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Myung-Joon Jeong, Anne-Laurence Dupont, E. René de La Rie. Degradation of cellulose at the wet-dry interface: I - study of the depolymerization. *Cellulose*, 2012, 19, pp.1135-1147. 10.1007/s10570-012-9722-4 . hal-01491167

**HAL Id: hal-01491167**

**<https://hal.science/hal-01491167>**

Submitted on 22 Mar 2017

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# Degradation of cellulose at the wet-dry interface: I—study of the depolymerization

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Received: 5 October 2011 / Accepted: 5 May 2012 / Published online: 22 May 2012  
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**Abstract** The degradation of cellulose in paper due to the formation of a tideline at the wet-dry interface when paper is suspended in water was explored. SEC/MALS was used to assess the molar mass, while ICP/MS, SEM/EDS and CE/UV provided a qualitative and quantitative analysis of the elements and inorganic ions present in the paper. Immediately after the formation of the tideline, no significant depolymerization was observed at the wet-dry interface, despite the accumulation of water soluble brown and/or fluorescent degradation compounds and salts containing sodium, chlorine, sulfur and calcium. Various artificial aging configurations were applied to the paper with tidelines to evaluate the effect of the material accumulated at the wet-dry interface on the long-term stability of paper. The decrease in the molar mass of cellulose (above, at and below the tideline) differed depending on the type of aging, i.e. whether the entire sheet of paper was aged or whether small amounts of paper from the different areas were sampled and aged, individually or together, which evidences a complex degradation pathway. In

the former aging configuration the material accumulated in the tideline affected the degradation of the tideline area to the same extent or more than the other areas. When the different areas of the paper sheet were sampled and aged together, it was found that the presence of the tideline clearly affected the degradation of the other paper areas. Conversely, in that case, cellulose within the tidelines was the least degraded. The area below the tideline, through which the water migrated, showed the most significant degradation.

**Keywords** Cellulose · Molar mass ·  
Wet/dry interface · Artificial aging

## Introduction

Many historical papers and books display brown lines, so-called ‘tidelines’, which may form at the wet-dry interface upon water or moisture exposure (Bone 1950; Hofenk de Graaff 1994; Eusman 1995; Dupont 1996a; Madaras and Turner 1953). Tidelines exhibit not only brown discoloration but also fluorescence under UV (Pedersoli et al. 2000). Wet cleaning treatment is often carried out by paper conservators to remove the unsightly tidelines on valuable graphic documents. However especially when applied locally, wet treatments increase the risk of producing additional wet/dry interfaces and hence the risk of forming

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new tidelines. A better understanding of the tideline phenomenon is thus of relevance to the conservation, storage and the treatment of cultural objects made of paper. An understanding of the process is also of general relevance to the understanding of cellulose degradation chemistry.

In spite of various research efforts, the degradation products present in the tidelines have still not been fully identified due to the apparent complexity of the mixture but also due to the presence of extraneous material such as natural components and additives in the paper. Acetic acid, formic acid, formaldehyde, and other degradation products from paper such as neutral- and acidic sugars (D-glucose, D-arabinose, D-galactose, D-glucuronic acid, D-gluconic acid) and their  $\delta$ -lactones have been identified (Bogaty et al. 1952; Hofenk de Graaff 1994; Dupont 1996b). The organic acids, products of cellulose oxidation, are of special interest considering that cellulose is subjected to degradation by acid-catalyzed hydrolysis during the lifetime of paper. Cellulose hydrolysis occurs naturally at a very low rate under normal atmospheric conditions, and is accelerated in the presence of acids (Fengel et al. 1984). A decrease in the degree of polymerization directly affects mechanical properties of paper, such as tensile, tear, bursting strength and folding endurance (Venter 1968; Levlin et al. 1999). Hydroperoxides, also shown to be generated during tideline experiments (Souguir et al. 2008), are evidence that oxidation reactions take place. It is therefore also likely that free radical species, such as peroxy and hydroxyl radicals are being formed. Metal ions, such as Fe, Cu and Mn, catalyze decomposition of hydroperoxides, and hydrogen peroxide via the Fenton reaction, thereby generating hydroxyl radicals.

For a better understanding of the effects of tideline products on the stability of paper it is important to study these depolymerization reactions at the wet-dry interface and in neighboring areas upon accelerated aging. It was decided to use artificial aging at 100 °C in closed tubes. It has been shown that acids, produced by oxidation reactions, catalyze hydrolytic depolymerization of cellulose during artificial aging (Meller 1955; Shahani and Harrison 2002). It has been suggested that oxidation reactions also directly contribute to the depolymerization (Hastrup et al. 2011), but to what extent this occurs is not yet clear.

In previous research it was found that a sheet of paper subjected to a tideline experiment and

subsequently artificially aged underwent faster depolymerization at the tideline than in other areas, and more degradation occurred in the area that had undergone the passage of water (area below the tideline) than in the area that had not been wetted (area above the tideline) (Souguir et al. 2008). However the influence of the tideline on neighboring paper areas as a result of cross-contamination during aging had not been explored. In this research, the molar mass and molar mass distribution (MMD) of cellulose sampled in the tideline and in the neighboring areas after accelerated aging were evaluated using size-exclusion chromatography with multi angle light scattering detection (SEC-MALS). The elemental composition and the inorganic anions content of the paper were also examined. A simple paper made of pure cellulose with no additives was chosen so as to simplify the experimental model.

## Experimental

### Materials and chemicals

Pure cellulose Whatman No.1 paper sheets (15 cm  $\times$  28 cm) composed of 100 % cotton cellulose fibers were used to produce tidelines. *N,N*-dimethylacetamide, lithium chloride anhydrous and methanol were purchased from Fluka.

### Production of tidelines

The papers were suspended vertically; the lower end immersed 2 cm deep in deionized water (Millipore) during 8, 16 and 48 h at a temperature (T) of 23 °C and relative humidity (RH) of 50 %. The wet/dry interface stabilized in about 2 h. After formation of the tideline, samples were dried in ambient air and equilibrated for at least 1 day in the same T/RH conditions as stated above.

To obtain a second tideline on the same sample, the sheet was dried in ambient conditions for 24 h after the formation of the first tideline, and placed again in water according to the same procedure. In that case, the migration time for the first and second tidelines was 16 h each. The secondary tideline formed below the first tideline.

