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# Influence of the artificial weathering on thermal stability of paper-based materials

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**Abstract**

In this research the thermal stability of paper and its components are investigated, in order to evaluate the effect of the artificial weathering treatments, carrying on measurements of thermal gravimetry; also some SEM observations are performed to follow the degradative phenomena. Our work allowed to correlate the level of degradation of the artificially aged paper samples with that of the naturally aged ones.

TGA curves of the weathered samples show changes in respect to the starting materials; particularly, the chemical oxidation appears as the most degradative action in respect to the other physical treatments.


*Keywords:* Cellulose; Paper; SEM; TGA; Thermal stability

## 1. Introduction

Paper consists mostly of cellulose fibres, whose molecules are linear polymers of β-D-glucopyranose monomers linked by β-1,4-glycosidic bonds.

Cellulose is obtained from different plants (i.e. cotton, flax, bamboo, maize, sisal and hemp), from cotton and linen rags and from wood [1]. Depending on its source, each type of cellulose has particular characteristics that influence the properties and the stability of paper: for example, cellulose from native wood exhibits a degree of polymerisation (DP) up to 10,000, whereas for that from native cotton DP can reach values of 15,000 [2]. Consequently paper made by pulp wood has poorer quality in respect to that obtained from rags.

In addition to cellulose, paper contains also hemicelluloses, lignin and additives (inorganic fillers, dyes, pigments, metal ions, etc.) in different amounts depending on the source of cellulose and on the final use of the material, respectively.

Paper stability is a property related to the production processes and to the environmental conditions (temperature, humidity, presence of micro-organisms, etc.) in which the paper is stored. During the time paper undergoes unavoidable ageing processes that cause mainly the degradation of cellulose: these phenomena can involve acid substances and the moisture present in the material (acid hydrolysis), oxidative agents and the atmospheric $O_2$ (oxidation), micro organisms (biodeterioration), or the light (photodegradation). All these factors act cooperatively and lead to both the progressive shortening of the polymeric chains and the variation of the crystalline content of cellulose. At macroscopic level, the paper appears not only weaker, because its mechanical resistance is noticeably reduced, but also sometime the appearance becomes completely different from the original one [3].

In order to understand and explain the degradation processes occurring on paper during its life, it is necessary to perform a complete study of well-defined specimens, subjected to artificial weathering carried out in strictly controlled conditions. In this research we chose as "model samples" different paper-based materials, such as filter paper (Whatman), newsprint paper and paperboards and we selected three "physical" and one "chemical" methods to age the paper: at the first category belong the treatments in oven, in solarbox and in climatic chamber, whereas the chemical treatment consists in the oxidation with sodium metaperiodate ($NaIO_4$).

Periodate oxidation is a highly regioselective reaction: the oxidative agent attacks merely the C2–C3 bond on the glycosidic

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ring and converts the 1,2-dihydroxyl groups in two aldehyde groups, without modify the glycosidic bonds and without significant side reactions [4,5]. The resulting product is the dialdehyde cellulose (DAC) [6]. Since periodate oxidation of cellulose proceeds gradually from the amorphous to the crystalline phase, prolonged reaction time and higher oxidant concentration are necessary to access into the inner region of the polymer. Nevertheless, for verifying if this treatment can be considered as a correct way to simulate the degradation occurring on the paper stored in normal archives conditions, the oxidative reaction with sodium metaperiodate has been performed in mild conditions. Indeed in a previous study [7] we demonstrated how prolonged reaction time and high oxidant concentration lead to a progressive and deep destruction of cellulose-based materials that lose their typical characteristics and properties. Therefore, starting from these results, in the present research the oxidative treatment has been carried out in the following conditions: [$NaIO_4$] 0.1 M for 2 h; this can be considered suitable for our aims.

Depending on the type of samples, each weathering treatments induced several modifications in the structure and in the components of paper itself that have been followed by electron microscopy and thermal analysis.

Observations carried out by scanning electron microscopy (SEM) magnify the typical paper morphology, highlighting some effects of the weathering treatments; energy dispersive spectrometry (EDS) allows determining both the elemental composition and the nature of filler present in the samples.

Generally, thermal analysis represents a reproducible and practically convenient method to characterise heterogeneous organic materials, as paper. Differential scanning calorimetry (DSC) allows a rapid detection and measurement of the physicochemical changes that a polymer undergoes when subjected to heating, whereas, thermogravimetric analysis (TGA) provides a method for the determination of mass change in the polymer as a function of time and temperature: thus, both these techniques reflect reactions which occur at the molecular level of a polymeric material. In literature a large number of studies on thermal decomposition of cellulose, the main component of paper, were published, highlighting a lot of important practical interests regarding different fields (fire safety [8], production of chemicals [9], high temperature applications [10], etc.). In the case of paper, the thermal behaviour of its main components, as cellulose, hemicelluloses, lignin and fillers can be well investigated with DSC and TGA [11,12].

