Characterization of changes induced by ageing to the microstructure of pure cellulose paper by use of a gravimetric water vapour adsorption technique

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Abstract

The changes induced to paper microstructure by accelerated ageing were studied by use of an automated gravimetric technique based on water vapour adsorption. The technique applies especially to cases that the adsorption and desorption of water is involved, such as paper recycling, hornification, ageing and aqueous conservation treatments. The logistics for the calculation of the specific surface area of the examined samples are presented and the f-plot technique is applied for the visualization and interpretation of the results, which indicated that ageing reduced the adsorption and the swelling capacity of paper, resulting in a more compact structure, increasing crystallinity and promoting hornification.

Key Words

Paper microstructure, adsorption, water vapour, specific surface, BET, f-plot, accelerated ageing, hornification.

This is an edited author’s version of the final submitted manuscript (post-refereed) of the article: *Characterization of changes induced by ageing to the microstructure of pure cellulose paper by use of a gravimetric water vapour adsorption technique*, by Spiros Zervos, published in Cellulose, Volume 14, Number 4 / August, 2007, DOI10.1007/s10570-007-9125-0.
The original publication is available at www.springerlink.com , at
http://www.springerlink.com/content/j4066121647584w5/fulltext.pdf [pdf version],
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Introduction

The microstructure of paper can be studied by various techniques, which apply to different research contexts and present different advantages and disadvantages: nitrogen and water vapour adsorption (Weatherwax 1977; Roberts 1996; Klemm et al. 1998), mercury (Hg) porosimetry (Vertommen et al. 1998; Westermarck 2000; Levis and Deasy 2001), small angle X-ray scattering (SAXS, Lin et al. 1987; Kato and Cameron 1999a), solute exclusion technique (Stone and Scallan 1967), and more recently, advanced analytical techniques such as NMR (Ek et al. 1995; Haggkvist et al. 1998; Topgaard and Soderman 2002). With these techniques, several microstructure parameters can be determined, such as open porosity, average pore radius, specific surface area, apparent and corrected density and pore size distribution. Most of these techniques are laborious, need sophisticated equipment and require extreme conditions such as high vacuum (Hg porosimetry, nitrogen adsorption) or very low temperatures (nitrogen adsorption). The interpretation of the results is based on complex theoretical background and in the case of Hg porosimetry, assumptions concerning the pore shape must be made for the determination of the pore size distribution and specific surface (Gregg and Sing 1982). Although Hg porosimetry has been often used for the studying of paper microstructure, the very high pressures that are used are suspected to deform the paper microstructure and introduce considerable errors (Gregg and Sing 1982; Chesson et al. 1997; Vertommen et al. 1998).

In contexts such as paper recycling and hornification, paper ageing (natural or thermally accelerated) and aqueous paper conservation interventions, changes in paper microstructure are induced primarily by interaction with water (except from ageing, where depolymerization and crosslinking also play important role, Kato and Cameron 1999b). The results of these processes also affect immensely the way treated paper interacts with water. Kato and Cameron (1999b), in their review of the relationship between thermally accelerated ageing and hornification, define the term ‘hornification’ as the irreversible changes in water sorption behaviour that result from water removal, either at ambient or elevated temperature, with lower flexibility, lower water retention, and increased brittleness being its main characteristics. They stress the importance of this phenomenon to the pulp and paper industry, especially concerning the understanding of the mechanisms responsible for the loss of recycled fibre quality. Hornification is attributed to the formation of irreversible intra-fibre hydrogen bonding between microfibrils.

The interpretation of the mechanism of the induced changes in strength and other properties due to the above mentioned processes (Kato and Cameron 1999a; Moropoulou and Zervos 2003), but also the need for a model that could predict them, require the understanding of the changes induced to the microstructure of paper. Absolute values are not of primary interest; the trends of the changes of parameters such as pore size and specific surface need to be clarified. In one of the very few relevant studies, Kato and Cameron (1999a) used small angle X-ray scattering (SAXS) to study the changes induced to the microstructure of paper due to ageing. They found that the size of the voids was very slightly affected by ageing, but the swelling capacity of paper was markedly diminished, with less and larger voids after ageing and wetting.

