



Oxidative degradation of non-recycled and recycled paper

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Received: 13 May 2020 / Accepted: 10 August 2020 / Published online: 28 August 2020
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Abstract The degradation of paper-based materials involves several and complex mechanisms, such as hydrolysis and oxidation. The behaviour of different types of pulps can be very variable. In this study, the difference upon oxidation of contemporary non-recycled and recycled papers, which now constitute a considerable fibre source, is investigated. A 0.015 M potassium periodate solution is used to oxidise five types of paper, two non-recycled and three recycled, for 0.5, 1, 2 and 4 h. The effects of such oxidation treatments are evaluated in terms of carbonyl content and degree of polymerisation (DP). A modified procedure of the Szabolcs's method and viscometry are used to measure the carbonyl content and DP, respectively. The carbonyl groups are found to

increase more rapidly in the recycled papers than in the non-recycled ones. On the contrary, oxidation causes a larger decrease of the DP values in the non-recycled papers, the paper made of pure cellulose being the most sensitive in terms of depolymerisation. The DP values measured for pure cellulose paper are in line with previously reported data. Moreover, in accordance with the Ekenstam equation, the plots of the reciprocal of DP as a function of oxidation time show good linear correlations for all types of paper investigated. Pseudo rate constants are thus calculated from the slopes of these plots, those of the non-recycled papers being found to be higher than those of the recycled papers.

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Graphic abstract



Keywords Periodate oxidation of paper · Recycled paper · Carbonyl content · Degree of polymerisation

Introduction

Technologies and raw materials for papermaking have radically changed over the centuries (Hunter 1978). While around 1850 wood fibres (softwood and hardwood) started being used to manage the ever-increasing demand for paper and deficiency of rag fibres, currently a growing part of paper manufacturing involves recycled fibres due to economic and environmental issues (CEPI 2017). The 2018 monitoring report published in the context of the European Declaration on Paper Recycling 2016–2020 outlines that the recycling rate in Europe reached 71.6% in 2018, increasing by 47% since 1998 (EPRC 2019). Unlike the well-studied Western historical paper for which significant research has been carried out over the past decades, scientific research on contemporary recycled paper is quite limited. It has previously been reported (Coppola et al. 2018a) that accelerated degradation experiments, carried out exposing recycled and non-recycled papers to extreme conditions of temperatures (50–80 °C) and relative humidity levels (26–98%), led to a systematic difference between the degradation rates of the recycled and non-recycled paper, albeit negligible considering the experimental limits. This finding could be traced back to a different extent of oxidative degradation. Therefore, in the present study, the extents of oxidative degradation in different papers are evaluated measuring its effects on DP in order to give insight into the behaviour of

contemporary recycled and non-recycled paper upon oxidation.

In general terms, the paper produced centuries ago and that manufactured nowadays can be considered as the same product, that is a sheet material made of a network of various fibres (e.g., rag, straw, wood, recycled) which have been deposited from an aqueous suspension (Roberts 1996). However, different types of paper can degrade with different rates (Barański et al. 2000, 2003), so that studies of degradation can allow predictions on their durability. Knowledge of mechanisms of cellulose degradation is a fundamental issue in preventive and interventive conservation of both historical and contemporary documents.

Regardless of its source, the main structural component of paper is cellulose, a linear condensation polymer consisting of D-anhydroglucopyranose units linked by β -1,4-glycosidic bonds. The morphological structure of cellulose can be very complex because of the ability of hydroxyl groups to form both inter- and intra-molecular hydrogen bonds (Nevell and Zeronian 1985). The complexity of the cellulose-based materials is reflected by the numerous degradation reactions which can occur (Zervos 2010; Area and Cheradame 2011), acid-catalysed hydrolysis and oxidation being among the main chemical reactions (Sistach et al. 1998; Porck 2000; Margutti et al. 2001). Hydrolysis takes place with the protonation of a glycosidic oxygen atom by a hydrogen ion, followed by the breakage of a glycosidic bond and splitting of the cellulose chain with consequent decrease in the degree of polymerisation (DP) (Nevell 1985a). Oxidation can proceed through several reaction paths, such as oxidation of the primary and secondary hydroxyl groups of the pyranose ring to carbonyl and carboxyl