In a previous paper a detailed investigation by DSC, concerning the thermal degradation of oxidised cellulose-based materials compared with the corresponding unaged ones, has been already reported [7]. In the present research we studied by TGA the influence of the weathering treatments on the thermal stability of paper-based materials: this property was reduced by the ageing processes, in different way depending on the amount of the degradation mechanisms occurring mainly in the cellulose. Also the presence of some additives influences the behaviour of paper during the thermal degradation.

TGA has been applied to characterise not only the selected paper-based materials, but also some ancient documents selected in the framework of the European project Papertech [13], with the aim to correlate the level of degradation of the artificially aged samples with that of the old ones that underwent a natural weathering. In this way helpful information to be used in paper restoration and conservation has been obtained, considering the opportunity of including thermal analysis in a diagnostic protocol to characterise the paper and its degradation.

## 2. Experimental part

### 2.1. Materials

Some paper-based materials, not died and/or printed, have been selected to study the thermal stability of cellulose:

- Whatman paper for chromatography (Carlo Erba, Italy; grammage: 70 g/m$^2$). Manufactured from high quality cotton linters (minimum α-cellulose content: 98%).
- Murillo paperboard (Fabriano Factory, Italy; grammage: 360 g/m$^2$). Uncoated paper, made with 100% of bleached short fibres, coming from trees. The product is acid free, with alkaline reserve, guaranteeing long life. It contains cellulose, no lignin and about the 10% of inorganic fillers.
- Watercolour paperboard (Fabriano Factory; grammage: 200 g/m$^2$). Acid free paper, made with 25% of cotton fibres, 15% long fibres pulp and 70% short fibres pulp. The product has alkaline reserve, guaranteeing long life and it contains cellulose, no lignin and about the 5% of inorganic fillers.
- Paper for restoration (Fabriano Factory; grammage: 390 g/m$^2$). Natural white, moulmade watermarked paper, made of 100% totally chlorine-free pulp of cotton. The product is wood and acid free, with alkaline reserve, to guarantee the longest life; it contains cellulose, no lignin and about the 6% of inorganic fillers.
- Newsprint paper (Cartiere Burgo, Italy; grammage: 65 g/m$^2$). Made largely from mechanical pulp and/or waste paper; it contains blanched cellulose, recycled fibres after deinking, starch, a noticeable amount of fillers (≅20%) and optical correctors.

The selected naturally aged paper samples (see Table 1) have different provenience, age and composition; therefore these samples give the possibility to investigate the effect of the natural weathering at various level of degradation. All these printed samples present evident traces of photodegradation and oxidation (yellowing and browning), due both to the additives used in the production (inks, sizing, fillers, etc.) and to the storage conditions.

### 2.2. Artificial weathering

Five sheets of each model sample have been weathered in the following ways:

- In oven at 100 °C for 500 h in the dark.
- In solarbox Angelantoni SB3000E at 65 °C (R. H. 25%) for 500 h, under a Xe-arc lamp (power 1000 W/m$^2$).

Table 1
List and description of the ancient samples

| No. | Type | Age | Provenience | Description |
|---|---|---|---|---|
| 1 | Book “Privat und offentliche recht der gegenwart” | 1903 | Austria | Ten printed sheets, with evident traces of oxidation on the borders |
| 2 | Magazine “L’illustrazione Italiana” | 1919 | Italy | Ten printed white pages and a blue cover with evident traces of oxidation on the borders |
| 3 | Magazine “Rivista di diritto commerciale” | 1941 | Italy | Ten printed sheets, with traces of oxidation on the borders |

- In climatic chamber Angelantoni Challenge 250 E at 60 °C (R. H. 70%) for 500 h, under a UV lamp (power 150 W/m$^2$).
- Chemical oxidation with sodium metaperiodate ($NaIO_4$). The ratio sample/solution has been kept for all experiments 1 g of sample for 100 ml of water. The samples have been mixed in a closed vessel with the metaperiodate solution 0.1 M and the mixture has been stirred gently at room temperature in the dark for two hours. At the end of the oxidation processes the samples have been filtered, washed with deionised water up to neutral conditions (pH 7) and dried.