In the above mentioned study, Kato and Cameron used water as a structural probe. They determined the size of the voids in the dry and the wet state and drew conclusions concerning structure capability to expand. The use of water adsorption recording over a continuous range of RH utilizes water in two roles: first, it serves as the means for the study of the microstructure, by monitoring the quantity of the adsorbed water and second, it simultaneously affects paper structure, serving as a structural probe. Thus, it can manifest stereochemical effects that impede the swelling of cellulose, such as those caused by hornification. According to the previous discussion, methods based on water adsorption possess an advantage for the studying of cellulose microstructure changes caused by interaction with water.

In this study, we utilize an automated gravimetric technique for the characterization of changes in paper microstructure, based on "CISorp Analyzer", an instrument made by CI Electronics Ltd (Mangel 1999). The instrument records the water vapour adsorbed by the sample as relative humidity changes according to a user-defined program. We also present the logistics for the calculation of the specific surface of the samples examined and apply the f-plot technique for the visualization and interpretation of the results. The method is relevant to cases that microstructure changes are of interest, especially cases that the adsorption of water is involved. Here, it is applied for the studying of the microstructure changes induced by accelerated ageing to pure cellulose paper. Such studies are also relevant to paper recycling and hornification and may help shed some light to the changes induced to historic paper by aqueous conservation treatments.

Theoretical Considerations

Specific Surface Area Determination

The BET Equation can take the following general form (Gregg and Sing 1982):

$$\frac{P}{(P_o - P)\cdot V_a} = \frac{C-1}{V_m \cdot C}\cdot\frac{P}{P_o} + \frac{1}{V_m \cdot C} \Rightarrow \frac{P}{(P_o - P)\cdot V_a} = A\cdot\frac{P}{P_o} + B \qquad (1)$$

where $A = \frac{C-1}{V_m \cdot C}$, $B = \frac{1}{V_m \cdot C}$, P: equilibrium pressure, P_o: saturation pressure, V_a: volume of adsorbed gas (ml) per g of material, V_m: volume of the adsorbed gas (ml) corresponding to monomolecular layer per g of material and C: constant (the volumes are expressed in normal conditions).

When the adsorbate is water vapour, $\frac{P}{P_o} = RH$ (2), where P: water vapour pressure at equilibrium, P_o: water vapour pressure at saturation, RH: relative humidity (expressed as a fraction).

The combination of equations (1) and (2) results equation (3):

$$\frac{RH}{(1-RH)\cdot V_a} = A\cdot RH + B \qquad (3)$$

According to the classic treatment, which is valid for isotherms of type II and IV (Gregg and Sing 1982, p. 168, 285), $\frac{RH}{(1-RH)\cdot V_a}$ is plotted against RH for RH values between 0.05 and 0.30. The slope of the straight line equals A and the intercept equals B. From the values of A and B, the values of C and V_m are calculated from the formulae:

$$C = 1 + \frac{A}{B} \quad \text{and} \quad V_m = \frac{1}{B\cdot C}$$

The specific surface of the sample in m^2/g of dry paper is given by:

$$S_{BET} = \frac{a\cdot V_m \cdot N_A \cdot 10^{20}}{22400}$$

where $\alpha = 10.6$ Å^2 (Gregg and Sing 1982, p. 238): surface occupied by one water molecule, V_m: water vapour volume in ml under normal conditions, corresponding to monomolecular layer and N_A: Avogadro constant.

Evaluation of microstructure changes - f Plot

When mesopores are present, adsorption measurements allow for the determination of the pore size distribution. A model for the pore shape is assumed and the capillary condensation region of the isotherm is analyzed according to the Kelvin equation (Gregg and Sing 1982). The CIsorp technique is not optimized for such an analysis, but qualitative conclusions concerning changes in pore size distribution after a treatment can still be drawn by the comparison of the adsorption isotherms before and after the treatment. Increased adsorption at low relative humidities indicates an increase in the surface area corresponding largely to the micropore range while an increase in adsorption at medium and high relative humidity indicates an increase in the surface area corresponding to the mesopore range. This comparison can be made easier and more depictive by the use of f-plots. An f-plot can be constructed by calculating the ratio of the ordinates of the isotherms of the treated and the reference sample at regular intervals of relative pressure (here RH) and plotting the ratio f of the two ordinates against relative pressure. Changes in the shape of the isotherm cause deviations of the f-plot from the horizontal (Gregg and Sing 1982, p. 100).