## Tideline extractives

The compounds accumulated at the tideline (about 120 mg) were extracted by stirring the paper samples for 1 day in 3.0 ml of deionized water. The extractives were dried at ambient condition after filtration using 0.2  $\mu\text{m}$  pore PTFE filter (Millipore). For calculating the extractives content in the tideline, the sample was dried in an oven ( $105 \pm 1$  °C) for 24 h. Solvent extractives content in Whatman No.1 was measured according to a modified standard method TAPPI T 204 cm-97 where, instead of dichloromethane or a mixture ethanol/benzene, acetone was used as it is less toxic and has been shown to give higher extraction yields (Jansson 2009).

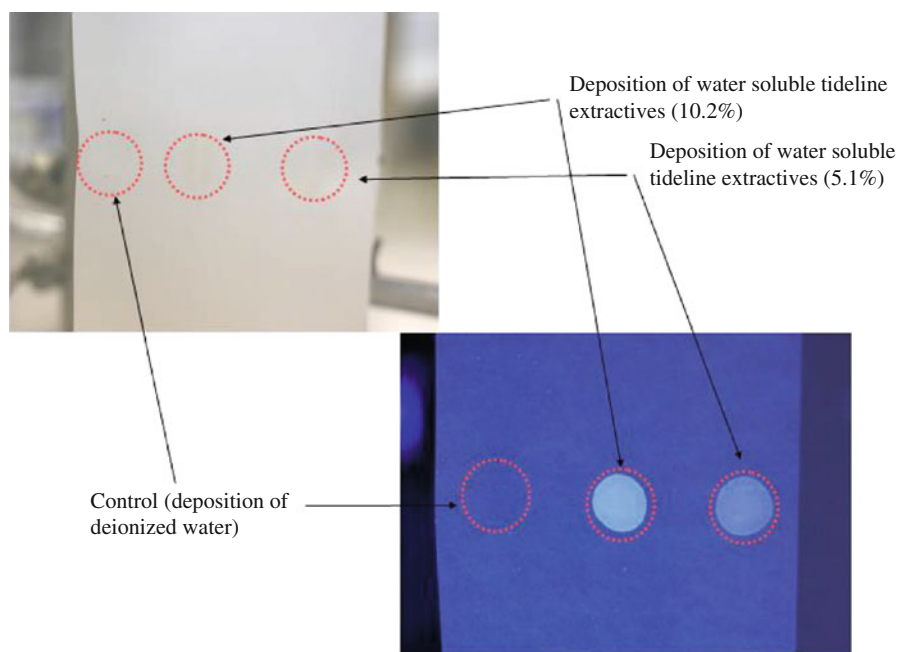
To evaluate the impact of tideline material on clean paper, the dried extractives were re-dissolved in water at 13 and 26 % (wt/vol). A 15  $\mu\text{l}$  drop of each concentrated tideline solution was deposited on clean paper (Fig. 1). The final content of the extractives in the paper in the small circular wetted area was 5.1 and 10.2 % (wt extract/wt paper), respectively.

## Artificial aging

In order to better evidence trends in the degradation and possibly extrapolate the data to historical artifacts, papers were artificially aged. One aging

procedure (type A) was carried out in large tubes where an entire sheet of paper with a tideline or, alternatively, a sheet of paper with drops of tideline water soluble extractives was placed (Wheaton hybridization tubes, 35 mm internal diameter (ID)  $\times$  147 mm, 144 ml), according to ASTM standard method D6819-02e02 (ASTM 2002: Standard Test Method for Accelerated Temperature Aging of Printing and Writing Paper by Dry Oven Exposure Apparatus). In the second and third aging procedures (types B and C), smaller vials were employed (9 ml crimp cap vials with PTFE/butyl cap). In type B, namely ‘single-sample’ aging and in type C, namely ‘multi-sample’ aging, samples taken in different areas of the sheet were aged individually (no tideline present) or in the presence of tidelines, respectively. The mass of paper placed in the vial was then scaled down to 250 mg in order to follow the ratio of sample weight to vial volume as in the ASTM D6819-02e02 standard. The preconditioning of the paper and the vials prior to aging was the same as in ASTM D6819-02e02 (23 °C, 50 % relative humidity). After aging, the samples were cooled at room temperature for 1 h before opening the tube or vial. In all cases the aging was carried out at 100 °C for 2 and/or 5 days. Table 1; Fig. 2 describe and illustrate the different aging types and conditions.

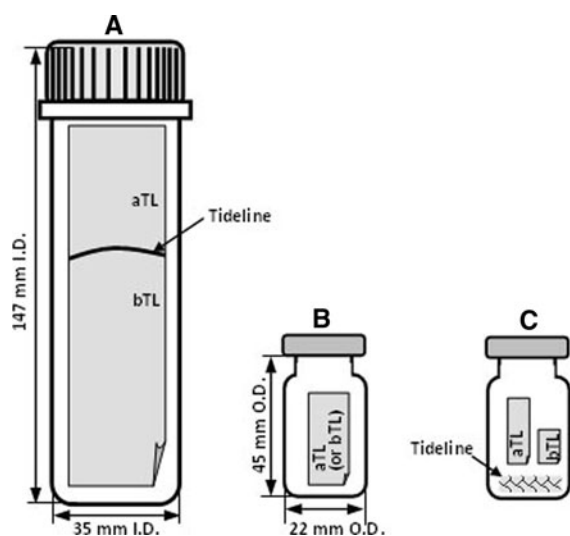
**Fig. 1** Tideline water soluble extractives deposited on Whatman paper No. 1 under visible (top) and ultraviolet (bottom) light



**Table 1** Weight and proportion (% wt/wt) of each sample to total weight of paper used for each aging type (A, B and C)

|     | A                                   | B                                             | C                                            |                    |                  |                   |
|-----|-------------------------------------|-----------------------------------------------|----------------------------------------------|--------------------|------------------|-------------------|
|     |                                     |                                               | Multi-sample aging in crimp cap vials (9 ml) |                    |                  |                   |
|     | Whole sheet aging in tubes (144 ml) | Single-sample aging in crimp cap vials (9 ml) | C1                                           | C2                 | C3               | C4                |
| aTL | About 4.0 g                         | 250 mg<br>(100 %)                             | 225 mg<br>(90 %)                             | 187.5 mg<br>(75 %) | 125 mg<br>(50 %) | 125 mg<br>(50 %)  |
| bTL | About 4.0 g                         | 250 mg<br>(100 %)                             | –                                            | –                  | –                | 62.5 mg<br>(25 %) |
| TL  | About 10 mg                         | –                                             | 25 mg<br>(10 %)                              | 62.5 mg<br>(25 %)  | 125 mg<br>(50 %) | 62.5 mg<br>(25 %) |