### 2.3. Scanning electron microscopy (SEM–EDS)

The morphological observations of the specimens have been carried out by SEM associated with EDS microprobe. SEM images have been recorded using the Secondary Electron detector at two different magnifications: 500× and 2000×. EDS allowed the determination of the elemental composition of each sample, in order to identify the nature of fillers. A Scanning electron microscope Stereoscan 440 Leica-Cambridge associated with an EDS microprobe Link-Gun Oxford have been used, after metallization of the specimen with a very thin layer of graphite, to obtain a good conductivity.

### 2.4. Thermal analysis

A PerkinElmer TGA 7 has been used with nitrogen flow (4 cm$^3$ min$^{-1}$); the samples (3–5 mg) have been heated from 50 to 900 °C at the rate of 10 °C min$^{-1}$. The weight loss and its first derivative have been recorded simultaneously as a function of temperature. Each analysis has been performed twice on three specimens gathered from every paper sheet. Therefore, the results reported in the following are an average of several measurements.

## 3. Results and discussion

### 3.1. SEM–EDS analysis

The typical Whatman paper morphology shows a fibrous structure (Fig. 1a); EDS analysis detects the presence only of carbon and oxygen, that are the components of the cellulose; no other elements are found, because Whatman paper does not contain any additives. After weathering in oven and oxidation with $NaIO_4$ no evident modifications occur; on the contrary, after ageing in solarbox and in climatic chamber changes in the paper morphology are evident. Indeed, both these latter induce the breaking of fibres (Fig. 1b), so reducing the mechanical resistance of paper.

As shown in Fig. 2a, Murillo contains a big amount of fillers, and actually EDS analysis detects the presence of C, O and Ca, constituting the calcium carbonate [$CaCO_3$]: this filler is the alkaline reserve of paper that allows the prolonging of its life. After the weathering in oven no evident modifications occur and no compositional variations are revealed in the EDS analyses. The oxidation does not modify appreciably the Murillo morphology, but it is evident the formation of many lamellar crystals on the paper surface (Fig. 2b and c), in which the EDS analysis detected only the presence of Ca, O and I: they could be crystals of $Ca(IO_3)_2$, formed by reaction between $CaCO_3$ and $NaIO_4$. Their amount is relevant, because the quantity of $CaCO_3$ as filler is high.

EDS analysis of Watercolour detects, besides C and O, also Si, Al and Ca: they come from the fillers of paper, kaolin

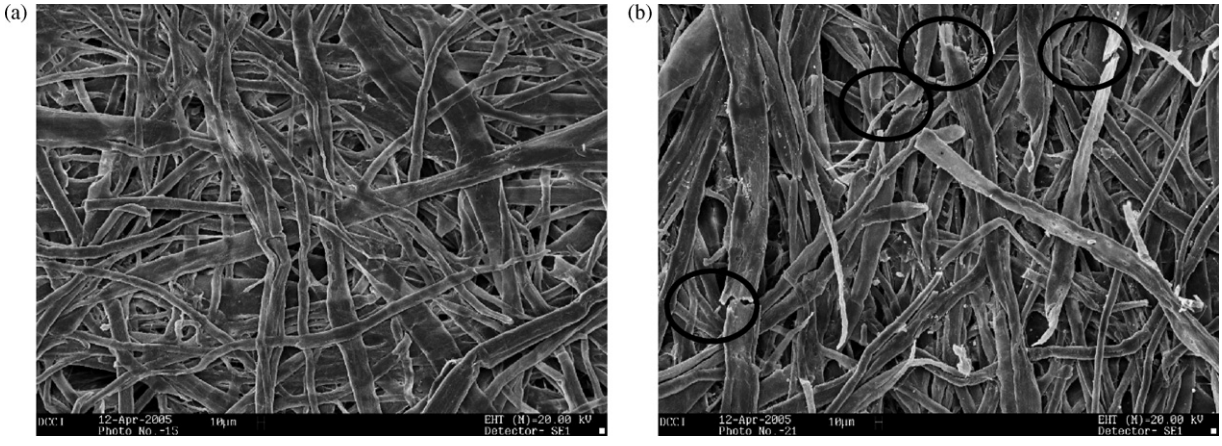


Fig. 1. SEM micrographs [500×] of Whatman paper: (a) unaged and (b) aged in solarbox (in the circles the broken fibre are highlighted).