Experimental

The CISorp Analyzer was used for the recording of the adsorption-desorption isotherms. The instrument is computer-controlled and records the changes of the sample mass as relative humidity in the sample chamber changes according to a user-defined program. The steps of the RH changes were specified at 5% up to 20%, than at 10% up to 90% and than at 5%. The same steps were defined for desorption. The instrument monitors the sample mass and when it is stabilized (there is a user defined stabilization criterion) proceeds to the next step of the program. Since the instrument has two scales, two similar samples can be analyzed at the same time in one determination. The accuracy of the scales is ±1μg and of the RH and temperature sensors ±1%RH and ±0.3ºC respectively (Anonymous b; Mangel 1999). The accuracy of the RH sensor was independently tested and found within the limits reported by the instrument manufacturer. The scales were calibrated before the experiments.

The recording was performed at 23ºC. The samples were dried in a desiccator for 2 hours (RH inside desiccator 18-20%) and then they were further dried at 50 ºC in dry nitrogen stream inside the weighting chamber of the instrument. The dry sample mass was taken as reference for the calculation of the mass changes. The sample mass was in the order of 40 mg. In every experiment, approximately equal masses of similarly treated samples were simultaneously analyzed in the two scales, so that equilibrium was reached at about the same time for both samples. Two replicate determinations for every ageing period were performed, with two specimens of the same ageing period in each determination, placed on the two scales. The experiments were performed in two replicate rounds, each round consisting of three determinations corresponding to the three ageing periods (0, 90 and 150 days). Thus, the determinations were 6 in total, and the analyzed samples were 12. The output of the instrument is in the form of a graph or a table of the percentage of the sample mass change (water uptake %, which is equal to the percentage of the weight of the adsorbed water over the weight of the dry paper) as a function of the relative humidity. The tables were inserted in a spreadsheet for further elaboration.

The volume of the adsorbed water vapour (V_a in ml under normal conditions) per g of paper was calculated from the CISorp results (water uptake %) by the formula:

$$V_a = \frac{(\text{water uptake \%})\cdot 22400}{18\cdot 100}$$

The crystallinity of the samples was determined according to the Crystallinity Index proposed by Segal et al. (1959): $CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100$, where CrI: Crystallinity Index, I_{002}: maximum intensity of diffraction at 2θ=22.8° and I_{am}: intensity of diffraction at 2θ=18.0° (intensities in arbitrary units). The samples were ground by a cutting mill to pass a 500μm screen (ball milling is known to reduce the crystallinity of cellulose, Segal et al. 1959; Millett et al. 1979; Klemm et al.1998, p. 104). A Siemens D5000 diffractometer was used (λ=1.5406Å, V=40KV, i=30mA). The rotation speeds of the detector and the sample holder were adjusted so that they moved from a 2θ angle of 10° to 27° in 14 minutes. The spectra were smoothed with a 'pick width parameter' value of 2. A graphical plotter was used and the intensities were measured by a ruler. The reported values are the average of 4 determinations.

The samples consisted of Whatman No 2 filter paper, which has been widely used to model pure cellulose, since it consists of pure cotton cellulose with no additives, fillers or sizing (Anonymous a). Ageing took place in sealed vessels at 80ºC and 76% RH for 90 and 150 days. It should be noted here that the aged samples were recognizable paper, which retained a significant portion of its original strength (see table 1). Specifics on the preparation of the samples and the ageing procedure have been presented elsewhere (Zervos and Moropoulou 2005).

