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Selective oxidation of cellulose, mediated by *N*-hydroxyphthalimide, under a metal-free environment

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Three types of cellulosic samples, including microcrystalline, never-dried sulfite pulp, and Cellets, were selected to test the oxidative capacity of a new oxidation protocol involving the redoubtable *N*-hydroxyphthalimide (NHPI) catalyst. All reactions were performed under mild conditions, at room temperatures and at atmospheric pressure, in the presence of sodium hypochlorite and sodium bromide. The generation of the reactive radicalic species, *i.e.* phthalimide *N*-oxyl (PINO) from its parent hydroxylamine, NHPI, in the presence of sodium hypochlorite, has been firstly proved by using the UV-Vis technique, followed next by the reaction with each cellulose type sample for a designated period of time, varying the amount of the NaClO introduced in the reaction. The main finding of this new proposed protocol resides in the elimination of any metal cocatalyst required for the generation of the non-persistent free radical PINO, as has been previously used. The obtained amounts of the carboxylic groups after oxidation, determined using potentiometric titration, are satisfactory, whereas the degree of polymerization of the resulted products has still superior values, as compared to many other methods used today. All the oxidized samples exhibited an increased crystallinity compared to the unoxidized samples as revealed by X-ray diffraction experiments. This new approach not only avoids the introduction of an additional chemical reagent, but also provides an easy and convenient alternative to those existing today for the preparation of oxidized cellulose products having high amounts of carboxylic groups and remarkably, less depolymerized.

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Introduction

Due to the tremendous development of modern society, we observe a continuous competition between industrial companies to find, produce and introduce to market new materials, better, cheaper, healthier than those existing today. Moreover, the consciousness of the finite character of the traditional raw materials based on petroleum, combined with the high concern associated with global warming, pollution, and contamination of the environment, assiduously lead to the reconsideration of natural resources as ideal candidates to be used for our daily life products' fabrication. In this context, the most abundant natural polymer on Earth has been already implemented as a key source for a wide variety of products ranging from food, cosmetics, secured papers, medicine, pharmacy, flexible displays and many others.[1] The cellulose used in these applications significantly differs from those originating from trees or tall plants, which serve as skeleton support. Obviously, from extraction to the end-product, cellulose suffers a long chain of processes including delignification, extraction, purification, and often derivatization (functionalization). Taking advantage of the presence of the many hydroxyl functional groups in anhydroglucose functional groups, cellulose is highly susceptible to chemical conversion to value-added products, *i.e.* cellulose derivatives. The most common processes involving the chemical modification of cellulose include oxidation, esterification, etherification, amination, and radical polymerization.[1] However, the classical chemistry applied to synthetic polymers is not suitable for cellulose, since its chemical and physical particularities (biocompatibility, biodegradability, rigidity, high crystallinity, and insolubility in common organic solvents) are a consequence of its specific way of production, namely biosynthesis. As for the selective oxidation of cellulose, a lot of research has been dedicated to design more economical and reliable processes for the selective conversion of the three hydroxyl groups in the cellulose anhydroglucose unit. Especially the primary OH group in the cellulose unit represents a focus site regarding

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chemical oxidation research, due to its higher reactivity over the two secondary OH groups and the importance of the resulting carboxyl derivative. Carboxy celluloses, obtained by the oxidation of cellulose, are amongst the most studied derivatives of cellulose, due to their tremendous applications including pharmaceutics, drug and gene delivery, food industry, cosmetic products, polymer composites, wound dressing gauzes, as well as the adsorption of a wide range of chemicals, such as dyes, metals, proteins, and various polymers.[2–4] A stable radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) has been introduced to mediate the selective oxidation of the primary OH groups in cellulose, in the presence of sodium hypochlorite and sodium bromide, at room temperature and pH around 10.[2–5] A TEMPO-mediated oxidation protocol, even if it is claimed to be highly selective, suffers yet from at least two major drawbacks: firstly, it causes a major depolymerization of the cellulose backbone after oxidation, leading to oxidized products with poor mechanical properties, and secondly, it is a toxic reagent to aquatic life, and therefore cannot be discarded into the wastewater network, being continuously accumulated in the environment, raising concerns regarding its recycling, thus increasing the overall costs of the process. Alternatives to this protocol have been continuously searched for, and *N*-hydroxyphthalimide (NHPI) is considered as one of the best modern catalysts, having high oxidation performance, when the active species, the phthalimide-*N*-oxyl radical (PINO) is formed through the homolytic scission of the >N–O–H bond.[5–12] Generation of the PINO radical is possible only if a suitable cocatalyst, able to abstract a proton from the O–H bond in NHPI, is present. Fig. 1 schematically shows the multitude of possibilities for PINO radical generation, which include the presence of metal salts, generally transition elements such as cobalt, manganese, lead, copper, iron, nickel, and even their mixtures.[8] Another approach consists of the use of non-metal cocatalysts, which mainly imply the presence of peroxides, nitrogen dioxide or nitric acid, aldehydes, anthraquinone, hexafluoroacetone, and even enzymes of the lacasse family.[8]