groups (Margutti et al. 2001), as well as free radical reactions (Kolar 1997; Jeong et al. 2014). Oxidising agents have been classified as non-specific or specific (Margutti et al. 2001), according to the positions of the pyranose ring they attack (random or defined, respectively). Sodium hypochlorite is considered a non-specific oxidant and may give rise to different products. In contrast, the periodate oxidation of cellulose leads to breaking of the bond between the C2 and C3 ring atoms, with formation of 2,3-dialdehyde cellulose (Varma and Chavan 1995). Oxidation reactions themselves can cause ring opening and increase of acidity due to the formation of carboxyl groups, weakening the glycosidic bonds and inducing hydrolytic depolymerisation (Margutti et al. 2001). Moreover, the formation of electron-acceptor groups such as carbonyl groups in the neighbourhood of the glycosidic oxygen has been held accountable for favouring hydrolysis (Krässig 1993). Therefore, cellulose degradation should be regarded as a mixed hydrolytic and oxidative mechanism, where the two reactions are autocatalytically accelerated (Sistach et al. 1998; Łojewska et al. 2005). In a very recent study (Tétreault et al. 2019), which describes a model for simulating the degradation of paper-based materials, oxidation was not included in the model due to the lack of data.

The prevalent mechanisms of degradation and their rates are functions of both paper properties (e.g., pH, lignin content, metal ions) and storage conditions (e.g., temperature, humidity, gaseous pollutants). It is well known that most of the paper produced between 1850 and 1950 using rosin sizing is acidic, and thus prone to a faster degradation than that produced before with other sizing materials (e.g., flour, gelatine) (Strlič et al. 2005a). pH plays a crucial role in the acid-catalysed hydrolysis, the lower the pH, the faster the degradation. A number of methods have been proposed to measure pH either by extraction (Strlič et al. 2004; ASTM D778-97 2007; TAPPI T509 om-15 2015) or surface determination (TAPPI T529 om-14 2014).

The chemical and physical paper properties may be altered to different extents depending on the main degradation mechanisms. For instance, yellowing is ascribed to the formation of carbonyl groups (Mosca Conte et al. 2012). Degradation experiments, during which paper samples are exposed to extreme conditions of temperature,

humidity and/or pollutants, have been carried out to determine the effects and rate of degradation by measuring the property of interest as a function of time with suitable techniques (Zou et al. 1996; Porck 2000; Margutti et al. 2001; Strang and Grattan 2009; Whitmore and Bogaard 2009; Kačík et al. 2009; Strlič et al. 2011; Coppola et al. 2018a). The determination of DP, a measure of the average molecular weight, is among the most investigated chemical properties of cellulosic materials. Although more precise techniques are now available, such as size exclusion chromatography (Strlič and Kolar 2003; Dupont and Mortha 2004; Łojewski et al. 2011), viscometry is still the most commonly used technique due to its relatively simple and fast procedure (Strlič et al. 2005b). DP measurements are especially important in connection with kinetic studies of paper degradation. Measurements of the extent of oxidised groups in cellulose is also important. The determination of oxidised carbonyl groups and DP is meaningful also for non-degraded cellulosic materials, where the presence of oxidised groups can be due to the pulping and bleaching processes (Biermann 1996), and for evaluation of appropriate conservation procedures (Bicchieri et al. 1999, 2016; Malesic et al. 2002). The determination of carbonyl groups presents inherent difficulties, such as low average contents (in the $\mu\text{mol g}^{-1}$ range) and possible incompleteness of derivatisation reactions due to problems of accessibility to functional groups (Röhrling et al. 2002). To estimate the amount of carbonyl groups in cellulose several analytical procedures have been reported (Szabolcs 1961; Nevell 1985b; Strlič and Pihlar 1997; Bicchieri et al. 1999; Röhrling et al. 2002; TAPPI T430 cm-09 2009), such as the determination of copper number (TAPPI T430 cm-09 2009), the cyanide method (Nevell 1985b) and fluorescence labelling (Röhrling et al. 2002). Fourier transform infrared (FTIR) spectroscopy has been also applied to investigate the formation of carbonyl groups (Margutti et al. 2001), however, the presence of non-bonded water can mask possible changes in the carbonyl region, not allowing easy recognition of oxidised functional groups (Ali et al. 2001; Coppola et al. 2018b).

In the present study, the effects of oxidation on paper samples immersed in a solution with a

specific oxidising agent (periodate), for different durations, were evaluated in terms of DP and carbonyl contents. Five different paper types, virgin non-recycled and recycled papers, were analysed in order to evaluate possible differences in the degradation effects. In particular, the present results focus on the correlation between oxidation time and carbonyl content, and between carbonyl content and DP.

