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Comparison study of TEMPO and phthalimide-*N*-oxyl (PINO) radicals on oxidation efficiency toward cellulose

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ABSTRACT

Regenerated cellulose fibers, type viscose, have been oxidized with sodium hypochlorite and catalytic amounts of sodium bromide by using two different protocols: first, involving the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and second, employing *N*-hydroxyphthalimide (NHPI). The reactions were carried out at room temperature and pH = 10.5 for 2.5 h. Viscose oxidized samples were analyzed and compared in terms of the negative charged groups content, as determined by potentiometric titration and methylene blue adsorption, morphologies and crystallinities changes, as well as changes in the degree of polymerization. The highest content of the carboxylic groups and the best preservation of the morphology and molecular weight of the original material have been found in the case of using NHPI/anthraquinone as oxidation mediators. TEMPO-mediated oxidation leads to the highest depolymerization and cause significant degradation of the cellulosic material.

1. Introduction

The oxidation of primary hydroxyl groups in polysaccharides is one of the most studied route of their functionalization, which yields valuable oxidized products such as polyuronic acids and aldehydes, to be further used in various fields as drugs, dyes, glues, thickeners, additives to foodstuffs, cosmetics and many other (Dumitriu, 1998). The oxidation of polysaccharides skeleton can be achieved by using different oxidizing agents (Ponedel'kina, Yu Khaibrakhmanova, & Odinokov, 2010), the majority of them are unfortunately non-specific, and therefore the oxidation reaction is strongly affected by side-products formation. For specific applications of cellulose, in medical or high tech devices, is highly required to obtain materials with improved properties controlled by the selectivity of the process and by the degree of oxidation.

Nanofibrillated cellulosic materials have become a hot topic due to their higher reinforcing potential confirmed by the huge enhancement in the tensile modulus (Besbes, Alila, & Boufi, 2011). Cellulosic bionanofibers have also unique biological activities. It was very recently reported (Shimotoyodome, Suzuki, Kumamoto, Hase, & Isogai, 2011), that cellulose nanofibers administered with glucose and glyceryl trioleate to mice reduce the postprandial blood glucose, plasma insulin, glucose-dependent insulinotropic polypeptide, and triglyceride concentrations. The nanofibrillated material consist of interconnected fibrils and microfibrils, 10–100 nm width and lengths ranging from hundreds of nm to several micrometers depending on the source of cellulose. One of the easiest ways toward preparation of individual nanofibrillated cellulose is to use the selective oxidation of primary hydroxyl groups in cellulose, method recently introduced by Isogai et al. (Isogai, Saito, & Fukuzumi, 2011; Saito & Isogai, 2004; Saito, Kimura, Nishymama, & Isogai, 2007; Saito et al., 2009). Currently, there are two major routes to selective convert the primary hydroxyl groups in cellulose to carboxylic ones: (a) first protocol involved cyclic sterically hindered stable nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (1), and derivatives, 2,2,5,5-tetramethylpyrrolidine-1-oxyl (2), its 3-carboxylic (or amide) derivatives and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrroline-1-oxyl (3), Fig. 1.

These compounds are uncommonly stable due to the lack of any α-hydrogen atoms, which precludes disproportionation of these

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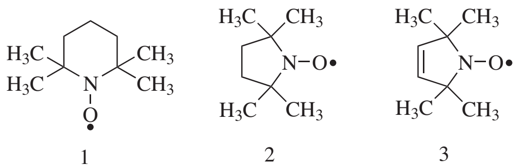

Fig. 1. Some stable nitroxyl radicals used for the cellulose selective oxidation.

radicals. The introduction of TEMPO-mediated oxidation, in which sodium hypochlorite and sodium bromide were used as reagents in aqueous media, was first applied to cellulose by Isogai and Kato as early as 1998 (Isogai & Kato, 1998).

