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Atomic force microscopy characterization of the ageing of pure cellulose paper

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Abstract

Atomic force microscopy was used to characterize the effects of chemical reactions induced by accelerated ageing in a climatic chamber (80 °C, R.H. 65%) on Whatman no. 1 chromatography paper surface, in order to study ageing consequences on sub-micron structures in cellulose. Evaluation was carried out by means of a comparison of topographic data with chemical characterization, in addition to spectrophotometric measurement in the UV–vis–NIR range. Imaging of samples at several treatment stages showed a non-homogeneous decomposition of the fibre surface into fibril bunches. Over paper sheet surfaces, occurrence of this phenomenon increases with ageing. Spectrophotometry measurements showed a strong variation of contributions in the UV–vis bands, both in the yellow chromophores region and in the carbonyl formation region, which was consistent with the hypothesis that a predominant oxidation mechanism is involved.

Keywords: Cellulose; AFM; Oxidation

1. Introduction

Analysis related to conservation of cultural heritage is concerned with targets that experience a superposition of spontaneous and non-reversible interactions, taking place for macroscopic durations, often in unknown conditions. In most cases the targets are also unique. As can easily be imagined, approaches and methods that are successful in the structure characterization of linear systems have frequently proved to be not applicable in this field of material science.

Relying on the understanding of physical, chemical and biological interactions responsible for deterioration phenomena, conservation science is actually an applied science, aimed at the major tasks to be performed in order to reduce degradation effects, and—whenever possible—prevent them from occurring.

Research in this field is, therefore, strongly focused on the development and improvement of non-destructive or micro-destructive techniques, capable of detecting ageing markers.

This work is concerned with library materials conservation, and reports the results of an initial experiment to assess the use of atomic force microscopy (AFM) on paper, which is the most commonly used writing support, to monitor the ageing of cellulose.

Other measurements are currently being gathered in order to verify the behaviour of cellulose at different degradation stages (e.g. acidic and oxidative degradation) [1]. The goal is to find a correlation between morphological alteration and specific degradation-patterns so as to understand which process had taken place on real samples (i.e. books, documents, etc.).

Cellulose degradation occurs as a result of internal or external factors, such as intrinsic acidity of the paper or storage in an unsuitable place. Degraded papers show an evident fragility and a yellowing, which in some cases compromises the legibility of the text.

The main degradation mechanisms involved are oxidation and hydrolysis [2,3]. The first one causes the formation of both C=C double bonds on the anhydroglucose ring and of carbonyl groups, which can be further oxidized to carboxylic groups depending on the position of C=O groups in the anhydroglucose chain. Oxidation can lead both to the breaking of the cellulose chain (depolymerisation) or to the opening of

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the rings, thus making alkaline or acidic attacks to the macromolecule easier. Hydrolysis breaks the chain and causes a fragmentation of the structure, and can occur both in acidic and alkaline environments, but at room temperature only the acidic process can take place.

During the first ageing stages—natural or accelerated—there are no significant variations in mechanical properties: degradation evidence is only provided by measuring chemical processes. Oxidation induced by environmental conditions, in fact, causes carbonyl and carboxyl groups formation, with great impact on paper permanence and durability, even if mechanical characteristics are not affected in the short term.

The approach used in the present work is to discover whether structural properties in a controlled degradation of a model system can be correlated with physical quantities measurable in a non-destructive or micro-destructive way.

AFM imaging has provided significant results in the characterization of cellulose single fibres [4] and crystalline surfaces [5], and has recently been applied on pulps and pulps' main components, allowing for the identification of the fibres' structure and surface properties [6].

In the manufacturing and production framework, which is strongly focused on coated papers, AFM imaging directly on paper cannot be used for fibres characterization, but is an established technique aimed at coating quality characterization [7]. Cultural heritage conservation, on the other hand, is concerned—in most cases—with non-coated paper surfaces, and it is, therefore, a field in which AFM imaging can be considered a promising technique.

AFM micro-destructivity features allow for the measurement of 'as prepared' samples, with no instrumental requirements. Moreover, the wide range of applications of this instrument has prompted technology leading to the development of completely non-destructive devices.

In this study, AFM is used together with chemical characterization and UV–vis–NIR spectroscopy, in order to highlight the relationships between fibre surface behaviour and chemical processes during controlled degradation.

2. Experimental

2.1. Materials and methods

The system investigated is pure cotton chromatography paper Whatman no. 1. sheets were subjected to temperature and moisture-stimulated accelerated ageing (AA in the following) in a climatic chamber, in an air environment (80 °C; R.H. 65%), according to ISO 5630-3/1996 standard. The choice of samples and treatment was determined by the fact that a sample series of the same paper type is being observed throughout natural ageing (NA in the following) at 23 °C and 50% R.H. at the Istituto Centrale per la Patologia del Libro (I.C.P.L.) laboratories and relationships between the two ageing processes are being reported. In particular, it was established that, for Whatman no. 1, 7 days of AA correspond to 10 years of NA conditions [8].

It is to be remarked that this statement cannot be extended immediately to all paper types, or to the same paper type in other storage conditions. There is, in fact, no absolute description of the normal, natural ageing process, since there are so many paper-dependent internal factors, as well as external factors varying with time and storage-conditions that influence the stability of paper, so much so that it seems impossible to predict unequivocally the natural ageing observed in a particular sheet of paper. Even more complex is the situation found in a stack of paper, like a book or file, or a complete library or archive collection. Comparative studies on identical copies of books stored under different conditions show that degradation is strongly related to the storage conditions to which the object has been exposed in the course of time [9].