Experimental

Materials

Five types of paper, two made of non-recycled fibres and three made with different proportions of recycled fibres, were analysed. The two samples made of non-recycled fibres are Whatman filter paper No 1 (Maidstone, UK) and Arcoprint 1 EW paper (Fedrigoni, Italy). The three samples with 30%, 80% and 100% of recycled fibres are, respectively, Nautilus (Mondi, UK), Woodstock (Fedrigoni, Italy) and OfficeDEPOT (OfficeDEPOT, US). Below these five types of paper are designated with the labels: Wh for Whatman, A for Arcoprint 1 EW, RN for Nautilus, RW for Woodstock, and RU for OfficeDepot. The recycled fibres of RW are pre-consumer, namely, for instance, derived from manufacturing scrap, while those of RU are post-consumer, thus reclaimed after having been used from a consumer (CEPI 2009). In our previous works (Coppola et al. 2017, 2018a), the fibre furnish analysis and phloroglucinol test were carried out and turned out that all samples, except Wh, are made of chemical pulps with both softwood and hardwood fibres. Additionally, all paper samples, except Wh, have a substantial amount of ash (more than 10%) and traces of lignin (Coppola et al. 2017, 2018a).

Oxidation

The samples were oxidised by immersion in potassium metaperiodate (KIO_4) 0.015 M aqueous solutions for 0.5, 1, 2 and 4 h at 20 ± 5 °C. For each sample, about 400 mg of paper were immersed in 50 mL of oxidising solution. Immediately after oxidation, the oxidised samples were immersed in distilled water for 15 min, washed thoroughly and air-dried.

Analytical methods

The non-degraded and degraded (oxidised) paper samples were analysed in terms of acidity, DP and carbonyl content.

The cold extraction method with the modifications suggested by Strlič et al. (2004) was carried out to measure the pH of all paper samples. The samples were weighed (6.6 ± 0.6 mg) and put into 1.5 mL vials, where a determined volume (462 ± 42 μL) of MilliQ water was added. The pH of the cold extraction was measured using a semi micro-combined glass electrode (32200383, XS Instruments, Italy). For each sample, pH was measured in triplicate. The pH value, rounded to the nearest 0.1 decimal digit, was acquired when a constant reading was reached. The mean uncertainty for alkaline paper using this procedure was evaluated to be ± 0.3 (Strlič et al. 2004).

A Bruker ATR-FTIR spectrometer with OPUS software (Vers. 7.5) was used to measure the absorbance spectra of non-degraded samples over the range $4000\text{--}400$ cm^{-1} . 64 scans were acquired with a resolution of 4 cm^{-1} to calculate the crystallinity index using the ratio between the absorption at 1372 and 2900 cm^{-1} (Kato and Cameron 1999; Łojewski et al. 2010).

The DP values were determined by viscometry using the cupriethylenediamine (CED) solvent as indicated by the standard ISO 5351 (2010). However, prior to dissolution, a reduction pre-treatment was carried out to stabilise oxidised cellulose, because of detrimental effects of CED due to its alkaline pH (about 11) (Strlič et al. 1998). Therefore, degraded and non-degraded samples were reduced with a NaBH_4 0.01 M aqueous solution for 24 h under room conditions. After reduction, the samples were rinsed with diluted acetic acid (pH 5) and washed thoroughly with distilled water. The air-dried stabilised samples were weighed, then immersed and stirred in a precise volume of distilled water. When a pulp was obtained, an equal volume of fresh CED 1 M was added, and the solution mixed again until the sample was completely dissolved. The efflux time of each solution passing through an Ubbelohde viscosimeter (532 10 I, Schott Geräte, Germany) at 25.0 ± 0.1 °C was measured automatically using a ViscoSystem (AVS 310, Schott Geräte, Germany). The product between the measured efflux time and viscosimeter constant (0.0086 s^{-1}), obtained from the calibration procedure (ISO 5351

2010), gives the viscosity ratio (η_{ratio}). For values of η_{ratio} from 1.0 to 19.9, the standard ISO5351 (2010) provides the corresponding values of the product between the intrinsic viscosity $[\eta]$ (mL g^{-1}) and the known mass concentration ρ of the sample (g mL^{-1}), calculated subtracting dry and ash contents from the weight of the sample. It was thus possible to calculate the DP values using the Mark–Houwink–Sakurada equation (Flory 1953) with the coefficients proposed by Evans and Wallis (1987):

$$\text{DP}^{0.85} = 1.1[\eta] \quad (1)$$

The DP calculated for each paper sample was the average of two independent measurements. The mean uncertainty of DP determinations was evaluated to be less than 2%, except for the RN paper (9%).