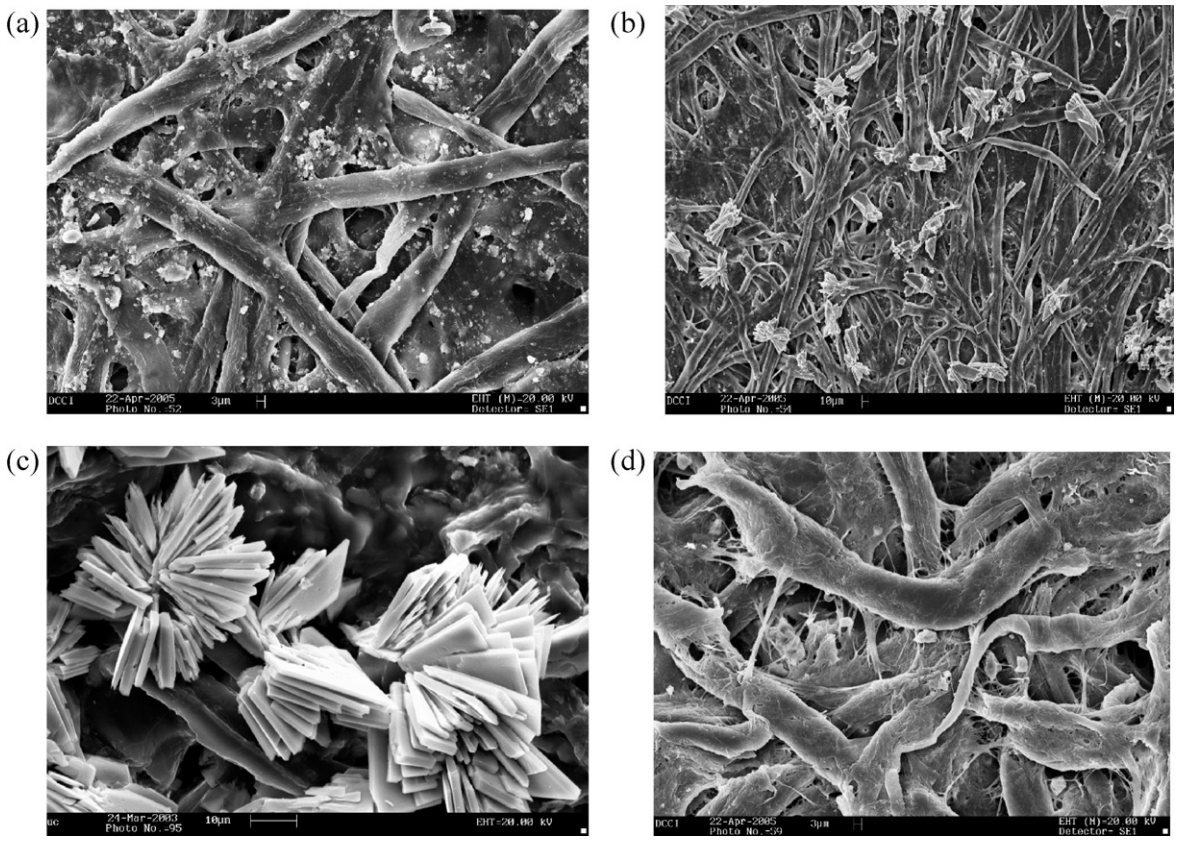


Fig. 2. SEM micrographs of: (a) unaged Murillo [2000×]; (b) oxidised Murillo [500×]; (c) lamellar crystals [2000×] and (d) unaged Paper for Conservation [2000×].

$[Al_2Si_2O_5(OH)_2]$ and calcium carbonate, that are the alkaline reserve of paper. Also in this case, after the weathering in oven no evident modifications in the morphology occur and no compositional variations are revealed in the EDS analyses, whereas after oxidation it is evident the formation of lamellar crystals on the paper surface, without any change in the paper morphology. In this case the amount of crystals is very small, because the quantity of $CaCO_3$ as filler is limited.

SEM observations of Paper for Conservation (Fig. 2d) show the presence of an adhesive among the fibres that is added during the sheets preparation. In order to determinate the nature of the adhesive, this paper has been extracted with acetone and the extracted fraction has been analysed by FT-IR; the peaks in the spectrum revealed that the adhesive is poly(vinyl acetate). EDS analysis detects the presence of C and O coming not only from cellulose, but also from poly(vinyl acetate); also a small amount of Ca is found that constitutes the filler ($CaCO_3$). The oxidation does not modify appreciably the morphology; also in this case few lamellar crystals containing Ca, O and I are present on the paper surface.

Newsprint paper is made by fibres with various dimensions and a large amount of fillers, in which the EDS analysis detects Ca, Si, Al, K and Mg, constituting calcium carbonate, kaolin and magnesium carbonate [$MgCO_3$]. After the weathering in oven and in solarbox no evident modifications occur and no compositional variations are revealed in the EDS analyses. Being performed in mild conditions, the oxidation does not modify appreciably the newsprint paper morphology, but, since the amount of fillers is relevant, many lamellar crystals are formed on the paper surface.

The naturally aged documents have been observed by SEM–EDS as well, in order to have information on their morphology and elemental composition.