The maximum accelerated ageing time was fixed at 49 days, since it was demonstrated [8] that the same treatment, for the same duration, caused significant chemical reactions without affecting mechanical properties. Samples were also collected at intermediate ageing stages after 7, 14, 21, 28, 35 and 42 days in the ageing chamber.

As regards the evaluation of viscosity, average degree of polymerisation (DP), acidity and carboxyl content, chemical characterization of samples followed the American Society for Testing and Materials (ASTM) and the Technical Association for the Pulp and Paper Industry (TAPPI) specifications (ASTM D1926-00, ASTM D1795-96(2001) e1 and TAPPI T 435 om-02). Carbonyl content measure was performed according to a method developed at the I.C.P.L. as described in a previous paper [10].

Visible spectra were measured using a Minolta Chroma Meter CR22. Colour coordinates are shown according to the CIE $L^*a^*b^*$ system.

The atomic force microscope used in this study was a SNOM/AFM instrument assembled in collaboration with ISM-CNR [11], operating in air, and using a quartz fibre probe with a conical tip (diameter $\cong$ 50 nm). Such a set-up will allow for near-field optical microscopy measurements to be taken.

The fibre probe is held to a piezoelectric bimorph parallel to its axis, and is forced into oscillation—close to its resonance frequency—normal to such direction. As it approaches the sample, the fibre tip becomes sensitive to the repulsive effect resulting from surface interaction.

In order to outline a reproducible method, a non-contact operating mode was preferred to a contact mode so as to avoid the possibility of surface damage occurring, which is experienced with non-coated papers and other soft materials.

The non-contact operation point is then fixed at a proper rate of original signal value (typical values are between 85 and 90%; 90% of original signal value was used in this experiment).

As far as image processing is concerned, no other filtering other than flattening and plane alignment fitting—to remove background slope, when necessary—were applied to data sets.

Absorbance in the 200–2500 nm range was measured by means of a Varian Cary 5 spectrophotometer, equipped with LabSphere integrating sphere and internal mount. By positioning the sample at the centre of the sphere, both the transmittance and reflectance of the sample are measured simultaneously.

Table 1
Chemical properties of Whatman no. 1 at different ageing stages

Ageing days	pH (±0.02)	DP	C=O, mmol/100 g paper	COO (±2%), mmol/100 g paper	L^*	a^*	b^*
0	5.40	1521±30	3.35±0.25	0.33	96.63	0.12	1.16
7	5.32	1305±26	4.06±0.20	0.36	95.68	0.06	2.21
14	5.21	1202±24	5.67±0.28	0.43	95.83	0.14	2.8
21	5.15	1090±22	7.31±0.37	0.47	95.61	0.19	3.15
28	5.00	1070±22	9.49±0.62	0.49	94.77	0.34	4.09
35	4.80	1040±20	11.70±0.65	0.51	94.41	0.39	4.82
42	4.76	1048±21	12.50±0.60	0.52	93.72	0.54	5.55
49	4.68	1045±21	13.09±0.28	0.53	92.52	0.64	6.23

This 'transflectance' measurement (transmittance plus reflectance, T_F) allows the sample's absorbance to be obtained directly, following the equations given below:

$$A = -\log(T + R) = -\log T_F$$

3. Results and discussion

3.1. Carbonyl/carboxyl formation and degree of polymerisation during ageing

According to the samples' chemical characterization data, as presented in Table 1, carbonyl and carboxyl groups content increase vs. time following a sigmoidal growth pattern between initial value and the maximum level, indicating reaction equilibrium. Both data sets show a satisfactory fit (Fig. 1) with a Boltzmann distribution, where the parameter indicating molecule content before treatment, at time $t=0$d, was fixed at the value estimated from measured data.

Comparison of the two datasets shows that carbonyl content quadruples between the initial and saturation value, and the process speed increment becomes definitive after around 24 days of ageing (from fitted flex position). Carboxyl increment, on the other hand, is almost 1.8 times the value for an unaged sample, and the process reaches saturation earlier with respect to carbonyl formation (fitted flex position is after almost 12 days ageing, and measured data are consistent with the fitted final value after 35 days ageing). At the same time, pH values decrease, according to the increase of acidic carboxylic functions present in the macromolecule.

A thorough model of pure cellulose paper degradation, providing a kinetic equation of DP decay and an idea of how to predict the life expectancy of paper, was proposed [12,13], and then extended [14] with a first-order correction so as to better describe behaviours over long reaction times, when paper DP value falls below 200.

Such a model is a reliable description, and is applicable to softwood and most hardwood cellulose papers, and it is commonly accepted in conservation science [15] as well as in the paper industry [14].