The use of UV-vis irradiation of NHPI solutions in acetonitrile, at wavelength λ = 365 nm, to obtain the PINO radical was also reported.[8] Several studies implying the use of NHPI for cellulose selective oxidation have already been published, and the presence of sodium hypochlorite and sodium bromide as actual oxidants is decisive.[13–19] Another study in this field avoided the use of harmful sodium bromide owing to the presence of copper(II) salts, able to perform the oxidation of cellulose in the presence of NHPI.[20] Certainly, the use of molecular oxygen as the ultimate oxidizing agent is highly desired, due to its low cost, non-toxicity and avoiding many social and environmental issues raised by the use of common polluting and toxic oxidizing agents. In this respect, we have recently developed an oxidizing protocol for cellulose oxidation using NHPI and molecular oxygen.[21] Unfortunately, the amount of the negatively charged groups was quite modest and further research in this area is needed. The utilization of an additional reagent when using NHPI as the oxidizing agent, required for its conversion into the active radical species, PINO, seems to be a drawback, increasing the cost of the overall oxidation process, and imposing a supplemental step necessary for product separation and purification. In this paper, we propose a new, innovative protocol for cellulose oxidation using NHPI in a metal-free system. The generation of the active radical species PINO becomes possible owing to the presence of sodium hypochlorite and sodium bromide, as actual oxidants, reagents also employed in the case of the well-established TEMPO-mediated protocol. The hypohalides present in the system take over the role of the metal cocatalyst, oxidizing in the first stage of the process the NHPI to its free radical counter partner, PINO, able to initiate the catalytic cycle of oxidation.

Experimental

Materials

Avicel® PH 101 microcrystalline cellulose (Mc) purified, partially depolymerized α-cellulose, with an average degree of polymerization (DP) of 140, was purchased from Sigma-Aldrich. The second used cellulose sample, *i.e.* Cellets 350 (C) with a particle size distribution between 350 and 500 μm, and a degree of polymerization of 350 has been received as a free sample from http://www.cellets.com. Never-dried softwood (spruce) bleached sulfite pulp (SBS) with a degree of polymerization of 2800 having a moisture content of 88% was donated by Lenzing AG. The pulp (50 g) was soaked before use in diluted hydrochloric acid (4500 mL) at room temperature, and pH ~ 2 and for 0.5 h, and then washed repeatedly with water by filtration. 2,2,6,6-Tetramethyl-1-piperidinyloxy radical (TEMPO), NHPI, sodium bromide, 9% (wt) sodium hypochlorite and other chemicals and solvents were of pure grade (Sigma Aldrich), and used without further purification.

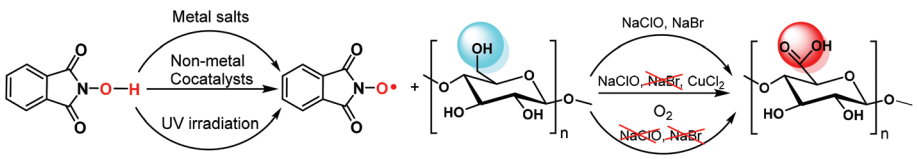

Fig. 1 Synthetic representation of the PINO radical generation from its hydroxyl precursor (NHPI) in the presence of (i) metal salts, (ii) non-metal catalysts, and (iii) UV irradiation, followed by its powerful catalytic activity for cellulose oxidation under various environments.

Analytical techniques

Determination of the carboxylic group contents using potentiometric titration. The content of the carboxylic groups in the oxidized cellulose samples was determined using the potentiometric titration method as detailed in our previous reports.[13–15] All given values are the mean values of 3 parallel measurements, the standard deviation of measurements being within 4%.

Degree of polymerization (DP). The degree of polymerization (DP) was determined viscometrically after dissolving the cellulose samples in cuoxam, the method being described in a previous study.[21] All cellulose solutions (oxidized and unoxidized) in the viscometer were employed for one measurement only to reduce the risk of possible degradation of the sample. The viscosity (η) was calculated using the efflux times of the cellulose solution (t), the blank cuoxam solution (t_0), and from the concentration of cellulose in solution (c). DP is calculated from the specific viscosity:

$$\eta_{\text{spec}} = \frac{\eta - \eta_0}{\eta_0} \quad (1)$$

according to:

$$\text{DP} = \frac{2000 \cdot \eta_{\text{spec}}}{c \cdot (1 + 0.29 \cdot \eta_{\text{spec}})} \quad (2)$$

where c is the cellulose sample concentration in g L^{-1}.