In Fig. 3a the fibrous morphology of a printed area of the Austrian book is reported. EDS analysis detects, besides the cellulose, Si, Al, Ba, S, that form the fillers of paper: kaolin and barium sulphate [$BaSO_4$]. In correspondence of the inked region, no other elements are detected; and, therefore, probably, the ink is organic.

Also in "L'illustrazione Italiana" a large amount of fillers is present, that EDS analysis reveals being kaolin and barium sulphate. In Fig. 3b the inked blue cover is shown; the blue colour is due to the Prussian blue, as revealed by the presence of Fe and C. In correspondence of the inked region small spheres containing Fe, S and O are detected; they could be iron gall ink particles, since this ink is obtained by mixing iron sulphate with tannic acid, Arabic gum and water [14]. EDS analysis on the white pages shows the presence the same elements detected for the blue cover; in addition, it is evident the presence of another type of a Fe-based ink, because S is absent.

The morphology of the "Rivista di diritto commerciale" is analogous to those of the other naturally aged samples. Besides C and O that constitute the cellulose, EDS analysis detects the presence of Si, Al, and Ca that form the fillers of paper: kaolin

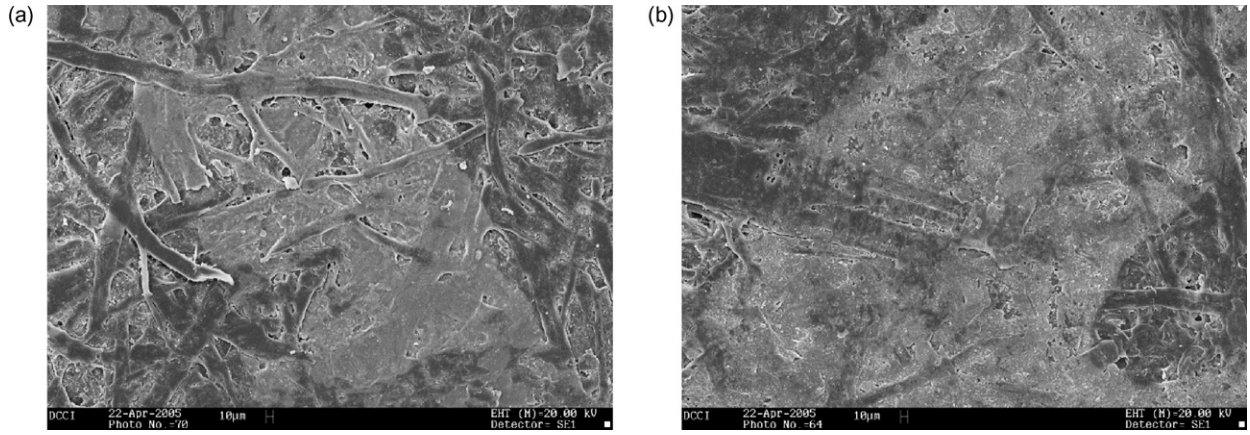


Fig. 3. SEM micrographs [500×] of: (a) the Austrian book and (b) the printed blue cover of "L'illustrazione Italiana".

and calcium carbonate. In correspondence of the inked region, no other elements are detected; therefore, probably, the ink is organic.

### 3.2. TGA analysis

TGA can be considered as the most suitable tool to investigate the thermal stability of cellulose-based materials, as paper, textiles and papyrus, before and after weathering [15]: the maximum of the derivative curve is taken as the decomposition temperature of cellulose. In accordance with the literature, it has been established that no degradation takes place until 200 °C. Above this temperature thermal stability gradually decreases and the cellulose decomposition occurs. Generally, at temperatures less than 100 °C the water loss in all the samples takes place [16].

Usually, the effect of the ageing treatments on the thermal stability of cellulose is revealed with the shift of the derivative curve maximum to lower temperature, in comparison with that of the unaged sample [7,17]. Moreover, TGA analysis gives an insight into the presence of fillers and inorganic compounds in the sample by detection, in the derivative curves, of their decomposition at temperatures usually higher than the decomposition temperature of cellulose. In a first approximation we can assume that cellulose does not interact with the fillers. Thus, we can consider the decomposition of cellulose and the fillers independently [18–20].

In our discussion TGA results, coming from the recorded weight loss curves and their correspondent derivative curves before and after weathering, are reported in terms of:

- Decomposition Temperature of cellulose ($Td_{cell}$).
- Decomposition Temperature of fillers ($Td_{fillers}$).
- Residual weight % (RW %) at 900 °C. This value includes the amount of chairs, unburned components (i.e. inorganic fillers) and final decomposition products produced during the analysis.