TL tideline, aTL above tideline, bTL below tideline



**Fig. 2** Scheme of the different types of accelerated aging. **A:** entire sheet with a tideline (as represented) or sheet with drops of tidelines extracts in 144 mL tube, **B:** single-sample aging (samples aged individually) in 9-mL vial; **C:** multi-sample aging (aTL and/or bTL with TL) in 9-mL vial

### Color measurements

Color measurements were carried out with a hand-held spectrophotometer SP 64 (X-rite) equipped with an integrating sphere. The configuration adopted was in reflectance mode (spectral range 400–700 nm in 10 nm steps), with the specular component included, using the 5 mm diameter aperture. The colorimetric coordinates values  $(L, a, b)^*$  were calculated in the CIE\*Lab76 Color System, with the D65 Standard Illuminant and 10° Standard Observer (Markus 1998). Based on the  $(L, a, b)^*$  values measured the total

colour change  $\Delta E^*$  occurred on a given sample was calculated as follows:

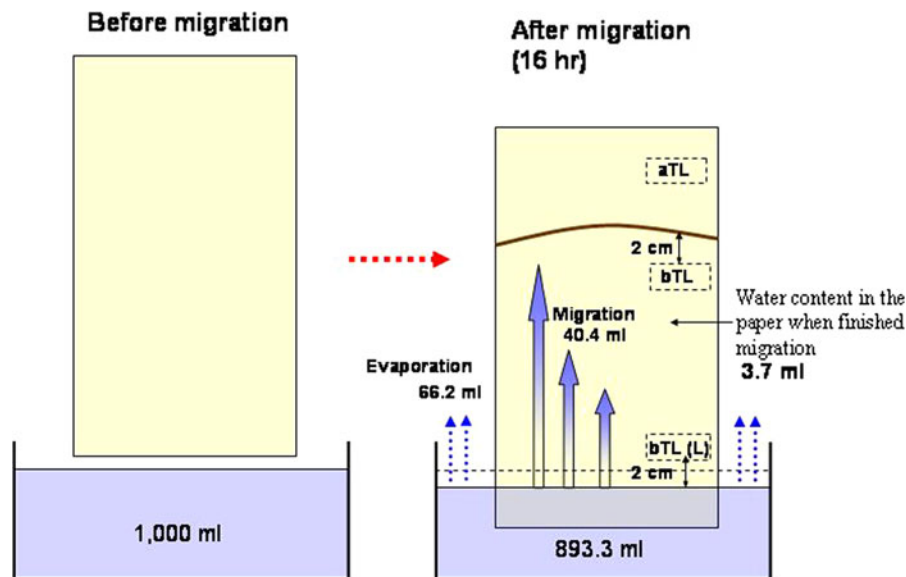
$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}.$$

### Molar mass determinations

Three to four areas in the paper were analyzed after the tideline experiment (Fig. 3): the tideline (TL), the area above the tideline (aTL), the upper area below the tideline (bTL) and, in some cases, the lower area below the tideline near the water level (bTL (L)).

The macromolecular characterization of cellulose was carried out by measuring the molar mass and molar mass distribution (MMD) using size-exclusion chromatography with multiangle light scattering and differential refractive index detection (SEC-MALS-DRI). The dissolution of the paper samples prior to the analysis was carried out in *N,N*-dimethylacetamide with 8 % lithium chloride according to a procedure detailed in a previous publication (Dupont 2003). An isocratic HPLC pump 515 (Waters), autosampler ACC-3000T (Dionex), Dawn EOS MALS detector (Wyatt Technologies), and 2414 (Waters) differential refractive index (DRI) detector were part of the chromatographic set-up. The separation was carried out on a set of three polystyrene divinyl benzene (PSDVB) columns Phenogel Linear(2) (5- $\mu$ m particle-diameter mixed bed pores columns, Phenomenex) preceded by a guard column Phenogel (5- $\mu$ m, Phenomenex). The columns compartment and the MALS detector were thermostated at 60 °C, the DRI was set to 55 °C. The mobile phase was *N,N*-dimethylacetamide with 0.5 % lithium chloride (wt/vol). The system was

**Fig. 3** Scheme showing water migration and evaporation during the tideline experiment and the different sampling areas in the paper sheet (16 h migration, Whatman filter paper No. 1, 28 cm × 15 cm)



operated at a flow rate of  $0.4 \text{ mL min}^{-1}$  with an injection volume of  $100 \text{ }\mu\text{L}$ . Each sample solution was run two times non-consecutively. The repeatability of the method as previously determined was  $\text{RSD } \% = 2.5$  on  $M_w$  for 3 separate cellulose samples analyzed two to three times non-consecutively.

#### Inorganic content in the paper

Several techniques were used to assess the elements and inorganic salts content in the paper samples.

#### *Inductively coupled plasma mass spectroscopy (ICP/MS)*

An ELAN DRC instrument (Perkin Elmer) was used. The decomposition of the paper samples was carried out in nitric acid for 20 min using the microwave sample preparation system (Q15, Questron Technologies) at 400 W (Lee et al. 2011). The decomposed samples were diluted 1,000 times in deionized water, and then filtered using  $0.45 \text{ }\mu\text{m}$  pore PTFE filter (Millipore). The content in the elements Na, Mg, Al, Si, P and K was measured.

#### *Scanning electron microscope and energy-dispersive spectroscopy (SEM/EDS)*

A variable pressure scanning electron microscope JEOL JSM-5410LV was used to examine the samples.

The accelerating voltage was 20 kV and the pressure was 0 Pa. Samples were observed using back-scattered electron imaging. The mapping was done over the same area by energy dispersive X-ray spectrometry (EDS) by means of an Oxford Instruments Link PentaFET Si(Li) detector and the software ISIS Link. The EDS operating conditions were as follows: accelerating voltage 20 kV, ATM windows, take off angle  $30^\circ$ , working distance 20 mm, count time 50 s, approximate dead time 15 %.