Weight loss of the oxidized samples. The weight loss (%) of the oxidized samples was determined using eqn (3):

$$W_{\text{loss}}\,(\%) = \frac{W_{\text{O}} - W_{\text{OX}}}{W_{\text{O}}} \times 100 \quad (3)$$

where W_{O} and W_{OX} represent the weight of the initial (unoxidized) and oxidized sample, respectively. The weight measurements were repeated 10 times for each oxidized sample. The presented results are the mean values of the weight loss percentage.

UV-Vis measurements. The UV-Vis absorption spectra of NHPI solutions in acetonitrile or water–acetonitrile 1 : 1 (vol) mixture were recorded using a SPECORD 200 Analytik Jena spectrometer.

FT-IR measurements. An amount of about 1 mg of dry cellulose sample (or oxidized sample) was pressed into a pellet containing 200 mg of potassium bromide. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 instrument, with the accumulation of 32 scans and a resolution of 2 cm^{-1}, in the 4000 to 500 cm^{-1} range.

Environmental scanning electron microscopy (ESEM) and weight loss experiments. The ESEM microphotographs were acquired on samples fixed by means of colloidal silver on copper supports. The samples were firstly covered by sputtering using a thin layer of gold (EMITECH K 550×). The as obtained coated surface was then examined using an Environmental Scanning 200 instrument, operating at 5 kV with secondary electrons in the high vacuum mode. The morphological changes that occurred in the oxidized samples, as a result of the carboxylic groups' introduction and also due to the weight loss after oxidation, were carefully monitored.

Crystallinity determination by X-ray diffraction (XRD). A D8 Advance Bruker diffractometer was used for analysing the unoxidized and oxidized samples. Analyses were performed in the 5° to 35°2θ range with data acquisition taken at 0.02° s^{-1} using the reflection method. The voltage and current parameters were set at 30 kV and 36 mA, respectively. The crystallinity of each sample was calculated using the formula (4):

$$\text{Relative crystallinity} = (I_{\text{crystalline}} - I_{\text{amorphous}}) \times 100\%/I_{\text{crystalline}} \quad (4)$$

where $I_{\text{crystalline}}$ was identified with the intensity at 22.54°, and $I_{\text{amorphous}}$ was the intensity at 14.28°.

Methods

PINO-mediated oxidation of cellulose. The three sorts of cellulose materials were subjected to PINO-mediated oxidation following a procedure briefly described as follows: cellulose (2 g, 12.3 mmol anhydroglycosyl units or AGUs) was introduced in 300 mL deionized water/acetonitrile solution (5 : 1 vol) containing NHPI (0.163 g, 1 mmol) and sodium bromide (1.65 g, 16 mmol). For the SBS sample, the amount of added water increased up to 400 mL for smooth stirring using a magnetic stirrer. The pH was adjusted to 10, and then a 9% (wt) NaClO solution (20 mmol in one series of trials or 40 mmol in another series of experiments) was added to the cellulose slurry, and kept at room temperature under vigorous stirring for fixed periods of time (5 or 24 h) carefully monitoring the pH value, maintained during the reaction at pH = 10 by using a 0.5 M NaOH solution (to compensate for the decrease of the pH due to carboxylic group formation).

Results and discussion

The simple introduction of NHPI in the reaction is not necessarily enough to promote the oxidation catalytic cycle. The key species able to start the process is represented by the PINO free radical, originating from its hydroxyl parent NHPI. Therefore, the PINO radical presence is compulsory to realize the expected oxidation process. In our approach, the introduction of sodium hypochlorite alone or in combination with sodium bromide plays a double role: (i) ensures the conversion of NHPI to PINO, similar to the systems that include metal salts, and (ii) further oxidizes the PINO radical to the nitrosonium cation, the actual oxidant of the primary OH groups in the cellulose unit. PINO radical formation from NHPI is a rather slow process in the presence of sodium hypochlorite, but becomes quite fast when sodium bromide is introduced supplementary to NaClO. The UV-Vis experiments, Fig. 2, show that the UV-Vis maximum adsorption band of NHPI from 300 nm is replaced by a new adsorption band, centered at 420 nm, when NaClO is added to NHPI, as a result of PINO radical formation. This maximum band becomes more prominent when sodium bromide is supplementarily introduced