The comparison among the unaged model samples is shown in Fig. 4; the corresponding TGA results are collected in Table 2.

All the model paper samples show the cellulose decomposition in the range 380–400 °C, also when fillers are present in the material; Paper for Conservation shows the highest thermal stability.

In the case of the filled papers at 700–750 °C the decomposition of inorganic compounds occurs. As already revealed by EDS analysis, except the Whatman paper made only by cellulose, all the model samples contain different amount of inorganic fillers, particularly the calcium carbonate ($CaCO_3$): it is well known that at 750–800 °C $CaCO_3$ is transformed in CaO with formation of $CO_2$; therefore the peak detected in the thermograms is due to the calcium carbonate decomposition. In the case of Watercolour no peaks corresponding to the fillers are observed, even if the EDS analysis detected their presence; this fact can be explained considering that their amount is too small to be revealed. The residual weight % at 900 °C changes with the paper type; newsprint paper has the biggest residual weight, since the amount of fillers is very high (≈20 wt.%).

As expected, each ageing treatment modifies the thermal stability of paper, depending on the type of weathering performed. Moreover, in some cases the ageing induces variations in the composition of the inorganic fillers, as already detected by EDS

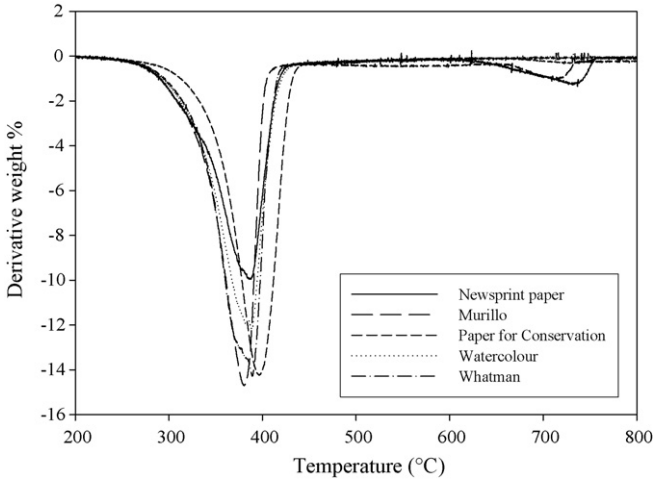


Fig. 4. Weight derivative curves for the unaged model samples.

Table 2
TGA results for the model paper samples before and after weathering

| Ageing treatment | $Td_{cell}$ (°C) | $Td_{fillers}$ (°C) | RW (%) |
|---|---|---|---|
| Whatman paper | | | |
| Unaged | 390 | – | 9.4 |
| Oxidised | 373 | – | 13 |
| Aged in oven | 385 | – | 8.6 |
| Aged in solarbox | 380 | – | 7.7 |
| Aged in climatic chamber | 382 | – | 9.1 |
| Watercolour | | | |
| Unaged | 390 | – | 14.2 |
| Oxidised | 348 | – | 21.5 |
| Aged in oven | 386 | – | 13.7 |
| Murillo | | | |
| Unaged | 383 | 718 | 4.5 |
| Oxidised | 364 | 713 | 16 |
| Aged in oven | 379 | 710 | 13 |
| Paper for Conservation | | | |
| Unaged | 399 | 732 | 10 |
| Oxidised | 370 | – | 13 |
| Newsprint paper | | | |
| Unaged | 389 | 718 | 20 |
| Oxidised | 347 | 713 | 21 |
| Aged in oven | 380 | 710 | 19 |
| Aged in solarbox | 372 | 710 | 20 |

analysis; for example in the case of the papers filled with calcium carbonate, this filler reacts with the sodium metaperiodate leading to the formation of the lamellar crystals of $Ca(IO_3)_2$.

In Fig. 5 the weight derivative curves for Whatman paper before and after weathering are reported; the corresponding TGA results are collected in Table 2. For the aged paper the cellulose decomposition happens at lower temperature, in respect to the unaged one; this behaviour is in accordance with the data reported in literature, showing the highest thermal stability for the unaged material [7]. The oxidation induces the most relevant decreasing in the decomposition temperature of cellulose and therefore, this weathering treatment represents the most degradative process for Whatman paper from the point of view of its thermal behaviour. The residual weight % at 900 °C is