(b) The second protocol for the mild and selective oxidation of cellulose was very recently proposed by Coseri et al. (Biliuta, Fras, Strnad, Harabagiu, & Coseri, 2010; Biliuta, Fras, Strnad, Harabagiu, & Coseri, 2011; Coseri et al., 2009). In this case, the non persistent nitroxyl radicals generated in situ from their hydroxyl precursors and an appropriate cocatalyst, are efficient mediators for cellulose oxidation. Some of the most known mediators for this kind of transformation are: *N*-hydroxyphthalimide (NHPI), *N*-hydroxybenzotriazole (HBT), and violuric acid (VA), Fig. 2. The use of these non persistent nitroxyl radicals, especially NHPI, becomes lately one of the most reliable method for the conversion of the OH groups to aldehydes or carboxylic acids for a wide range of organic substrates (Coseri, Mendenhall, & Ingold, 2005; Coseri, 2007, 2008, 2009a, 2009b).

The reaction mechanism for the cellulose selective oxidation is similar for both stable and non persistent nitroxyl radicals, involving the formation of nitrosonium cation, which is the actual oxidant, Fig. 3 (Shibata & Isogai, 2003).

In the present study we applied the above two protocols, i.e. TEMPO and NHPI-mediated oxidation of viscose fibers, and comparatively investigated: the amount of carboxylic groups formed as determined by potentiometric titration and indirectly by methylene blue adsorption method, changes in crystallinity occurred after oxidation by means of X-ray diffraction and iodine sorption value, and analysis of differences in the fibers morphology after oxidation as evidenced by environmental scanning electron microscopy (ESEM) and weight loss experiments. Also, the changes on the degree of polymerization occurred after oxidations were unequivocally determined by viscosimetric measurements. We believe this study can bring a more detailed picture of the experimental procedures used for the surface oxidation of viscose fibers performed via two parallel routes, i.e. stable versus non persistent nitroxyl radicals.

2. Experimental

2.1. Materials

As cellulose source, we have used viscose fibers provided by Lenzing AG Austria, with the following specifications (Kreze, Strnad, Stana-Kleinschek, & Ribitsch, 2001): linear density (dtex) 1.88, average length: 39 mm, average diameter: 14.3 µm, degree of polymerization: 235, molecular mass: 38,500, density: 1.5045 g cm^{-1}.

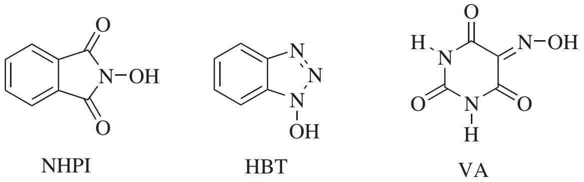

Fig. 2. The —OH bearing precursors for the non persistent nitroxyl radicals, used for the cellulose selective oxidation.

NHPI, TEMPO, sodium bromide, 3 mass% sodium hypochlorite solution, cerium (IV) ammonium nitrate (CAN), anthraquinone and other chemicals and solvents, purchased from Sigma Aldrich, were of laboratory grade and used without further purification.

2.2. Fibers preparation

The viscose fibers were added into an aqueous solution containing 200 mL of 0.1 M potassium chloride and 3 mL of 0.1 M hydrochloric acid. The fiber suspension was then stirred with a magnetic stirrer for about a half an hour in order to achieve complete wetting of the fibers and equal charge distribution.

2.3. Nitroxyl-mediated oxidation of viscose fibers

Viscose fibers (10 g) were immersed in deionised water (800 mL) in a 2 L flask. In one set of experiments, TEMPO has been used as stable nitroxyl radical to mediate the oxidation reaction, whereas in another set of experiments, NHPI has been used along with an appropriate cocatalyst, either CAN or anthraquinone to provide in situ, the non persistent phthalimide N-oxyl radical (PINO). In all experiments, sodium bromide (0.25 mmol/g cellulose) and an amount of 3% NaClO solution, corresponding to 5 mmol/g cellulose were added slowly to the cellulose slurry, and the pH of this mixture adjusted to be 10.5, at room temperature by adding a 0.4 mol L^{-1} NaOH solution, using a pH-meter. After stirring for 2.5 h, the oxidation was quenched by adding ethanol (ca. 12 mL). The resulted fibers were washed thoroughly with deionised water and ethanol. The water-insoluble fractions thus obtained were dried by lyophilization followed by vacuum-drying at 40 °C for 48 h, and weight to measure the mass recovery ratios.