#### *Capillary electrophoresis with UV detection (CE/UV)*

A P/ACE MDQ equipped with a photodiode array detector was employed (Beckman Coulter). The system operation, data acquisition, calibration, and quantitation were performed using 32 Karat 5.0 software (Beckman Coulter). The compounds were identified according to their migration time compared to standard compounds. UV detection was used at 233 nm. Data collection rate was set to 4 Hz. A bare fused silica capillary with  $75 \text{ }\mu\text{m}$  ID was cut to a total length of 61 cm (50.4 cm effective length to the detection window). Prior to injection the capillary was rinsed by flushing 1 min with NaOH 0.1 M followed by 1.5 min with deionized water. It was then conditioned for 1 min with the running buffer. CEofix Anions5 pH 5.4 (Beckman) was used as background electrolyte (BGE). The injection was made in hydrodynamic mode by applying a pressure of 0.7 psi for

4.5 s. A separation voltage of 30 kV was applied to the anodic end. The run temperature was 25 °C. After each analysis the capillary was rinsed for 2 min with deionized water. The sample was prepared with 60 mg of paper suspended in 2 mL water for 1 h. The extract was filtered with 0.22 µm pore PTFE filter before injection. The calibration curves for the quantitation of the anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were built with NaCl,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  using seven solutions of increasing concentration (25, 50, 100, 150, 200, 250 and 300  $\text{mgL}^{-1}$ ).

## Results and discussion

### Tideline extractives

Usually the tideline formed around 17 cm in height above the water surface (Fig. 3). On average 40.4 ml of water migrated through the area below TL in 16 h, 36.7 ml of which evaporated during the experiment and 3.7 mL remained in the paper at the end of the migration.

The average tideline (16 h-migration) dry extractives content was 8.88 % (wt/wt sampled area) with a small variation (RSD 12.4 %), which may be caused by slightly different temperature and relative humidity conditions and by slight variations in sample size. The acetone extractives content of Whatman No.1 (equivalent to aTL) was below 0.06 % (wt/wt), which does not account for the full amount of extractives produced by water migration in the tideline. Even considering that pre-existing naturally aged products in bTL as well as residual extraneous material other than cellulose in paper can contribute to the brown and fluorescent material present at the tideline, the large amount of TL water extractable material suggests that it originates from compounds formed during the experiment, at or below the wet/dry interface. The relatively large quantities of formic acid and acetic acid that form at the wet/dry interface and reform *de novo* upon successive tideline experiments, as well as the hydroperoxides found (Souguir et al. 2008), which contribute to paper degradation, further supports this hypothesis.

Table 2 shows the results of the ICP/MS analyses of the major mineral elements present in the samples. Aluminium, silicon and phosphorus were found in every area, while magnesium, potassium and

**Table 2** Major mineral elements content in ppm (wt/wt) of aTL and TL (ICP/MS)

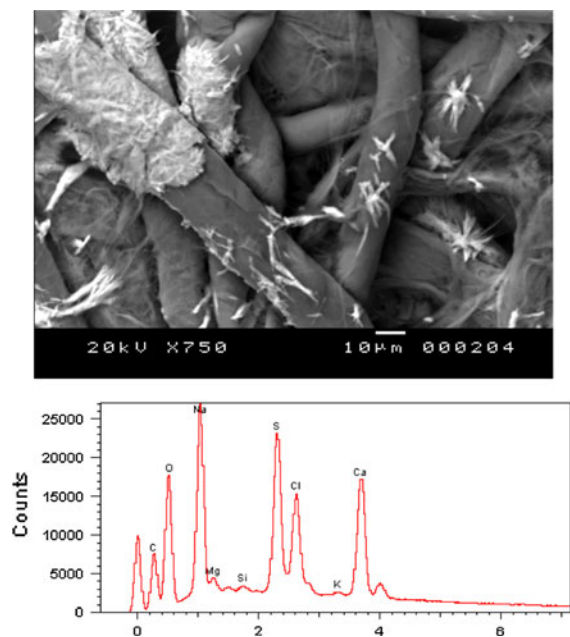
|            | aTL  | TL    |
|------------|------|-------|
| Sodium     | 55.6 | 811.9 |
| Magnesium  | 2.8  | 20.2  |
| Potassium  | 3.1  | 62.1  |
| Phosphorus | 35.8 | 30.5  |
| Silicon    | 41.9 | 42.7  |
| Aluminum   | 2.7  | 2.9   |
| Iron       | 3.05 | 3.15  |
| Copper     | 0.33 | 0.78  |
| Manganese  | 0.05 | 0.27  |

especially sodium, the latter being by far the most abundant, were found mostly accumulated at the tideline. These elements arise probably from the plant and the water used for pulping. Those that accumulated in TL may be in the form of salts, which can migrate with water. Small amounts of transition metals (Fe, Cu, Mn) were also evidenced. Their presence is known to favor Fenton reactions, which have been suggested to induce cellulose degradation (Hastrup et al. 2011; Rouchon et al. 2011).

The SEM/EDS analysis (Fig. 4) shows that crystals formed in the tideline area, which supports the ICP/MS results. While the morphology of the fibers at the tideline seems unaffected, the elemental composition of the crystals (S, Ca, Cl, Mg, Si, K) indicates that, in all likelihood, these are sodium and calcium salts (possibly  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$  or  $\text{CaSO}_4$ ). The presence of alkaline salts is consistent with the pH 7.6 obtained for the water soluble TL extract (measurement according to TAPPI T509 om-88) while both aTL and bTL had a pH of 5.8.

Figure 5 shows the electropherograms of the extracts of paper in the different areas with the anions identified and quantified with CE/UV. The presence of chlorides, sulfates and nitrates was evidenced in the paper extracts, which supports the above reported results. In all areas, chloride was the most abundant, and a significant amount was found in the tideline.