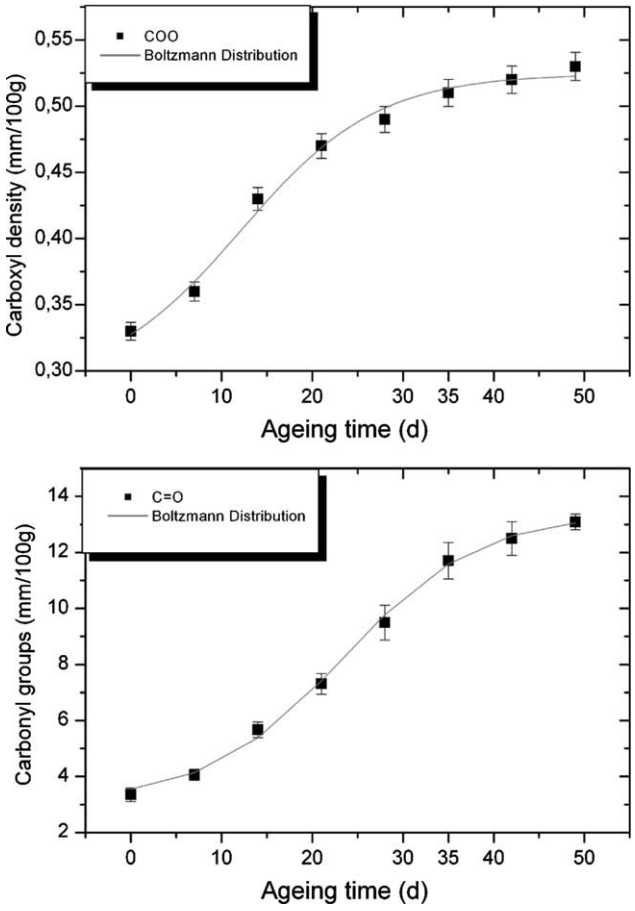

Fig. 1. C=O and COO– groups formation vs. ageing time.

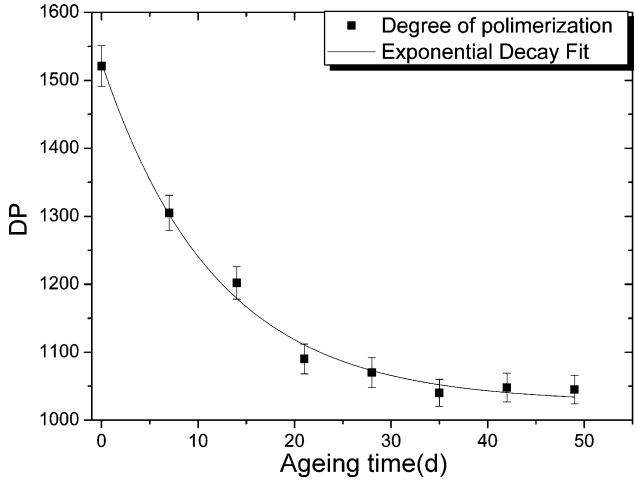

Fig. 2. DP behaviour during accelerated ageing.

Table 2
Accelerated ageing effect on chemical parameters of Whatman no. 1

Whatman no. 1 (paper sheets from different boxes)	pH (±0.02)		DP		C=O, mmol/100 g paper		COO (±2%), mmol/100 g paper	
	Unaged	28d	Unaged	28d	Unaged	28d	Unaged	28d
Box no. 1[a]	5.04	5.00	1521±30	1070±22	3.35±0.25	9.49±0.62	0.33	0.49
Box no. 2[b]	5.37	5.64	1320±40	870±40	0.46±0.01	1.14±0.02	7.35	7.79
Box no. 3[b]	6.58	6.02	1521±21	1123±20				
Box no. 2[b] hydrolized before ageing	4.90	4.96	230±20	180±20	4.5±0.4	4.9±0.5	7.37	8.06
Box no. 2[b] oxydized before ageing	5.52	5.40	810±20	304±9	0.55±0.01	5.0±0.5	8.28	8.99

[a] Paper sheet from this box is the one used in this experiment.
[b] Courtesy of I.C.P.L. Data related to paper sheets in these boxes belong to other experiments currently ongoing at I.C.P.L.

On the other hand, several experimental proofs showed [16] that degradation of cotton cellulose paper follows a decay behaviour that is different with respect to other types of pure cellulose paper, and does not fit the model. For this reason, experiments pertaining to cotton cellulose [10,17,18] usually do not apply specific fitting methods to DP decay interpretation.

Best fit, according to the chi-square test, of our DP data, appears to be an exponential decay, and this can be interpreted

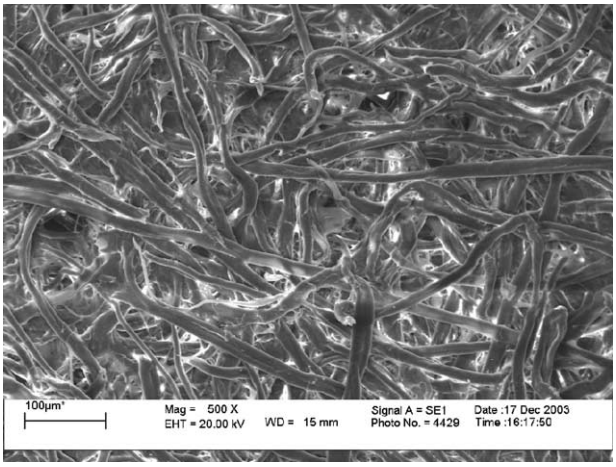

Fig. 3. SEM image of Whatman no. 1. Courtesy of Yoko Taniguchi and Malta Restoration Center.