3. Methods

3.1. 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}.

3.2. Potentiometric titration

The pH potentiometric titration of the fibers suspension was carried out with a two-buret instrument Mettler Toledo T70, in an inert atmosphere (N_2 bubbling). The burettes were filled with 0.1 M HCl and 0.1 M KOH. All solutions were prepared in Mili-Q water with low carbonate content ($<10^{-5}$ M). This was achieved by boiling and cooling under nitrogen atmosphere. The suspension was titrated in a forth and back manner between the initial pH = 2.8 to the preset pH = 11. The titration experiments were carried out at 0.1 M ionic strength, set to its appropriate value with KCl. The titrant was added dynamically within a preset interval of [0.001–0.25] mL. The equilibrium criteria for the timed addition was set to $dE/dt = 0.1/150$ s. Where 150 s was the minimum time to reach equilibrium conditions between two additions of the titrant, and the maximum time was set to 7200 s. The pH value was measured with a Mettler Toledo DG-117 combined glass electrode. A blank HCl–KOH titration was carried out under in the same conditions as stated above. All presented values are the mean values of 3 parallel measurements.

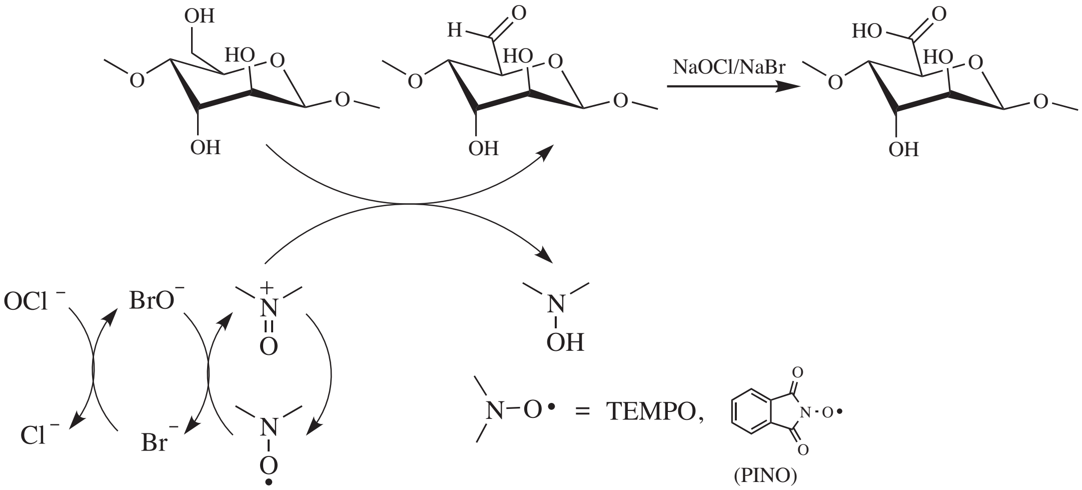

Fig. 3. Simplified oxidation cycle with NaOCl/NaBr tandem of the primary OH groups in cellulose, mediated by nitroxyl radicals.

3.3. *Environmental scanning electron microscopy (ESEM) and weight loss experiments*

The ESEM studies were performed on samples fixed by means of colloidal silver on copper supports. The samples were covered with a thin layer of gold, by sputtering (EMITECH K 550x). The coated surface was examined by using an environmental scanning 200, operating at 5 kV with secondary electrons in High Vacuum Mode.

Some degradation phenomena can accompany the oxidation reactions. As a result, morphological changes of the oxidized viscose fibers due to introduction of carboxylic groups and also weight loss can occur. The weight loss percentage of the oxidized samples was calculated according with the following equation:

$$W_{loss}(\%) = \frac{W_O - W_{OX}}{W_O} \times 100 \qquad (1)$$

where W_O and W_{OX} are the weight of the original and oxidized viscose fibers respectively. The weight measurements are repeated 10 times for each oxidized viscose fibers to obtain an average of the weight loss percentage.

