_2 bubbling). The solution was titrated from the initial pH = 2.5 to the preset pH = 11, with 0.1 M KOH. The potential of the solution was measured in pH, using a Mettler Toledo DG-117 pH glass electrode. The same solution was also titrated without the fibers sample as a blank acid – base titration for data evaluation purpose. The amount of negatively charged groups was calculated, by subtracting the blank titration from the sample titration. All presented values are the mean values of 3 parallel measurements, the standard deviation of measurements being within 4%.

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

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

2.5. X-ray photoelectron spectroscopy (XPS)

The compositional analysis of the studied samples was carried out by X-ray photoelectron spectroscopy (XPS) using a PHI-5000 VersaProbe photoelectron spectrometer (Φ ULVAC-PHI, Inc.) with a hemispherical energy analyzer (0.85 eV binding energy resolution for organic materials). The shape of the samples was "tablet" of dried fibers. A monochromatic Al Kα X-ray radiation ($h\nu$ = 1486.7 eV) was used as excitation source. The standard take-off angle used for analysis was 45°, producing a maximum analysis depth in the range of 3–5 nm. Spectra were recorded from at least three different locations on each sample, with a 1 mm × 1 mm area of analysis. Low-resolution survey spectra were recorded in 0.5 eV steps with 117.4 eV analyzer pass energy. In addition, high-resolution carbon (1s) spectra were recorded in 0.1 eV steps with 58.7 eV analyzer pass energy. The XPS data were acquired using the PHI SUMMIT XPS for VersaProbe software.

2.6. Crystallinity determination by X-ray diffraction (XRD)

Each sample was filled into the sample holder. The sample holder was loaded onto the X-ray diffractor (D8 Advance Bruker) to analyze from 5° to 35° 2θ with data acquisition taken at 0.02° s^{-1} by the reflection method. The operated voltage was 30 kV and the current was 36 mA. The crystallinity was calculated according with the formula (1):

$$\text{relative crystallinity}\,(\%) = \frac{\text{icrystalline} - \text{iamorphous}}{\text{icrystalline}} \times 100 \qquad (1)$$

where $I_{\text{crystalline}}$ was identified with the intensity at 21.5°, and $I_{\text{amorphous}}$ was the intensity at 12.6°.

3. Results and discussion

3.1. PINO-mediated oxidation of cellulose fibers

Copper chloride–TEMPO system was first reported by Semmelhack (Semmelhack, Schmid, Cortes, & Chou, 1984), the actual reactive species being Cu(II) which oxidize TEMPO to the oxoammonium cation. In this work, Cu(II) is used to generate the phthalimide N-oxyl (PINO) radical through an oxidation reaction of MHPI. The formed PINO is further oxidize in the presence of Cu(II) ions to generate the oxoammonium $PINO^+$, the actual oxidizing species (Fig. 2). Moreover, the reduced Cu(I) formation allows further reoxidation of NHPI, thus minimizing the catalyst loading