The carbonyl content was measured following the method originally proposed by Szabolcs (1961) and optimised by Strlič and Pihlar (1997). About 10 mg of paper samples were put in an open 10 mL glass tube. 0.5 mL of KOH 0.3 M and 0.5 mL of 2,3,5-triphenyltetrazolium chloride (TTC) 0.01 M were added, and heated in a water bath at 80 °C for 6 min. After immediate cooling to room temperature, the solution with the sample was filtered and rinsed with methanol in a laboratory flask until the 10 mL mark was reached. In alkaline medium, the oxidation of carbonyl groups (aldehydes and ketones, the latter previously converted into aldehyde through alkaline hydrolysis) into carboxyl groups, and the consequent reduction of TTC into triphenylformazane (formazane), with its typical red colour, allows the determination of carbonyl content by measuring the absorbance of formazane at 482 nm. The absorbance (Abs) of the resulting solution, kept in the dark due to light sensitivity, was measured within 60 min from the preparation. A UV-Vis Cary 60 spectrophotometer (Agilent Technologies Inc, US) with the CaryWinUV Scan software (Vers. 5.0.0.999) was used to measure the absorbance in the 400–600 nm wavelength range with a resolution of 1 nm. In order to determine the carbonyl content, a calibration curve was built measuring the absorbance at 482 nm of the reaction solutions with different amounts of a 0.0055 M aqueous solution of glucose: 0.025, 0.030, 0.040, 0.050, 0.060, 0.075, 0.100 mL, corresponding to 0.1375, 0.1650, 0.2200, 0.2750, 0.3300, 0.4125, 0.5500 μmol of glucose in 10 mL. Formazane

solutions follow Beer's law in the calibration region (Strlič and Pihlar 1997). Therefore, a calibration graph plotting Abs at 482 nm versus μmol of glucose allows to evaluate the carbonyl content (μmol). Figure 1 shows the calibration line ($R^2 = 0.994$) obtained, which is defined by the following equation:

$$\text{Abs}(482 \text{ nm}) = -0.43 + 2.91 \mu\text{mol}_{\text{gluc}} \quad (2)$$

It can be noted that the slope is very close to that found by Strlič and Pihlar (1997). According to Eq. 2, the concentration of glucose for which the absorbance measured is zero is equal to 0.15 μmol in 10 mL of solution. This limit of detection was ascribed to the inherent loss of formazane (Strlič and Pihlar 1997).

At least two measurements of carbonyl content were carried out on each paper sample. The mean uncertainty of carbonyl content determinations was evaluated to be about $\pm 6\%$, except for the RU paper (23%).

Results and discussion

Figures 2 and 3 show the total carbonyl contents per gram of paper and the corresponding DP values as a function of oxidation time for the non-recycled and recycled papers, respectively.

As expected, the carbonyl content increases, and the DP decreases with increasing oxidation time. According to Margutti et al. (2001), the acidity of the periodate solution can also contribute to