The presence of minerals and salts in the tidelines, such as silicates, calcium and sodium salts should contribute to the buffering of some of the acidity present, which would subsequently lower the hydrolytic degradation of cellulose at the tideline during aging. This also implies that the formate and acetate



**Fig. 4** SEM image of the fiber surface at the wet-dry interface (*top*) and EDS analysis of one of the crystallized salts spot (*bottom*)

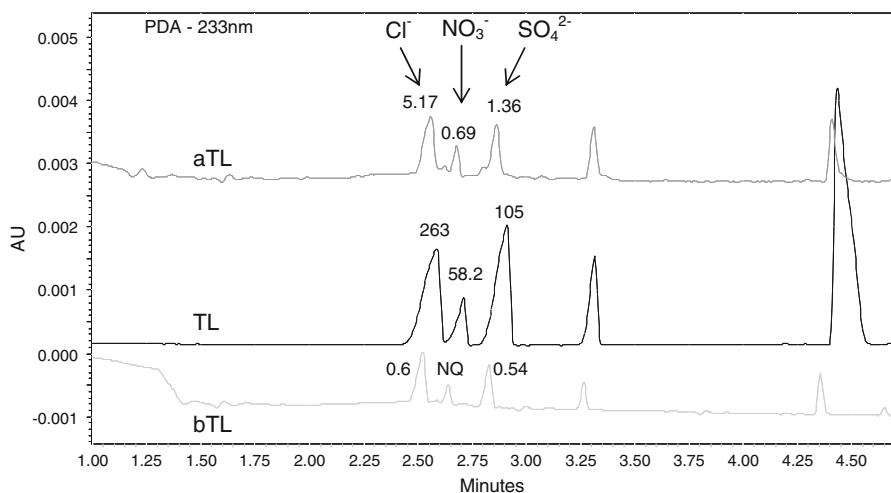
anions detected by CE/UV in large quantities in the tideline as reported in a previous publication by the authors (147.4 and 223  $\mu\text{mol g}^{-1}$ , respectively) (Souguir et al. 2008) would easily form salts, if they can react with the inorganic cations, since with  $\text{pK}_a$  of 3.77

and 4.79 respectively, both should be carboxylates at pH 7.6. However, it has to be recalled that the pH measurement is made on a bulk aqueous extract and it does not necessarily reflect the exact pH across the cellulose fibers at the supramolecular level. Indeed, as seen on the SEM image (Fig. 4), the minerals accumulated at TL are topically distributed in patches due to local recrystallizations, which implies that not all the organic acids produced during degradation in the cellulose fibers at the mesoscopic level will be able to interact to form carboxylic salts, and thus can also still be present in their protonated form in the areas where no crystals are present.

#### Molar mass determinations and color measurements

The weight-average molar mass ( $M_w$ ) of cellulose for aTL, TL and bTL before aging was similar, 548 ( $\pm 2.1\%$ )  $\text{kg mol}^{-1}$ , 555 ( $\pm 1.7\%$ )  $\text{kg mol}^{-1}$  and 543 ( $\pm 1.4\%$ )  $\text{kg mol}^{-1}$ , respectively, indicating that no measurable depolymerization took place during the experiment.

To evaluate the long-term effect of the presence of tidelines in paper, color measurements were carried out (except on the tideline which is too thin for the spectrophotometer probe) and the molar mass of cellulose of the samples artificially aged (types A, B



**Fig. 5** Electropherograms of aqueous extracts of paper (aTL, TL and bTL) with quantitation for the anions  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in  $\mu\text{moles per gram of paper}$  (NQ: not quantifiable, i.e. below LOQ). Peak at 4.3–4.4 min is formate. Capillary

75  $\mu\text{m} \times 61$  cm. BGE CEofix Anions5 pH 5.4. Hydrodynamic injection 0.7 psi, 4.5 s; applied potential 30 kV; temperature 25  $^\circ\text{C}$ ; detection 233 nm

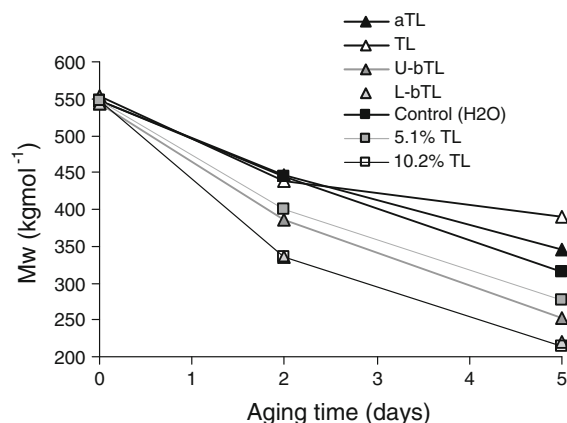
and C) was measured. As expected, the values of  $M_w$  of all the samples decreased upon aging.

#### Aging type A

**Sheet with drops of TL extractives** Table 3 shows the  $(L, a, b)^*$  and  $\Delta E^*$  values as a function of aging for the sheet of paper on which drops of tideline extractives were deposited. The two areas where the tideline extractives were deposited showed a larger color change and darkening upon aging than the rest of the paper. The color change in the affected area was more weighted towards coordinates  $(+a^*)$  (red) and  $(+b^*)$  (yellow) than for the control sample, which discolored with the expected general tendency of Whatman No. 1 paper upon aging (Piantanida et al. 2005). This result suggests that the areas with the tideline extractives are the most degraded. This was confirmed by the molar mass characterizations:  $M_w$  of cellulose in the area with tideline extractives was smaller than in the area without tideline extractives (Fig. 6). Moreover, the extent of the degradation increased with the concentration of the tideline extract deposited. These results show that the tideline extractives had a strong adverse effect on cellulose during aging.

**Sheet with a tideline** Table 4 shows the  $(L, a, b)^*$  and  $\Delta E^*$  values for the sheet of paper with a tideline before and after aging. The areas bTL (and bTL(L)) exhibited a larger discoloration than aTL (TL is too thin to be measured with the available instrumentation).

Table 5 shows  $M_w$  of cellulose as a function of aging time in the different areas of a whole sheet of paper containing a tideline (formed as shown on



**Fig. 6**  $M_w$  ( $\text{kg mol}^{-1}$ ) of cellulose as a function of aging time (type A) for paper with tideline extractives and for a sheet with a tideline (not pre-wetted paper)

Fig. 3), and subsequently artificially aged. The area that degraded the most was bTL, and especially more so in the lower area, bTL(L), which had the smallest  $M_w$  ('not pre-wetted' data). This is consistent with the colorimetric measurements.