3.4. *X-ray diffraction analysis*

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 $0.02^\circ\ s^{-1}$ by the reflection method. The operated voltage was 30 kV and the current was 36 mA. The crystallinity was calculated according with the following equation:

$$\text{Relative crystallinity} = \frac{I_{crystalline} - I_{amorphous}}{I_{crystalline}} \times 100\% \qquad (2)$$

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

3.5. *Iodine sorption value (ISV)*

ISV was determined according with the Schwertassek method: the fibers were treated with KI_3 solution, leave for 2 h to attain the equilibrium, and then filtered. A solution of 0.02 N sodium thiosulphate was used for titration of the resulted iodine solution. ISV (mg absorbed iodine/g cellulose), and the degree of crystallinity were calculated from the difference in iodine concentration between the filtrate and a blank solution as described by Hessler and Power (1954) and Schwertassek (1961).

3.6. *Viscosity average degrees of polymerization (DPv) measurement*

Intrinsic viscosities of the viscose fibers were obtained by a capillary viscometer using 0.5 M copper ethylenediamine (cuen) as the solvent. All these values were converted to viscosity average degrees of polymerization (DPv) according with the previous reported method (Sihtola, Kyrklund, Laamanen, & Palenlus, 1963).

4. Results and discussion

4.1. *Cellulose oxidation*

In order to have a full understanding regarding the catalytic efficiency of the most used nitroxyl radicals on cellulose fibers oxidation, we envisaged two separate oxidation protocols, firstly, the reactions were carried out by using the stable nitroxyl radical, TEMPO, and secondly, in a separate set of experiments, the viscose fibers oxidation was performed employing the non persistent PINO nitroxyl radical generated in situ from its hydroxyl precursor, NHPI in the presence of different cocatalysts, i.e. CAN or anthraquinone, Table 1. In all cases, the other parameters such as: the concentrations of the NaClO, which was set to 5 mmol/g cellulose, NaBr: 0.25 mmol/g cellulose, pH = 10.5, temperature: 25 °C and reaction time: 2.5 h were maintained constant. Table 1 shows the schematization of the experiments. In the preliminary runs,

Table 1
Oxidation reaction of viscose fibers oxidized with TEMPO or NHPI.

Run	Catalyst (mmol/g cellulose)	Cocatalyst (mmol/g cellulose)	Amount of negatively charged groups (mmol/kg)[a]
O	–	–	6
T1	TEMPO (0.015)	–	69
N1	NHPI (0.015)	Anthraquinone (0.015)	97
N2	NHPI (0.015)	CAN (0.015)	77
T2	TEMPO (0.150)	–	154
N3	NHPI (0.150)	Anthraquinone (0.150)	233
N4	NHPI (0.150)	CAN (0.150)	165

[a] Determined by potentiometric titration; variation between analyses was less than 2% in all cases.

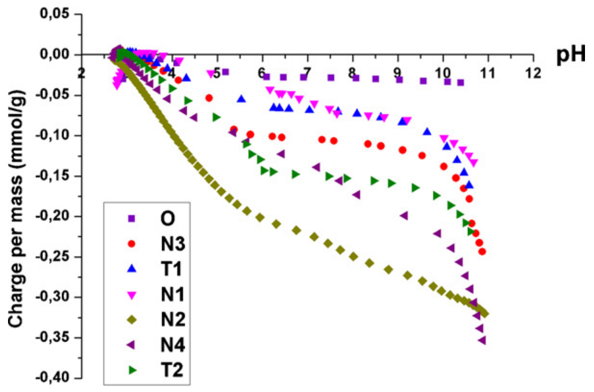

Fig. 4. Charge isotherms of the original (O) and oxidized fibers with TEMPO or NHPI.