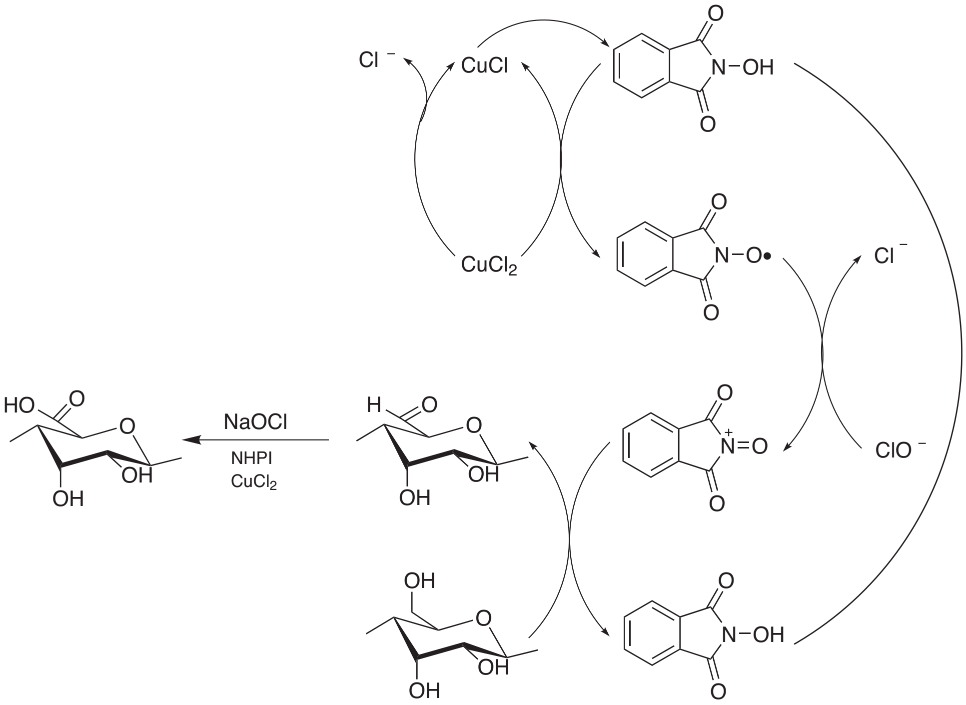

Fig. 2. NHPI–$CuCl_2$–NaOCl oxidation cycle of viscose fibers.

Table 1
Viscose fibers oxidation in the presence of NHPI and CuCl2, at room temperature.

Sample	Reaction time (h)	Amount of negatively charged groups (mmol kg^{-1})
CV	–	6
OCV (2 h)	2	162
OCV (4 h)	4	218

(Nechab, Einhorn, & Einhorn, 2004). The oxoammonium ions will convert the primary OH groups from cellulose to aldehyde groups, the catalytic cycle continuing to form carboxylic groups. Two samples of CV were oxidized using a different reaction time, *i.e.* 2 and 4 h, respectively. The amount of negatively charged groups as determined by potentiometric titration has been presented in Table 1.

From Table 1, it can be observed that the amount of carboxylic groups formed during the oxidation increase from 6 mmol kg^{-1} in the original sample, to 162 mmol kg^{-1} when the oxidation was performed for 2 h (sample OCV 2 h) and reach the maximum level of the amount of formed COOH groups within 4 h (sample OCV 4 h).

3.2. FTIR analyses

ATR spectra of the CV and OCV were recorded. As we have previously stated (Biliuta et al., 2011, 2010; Coseri, 2009b), the only difference between the starting material and oxidized fibers in the FT-IR spectra can be observed in the 1600–1800 cm^{-1} range. The apparition of the 1732 cm^{-1} band, attributed to carboxylate group in their acidic form is a clear indication of oxidation reaction (Fig. 3).

3.3. XPS analyses

XPS technique can detect only carbon and oxygen atoms in cellulose fibers, hydrogen atoms being undetectable. A low-resolution XPS scan is run to determine the percentages of the C and O atoms present at the viscose fiber surface before and after oxidation. The oxygen-to-carbon atomic ratio was calculated using area sensitivity factors, as an initial indication of surface oxidation. Accordingly with the molecular formula of cellulose – $(C_6H_{10}O_5)_n$ – the O/C atomic ratio value expected for pure cellulose is 5/6 = 0.83. However, for the original (untreated) viscose sample (CV) the O/C atomic ratio has been found to be 0.6. This lower number than theoretically value is not surprisingly, since it is well known that cellulose fibers are naturally covered with different non-cellulosic materials: waxes, proteins and pectin (Topalovic et al., 2007). Other reported "impurities" consists in lignin and fatty acids (Sahin, 2007). Therefore the cellulose backbone is "hided" under these laminar layers, and the amount of the carbon atoms as detected by XPS is always higher than theoretically value, due to these carbon reach contaminants. Nevertheless, the relative comparison between unoxidized and oxidized samples, performed by XPS, remain a powerful technique, who brings valuable information concerning the structural changes occurred after oxidation (Fras et al., 2005). It can be seen from Table 2, that the O/C atomic ratio

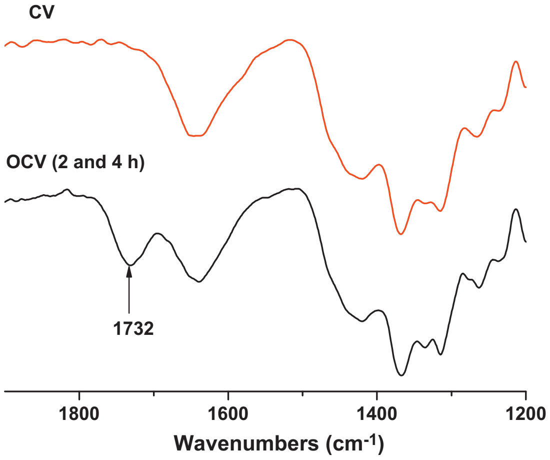

Fig. 3. FTIR spectra fragment of CV and OCV.