As moisture in paper can affect the rate of degradation, higher moisture content leading to more degradation during heat aging (du Plooy 1981; Welf 2005; Havlínová et al. 2009), the hydration state of the paper in the different areas was measured after producing the tideline (Table 6). Due to a difference in the temperature and relative humidity in the two locations where the measurements were done, it was observed that the moisture content of aTL area in 'condition 1' (5.39 %) was a little smaller than in 'condition 2' (5.70 %). In both cases, after climatic re-equilibration to TAPPI standard during one week,

**Table 3**  $(L, a, b)^*$  values of paper with and without tideline extractives as a function of aging time (aging type A: sheet with drops of tideline extract)

$\Delta E^*$  for any given sample is calculated using the corresponding unaged counterpart sample as reference

<sup>a</sup> The control sample was Whatman No. 1 on which an equivalent volume of  $\text{H}_2\text{O}$  was dropped

|                      | Aging period (days) | $L^*$ | $a^*$ | $b^*$ | $\Delta E^*$ |
|----------------------|---------------------|-------|-------|-------|--------------|
| Control <sup>a</sup> | 0                   | 96.89 | −0.08 | 2.10  |              |
|                      | 2                   | 96.42 | 0.14  | 3.96  | 1.92         |
|                      | 5                   | 95.36 | 0.38  | 5.56  | 3.76         |
| 5.1 % TL             | 0                   | 95.79 | −0.28 | 6.13  |              |
|                      | 2                   | 94.01 | 0.87  | 8.16  | 2.85         |
|                      | 5                   | 91.81 | 1.62  | 9.71  | 5.75         |
| 10.2 % TL            | 0                   | 94.71 | −0.22 | 9.30  |              |
|                      | 2                   | 92.46 | 1.56  | 10.33 | 3.21         |
|                      | 5                   | 89.63 | 2.44  | 11.29 | 5.91         |

**Table 4** ( $L^*$ ,  $a^*$ ,  $b^*$ ) values of paper with tideline as a function of aging time (aging type A)

| Aging period (days) | Area   | Not pre-wetted |       |       |              | Pre-wetted |       |       |              |
|---------------------|--------|----------------|-------|-------|--------------|------------|-------|-------|--------------|
|                     |        | $L^*$          | $a^*$ | $b^*$ | $\Delta E^*$ | $L^*$      | $a^*$ | $b^*$ | $\Delta E^*$ |
| 0 (control)         | aTL    | 96.74          | −0.19 | 1.91  |              | 96.60      | −0.14 | 1.80  |              |
| 2                   | aTL    | 96.06          | −0.03 | 2.90  | 1.22         | 95.99      | −0.05 | 2.94  | 1.29         |
|                     | bTL    | 95.76          | 0.05  | 3.38  | 1.79         | 95.84      | 0.03  | 3.26  | 1.70         |
|                     | bTL(L) | 95.73          | 0.06  | 3.31  | 1.75         | 95.29      | −0.02 | 2.75  | 1.72         |
|                     | aTL    | 95.42          | 0.10  | 4.28  | 2.73         | 94.74      | 0.29  | 5.01  | 3.73         |
| 5                   | bTL    | 94.72          | 0.31  | 5.44  | 4.10         | 94.04      | 0.54  | 5.94  | 4.96         |
|                     | bTL(L) | 94.59          | 0.36  | 5.55  | 4.27         | 94.22      | 0.49  | 5.73  | 4.74         |

$\Delta E^*$  for any given sample is calculated using the control (unaged) aTL sample as reference

**Table 5**  $M_w$ , ( $\text{kg mol}^{-1} \pm \text{RSD}\%$ ) of cellulose as a function of aging time (type A) for not pre-wetted and pre-wetted samples

| Aging period (days) | 0               | 2               |                 | 5               |                 |
|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                     |                 | Not pre-wetted  | Pre-wetted      | Not pre-wetted  | Pre-wetted      |
| aTL                 | 548 $\pm$ 2.1 % | 447 $\pm$ 4.4 % | 439 $\pm$ 4.3 % | 346 $\pm$ 4.2 % | 299 $\pm$ 1.0 % |
| TL                  | 554 $\pm$ 1.7 % | 439 $\pm$ 2.8 % | –               | 379 $\pm$ 8.8 % | –               |
| bTL                 | 543 $\pm$ 1.4 % | 386 $\pm$ 8.6 % | 374 $\pm$ 8.5 % | 252 $\pm$ 7.7 % | 225 $\pm$ 2.5 % |
| bTL (L)             | –               | 336 $\pm$ 2.1 % | 358 $\pm$ 1.2 % | 220 $\pm$ 1.3 % | 202 $\pm$ 3.4 % |

the moisture content in bTL(L) was about 0.7–0.8 points ( $\approx 12\%$ ) higher than in aTL (‘not pre-wetted’ data). The variation of moisture content in the different areas can be, at least partly, due to hysteresis effect, caused by breaking inter- and intramolecular hydrogen bonds between cellulose as result of the water absorption and desorption (Gruber et al. 2001 cited in Okubayashia et al. 2004). This result shows that the lower wetted part of the paper retains more moisture than the upper wetted part. The entire sheet was thus pre-wetted to cancel the hysteresis effect and ensure that the paper in aTL would re-equilibrate by water desorption, like bTL. The paper was then re-equilibrated at 23 °C and 50 % RH before the tideline experiments. In that case, the moisture content of aTL and bTL(L) were found almost similar (Table 6, ‘pre-wetted’ data). After aging, although  $M_w$  was slightly smaller after the pre-wetting than before for all the samples, it is noteworthy that bTL and bTL(L) were still more degraded than aTL; bTL(L) being as degraded as the paper sample with the 10.2 % concentrated TL drop (Table 5; Fig. 6). The  $\Delta E^*$  values of the samples aged 5 days are consistent with the  $M_w$  data, with, again, a larger discoloration in the area below the tideline (Table 4, ‘pre-wetted’ data).

This gradually increasing degradation in the area below the tideline must therefore be attributed to other factors than the small moisture content differences in the different areas of the paper while aging. As mentioned before, hydroperoxides and oxidation products such as small organic acids were shown to accumulate at the tideline (Souguir et al. 2008). These compounds and possibly also other oxidation products are likely to be formed in bTL during the water migration thus affecting the degradation of cellulose of that area.