Table 1, runs T1, N1, and N2 a concentration of 15 μmol/g cellulose of nitroxyl radical has been employed. The content of the amount of negatively charged groups have been determined by using potentiometric titration, Table 1 and Fig. 4. As can be observed, the amount of carboxylic groups increased from 6 mmol/kg viscose fibers in the original sample (O) to 69 mmol/kg in the case of using TEMPO (run T1), 77 mmol/kg for the NHPI/CAN system (run N2) and 97 mmol/kg in the NHPI/anthraquinone system. Interestingly, the oxidized systems using NHPI provides all the time the highest amount of carboxylic groups. The next step was to investigate the influence of the catalysts loading on the yield of carboxylic group formation. Thus, the runs T2, N3, and N4, have used larger amounts of nitroxyl radicals, i.e. ten times higher than initial experiments. We have found the same behavior, namely the TEMPO oxidation (run T2) gave the lowest amount of carboxylic groups, since for the oxidizing systems involving NHPI (runs N3 and N4) the detected amount of negatively charged groups was higher. Again, the NHPI/anthraquinone system was the most efficient, with a total of 233 mmol/kg carboxylic groups.

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

The easiest way to detect the oxidation product formation from cellulosic materials is represented by the FTIR technique. We had previously presented in detail (Biliuta et al., 2010; Coseri et al., 2009), the assignments and distributions of the most important FTIR peaks appeared after oxidation. Thus in this paper, we just remind that the major change in the FTIR spectra after oxidation is the presence of a new adsorption band around 1740 cm^{-1} which corresponds to the C=O stretching frequency of carboxyl groups in their acidic form. All the FTIR spectra are presented in Supporting information part.

4.3. ESEM and weight loss

The viscose fibers oxidized with either TEMPO or NHPI had incorporated certain amounts of carboxylic groups, depending on the nitroxyl type's radical and its concentration used in the reaction. The physical modifications of the cellulose fabrics are in detail studied using ESEM and weight loss measurements, see Supporting information and Table 2. The surface of viscose fibers was smooth and long for the N1 sample, resembling the structure of the original material (Biliuta et al., 2010; Coseri et al., 2009). Some fine pits and small plaques fragments are observed for the T1 and N2 samples, the surface of the cellulose fibers seems to become rougher with an increasing amount of tiny groves. It can be concluded thus, that NHPI/anthraquinone system is milder than the TEMPO and NHPI/CAN oxidizing systems. Increasing the nitroxyl radical concentration, the morphology of the viscose fibers starts to shows cracks in the fibers surface, melting-like aspects of some regions of the fibers surface, thus some fine particles being liberated into solution, especially for T2 and N4 samples. Again the NHPI/anthraquinone system seems to be the mildest for the oxidation, even when the concentration of both NHPI and anthraquinone was ten times higher than in the N1 sample. To confirm the morphological changes observed during ESEM analyses, weight loss measurements are performed. As Table 2 presents, there are evidence of increasing of the loss percentage in the following order: N1 > N2 > N3 > N4 > T1 > T2. One can conclude that the oxidizing systems including TEMPO cause the highest damage of the fibers surface, NHPI/CAN is somehow a harmful system, especially at higher concentrations of catalyst/cocatalyst. Unequivocally when PINO radical generation was achieved using NHPI and anthraquinone, the oxidation reaction occurs mild, and the morphology of the viscose fibers remained barely unchanged.

Table 2
Average weight loss (%) of viscose fibers oxidized with TEMPO or NHPI.