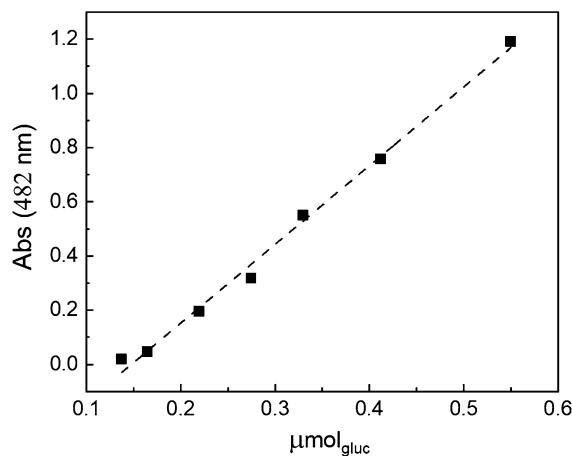


Fig. 1 Calibration line for the determination of carbonyl content

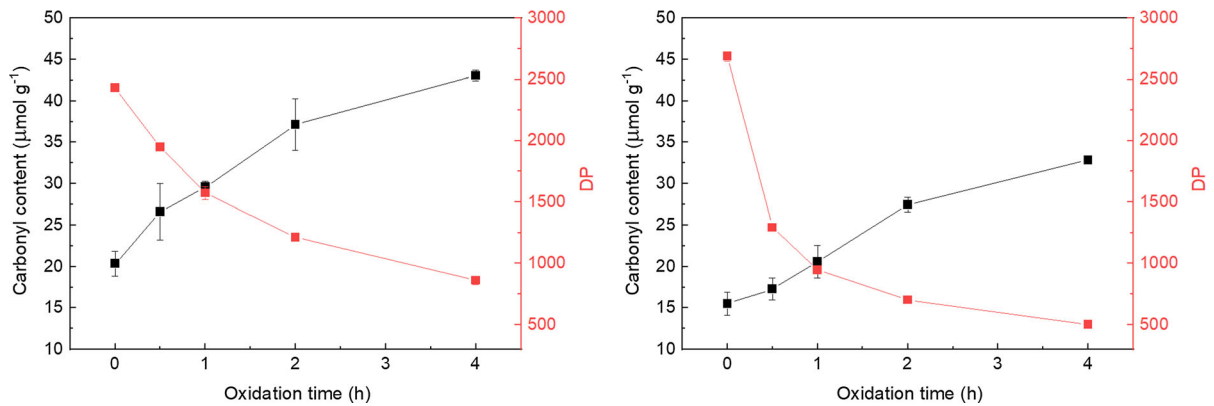


Fig. 2 Carbonyl contents ($\mu\text{mol g}^{-1}$) and DP values as a function of oxidation time for the A (left) and Wh (right) papers. Vertical lines indicate the standard deviations