Table 2
XPS analysis of the original and PINO-oxidized fibers.

Sample	Oxidation time (h)	Surface composition			Binding energy (eV)			
		O	C	O/C	284.8 C1 (at.%)	286.4 C2 (at.%)	287.8 C3 (at. %)	288.9 C4 (at. %)
CV	–	37.9	63.1	0.600	24.93	52.01	20.31	2.75
OCV	2	38.7	60.5	0.639	28.40	50.14	15.22	6.24
OCV	4	39.0	60.7	0.642	27.52	49.30	15.31	7.87

increased to 0.639, sample OCV – oxidized 2 h (OCV 2 h) and 0.642 sample OCV – oxidized 4 h (OCV 4 h).

To obtain detailed information, a high-resolution scan on the C 1s region for the unoxidized and oxidized samples was conducted in order to determine the types linkage and the amounts of carbon – oxygen bonds. The C 1s XPS spectra and deconvolution peaks of CV and OCV samples are presented in Fig. 4. The C 1s peak is deconvoluted into four sub-peaks: C1, C2, C3, and C4. C1 peak is attributed to the unoxidized carbon, C—C, and has the lowest binding energy: 284.4 eV. C2 peak corresponds to carbon linked to a single oxygen, —C—O, at 286.4 eV, C3 peak is assigned to O—C—O bond or a single carbonyl oxygen —C=O, at a binding energy of 287.8 eV, and finally C4 represents carbon atoms linked to a carbonyl and a non-carbonyl oxygen, O—C=O, and has the highest binding energy: 288.9 eV (Hua, Kaliaguine, Kokta, & Adnot, 1993). Pure cellulose is a homopolysaccharide of β-D-glucopyranose units. Five carbon atoms linked to one of the oxygens and one carbon linked to two oxygen atoms are contained by each monosaccharide unit. Therefore we would expect for the CV a curve-resolved XPS C 1s signal consisting only in two peaks (C2 and C3). The supplemental apparition of the two peaks C1 and C4 may be due to a contamination of fibers and/or to a chemical change in the fibers structure (Carlsson & Strom, 1991). The oxidation reaction which leads to the formation of HO—C=O groups increased the C4 contribution in the C 1s spectrum from 2.75% in the CV to 6.24% in OCV (2 h) and 7.87% in OCV (4 h) (Table 2).

3.4. Crystallinity determination of the CV and OCV as determined by X-ray diffraction (XRD)

The comparison of the diffractograms for CV, OCV (2 h) and OCV (4 h), shows only minor differences between them (Fig. 5). The diffraction peak positions remain almost unchanged after oxidation. The measured crystallinity was 25% in CV, 26.2% in OCV (2 h)