Run	Average weight loss (%)	Standard deviation (%)
T1	2.22	0.12
N1	0.82	0.08
N2	1.65	0.10
T2	8.16	0.39
N3	1.75	0.21
N4	2.17	0.31

4.4. X-ray diffraction analysis and iodine sorption value (ISV)

In Supporting information part, we present the X-ray diffraction patterns of the viscose fibers before and after oxidation. From X-ray diffraction pattern of each sample, we may conclude that the oxidation reaction conditions affect in some extent the fibre's structure. Original, untreated sample (O) has a crystallinity of 25% (Kreze et al., 2001; Kreze, Jeler, & Strnad, 2002). During oxidation reaction, due to introduction of carboxylic groups mainly in the amorphous regions and crystal surfaces (Dai, Dai, Yuan, Sun, & Zhu, 2011; Qin, Tong, Chin, & Zhou, 2011), the crystallinity showed an increasing trend. This trend is moderate for the samples T1, N1, N2, N3 and N4, whose crystallinity is only few percents higher than in O sample. However, a significant increasing of the crystallinity was observed for the T2 sample, whose crystallinity reach 42%. In this case we can suppose that this is due partial loss of the disordered regions during the oxidation reaction as well washing process, which cause an increasing of water-solubility products.

The ISV gives a measure of the cellulose accessibility areas toward an iodine solution and is expressed as mg of iodine adsorbed by one gram of cellulose. Generally, iodine bounds only to less ordered amorphous regions (Kreze et al., 2002). Iodine sorption mechanism differs from water sorption: iodine adsorbs only in a mononuclear layer to available hydroxyl groups of cellulose amorphous regions, since water adsorb in multimolecular layers. The three-iodide anion is incorporated into viscose fibers with partly positive hydrogen from hydroxyl groups of accessible region. When the hydroxyl groups are included in the crystallites or they are converted into different functional groups, like carboxylic ones, they become inaccessible to iodine, having result a lower ISV. Therefore, a low ISV means a reduction of the accessible hydroxyl groups for iodine adsorption or an increasing of the crystallinity, or both. In viscose oxidized fibers, a certain number of accessible primary OH groups are converted to carboxylic ones, which are less prone to absorb iodine than the original hydroxyl groups. Therefore we would expect that oxidized fibers exhibit lower ISV. Indeed, Fig. 5 clearly shows the above mentioned hypothesis: the highest ISV was found for sample O (original viscose fibers) which corresponds to

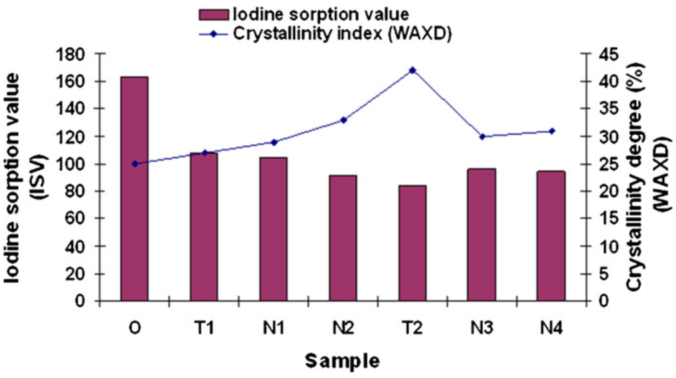

Fig. 5. Iodine sorption values (ISVs) of viscose fibers oxidized with TEMPO or NHPI and crystallinity degree as determined by WAXD.

the lowest crystallinity as determined by X-ray diffraction. Conversely, the T2 sample has the lowest ISV, and therefore the highest crystallinity as determined by using X-ray diffraction experiments. All the oxidized samples have lower ISV than original (unoxidized) sample, while their crystallinity is always higher than in original sample.

4.5. Changes in degree of polymerization of viscose fibers during TEMPO and NHPI-mediated oxidation

The DPv values of the original and oxidized samples are presented in Fig. 6.