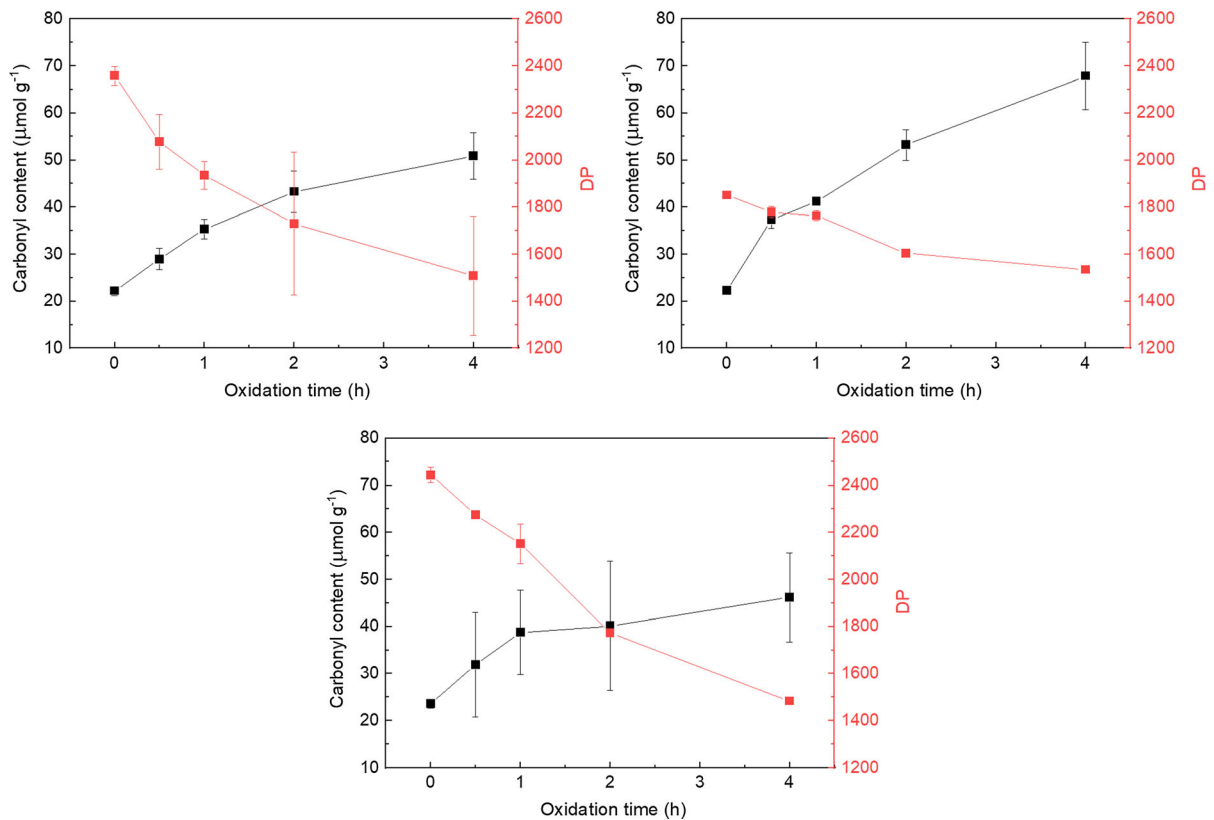


Fig. 3 Carbonyl contents ($\mu\text{mol g}^{-1}$) and corresponding DP values as a function of oxidation time for the RN (top left), RW (top right) and RU (bottom) papers. Vertical lines indicate the standard deviations

depolymerisation. The diagrams of Figs. 2 and 3 highlight at first glance that oxidation causes a sizeable decrease of DP values, especially for the two non-recycled papers. A decrease of about 65% and 80% from the initial DP was measured after 4 h of

oxidation for the A and Wh papers, respectively. The decrease of DP values of the three non-recycled paper is smaller, that is, about 40% for RN and RU, and less than 20% for RW. The highest increase in carbonyl content was measured for the RW paper, the carbonyl

content of the most oxidised sample being three times as large as that of the non-oxidised sample (see top right panel of Fig. 3). It can be noted that the values found for the carbonyl content of oxidised samples of the RU paper (see bottom panel of Fig. 3) are characterised by a large variance. In addition to an intrinsic error of the method for carbonyl content determinations, as reported by Strlič and Pihlar (1997), a tentative explanation for the higher error measured in RU could be ascribed to heterogeneity of this paper. The carbonyl contents of the other types of paper after 4 h of oxidation is about twice as large as that measured on the corresponding non-oxidised samples. The different behaviour in terms of DP decrease with increasing carbonyl content for the five types of paper considered is clearly shown in Fig. 4, where DP is plotted versus carbonyl content.

A negative linear correlation between DP and carbonyl content was found for all kinds of paper ($R^2_A = 0.98$, $R^2_{Wh} = 0.64$, $R^2_{RN} = 0.99$, $R^2_{RW} = 0.95$, $R^2_{RU} = 0.85$). The significantly smaller correlation coefficient found for Wh stems from the sizeable decrease of DP measured after only 30 min of oxidation.

Oxidation has been held accountable for favouring hydrolysis (Krässig 1993). Provided the DP value is sufficiently large and assuming no loss of monomers, the kinetic of paper degradation for random acid-hydrolytic reactions follows a first-order law with respect to the number of unbroken glycosidic bonds, which leads to the Ekenstam equation (Eq. 3) (Ekenstam 1936):

$$\frac{1}{DP} - \frac{1}{DP_0} = kt \quad (3)$$

where DP and DP_0 represent the degree of polymerisation of cellulose at time t and 0, respectively, and k is the rate constant (t^{-1}). In analogy with the Ekenstam equation, Fig. 5 displays plots of the reciprocal DP versus oxidation time (instead of the degradation time) for non-recycled and recycled papers.

Figure 5 shows that, at least for our relatively short oxidation times, the plots display good linear correlations. In accordance with Eq. 3, the slopes lead to the evaluation of the corresponding pseudo rate constants. Table 1 reports these values and the corresponding correlation coefficients (R^2).

This approach also highlights that the three recycled papers are less sensitive to the oxidation treatment in terms of depolymerisation. This behaviour can be ascribed to different extents of crystallinity of the samples, as suggested by Łojewski et al. (2010). The trend of crystallinity index values calculated as the ratio between the FTIR absorbance at 1372 and 2900 cm^{-1} (Kato and Cameron 1999; Łojewski et al. 2010) is $Wh < A < RW < RU < RN$. The higher crystallinity of the recycled papers can thus be associated with a higher resistance to depolymerisation. Interestingly, the most sensitive paper resulted to be Wh, which is made of pure cellulose, with no ash, lignin and additives, that is, the most expensive among the five papers considered. The high sensitivity of model paper likely stems from the absence of alkaline reserve. However, lignin content may also play a role