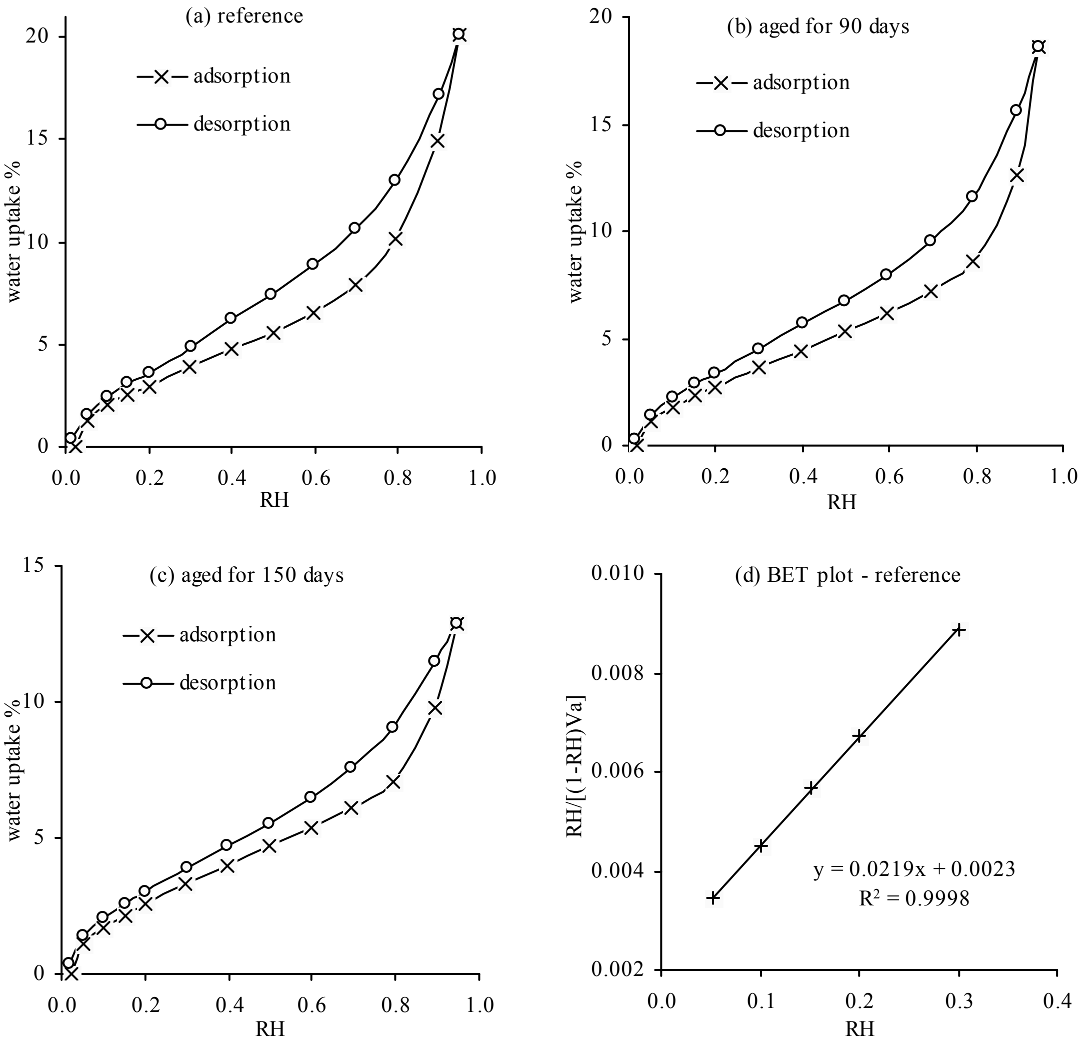

Figure 1: Adsorption isotherms of reference (a), aged for 90 days (b) and 150 days (c) samples; BET plot for reference sample (d).

Results

In figures 1a-c, the water vapour adsorption isotherms of reference (untreated), aged for 90 days and 150 days Whatman No 2 filter paper are presented. The ordinate represents the mass of the adsorbed water vapour per 100 g of dry paper (water uptake %), and is the mean of 2 determinations with two samples each (4 values in total).

The specific surface area of the samples was calculated according to the method presented above. The experimental results and the calculated values of the BET constants and of RH/[(1-RH)V_a] are presented in table 1. The constant C and the V_m were calculated from the plot of RH/[(1-RH)V_a] against RH (figure 1d). The coefficients of determination are very close to 1, indicating that the determined values are reliable. Table 1 also includes the percentage of the hydrolysed glycosidic bonds δ% and the tensile strength values of the samples, which have been published elsewhere (Zervos and Moropoulou 2005), but are also presented here because of their relevance to this work.

The standard deviations of the water uptake are presented in table 1. The standard deviations of the RH calculated from the six determinations were less than 0.001 at any point of the isotherms, while the higher standard deviation of the crystallinity index was 0.5.