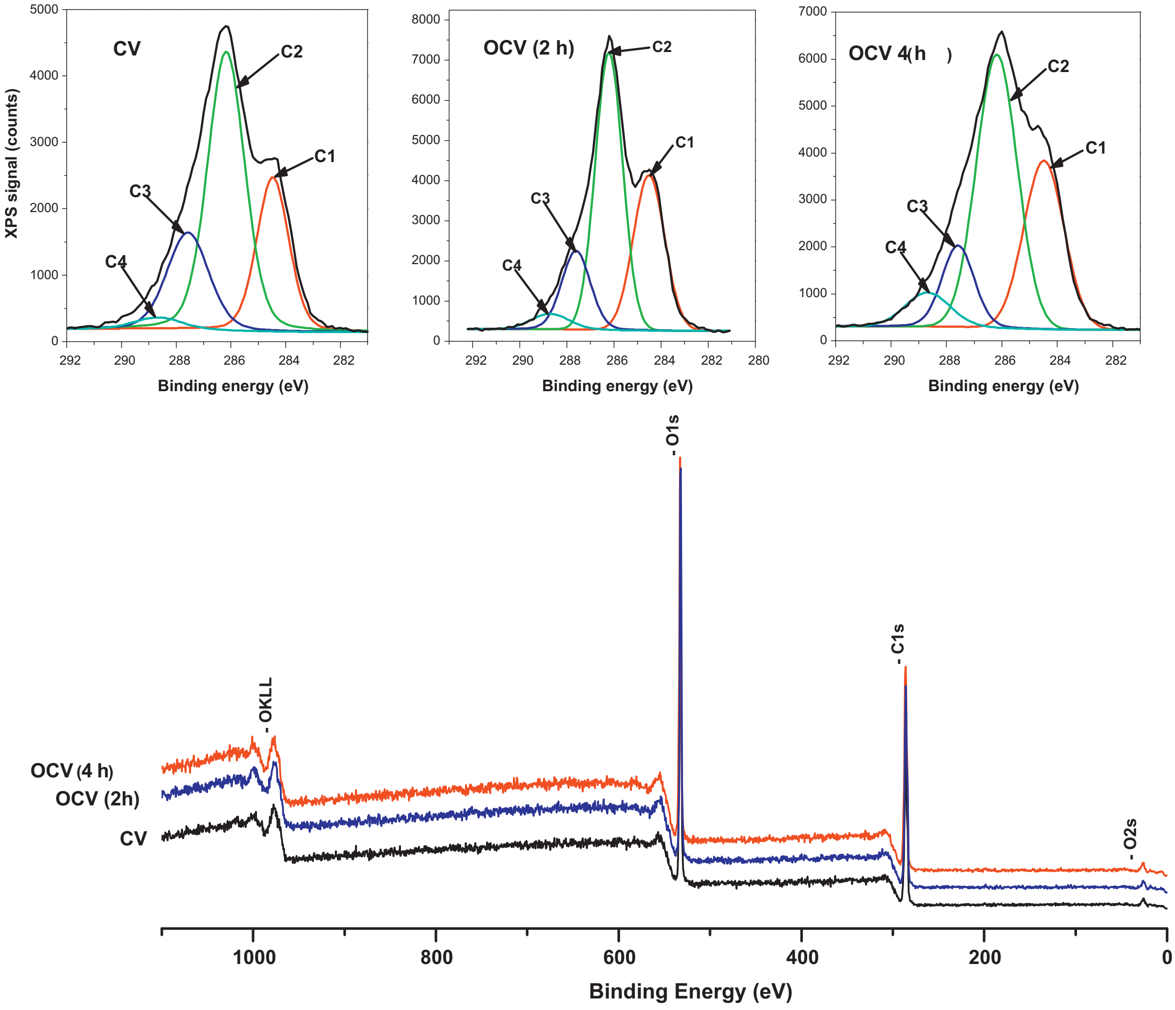

Fig. 4. XPS survey spectra and scan of C 1s region of the CV and OCV.

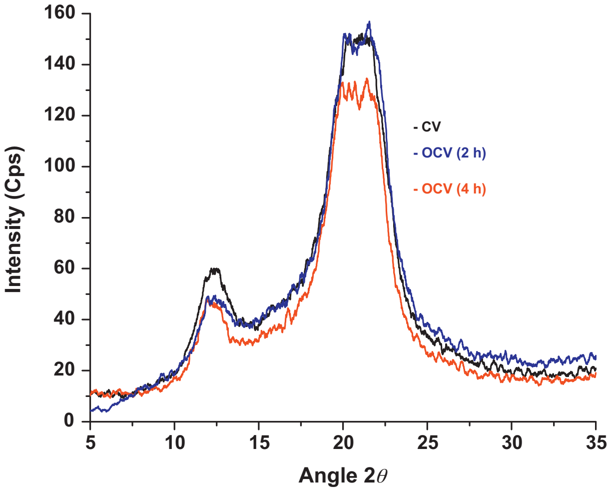

Fig. 5. X-ray diffraction patterns of CV and OCV.

and 28.7% OCV (4 h). The highest crystallinity value for OCV (4 h) sample can be explained not only due to the highest amount of carboxylic groups, but also due to the longest reaction time, that may lead to some destructive processes favored by the alkaline media, the amorphous regions being the most affected, those being liberated in the reaction solution mostly as water soluble fractions.

4. Conclusions

Viscose fibers were functionalized by newly NHPI–$CuCl_2$/sodium hypochlorite oxidizing system. The versatile functions of $CuCl_2$ allow the oxidation cycle to be promoted without the presence of any sodium bromide as was previously used in this type of reactions. The reactions took place at room temperature and pH = 10.5, the moderate conversion of primary OH groups to carboxylic ones being accomplished within 2 h.

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