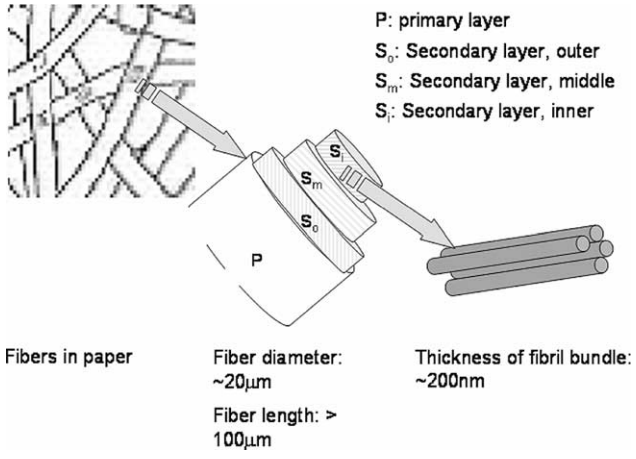

Fig. 4. Paper structure model and typical dimensions in cotton cellulose.

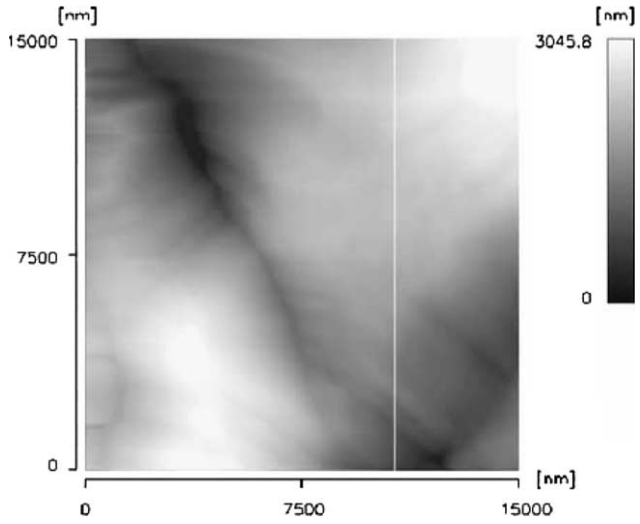

Fig. 5. Whatman no. 1 surface sample.

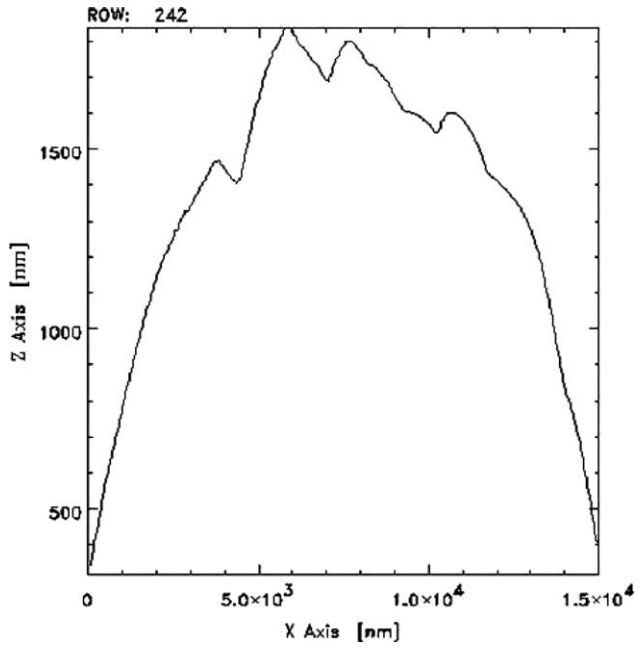

Fig. 6. Whatman no. 1 unaged sample cross section.

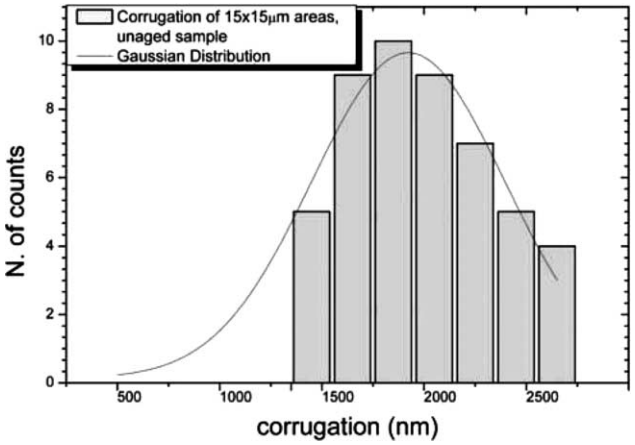

Fig. 7. Whatman no. 1, unaged sample, surface corrugation values.

as a superimposed chemical synergetic mechanism of oxidation and hydrolysis. Maximum decrease occurs, also in this case, in the first 21 days of ageing. DP measured values for data points at 28–35–42–49 days are compatible within the calculated error (Fig. 2).

A comparison of the present experimental data with those of other Whatman no. 1 sheets, deriving from different lots and subjected to identical procedures, demonstrates that no correlation can be found between ageing and a single characterization parameter. Samples from the same lot, treated in different ways, show (after the same storage duration and conditions) major differences in the parameters' values (Table 2). This supplies further proof of the knowledge already acquired [9,16,18–21], meaning that the correspondence between an accelerated ageing period and a natural ageing duration is not unique, but depends at least on the starting condition of the paper.

3.2. AFM results

Atomic force microscopy measurements were performed on paper sheets at different ageing stages (TQ, 7d, 28d, and 49d). For each sheet, samples measuring 1 cm × 1 cm were chosen from different locations (ranging from the border to the centre of the sheet). Images acquisition was performed on several areas of the same sample, using 15 × 15 μm frames; where appropriate, a more finely resolved outline of image details was obtained using 5 × 5 μm frames.