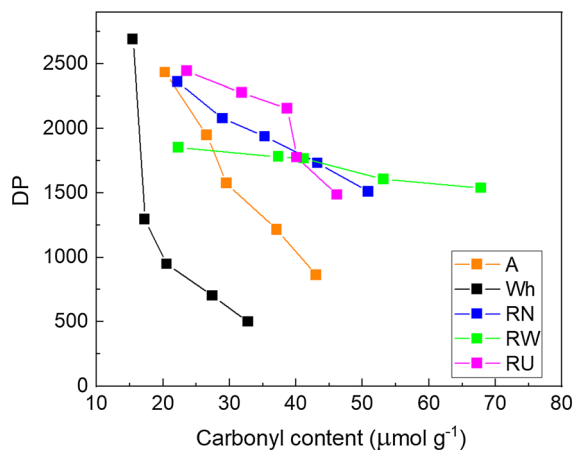


Fig. 4 DP as a function of carbonyl content ($\mu\text{mol g}^{-1}$) for the five types of paper considered

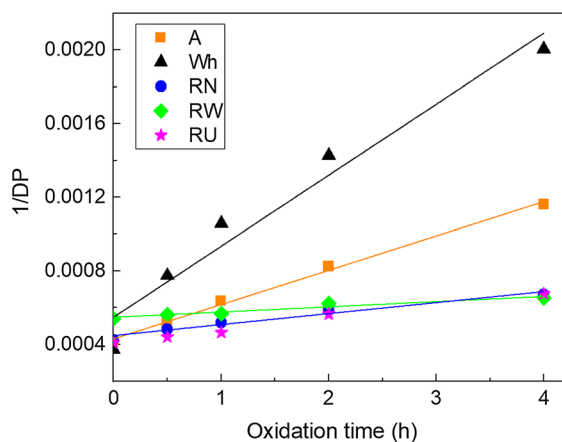


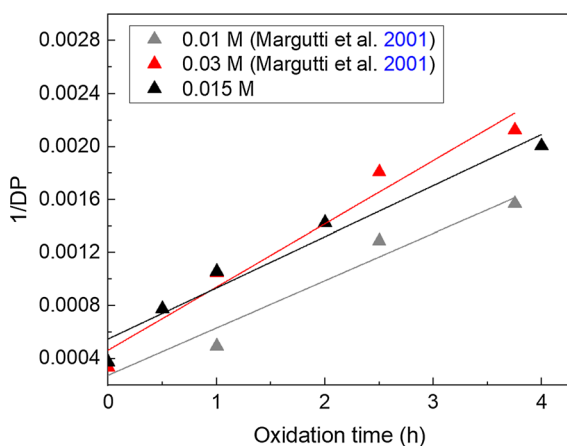
Fig. 5 Reciprocal DP as a function of oxidation time for the non-recycled and recycled papers considered

Table 1 Pseudo rate constants calculated for the papers considered with the corresponding uncertainties and correlation coefficients (R^2)

Paper sample	$k \times 10^5$ (h^{-1})	R^2
A	18.66 ± 0.71	0.996
Wh	38.62 ± 4.70	0.96
RN	5.985 ± 0.65	0.97
RW	2.840 ± 0.44	0.93
RU	6.814 ± 0.43	0.99

in these differences. It has been reported that lignin-containing pulps are significantly affected in terms of yellowing (due to an increase of carbonyl groups, which are chromophores) upon oxidation, while maintaining their strength and DP (Schmidt et al. 1995). Future developments of the present study could investigate the role of lignin.

A previous study (Margutti et al. 2001) has reported on the effects of different concentrations of sodium periodate oxidation on Whatman filter paper No 1 (Wh) in terms of $[\eta]$ and DP. Viscometry was performed using the CED solvent, but the DP values were calculated using Eq. 1 with different coefficients. Therefore, for the sake of direct comparison with the present DP values, those reported by Margutti et al. (2001) were recalculated using the coefficients suggested by Evans and Wallis (1987) (see Eq. 1). The comparison in terms of reciprocal of DP as a function

**Fig. 6** Reciprocal of DP as a function of oxidation time for Wh paper: present results (black) and data reported in Margutti et al. (2001) (red and grey)

of oxidation time for Whatman paper samples is displayed in Fig. 6.