The results also show that, unexpectedly, after 5 days of aging, TL was the least degraded sample (Table 5). Another observation is that there seems to be a fundamental difference in aging behavior between the paper on which drops of tidelines water extractives have been applied and the ‘real’ tideline produced on a paper vertically by water migration. The ‘real’ TL aged considerably less than any of the other samples. It is thus likely that the ‘real’ tideline contains material that was lost during the preparation of the aqueous extract, such as the alkaline compounds for instance, which, as mentioned earlier can counter-act the degradation of cellulose. Indeed when the dried TL aqueous extract was re-dissolved in water to obtain

**Table 6** Moisture content of the samples upon re-equilibrating in respective conditions

|         | Not pre-wetted |             | Pre-wetted <sup>a</sup> |
|---------|----------------|-------------|-------------------------|
|         | Condition 1    | Condition 2 | Condition 2             |
| aTL     | 5.39 ± 0.22    | 5.70 ± 0.06 | 6.41 ± 0.03             |
| TL      | 6.00 ± 0.21    | –           | –                       |
| bTL     | 6.00 ± 0.09    | –           | –                       |
| bTL (L) | 6.11 ± 0.43    | 6.51 ± 0.03 | 6.47 ± 0.05             |

Condition 1: 22.5 °C ± 0.5, RH 45 % ± 3, condition 2: 23.0 °C ± 0.5, RH 50 % ± 5

<sup>a</sup> Pre-wetted samples were immersed in deionized water for 1 h and re-equilibrated prior to the tideline experiment

**Table 7**  $M_w$  (kg mol<sup>-1</sup>) ± RSD% of the samples aged 5 days in the different configurations

| Sample  | Aging type |      |       |      |       |      |       |      |       |      |       |                  |
|---------|------------|------|-------|------|-------|------|-------|------|-------|------|-------|------------------|
|         | A          |      | B     |      | C     |      |       |      |       |      |       |                  |
|         |            |      |       |      | C1    |      | C2    |      | C3    |      | C4    |                  |
|         | $M_w$      | RSD% | $M_w$ | RSD% | $M_w$ | RSD% | $M_w$ | RSD% | $M_w$ | RSD% | $M_w$ | RSD%             |
| aTL     | 346        | 4.2  | 407   | 1.7  | 291   | 0.1  | 247   | 1.8  | 188   | 3.0  | 243   | N/A <sup>a</sup> |
| TL      | 379        | 8.8  | –     | –    | 345   | 1.1  | 331   | 2.8  | 309   | 8.0  | 349   | N/A              |
| bTL     | 252        | 7.7  | 367   | 0.1  | –     | –    | –     | –    | –     | –    | 212   | N/A              |
| bTL (L) | 220        | 12.5 | –     | –    | –     | –    | –     | –    | –     | –    | –     | –                |

<sup>a</sup> No RSD: only one measurement

the concentrated extract, it was observed that some of the crystals did not re-dissolve completely, probably due to limit of solubility, and were filtered out before the application on paper.

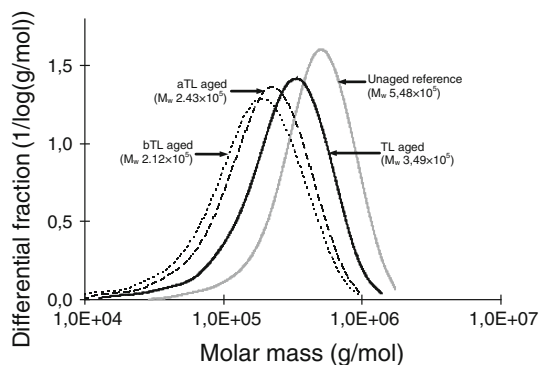
#### Aging types B and C

In the large tubes used for type A aging, the tideline accounted for about 0.25 % (wt/wt) of the entire paper sheet. In order to investigate whether the tideline material has an impact on the degradation of neighboring paper areas during aging, a larger percentage of tideline material with respect to the other areas (aTL and bTL) needed to be used. As TL material is available only in small quantities, the aging was carried out in smaller volume glassware (9 mL vials).

When aged with TL (multi-sample aging type C), aTL and bTL were more degraded than when aged individually (single-sample aging type B). Table 7 gathers the  $M_w$  data. In addition, the extent of the degradation of aTL increased with increasing percentage of tidelines present (aging types C1, C2, C3) (Fig. 8; Table 7). This result implies that some

material in the tideline favored the degradation of the other samples during the accelerated aging exposure. This, again, is consistent with the previous findings indicating the presence of larger concentrations of small organic acids and hydroperoxides in the tideline than in the other areas (Souguir et al. 2008). Some of these low molar mass species are either volatile or can migrate by contact so as to affect the degradation of neighboring paper samples in the vial. Not much information is available in the literature on the effect of volatile organic compounds (VOCs) on paper but it has been shown that organic acid vapors such as acetic acid and other VOCs can have an impact on the degradation of cellulose and on paper stability (Dupont and Tétreault 2000; Strlič et al. 2011).

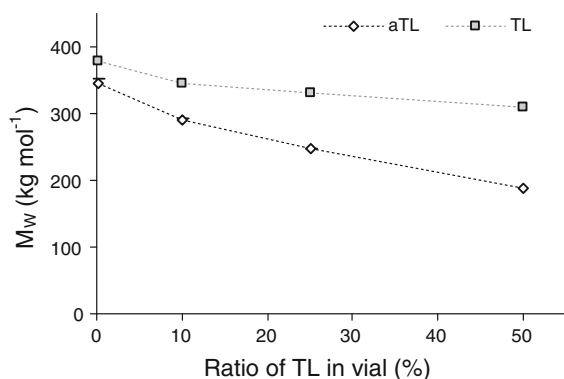
In type B aging, bTL was more degraded than aTL, which is consistent with the results obtained with type A aging (Table 7). Likewise, in type C4 aging, bTL underwent the largest decrease in  $M_w$ , while TL was clearly the least degraded of the three co-aging samples (Fig. 7). This corroborates the result shown earlier of the presence of alkaline salts in the tideline, able to partly counteract the hydrolytic degradation



**Fig. 7** Molar mass distribution of cellulose in the different areas of paper aged for 5 days (multi-sample aging type C4)

induced by the organic acids formed due to oxidation. It is also possible that some of the degradation compounds produced during the tideline experiment act as anti-oxidants. Phenolic compounds such as in lignin have been shown to inhibit autoxidative degradation of cellulose (Schmidt et al. 1995). Even though Whatman No.1 does not contain any lignin, aromatic compounds (furanic and phenolic) can arise from cellulose degradation (Lai 2001; Ramalho et al. 2009).