Using these frames, typical target objects are expected to be just portions of the fibre surface, as fibre diameter, for cotton

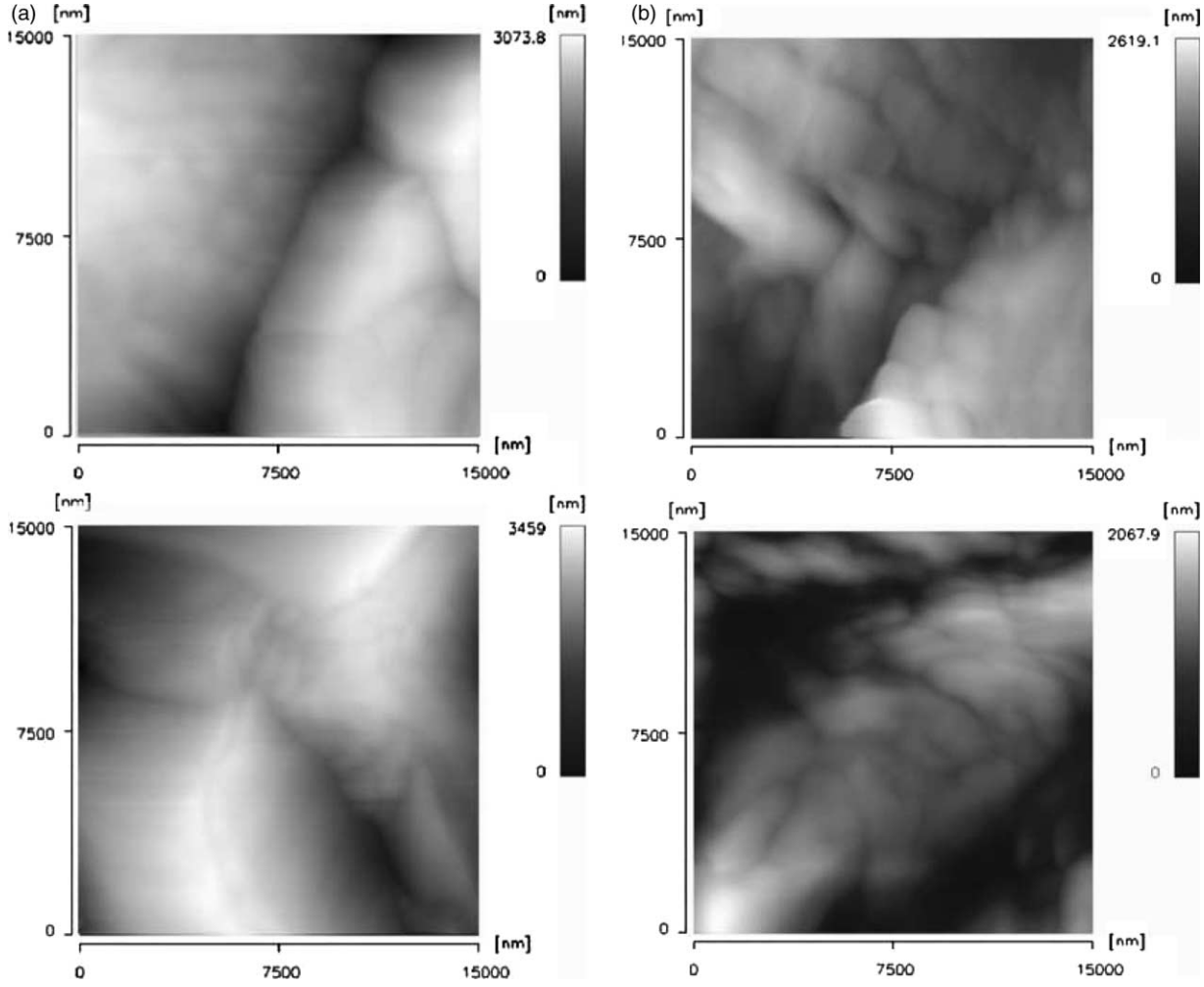

Fig. 8. AFM images of samples at different ageing stage: (a) unaged, (b) after 7 days ageing, (c) after 28 days ageing, (d) after 49 days ageing.