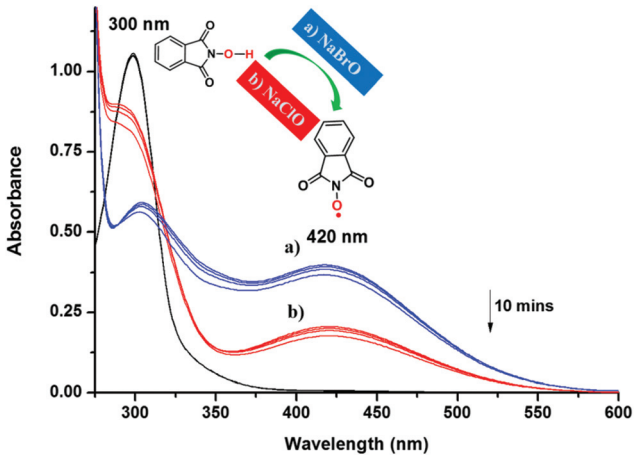

Fig. 2 UV-Vis absorption of a mixture of NHPI (0.5 mM) and NaOCl (50 mM), in the presence (50 mM) (a) or absence of NaBr (b), in acetonitrile/water 1 : 1 (vol).

into the NHPI/NaClO mixture. Indeed, the mixing of an acetonitrile solution of NHPI with an aqueous solution of NaClO/NaBr results in the appearance of a yellow color, as a result of PINO radical appearance.

PINO radical formation should be the result of a process consisting of hydrogen atom abstraction from NHPI by another species which might be already present in the system. It is known that NaClO is able to produce ClO$^{\bullet}$ radicals, able to abstract a hydrogen atom from NHPI.[22] When sodium bromide is supplementarily introduced in addition to NaClO, the first step consists of the formation of sodium hypobromide, which in turn will generate BrO$^{\bullet}$ radicals, much more reactive than the ClO$^{\bullet}$ radicals, see Fig. 3. Therefore, PINO radical formation seems to represent a much more feasible process if considering BrO$^{\bullet}$ as the main radical species responsible for hydrogen atom abstraction from NHPI. This assumption correlates quite well with the role of HBrO and HClO in cell lysis investigation,

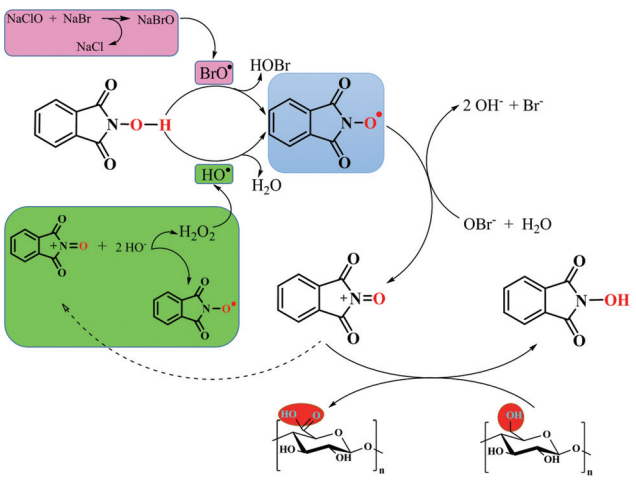

Fig. 3 Possible reaction pathways of the PINO radical formation from NHPI in the presence of free radical species, such as BrO$^{\bullet}$ or HO$^{\bullet}$.

which reveals that hypobromide radicals cause cell lysis faster than that induced by hypochlorite radicals at the same concentration.[22] Other authors found that BrO$^{\bullet}$ radicals induce red blood cell lysis about 10 times faster than ClO$^{\bullet}$ radicals[23] and are also responsible for membrane modification at lower concentrations than hypochlorite radicals.

Once the PINO radical is formed, in the second stage of the process the hypobromide ions present in the system oxidize the PINO radical to form nitrosonium species, the actual cellulose oxidant, Fig. 3, as extensively presented in our previous papers.[13,17,18] At this point, cellulose oxidation will selectively occur at C6, the primary hydroxyl groups being converted into carboxylic ones.

The presence of the nitrosonium ions in the reaction medium is likely to induce some side reactions by reacting with hydroxyl anions, hydrogen peroxide being thus produced. Hydrogen peroxide decomposition provides the existence of another reactive free radical species, namely the hydroxyl radicals. Therefore, it seems quite likely to have another source of free radicals, *i.e.* the HO$^{\bullet}$ able to perform hydrogen atom abstraction from NHPI, generating in this way the PINO radical. Concluding, two routes are possible for PINO radical formation by H atom abstraction from NHPI, both using free radical species, either BrO$^{\bullet}$ or HO$^{\bullet}$. To prove this hypothesis, butylated hydroxytoluene (BHT) (a radical scavenger) was introduced in the reaction mixture. A complete inhibition of the reaction was noted as a consequence, this confirming that PINO radical generation occurs following a free radical mechanism.[24] Table 1 contains the overall experiments carried out using the proposed metal free NHPI mediated oxidation of the three sorts of cellulose.