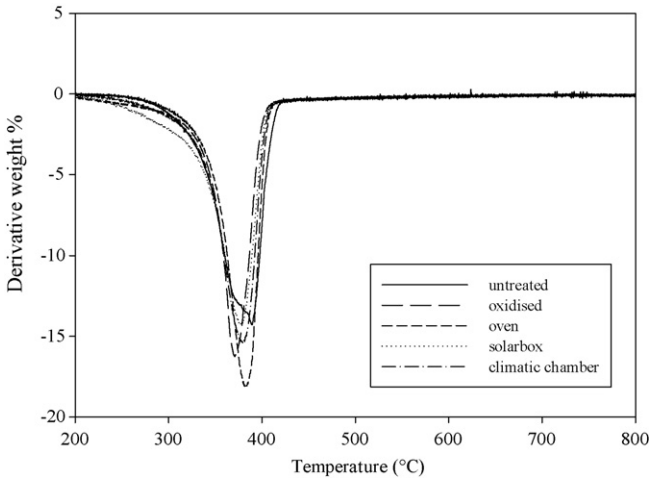


Fig. 5. Weight derivative curves for Whatman paper before and after weathering.

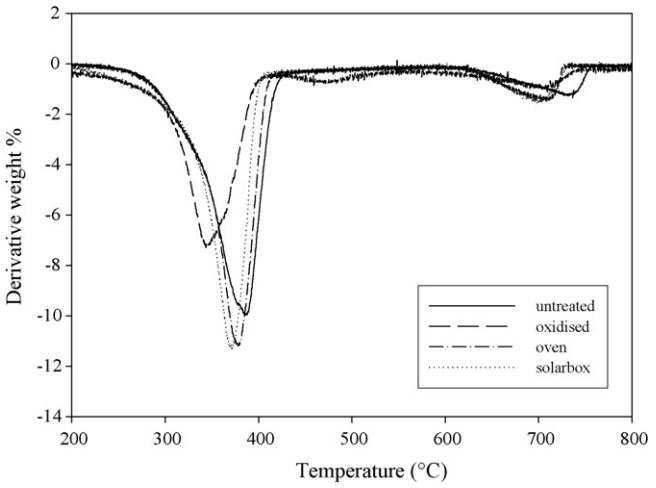


Fig. 6. Weight derivative curves for newsprint paper before and after weathering.

almost the same for all the samples (≅10%) because no variation in the composition before and after weathering has been found.

For the oxidised Watercolour cellulose decomposition takes place at very low temperature (see Table 2). The residual weight % at 900 °C is almost the same for the unaged and aged in oven samples (≅14%), whereas for the oxidised one it is greater (≈20%), due to the change in the composition (formation of lamellar crystals).

Also for the oxidised Murillo and Paper for Conservation the cellulose decomposition happens at very low temperature (see Table 2). On the contrary the ageing in oven does not modify the Murillo thermal stability that is comparable with that of the original paper. At 710–720 °C the decomposition of the inorganic filler ($CaCO_3$), detected by EDS analysis, occurs. The residual weight % at 900 °C is almost the same for both the specimens (≅10–15%), except for the original Murillo that is surprisingly very low, as said before.

In Fig. 6 the weight derivative curves for newsprint paper before and after weathering are reported; the corresponding TGA results are collected in Table 2. As expected, cellulose decomposition happens at the lowest temperature for the oxidised newsprint paper; the ageing in solarbox strongly reduces the thermal stability, more then the ageing in oven. These results are remarkable since fillers are claimed to prolong the lifetime of the paper. At 710–720 °C for each sample the decomposition of fillers ($CaCO_3$) occurs; the residual weight % at 900 °C is almost the same for the aged samples (≅20%) and for the unaged one.

The results above reported demonstrate in conclusion that each weathering treatments determine different effects on cellulose and on its stability. Whereas the raw materials show the highest thermal stability, cellulose decomposition takes place at the lowest temperature for the oxidised samples; generally, the ageing treatments in oven, in solarbox and in climatic chamber slightly decrease the decomposition temperature of cellulose. In conclusion, the oxidation with sodium metaperiodate is the most degradative treatment, because it induces considerable modifications in the cellulose structure, at level of the polymeric chains, enhancing and promoting the oligomers formation [21].

Table 3
TGA results for the naturally aged model samples

| Sample | $Td_{cell}$ (°C) | $Td_{fillers}$ (°C) | Residual weight % |
|---|---|---|---|
| Austrian book | 353 | – | 21 |
| L'illustrazione Italiana | 370 | 680 | 30 |
| L'illustrazione Italiana (blue cover) | 375 | – | 29 |
| Rivista di diritto comm | 370 | – | 27 |

The reduction of thermal stability can be explained assuming that the aged cellulose is already degraded with a large fraction of oligomers. Therefore, less energy is necessary for its decomposition.