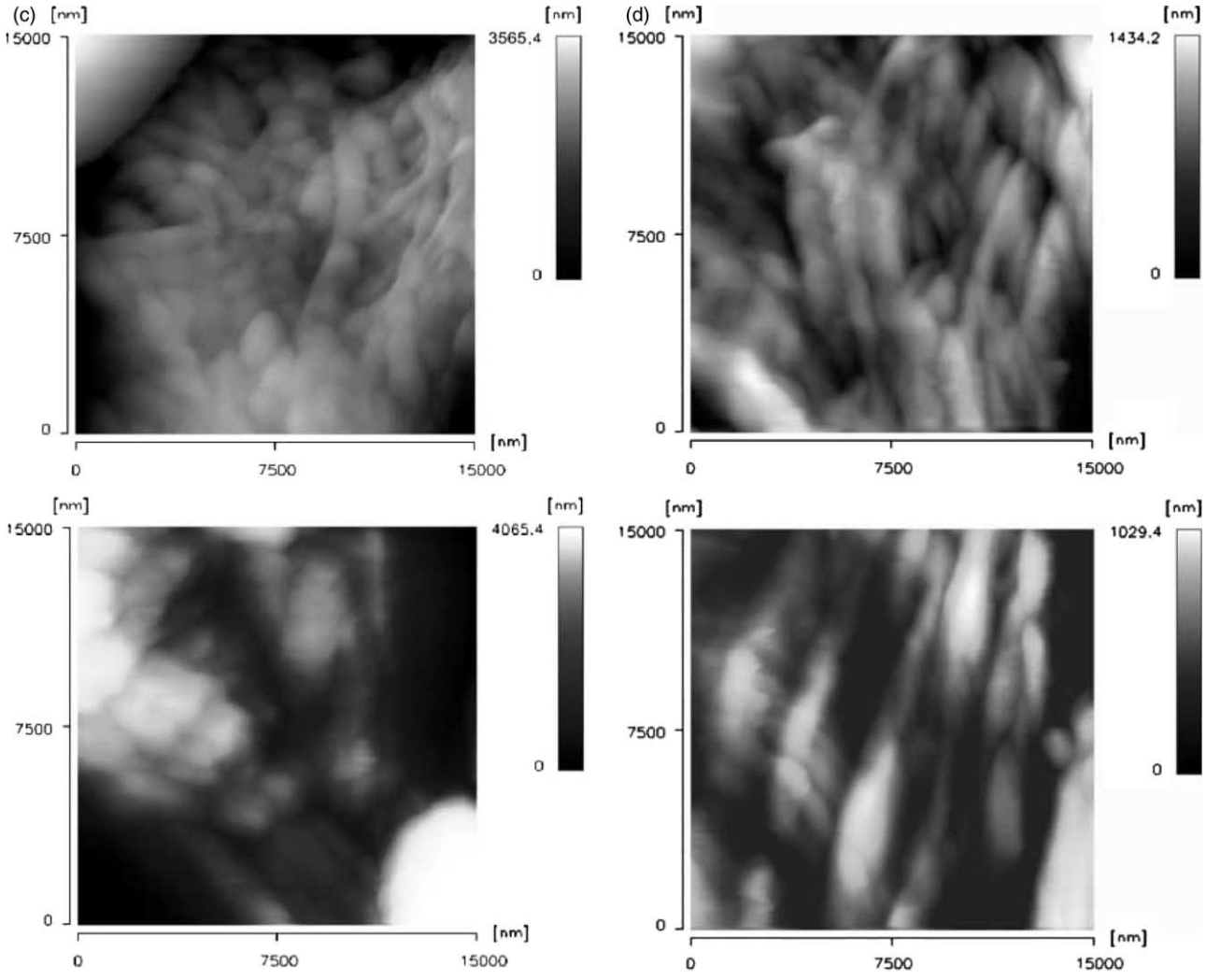

Fig. 8 (*continued*)

linter paper, is known (Figs. 3 and 4) to be mainly of about 10–20 μm [22,23].

Nevertheless, apart from surface imaging (Fig. 5), the dataset provided by AFM measurements allows for both a coarse evaluation of fibres width and the acquisition of statistics on corrugation distribution. So far as the unaged sample is concerned, observation of fibre images cross-sections demonstrates that values of fibre section interpolated at the lowest level (height = 0) lie mostly above 10 μm (Fig. 6), which is in good agreement with the paper structure model mentioned above.

In addition, data on surface corrugation provide a good insight on fibre compactness.

Consistency test on surface corrugation data related to a 15×15 μm frame resulted in a Gaussian distribution (Fig. 7) around a mean value of 1894 ± 27 nm, with sigma amplitude 586 ± 31 nm.

When making a merely qualitative comparison between images, samples with different ageing states showed fragmentation of the fibres surface, involving all three fibres dimensions (height, width and length), (Fig. 8). Occurrence of such fragmentation increases with increasing ageing time, with a significant morphology appearing after 21–28 ageing days, a morphology that is quite similar to the appearance of the more aged sample.

The suggested interpretation of such phenomena, in accordance with the previously discussed fibre structure [23] model, and with reported AFM imaging of cotton fibrils [4] is that the climate chamber treatment is likely to induce deterioration of the fibre cuticle, resulting in the removal of encapsulated fibril bundles and the unfastening of the bundles themselves. From the chemical reaction point of view, the above-mentioned data related to carbonyl increment are in agreement with such a hypothesis. Such phenomena would imply a decrease in surface compactness that is also reflected in the corrugation data, which are not, in this case, distributed around a specific value, but spread towards the smaller dimensions (Fig. 9), including values that were never found in unaged samples. Least square fit test of 7 days aged sample data also fitted with a Gaussian distribution, centred at 1534 ± 36 nm, with a sigma amplitude of 924 ± 80 nm. On the other hand, consistency test did not provide acceptable