Reference				Aged for 90 days				Aged for 150 days			
RH	water uptake %	SD	RH/[(1-RH)Va]	RH	water uptake %	SD	RH/[(1-RH)Va]	RH	water uptake %	SD	RH/[(1-RH)Va]
0.022	0.00	0.00		0.021	0.00	0.00		0.022	0.00	0.00	
0.052	1.28	0.01	0.00345	0.052	1.11	0.02	0.00398	0.052	1.08	0.02	0.00407
0.101	2.00	0.01	0.00451	0.101	1.81	0.03	0.00500	0.101	1.70	0.02	0.00531
0.151	2.52	0.02	0.00567	0.150	2.31	0.04	0.00615	0.151	2.16	0.01	0.00663
0.200	2.98	0.02	0.00674	0.199	2.72	0.03	0.00734	0.200	2.54	0.01	0.00790
0.300	3.88	0.04	0.00888	0.299	3.64	0.03	0.00942	0.299	3.29	0.01	0.01042
0.398	4.74	0.03		0.397	4.42	0.03		0.398	4.00	0.05	
0.498	5.61	0.03		0.496	5.31	0.04		0.497	4.68	0.05	
0.596	6.56	0.02		0.596	6.20	0.03		0.596	5.34	0.09	
0.695	7.90	0.05		0.694	7.18	0.04		0.694	6.08	0.12	
0.793	10.17	0.10		0.792	8.64	0.02		0.793	7.07	0.15	
0.896	14.95	0.10		0.896	12.59	0.03		0.896	9.76	0.19	
0.946	20.11	0.07		0.946	18.58	0.08		0.947	12.90	0.20	
A			0.0219				0.0223				0.0258
B			0.0023				0.0028				0.0027
R^2			0.9998				0.9991				0.9999
C			10.52				8.96				10.56
Vm (ml)			41.3				39.8				35.1
S_{BET} (m^2/g)			117.8				113.6				100.0
δ%			0.0000				0.1263				0.6125
TS (N/m)			1770				1760				1161

Table 1: Water uptakes corresponding to the adsorption part of the isotherms; calculated values of BET parameters, RH/[(1-RH)V_a] and specific surface (S_{BET}); percentage of the hydrolysed glycosidic bonds (δ%) and tensile strength (TS). SD: standard deviation of the water uptake.

Discussion

The shape of the isotherms is not exactly identical to any one of the six known types. They were initially characterized as either of type IV or V, since the hysteresis loop manifests the existence of mesopores which are characteristic of type IV or V isotherms (Gregg and Sing 1982, Mangel 1999, p. 583). The hysteresis loop is of type B (H3 according to the IUPAC description system, Gregg and Sing 1982, p. 287) and extends to the whole range of relative humidities. The constant C of the BET equation for the system under study (pure cellulose paper - water vapour) was found to have values around 10. Since C exceeds 2, the isotherms were definitely classified as type IV (Gregg and Sing 1982, p. 46, 168). For such values of C though, the calculation of the specific surface by the BET treatment has been a matter of controversy, since the formation of the multimolecular layer is supposed to start before the completion of the formation of the monomolecular layer (Gregg and Sing 1982). Furthermore, the BET theory has been criticized in general for ignoring adsorbate interactions and the heterogeneity of the substrate (Gregg and Sing 1982, p. 49; Roberts 1996, p. 74). Nevertheless, it has been used for the determination by water vapour adsorption of the specific surface of many different kinds of paper, pulps and cellulose products, some of them containing degraded, oxidized and generally modified cellulose: cellophane, filter paper, dilignified cellulose of different origins, refined pulps, scoured and bleached cotton, viscose cord rayon, mercerized microcrystalline cellulose (Roberts 1996, p. 74, table 5.2, p. 76; Haggkvist et al. 1998; Klemm et al. 1998, p. 28, table 2.1.11). The values obtained are in good agreement with other methods.