For comparison purposes, TEMPO-mediated oxidation of all cellulose samples was carried out, following exactly the same reaction conditions as in the case of NHPI-mediated oxidation (samples denoted as: McT24, CT24, and SBST24). The amount of carboxyl groups introduced expressed as mmol kg^{-1} depends on cellulose type, reaction time and the amount of sodium hypochlorite in the reaction. The maximal amount of the negatively charged groups formed following NHPI/NaClO/NaBr oxidation was detected when using microcrystalline cellulose oxidized for 24 h with 10 g NaClO per gram of cellulose, Fig. 4. The values do not significantly differ from those obtained by using the alternative TEMPO mediated protocol (samples McT24, CT24, and SBST24). To have a deeper insight into the influence of the oxidation reaction time on the amount of carboxylic group formation and on the degree of polymerization (DP) of the resulted products, we have done supplementarily a study to evaluate these parameters, using different oxidation times, in the range of 1 h to 24 h, Fig. 4. Larger reaction times seem to be beneficial for the higher amounts of COOH groups' formation, but detrimental for the DP value. A reasonable reaction time could be the choice in order to achieve a compromise between the two parameters, depending on the application envisaged for the oxidized product. Moreover, on increasing the reaction time, an increase of the weight loss of the initial sample is observed. As an example, the weight loss varies from 12% for SBS24 to 16%

Table 1 Cellulose oxidation in a metal free environment, using NHPI: amount of carboxylic group formation, average weight loss and degree of polymerization for the oxidized samples under various reaction times and volumes of sodium hypochlorite

Sample	Reaction time (h)	Volume of NaClO/g cellulose (ml)	Amount of negatively charged groups (mmol kg^{-1})	Average weight loss (%)	Degree of polymerization (DP)
Mc	—	—	6	—	140
Mc5	5	10	196	10 ± 0.12	120
Mc5′	5	20	288	10 ± 0.08	108
Mc24	24	10	486	18 ± 0.14	86
McT24	24	10	522	28 ± 0.22	62
C	—	—	12	—	350
C5	5	10	110	6 ± 0.10	310
C5′	5	20	162	10 ± 0.12	275
C24	24	10	264	16 ± 0.21	190
CT24	24	10	285	19 ± 0.27	130
SBS	—	—	18	—	2800
SBS5	5	10	116	2 ± 0.07	2200
SBS5′	5	20	264	3 ± 0.18	1980
SBS24	24	10	426	12 ± 0.24	1300
SBST24	24	10	488	16 ± 0.16	980

Mc = Avicel® PH 101 microcrystalline cellulose. C = Cellets 350. SBS = Never-dried softwood (spruce) bleached sulfite pulp.

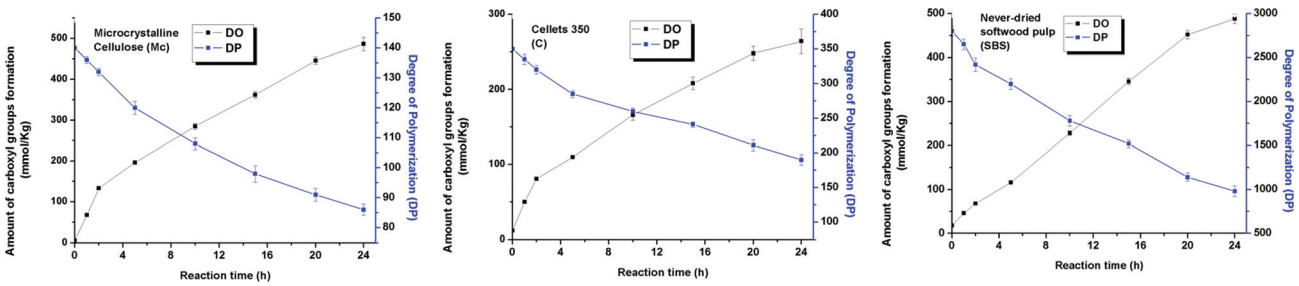

Fig. 4 The relationship between the oxidation reaction time and the amount of carboxyl groups' formation and the degree of polymerization, in the oxidation reaction of 1 g Mc, C, or SBS, with: 0.5 mmol NHPI, 8 mmol NaBr and 10 mmol NaClO, at room temperature and pH = 10.

for C24 and 18% for the Mc24 sample, respectively, which lead to a diminution of the yield of the oxidized products.