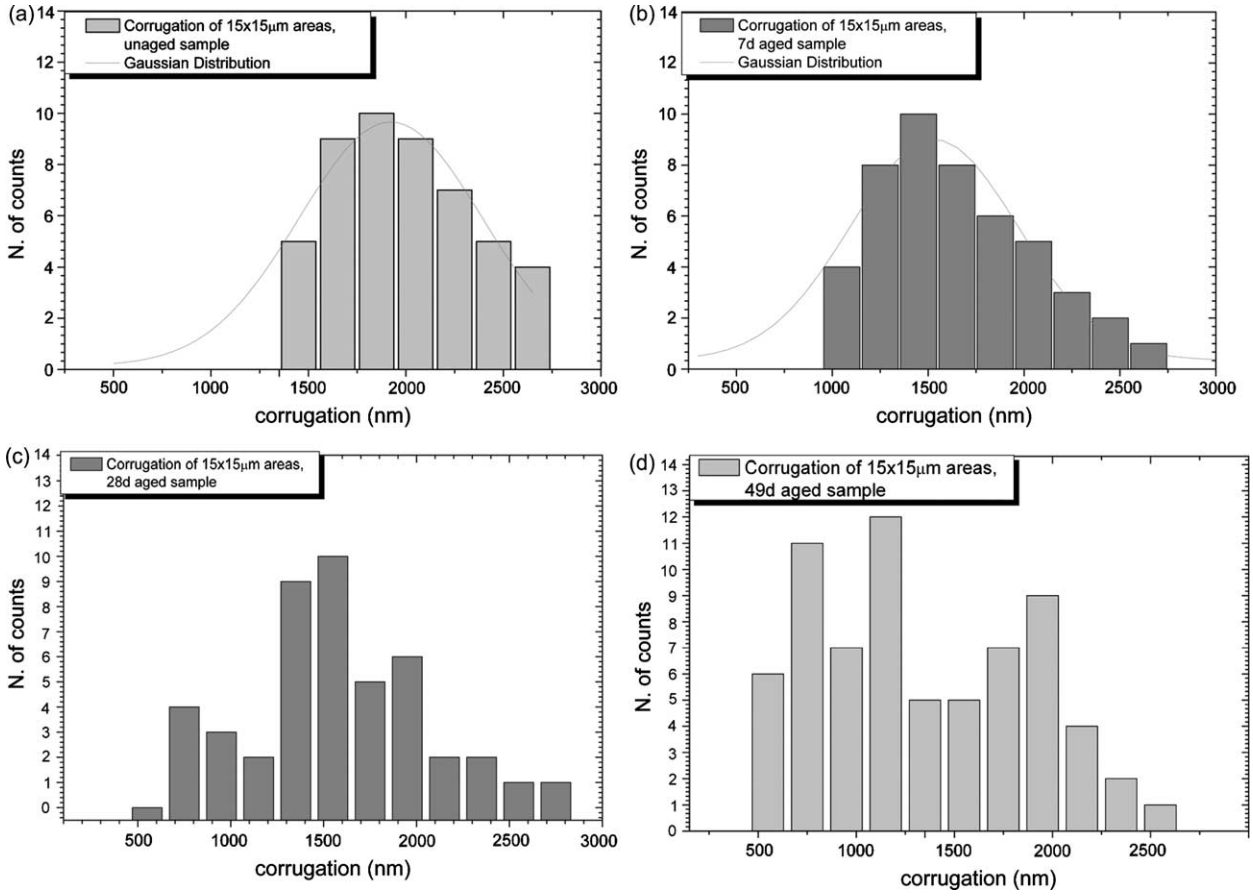

Fig. 9. Whatman no. 1 surface corrugation data: (a) unaged sample, (b) after 7 days ageing, (c) after 28 days ageing, (d) after 49 days ageing.

chi-square values for Gaussian, bimodal or multimodal fit of data related to the 28–49 days aged samples (Fig. 9(c) and (d)). Random distribution of surface corrugation is, therefore, the accepted interpretation.

Such behaviour is consistent with the hypothesis stated above, that the main effect is fibre cuticle deterioration.

3.3. Colorimetry

Analysis based on CIE $L^*a^*b^*$ coordinates variation showed minor colour variation, with ΔE values increasing with ageing to a maximum value of $\Delta E = 6.23 \pm .0.13$ (Fig. 10), mostly due to L^* and b^* variations, while a^* variation is almost insignificant (Table 1).

3.4. UV–vis–NIR spectrophotometry results

Transflectance measurements were performed on samples series in the UV–vis–NIR wavelength range 200–2500 nm. Several series were considered, including samples taken from different areas of the sheets, so as to take into account effects due to the non-uniform sheet thickness. The resulting absorbance spectra (Fig. 11) always reflect the NIR profile of cellulose, reported elsewhere [24], and an overall behaviour of absorbance increment with ageing is observed for all series in the UV–vis range, with a slope change in the 250–450 nm band.

Averages taken from each set of ageing stage data indicate that such an increase is not progressive but can be considered as having a definite impact, which occurs after 21 days of ageing. Compatibility is found, in fact, amongst averages from samples aged for 21, 28, 35, 42 and 49 days, whereas, on the other hand, all their spectra are found to be well separated from the unaged sample spectra (an example is shown in Fig. 12). Such results would lead to a conclusion that, after a certain ageing stage

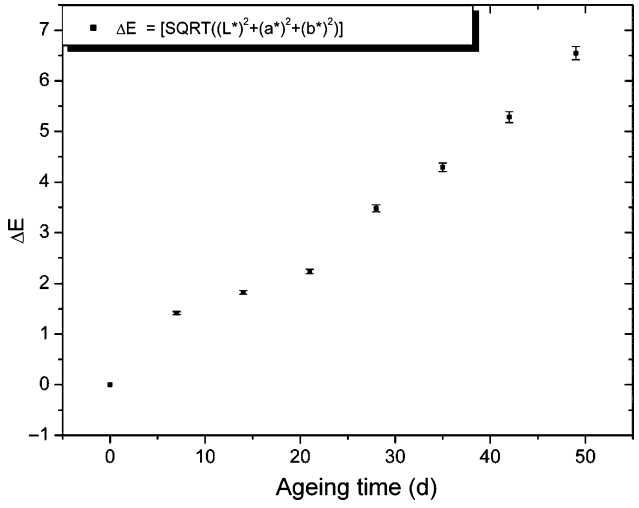

Fig. 10. ΔE variation vs. ageing time.