The specific surface area and the porosity of a given cellulose sample depend dynamically on the current temperature and especially on the relative humidity, but also on the history of hygrothermal changes the specific sample has undergone. When water is adsorbed from the dry state, a monolayer of water molecules starts to form on the external surface and the surface of the pores of cellulose. The water molecules are hydrogen bonded to the accessible OH groups of the cellulose. As relative humidity increases, more layers are formed, and cellulose starts to swell. The process of swelling causes closed pores to open, thus creating new active pores, and expands the existing pores. At the same time, capillary condensation of water starts occurring in the pores, first filling the smaller ones and proceeding to the larger ones (Klemm et al. 1998; Roberts 1996). The surface area calculated from the BET treatment (S_{BET}), depends very little on the swelling of cellulose, because it corresponds to the monomolecular layer, before considerable swelling starts to occur. Thus, differences in the S_{BET} due to different treatments reflect real differences in pore volume. In other words, when S_{BET} diminishes, it is because the treatment has brought about a real decrease in the overall pore volume. When comparing isotherms or using the f-plots though, lower adsorption at high relative humidities is an indication of reduced volume of large pores, but also of lower swelling capability.

In figure 2, the adsorption part of the 3 isotherms of the reference sample and the samples aged for 90 and 150 days are plotted together for comparison. Ageing shifts the isotherms closer to the x-axis, reducing the quantity of water vapour that the samples can adsorb. Such a diminution of the sorption capacity of cellulose could be attributed to either structural changes caused by hydrolysis, and in this case it is amenable to BET analysis, or to chemical changes others than hydrolysis (formation of new active groups in such concentrations that interfere with the adsorption capacity of cellulose), in which case the BET treatment does not apply.

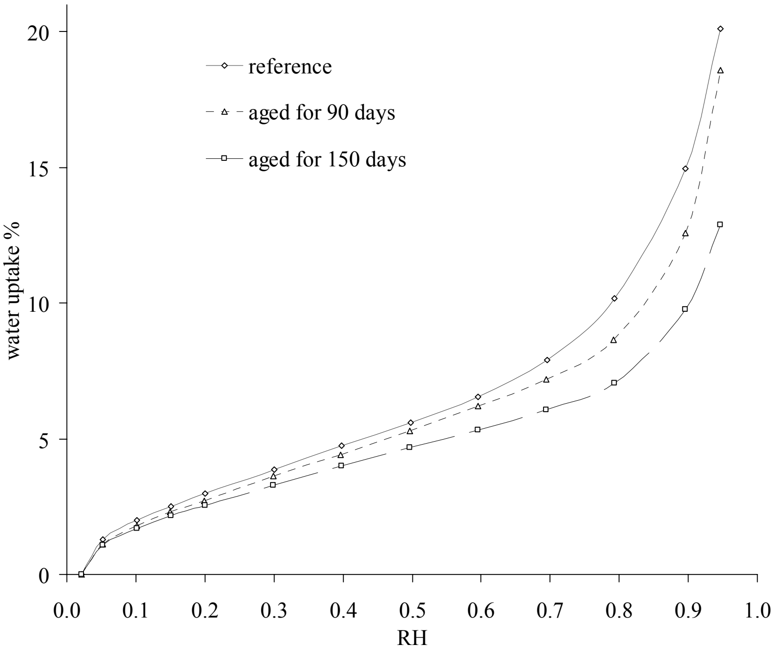

Figure 2: Isotherms of reference, aged for 90 days and 150 days samples (adsorption part only).

According to the relevant literature, the main degradation route of cellulose under the ageing conditions used here is hydrolysis, with negligible contribution from other type of reactions, such as oxidation, pyrolysis and thermal degradation (Feller et al. 1986; Zou et al. 1994, p. 399; Zou et al. 1996, p. 253, 257; Kato and Cameron 1999b, p.26). Whitmore and Bogaard (1994) studied the contribution of different degradation chemistries during the oven ageing of cellulose. They found that: "Degradation in the humid ovens (90°C, 50% RH and 80°C, 65% RH) produced one carbonyl per scission with no measurable concomitant carboxyl production, which is consistent with a purely hydrolytic scission chemistry". The almost exclusively hydrolytic character of cellulose degradation has also been verified by studying the composition of the degradation products (Erhardt et al. 1999, p. 503, 504). Therefore, chemical alterations such as the formation of new active groups that interfere with the adsorption capacity of cellulose cannot account for the reduced water adsorption of the aged samples. Accordingly, the diminution of the water adsorption capacity of the samples must be attributed to structural changes and in such case, the BET treatment can be applied to the aged samples, as applied to the virgin cellulose.