The original viscose fibers have the DPv value of 235. The DPv values of all the oxidized samples are clearly lower than that of the unoxidized one. It can be assumed that during oxidation reaction the cellulose chains are depolymerized in such extent depending on the mediator's nature and concentration, since all the others parameters remained constants. The highest depolymerization is observed in the case of using TEMPO as mediator, the DPv values lies in this case from 45 (sample T1) when 0.015 mmol TEMPO/g cellulose was used to 40 (sample T2) when ten times higher concentration of TEMPO was used in the oxidation reaction. Due to the fact that the oxidation reaction takes place mostly in the disordered regions and at the surface of the crystalline regions, the depolymerization will occur by β-elimination at C6 aldehyde groups which are the intermediated of this reaction (Coseri et al., 2012). Other depolymerization process can be promoted by the presence of different radical species appeared in situ during the TEMPO-mediated reaction (Shibata & Isogai, 2003). When smaller concentrations of NHPI were used to mediate the viscose fibers oxidation (samples N1 and N2), the resulted samples have a quite higher (as compared with sample T1) values of DPv of 90 and 88 respectively. Increasing the NHPI's concentration to achieve a higher content of the COOH group's formation, only a minor decrease of DPv values toward N1 and N2 samples was observed (samples N3 and N4). We can assume based on these results, that clearly, NHPI can be a milder alternative to TEMPO as mediator for the oxidation reaction of viscose fibers. The significant depolymerization during the TEMPO-mediated oxidation reaction was also previously reported in the case of TENCEL fibers when the DPv values dropped after oxidation from 380 in original material to 49, and also for Bemliese fibers, when the decrease was even more dramatically, from 680 in the starting fibers to 38 in the oxidized ones (Isogai, Yanagisawa, & Isogai, 2009).

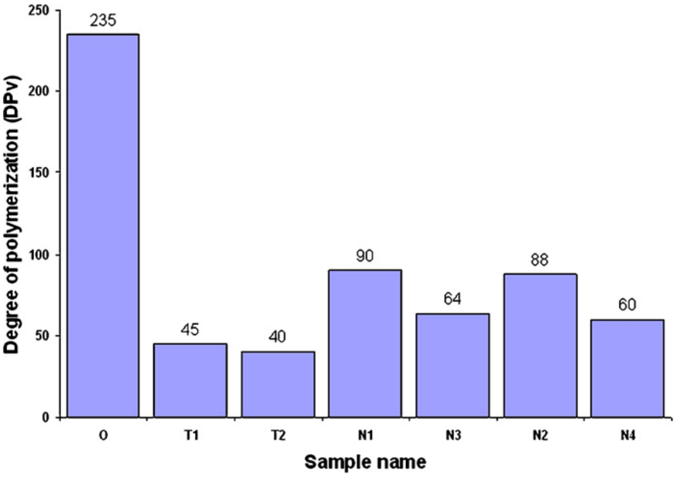

Fig. 6. Degree of polymerization (DPv) of the original (O) and oxidized viscose fibers.

5. Conclusions

The main goal of this paper was to perform a comparison study of the two most powerful agents for the selective oxidation of cellulose, namely TEMPO and NHPI, in terms of oxidation efficiency expressed as amount of negatively charged groups formation, crystallinity and morphology changes and mildness of the reaction. The primary evidence of the oxidation reaction was obtained by FTIR. The amount of negatively charged groups was directly determined by potentiometric titration and indirectly by using methylene blue adsorption method. The highest content of the carboxylic groups was found when NHPI mediate the oxidation reaction and either CAN or anthraquinone served as cocatalysts. The crystallinity of the viscose samples barely changed after oxidation with NHPI and small amounts of TEMPO. Increasing TEMPO concentration up to 0.15 mmol/g cellulose (amount largely used in the celluloses oxidation processes) leads to a jump of crystallinity to 42% (toward 25% in the original sample) as a result of considerable weight loss occurred mostly in the disordered regions, some fibers fragments being thus liberated in the solution. The obtained results of crystallinity changes during oxidation are confirmed by the iodine sorption value experiments. The morphology of the viscose fibers was unaffected when NHPI/anthraquinone was used for oxidation, but considerable damage was observed in the case of using 0.15 mmol TEMPO/g cellulose. We can conclude that NHPI/anthraquinone is the optimum oxidizing system for cellulose fibers, being the mildest, yielding the highest amount of carboxylic groups, preserving the morphology of the original sample and very important, giving the smallest depolymerization. Contrary, TEMPO, at least at concentrations of 0.15 mmol/g cellulose seems to be more harmful and aggressive oxidizing system as compared with NHPI/anthraquinone.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.08.047.

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