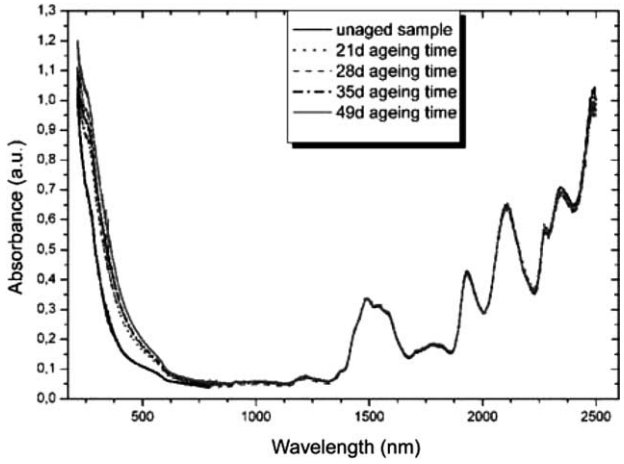

Fig. 11. UV–vis–NIR averaged spectra vs. ageing time from a sample series.

(around 21 days), some degradation process responsible for an absorbance increase becomes distributed over the whole sheet, almost independent of paper dishomogeneity.

A significant element of such process is connected with paper yellowing, of course, and involves the formation of yellow chromophores. Yet, according to observations of the spectrophotometric data, some other side effects attributable to the above-mentioned cuticle degradation are found.

From a comparison of aged vs. unaged spectra samples (Fig. 13), evidence is found which shows that a first variation of the increment profile happens between 7 and 21 days of ageing, and then another one between 21 and 28 days, which becomes stable in time. This appears to be in agreement with the analysis of the carboxyl and carbonyl formation processes and—as far as the second variation is concerned—with the surface behaviour revealed by AFM imaging. Absorbance increment reaches a maximum at around 260 nm, which is consistent with the typical wavelength range of carbonyl formation in compounds [25]. A significant increase can also be observed in the ultraviolet band between 300 and 360 nm, which can be ascribed to the formation of yellow chromophores [25], as is also verified by the variation of the CIE b^* coordinate (Table 1).

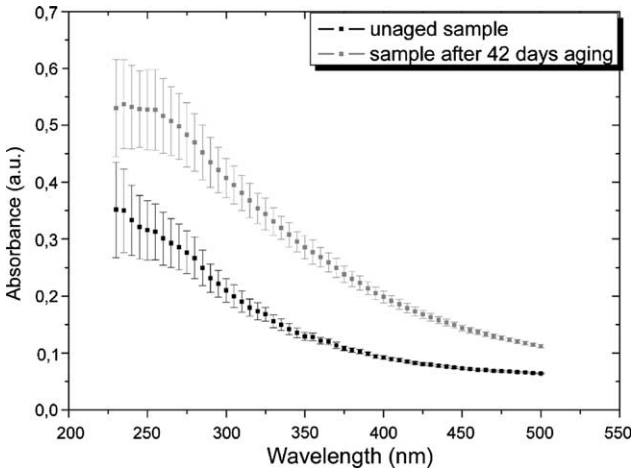

Fig. 12. Statistics from all the unaged and 42 days aged samples.

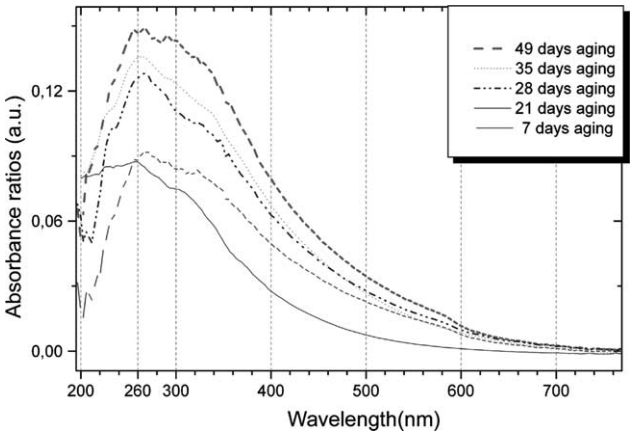

Fig. 13. Absorbance increment of aged samples with respect to the unaged one.

4. Conclusions

Atomic force microscopy has a potential application as a micro-destructive technique for the evaluation of pure cellulose paper degradation. Imaging of standard samples throughout an accelerated ageing treatment showed a surface deterioration due to superimposition of slight oxidation and hydrolysis processes.

Such processes are verified destructively, by means of a quantitative chemical characterization, and non-destructively, by means of spectrophotometric absorbance measurements, which provide semi-quantitative information. Chemical data indicate a minor DP decrease, and carbonyl and carboxyl groups formations as the main concurrent processes, where the dominant impact is ascribable to carbonyl formation. Speed rate change of carbonyl formation process is fitted between 21 and 28 days. The absorbance component, around 260 nm, and consistent with carbonyl formation reported in literature, shows a significant increase during the first weeks of treatment and a stabilization trend after 28 days of treatment.

Whereas mechanical and colorimetric techniques do not show significant variation after the ageing period considered, AFM is sensitive to induced deterioration and offers a new insight into the morphological behaviour of cotton cellulose fibre surfaces during degradation. Moreover, even if AFM is not sufficient to determine the nature of the process in as much detail as the destructive evaluation can provide, it does allow for a micro-destructive quantitative distinction to be made between the initial and final stage.

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