Interestingly enough, when using TEMPO the weight loss was found to be even higher for all three cellulose samples oxidized for 24 h, reaching almost 30% for the McT24 sample. Another parameter of significant importance is the degree of polymerization of the oxidized samples. It is well known that one of the major drawbacks of the TEMPO oxidation protocol is the occurring sharp depolymerization affecting the oxidized products.[25] When NHPI is used in combination with NaClO and NaBr, higher DP values are expected. Indeed, all three oxidized cellulose samples still show higher DP values as compared to those issued from the TEMPO mediated protocol (Table 1, Fig. 4).

FT-IR

The first insight into the oxidation process was acquired through FT-IR. Fig. 5 shows the FT-IR spectra of three cellulose

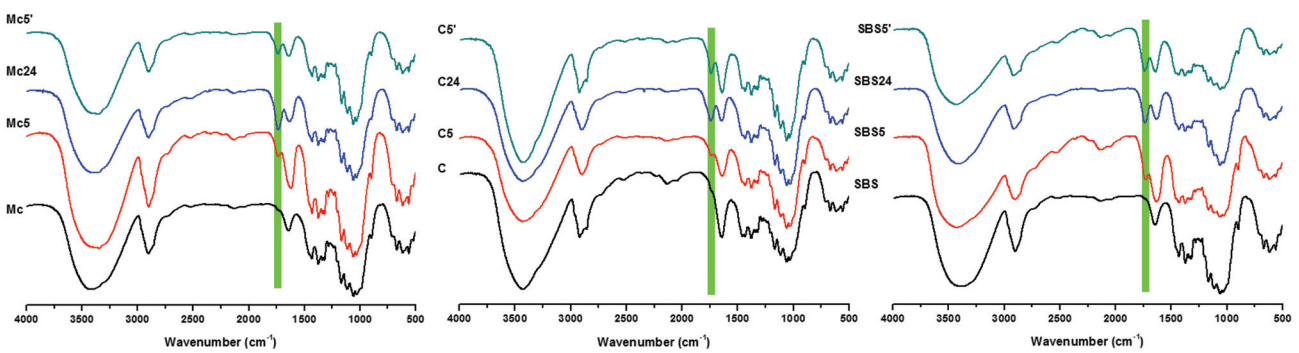

Fig. 5 FT-IR spectra of the native and oxidized cellulose samples.

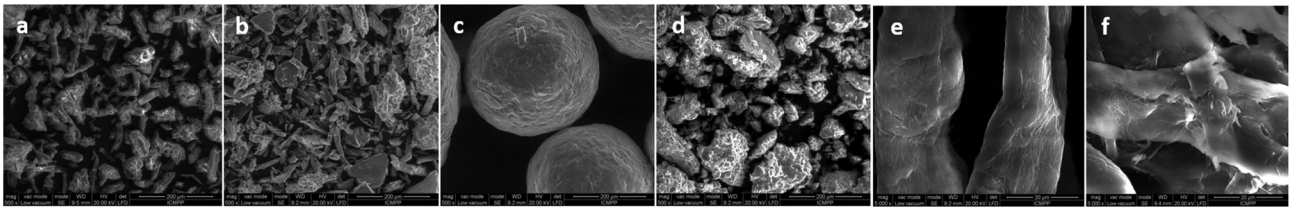

Fig. 6 SEM microphotographs of selected Mc (a), Mc5 (b), C (c), C5 (d), SBS (e), and SBS5 (f) samples.

materials before and after oxidation. Before oxidation, typical cellulose FT-IR absorption peaks are seen, as follows: a broad peak between 3000 and 3700 cm^{-1}, corresponding to the stretching vibration of the plethora of O–H groups, and the peak centered at 2900 cm^{-1} attributed to the C–H stretching originating from CH and/or CH_2 groups. The sharp absorption peak at around 1640 cm^{-1} reveals a water –OH bending vibration, since the characteristic peaks of the C–O–C stretching vibration are visible at 1164 cm^{-1}, anti-symmetric, and 1059 cm^{-1}, ring deformation, respectively. Other noticeable absorption peaks are present at 1431 cm^{-1}, $-CH_2$ symmetric bending vibration and 1373 cm^{-1}, C–H bending vibration.

Following oxidation, the main feature of all FT-IR spectra resides in the appearance of a new absorption peak, centered at 1735 cm^{-1}, assigned to the C=O bond formation in carboxylic groups. The intensity of this peak is proportional to the amount of the introduced COOH groups. The other significant changes in the FTIR spectra are noticed in the absorption decrease of both peaks attributed to the C–H stretching originating from CH_2 groups, those from 2914 cm^{-1} and 1431 cm^{-1}.