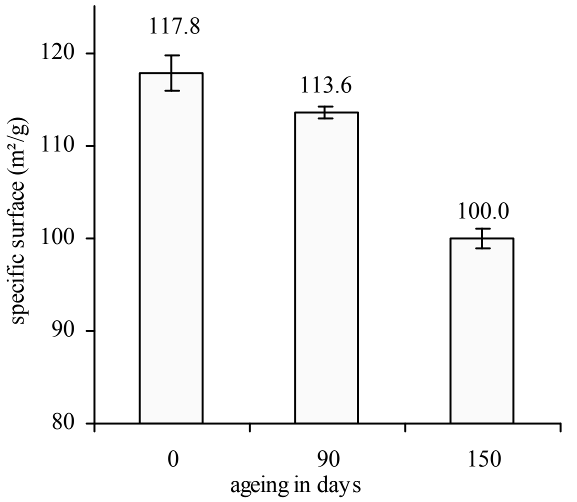

Figure 3: Specific surface of reference, aged for 90 days and 150 days samples; error bars represent confidence intervals at 0.05 significance level.

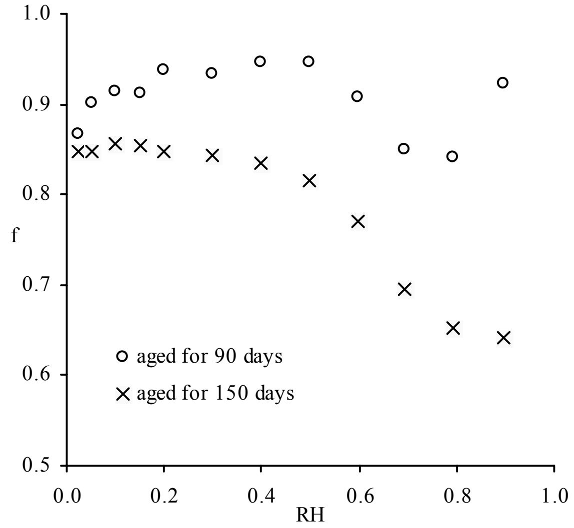

Figure 4: f plots of the aged samples; f (ratio of the ordinates of the isotherms of the aged and the reference sample at regular intervals of RH) plotted against RH.

The calculation of the specific surface by the BET treatment permits a quantitative comparison of the adsorption potential of the three samples (figure 3). The application of the student-t test showed that the reduction of the specific surface of the samples is statistically significant. The reduction of the adsorption ability of the samples indicates that as ageing advances, the size of the pores is reduced and the structure of paper becomes more compact.

In order to visualize the results and make the comparison easier, we constructed the f-plot of the aged for 90 and 150 days samples with the untreated as reference (figure 4). It can be seen that up to 50% RH, the pores corresponding to this range of relative pressures have been rather equally affected and the adsorption capacity of the aged samples has been reduced to the 0.85-0.95 of the original. For higher RH though, the adsorption capacity of the aged samples drops significantly, indicating that the larger pores of the aged samples have been affected more than the smaller ones and that the expansion of the structure becomes more hindered as the RH surpasses 50%. This is particularly evident in the case of the 150 days aged sample. Such a reduction of the adsorption capacity at high relative humidities is an indication of hornification.

The reduction of the water adsorption capacity and the decrease of the specific surface of the samples due to accelerating ageing are consistent with the current theories about paper ageing. It has been discussed above that the main degradation process of paper during accelerated ageing is the depolymerization of cellulose. The high temperature and the humidity involved in accelerated ageing promote the mobility of the cellulose chains and the scission of the cellulose macromolecules at random sites facilitates a more compact arrangement of the fragmented cellulose molecules (Atalla 1981). As a result, the microstructure partially collapses, the crystallinity increases (figure 5) and the water adsorption and swelling capacity of paper decrease.