The results also show that the degradation of TL was proportional to its own percent weight in the vial, albeit to a much lesser extent than for aTL (Fig. 8). This is consistent with the hypotheses presented earlier. On the one hand in TL part of the organic acids are in the form of organic salts and part in the protonated form. The latter are volatile enough to contaminate neighboring paper and enhance hydrolytic degradation. The presence of larger amounts of

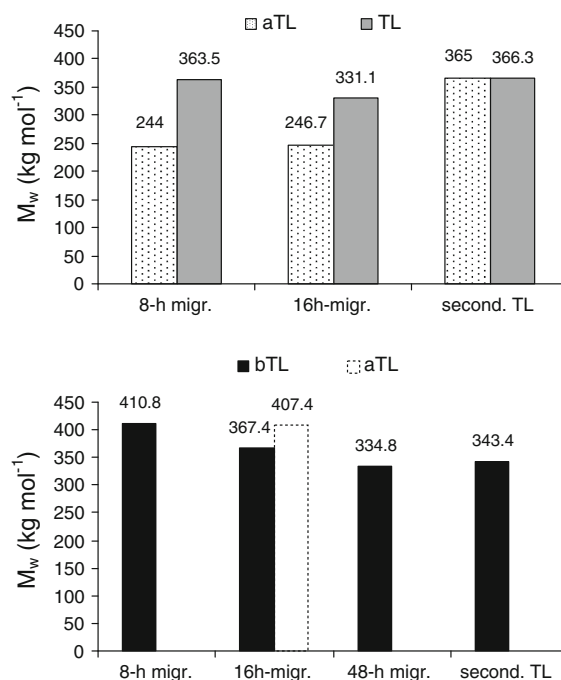


**Fig. 8**  $M_w$  (kg mol<sup>-1</sup>) of aTL and TL samples aged 5 days (various amounts of TL relative to aTL in the vial): whole sheet aging type A (0.25 %) and multi-sample aging types C1, C2, C3 (10, 25 and 50 %, respectively)

TL material produces a more concentrated acidic atmosphere in the vial, leading to a proportionally higher degradation of the cellulose of all samples in presence. On the other hand bTL is subject to a larger degradation. This is due to the formation of oxidized species during water migration to the wet/dry interface, which promote degradation.

Lastly, it was thought that water migration time could also be a factor affecting the degradation.  $M_w$  of papers in which the tideline was produced using different migration times was evaluated. Figure 9 (top) shows the results for the samples aTL and TL, when the tideline was produced in 8 h as compared to 16 h (after 5 days of multi-sample aging type C2). Results for 48 h migration are not shown as such a long time resulted in a wider yet more diluted tideline area, due to the slow recession process of the wet/dry interface upon prolonged time.

As observed for 16 h migration earlier, in the 8 h experiment, aTL degraded more than TL upon accelerated aging (Fig. 9 top). No difference in the degradation upon aging of aTL samples in terms of



**Fig. 9**  $M_w$  (kg mol<sup>-1</sup>) of samples produced with different migration times and aged 5 days. *Top.* aTL and TL after multi-sample aging type C2. *Bottom.* bTL after single-sample aging type B

migration time was observed, but for TL, the sample produced in 8 h migration was slightly less degraded than the sample produced in 16 h. This indicates that acids and other oxidized species in TL build up with time of migration. It is worth noting that the secondary tideline, despite presenting brown discoloration and fluorescence (although less intense than the primary tideline), did not affect the cellulose molar mass of aTL more than that of TL itself. However the lower  $M_w$  than that obtained when aTL was aged as a single sample, namely  $407 \text{ kg mol}^{-1}$ , shows that cross-contamination of secondary TL to aTL during aging still occurred, although to a lesser extent. Previous research by the authors showed that formic and acetic acids are produced continuously in successive tide-lines produced consecutively, but that their concentration decreased, with ratios first tideline to secondary tideline of 2 and 6 for formic and acetic acids, respectively (Souguir et al. 2008).

The degradation of bTL upon type B aging, conversely, increased as a function of water migration time, with bTL of the 48 h migration sample being the most degraded (Fig. 9 bottom). Here, for the secondary tideline experiment, bTL area was wetted during 32 h. Its  $M_w$  was indeed intermediary between that obtained for the 16 and 48 h samples. This result implies that the area of the paper through which the water travels undergoes continuous degradation during the experiment and supports the in situ formation of oxidized compounds able to promote the degradation, as suggested earlier. This consolidates further the hypothesis that reactive species are being formed during the migration of water and keep forming in the wetted area as long as the experiment continues.

## Conclusion

The evaluation of paper degradation at the wet-dry interface using size-exclusion chromatography showed that there was no obvious cellulose depolymerization immediately after the tideline formation. Conversely, during artificial aging in a confined environment it was found that the presence of tideline material strongly increased cellulose degradation. This was observed not only at the tideline location but also in co-aging neighboring areas aTL and bTL. The degradation pathway seems rather complex as a counter-degradation effect of the cellulose in the

tideline was also evidenced. The latter was attributed to the formation of alkaline salts that migrate with water and are able to buffer part of the acidity present. The elements and salts evidenced by ICP/MS, SEM/EDS and CE/UV can arise from the paper manufacturing. The different aging properties of cellulose at the tideline could thus be due to the presence of compounds which tend to slow the degradation (anti-oxidative material) as well as compounds that tend to promote it, such as organic acids (protonated form) and hydroperoxides. Some of these pro-degradation compounds are volatile as they were shown to affect the degradation of the neighboring paper areas in the aging vial during aging. Time of migration was shown to especially affect the area below the tideline, confirming the continuous formation of reactive species with time. The primary focus of this study was the examination of the depolymerization of cellulose during aging and more work has to be carried out to better understand the role of oxidative reactions during tideline experiments and relate them with the present findings. This will be the subject of a forthcoming (part II) publication.

**Acknowledgments** The CNRS, the Andrew W. Mellon Foundation and the Korea Research Foundation Grant funded by the Korean Government [KRF-2008-357-C00001] are acknowledged for financial support. Warm thanks are also due to Christopher Maines, Suzanne Lomax and Zied Souguir for useful discussions. We are also grateful to Sabrina Paris, Marie Schuler and Julien Barthez for their technical help.

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