SEM

The microphotographs acquired by using ESEM present comparatively the morphological changes that occurred in cellulosic materials after NHPI/NaClO/NaBr oxidation, Fig. 6. It can be seen that after oxidation the morphology of the cellulose surface is quite altered, the major modifications being on sample C5. On this sample, the initial granular structure with a mean diameter of 350 μm (sample C) is almost totally compromised, the oxidized sample showing crumbly residual like fragments.

On two other oxidized samples (Mc5 and SBS5) the occurred changes are not very obvious, especially those derived from Mc. Regions of surface rupture are seen for the SBS5 sample, fragmentation of the microfibrils being conspicuous. All these modifications could be to a large extent attributed more to cellulose exposure to alkaline media rather than to the toxicity or the harsh nature of the reactants.

X-Ray

X-ray diffraction patterns of both unoxidized and oxidized samples are given in Fig. 7. All presented diffractograms show typical cellulose peaks with reflections at 2θ about 14.3° and 34.8°, respectively, assigned to the (110) and (004) crystallographic planes. The reflections at 16.6° and 22.5° are assigned to the (110) and (200) crystallographic planes in cellulose. The great similitude in the diffraction patterns for unoxidized and oxidized samples is a strong argument for the selective introduction of carboxylic groups on the crystal surface, rather than

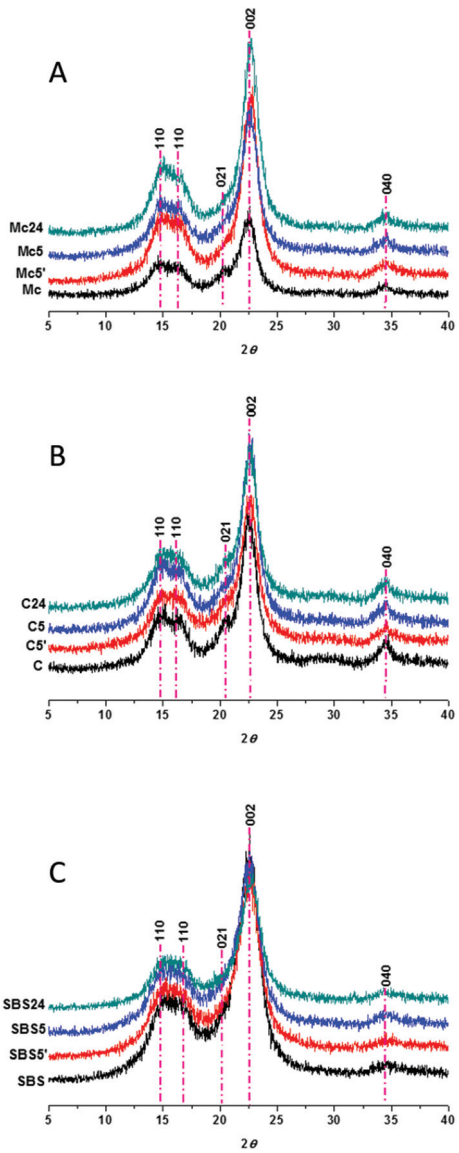

Fig. 7 X-ray diffraction patterns of original (unoxidized) and NHPI/NaClO/NaBr oxidized samples of microcrystalline cellulose (A), Cellets (B), and never-dried pulp (C).

inside the crystallites. Moreover, in the unoxidized samples, a peak at 20.6° (labeled 021), assigned to the amorphous phases,[26] can be easily detected. Following the oxidation reaction, the (021) peak of the amorphous phase shows a noticeable tendency of flattening in all oxidized samples, thus supporting the hypothesis that cellulose amorphous regions are to a large extent removed during the oxidation process.

The degree of crystallization (DC) has been calculated as presented in the Experimental section. For the unoxidized (Mc, C, and SBS) samples, the calculated DC has been found to be 42%, 58% and 43%, respectively. After oxidation, an increase of the DC has been observed, with the highest DC values for the samples oxidized for 24 h: 52% for sample Mc24, 64% for sample C24, and 54% for sample SBS24. The increase of the DC value after the oxidation reaction could be a consequence of the peeling of some fragments from cellulose's amorphous regions due to exposure to the alkaline medium during the oxidation reaction, but also due to the formation of carboxyl groups, mainly in the amorphous regions and the surface of cellulose crystals. Nevertheless, the higher DC values found for the oxidized samples denote a selective oxidation process, occurring at C6, contrasting with the periodate oxidation system, when the opening of the anhydroglucose unit of cellulose leads to a sharp decrease of the DC.[27]

Conclusions

The high catalytic activity exhibited by NHPI to a myriad of low molecular organic substrates, through its free radical derivative PINO, has been expanded toward several cellulosic materials in a simple oxidation protocol, employing sodium hypochlorite and sodium bromide, under mild reaction conditions, room temperature and atmospheric pressure.