A good linearity is also observed for the data previously reported (Margutti et al. 2001). It is worth noting that the plot obtained in the present study by oxidation in 0.015 M KIO_4 is placed in the middle between those derived from Margutti et al. (2001). Table 2 compares the evaluated pseudo rate constants for Wh oxidised in 0.01 and 0.03 M NaIO_4 with that obtained here.

It has recently been reported (Coppola et al. 2018a) that the degradation rates found for RW and A, aged at different conditions of temperature and water vapour pressure, are comparable within the experimental uncertainties, although those found for the recycled paper (RW) are slightly higher than those found for the non-recycled paper (A). The present results show that the extent of depolymerisation due to oxidation with periodate, in contrast to that due to accelerated ageing, is influenced by the type of paper.

It is well known that pH plays a crucial role in the kinetics of paper degradation. An increase of pH from 4 to 8 was found to cause a decrease of the degradation rate of pure cellulose by a factor of 3 (Kočar et al. 2005). Table 3 reports the pH values measured for the five types of paper considered here, following the procedure reported by Strlič et al. (2004).

It is to be noted that the pH values of the A and RW papers are in good agreement with those found in a previous study (Coppola et al. 2018a). However, it is worth noting that a decrease of the pH values by at least one unit upon addition of an electrolyte (few drops of NaCl solution) was observed. This finding is plausibly to be ascribed to an instrumental error when the ionic strength is extremely low (Strlič et al. 2004). Accordingly, the pH of Whatman paper should be nearly neutral (Kočar et al. 2005; Neves et al. 2009), as it is made of pure cellulose, free from additives.

Table 2 Pseudo rate constants (see text) for Wh paper obtained in the present study and those derived from Margutti et al. (2001)

Oxidant	Concentration [mol L^{-1}]	$k \times 10^5$ (h^{-1})	R^2
NaIO_4	0.01	35.75 ± 4.94	0.96
NaIO_4	0.03	47.76 ± 6.44	0.96
KIO_4	0.015	38.62 ± 4.70	0.96

Table 3 pH values (average of three measurements) and standard deviations of the non-oxidised papers

Paper sample	pH
A	8.4 ± 0.2
Wh	8.5 ± 0.3
RN	9.3 ± 0.2
RW	8.6 ± 0.1
RU	9.1 ± 0.1

Probably, further work on the correct procedure and equipment to determine pH values in solutions with very low ionic strength should be carried out. Regardless of these limits, the pH values measured for all kinds of paper did not change significantly with the oxidation time. The pH values of the three recycled papers analysed resulted to be somewhat higher than those of the non-recycled ones (see Table 3). This finding can account for the lower rate of degradation in terms of DP. However, this is not the only factor as the A and RW papers have comparable pH values but sizeably different pseudo rate constants (see Table 1).

Conclusions

The effects of periodate oxidation on five different types of paper, recycled and non-recycled, were evaluated. Previous accelerated ageing experiments have shown that two types of paper analysed in the present study (the non-recycled and recycled papers labelled A and RW, respectively) degrade similarly. However, the present results indicate that oxidation influences the chemical properties (degree of polymerisation (DP) and carbonyl content) of the investigated paper types to different extents, thus stimulating further work to study these different behaviours. The formation of carbonyl groups in the recycled papers is found to be larger than that in the non-recycled ones. Nevertheless, the present results show that the oxidation process causes a larger degradation in the non-recycled papers in terms of reduction of the average DP, as measured with viscometry. Regardless of these differences, the present findings suggest that oxidation by the specific agent periodate, which attacks the C2–C3 ring bond, favours random hydrolysis with scission of the glycosidic bonds. The degradation data obtained in the present study for the model Whatman paper (Wh)

oxidised with a periodate solution are comparable to those previously reported in the literature.

For the first time, this study shows that, in accordance with the Ekenstam equation, the reciprocal of DP as a function of oxidation time is found to give good linear correlations for all types of paper investigated. The degradation rates calculated for the non-recycled papers result to be higher than those of the recycled papers. The most sensitive paper in terms of DP decrease results to be the model Wh paper made of pure cellulose, in line with the absence of alkaline reserves. More in general, the three less expensive (recycled) papers analysed here prove to be degraded to a lesser extent by the action of a specific oxidant.

Acknowledgments AM and FC thank the Italian Ministero dell'Istruzione, dell'Università e della Ricerca for financial support.

Funding Open access funding provided by Alma Mater Studiorum - Università di Bologna within the CRUI-CARE Agreement.

Availability of data and material Data generated during this study are included in this article.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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