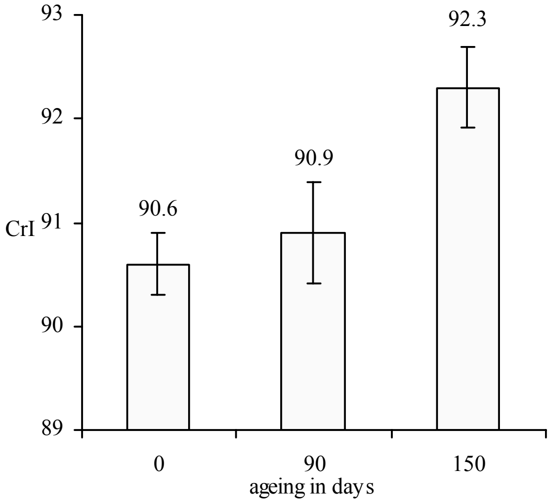

Figure 5: Crystallnity Index of reference, aged for 90 days and 150 days samples; error bars represent confidence intervals at 0.05 significance level.

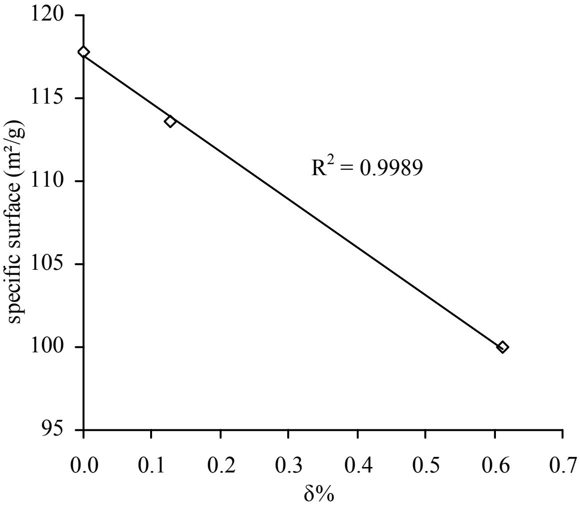

Figure 6: Plot of the specific surface against the percentage of the hydrolysed glycosidic bonds δ%

It has been shown that the depolymerization of cellulose for ageing in sealed vessels is an autocatalytic process, and that the percentage of the hydrolysed glycosidic bonds δ% increases exponentially with the time of ageing (Zervos and Moropoulou 2005). Both the pattern of the specific surface decrease and the f-plot indicate that the diminution of the sorption capacity follows a similar law. In order to ascertain that, the S_{BET} was plotted against δ%. The results of the linear regression are presented in figure 6, and although the points are few, they seem to support the notion that the sorption capacity is related roughly linearly to the extent of hydrolysis rather than to the time of ageing (within the limits studied). Therefore, although the first part of ageing (90 days) is longer than the second (60 days), the changes are greater in the second part, where hydrolysis is far more extensive (see table 1, δ% values). This observation lends further support to the point expressed above, that the hydrolysis of cellulose is responsible for the diminution of the sorption capacity of the aged samples.

Conclusions

The application of the presented gravimetric technique allowed for the calculation of the specific surface of the paper samples. It is inexpensive, relatively fast and easily applied at ambient temperatures and normal atmospheric pressure. The fact that the adsorbate is water vapour is the great advantage of the method in contexts that the material under study swells by adsorbing water and the system under study involves interaction with water. The use of the f-plot facilitated the comparison of samples before and after a treatment, by visualizing the differences in adsorption at all the range of relative humidities.

The technique was used for the study of the changes induced to paper by accelerated ageing. The results indicated that ageing reduced the adsorption and the swelling capacity of paper, the effect being more intense at high relative humidities. Apparently, ageing reduced the size of the pores, promoted hornification and resulted in a more compact structure.

Acknowledgements

I would like to thank professor A. Moropoulou of National Technical University of Athens (NTUA), School of Chemical Engineering (SCE), for her support and assistance. The experimental part of the research presented here took place at the Section of Materials Science and Engineering, SCE, NTUA.

Abstract

The changes induced to paper microstructure by accelerated ageing were studied by use of an automated gravimetric technique based on water vapour adsorption. The technique applies especially to cases that the adsorption and desorption of water is involved, such as paper recycling, hornification, ageing and aqueous conservation treatments. The logistics for the calculation of the specific surface area of the examined samples are presented and the f-plot technique is applied for the visualization and interpretation of the results, which indicated that ageing reduced the adsorption and the swelling capacity of paper, resulting in a more compact structure, increasing crystallinity and promoting hornification.

Key Words

Paper microstructure, adsorption, water vapour, specific surface, BET, f-plot, accelerated ageing, hornification.

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