The main finding resides in the total absence of any metal cocatalyst, a prerequisite for the PINO radical generation *via* the one electron oxidation of PINO. The designed oxidation protocol takes advantage of the two already present reagents, *i.e.* NaClO and NaBr, as efficient co-oxidizing agents for NHPI to generate the PINO radical, able to initiate the whole oxidative cycle. Under these circumstances, not only is metal participation avoided, but also the amount of the carboxylic groups introduced in the anhydroglucose unit of the cellulose chain is comparable to the one obtained using the well-established, yet more expensive, TEMPO radical. Moreover, the degree of polymerization values determined for the oxidized products obtained by using the newly reported protocol are significantly higher than those produced by other oxidation methods, improving in this way a sensitive issue, often limiting the use of oxidation reactions on cellulose as a potential functionalization pathway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 J. Credou and T. Berthelot, *J. Mater. Chem. B*, 2014, **2**, 4767–4788.
2 P. S. Chang and J. F. Robyt, *J. Carbohydr. Chem.*, 1996, **15**, 819–830.
3 T. Saito and A. Isogai, *Biomacromolecules*, 2004, **5**, 1983–1989.
4 T. Saito, Y. Okita, T. Nge, J. Sugiyama and A. Isogai, *Carbohydr. Polym.*, 2006, **65**, 435–440.
5 S. Coseri, *Eur. J. Org. Chem.*, 2007, 1725–1729.
6 S. Coseri, *Mini-Rev. Org. Chem.*, 2008, **5**, 222–227.
7 S. Coseri, *J. Phys. Org. Chem.*, 2009, **22**, 397–402.
8 S. Coseri, *Catal. Rev. Sci. Technol.*, 2009, **51**, 218–292.
9 L. Melone, M. Petroselli, N. Pastori and C. Punta, *Molecules*, 2015, **20**, 15881–15892.
10 L. Melone, S. Prosperini, G. Ercole, N. Pastori and C. Punta, *J. Chem. Technol. Biotechnol.*, 2014, **89**, 1370–1378.
11 L. Melone and C. Punta, *J. Org. Chem.*, 2013, **9**, 1296–1310.
12 F. Recupero and C. Punta, *Chem. Rev.*, 2007, **107**, 3800–3842.
13 S. Coseri, G. Nistor, L. Fras, S. Strnad, V. Harabagiu and B. C. Simionescu, *Biomacromolecules*, 2009, **10**, 2294–2299.
14 G. Biliuta, L. Fras, S. Strnad, V. Harabagiu and S. Coseri, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 4790–4799.
15 G. Biliuta and S. Coseri, *Cellulose*, 2016, **23**, 3407–3415.
16 M. Dobromir, G. Biliuta, D. Luca, M. Aflori, V. Harabagiu and S. Coseri, *Colloids Surf., A*, 2011, **381**, 106–110.
17 S. Coseri, G. Biliuta, L. Fras-Zemljic, J. Stevanic Srndovic, T. Larsson, S. Strnad, T. Kreze, A. Naderi and T. Lindstrom, *RSC Adv.*, 2015, **5**, 85889–85897.
18 G. Biliuta, L. Fras, M. Drobota, Z. Persin, T. Kreze, K. Stana-Kleinschek, V. Ribitsch, V. Harabagiu and S. Coseri, *Carbohydr. Polym.*, 2013, **91**, 502–507.
19 S. Coseri, G. Biliuta, B. C. Simionescu, K. Stana-Kleinschek, V. Ribitsch and V. Harabagiu, *Carbohydr. Polym.*, 2013, **93**, 207–215.
20 S. Coseri and G. Biliuta, *Carbohydr. Polym.*, 2012, **90**, 1415–1419.
21 G. Biliuta, L. Fras, V. Harabagiu and S. Coseri, *Dig. J. Nanomater. Biostruct.*, 2011, **6**, 293–299.
22 C. L. Hawkings, B. E. Brown and M. J. Davies, *Arch. Biochem. Biophys.*, 2001, **395**, 137–143.
23 M. C. Vissers, A. C. Carr and A. L. Chapman, *Biochem. J.*, 1998, **330**, 131–138.
24 S. J. Singh and R. V. Jayaram, *Catal. Commun.*, 2009, **10**, 2004–2007.
25 S. Coseri, *Biotechnol. Adv.*, 2017, **35**, 251–266.
26 H. Jiang, Y. Wu, B. Han and Y. Zhang, *Carbohydr. Polym.*, 2017, **174**, 291–302.
27 U. J. Kim, S. Kuga, M. Wada, T. Okano and T. Kondo, *Biomacromolecules*, 2000, **1**, 488–492.