We must underline that the normalisation of some characteristics of the samples, such as their weight and thickness, does not affect our conclusions: first of all, because some comments concern the behaviour of each single kind of paper and, secondly, because some statements come from the observation of the general trends. This last consideration takes into account the reliability of all the measured $Td_{cell}$ values, since a 10% of error comes from both instrumental and operator inaccuracy.

In Fig. 7 the comparison among the three naturally aged samples, i.e. Austrian book, "L'illustrazione Italiana" and "Rivista di diritto commerciale", is reported in terms of the weight derivative curves; the corresponding TGA results are collected in Table 3. For the Austrian book the cellulose decomposition happens at the lowest temperature (353 °C), whereas the other samples show a higher and similar thermal stability. No peaks related to the fillers are clearly revealed for all the samples. It is important to note that EDS analysis detected the presence of fillers in all the papers, but probably their amount is under the detection limit of TGA.

TGA analysis allows the comparison of the thermal behaviour of ancient samples at different degradation level, highlighting how some characteristics are in function of their composition and provenance. Moreover, these results could be related to those attained from the thermal analysis of model samples, to explain better how different ageing agents act on paper and on its stability: in conclusion, it is clear that the ancient papers underwent some degradative phenomena that reduce considerably the thermal stability of cellulose (see Table 2), phenomena which are related to their exposition to the degradative agents. This point will be the topic of further studies.

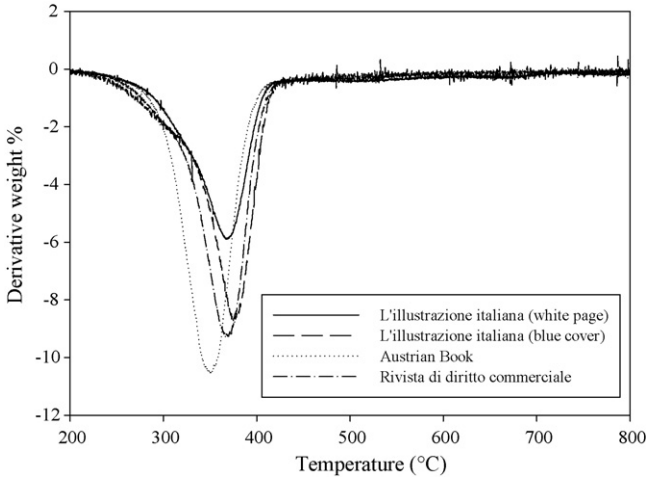


Fig. 7. Weight derivative curves for the naturally aged model samples.

## 4. Conclusions

It is well known that thermal data contain information related to the structural properties of the materials and may be used to predict properties that are directly related to their physical performance. Thermal analysis, and in particular TGA, represents an important tool to assess the conservative state of paper. This step is fundamental during any restoration works, since it allows knowing deeply the degradation level of artworks.

Starting from the results reported in this paper it is clear as TGA analysis allows to monitor the degradation level in paper, because it performs a complete investigation of the thermal behaviour of paper and the influence of the main degradative agents (light, heating, oxygen and enzymes) on it. TGA curves of the weathered samples show changes in respect to the starting materials; particularly, the signals corresponding to the main cellulose decomposition shifts to lower temperature for the aged samples, in different ways depending on the type of weathering performed. The chemical oxidation with sodium metaperiodate appears as the most degradative treatments, inducing inner modifications in the cellulose structure at the level of polymeric chains; therefore this procedure does not supply a significant simulation of the oxidative degradation of paper in normal archives conditions.

During the other ageing treatments the chemical composition of cellulose changes very weakly. Nevertheless, the negligibly small changes in chemistry of cellulose after the ageing considerably influence the thermal behaviour of cellulose at high temperatures. Probably, these changes lead to the formation of defects (nuclei) in cellulose. These defects promote the decomposition of cellulose at high temperatures.

Oxygen does not penetrate into the cellulose matrix. Thus, the aging of paper indoors being in darkness can lead only to oxidation of surface cellulose. The paper can be kept in darkness during infinitely long time, say, one million years. Indeed, thermal decomposition of cellulose occurs with the high activation energy. Thus, if ignoring the damage of the surface, cellulose is unchangeable.

In contrast to oxygen, which attacks only the surface of cellulose, UV can penetrate in depth of cellulosic fibres. Indeed, cellulose is more or less transparent for the UV radiation. Thus, the mechanical deterioration that is inconsiderable in the case of darkness (damage of only surface cellulose) becomes con-

siderable in the case of the hard UV. Indeed, in all the cases of weathering without UV the paper does not change the morphology.

In the future, TGA analysis will be applied to the weathered paper herein considered after the application of suitable polymeric materials acting as consolidants for the paper, this in order to evaluate if and how the thermal stability can be improved after a conservative intervention.

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