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Investigating the Causes of Paper Strength Loss after Aqueous Treatments

Abstract

Previously published studies on 8 different papers showed that aqueous treatments (i. e. washing and deacidification) resulted in the general decrease of tensile strength and the increase of stretch at break, which were statistically significant in most cases. A search revealed similar findings scattered in the relevant literature. As a result, a study was launched in order to investigate the causes of paper strength loss after aqueous treatments.

Hornification, a phenomenon related with strength loss after drying, has been widely investigated by the paper industry. The term is used for the irreversible changes that occur after the first drying of cellulosic fibers, resulting in the reduction of water retention value and tensile strength. Both properties are very important in paper recycling.

Under the assumption that changes at the microstructure level – similar to the ones occurring as a result of hornification – may be responsible for the strength loss, various microstructural parameters were studied, mainly on a model pure cellulose paper (Whatman Nr. 2 filter paper) and occasionally on a number of historical samples. The following methods were used:

- Air resistance determination (Gurley method)
- Determination of the Specific Surface Area of cellulose by a water vapour sorption method (CIsorp), described in detail elsewhere. The method of the f-plots was utilized for the comparison of the absorption isotherms.
- Determination of volume changes, deduced by the changes in the dimensions of the sheets of paper
- Determination of Crystallinity Index
- Mercury porosimetry for the evaluation of porosity changes

The results were not conclusive in all cases, but generally showed that after washing, the specific surface area and the porosity of the Whatman samples increased. Evidence also indicated that the surface area corresponding to smaller pores slightly decreased, while that corresponding to the larger pores increased.

A tentative mechanism is proposed that accounts for the microstructural changes, strength loss and higher stretch at break observed after aqueous treatments. Further investigation is needed to ascertain the validity of the suggested mechanism and the possible connection with hornification. An experimental approach is proposed.

1 Introduction

In previous publications, we reported on the effects of two model aqueous conservation treatments (washing with deionized water and deacidification with semi-saturated calcium hydroxide solution) on the mechanical properties of 8 different paper samples. Our results showed that after the treatments, the tensile strength of all but one paper sample decreased, with the decrease being statistically significant in 6 out of 8 cases. They also showed that folding endurance exhibited a statistically significant decrease in 2 cases while stretch at break an overall increase, which was statistically significant in 5 out of 8 cases.[1]

The observed strength decrease was considered a rather surprising but also alarming finding, since it was observed for both sized and unsized paper samples[2] and contradicted the generally accepted tenet that aqueous treatments have an overall positive impact on the strength properties of paper.[3] A literature search revealed several scattered reports concerning strength loss after various aqueous treatments.[4]

1 Moropoulou/Zervos (2003); Zervos (2007b)

2 Moropoulou/Zervos (2003)

3 Hey (1979); Dupont (1996)

4 Wilson et al. (1981), p. 99; Lienardy/van Damme (1990); Green/Leese (1991); Sistach (1996); Adamo et al. (1998), p. 45; Moropoulou/Zervos (2003)

The next step was to search the literature for a possible explanation. In most of the cases where strength loss was reported, it was considered unimportant or irrelevant and left uncommented. In rare occasions, an arbitrary explanation was put forward and the strength loss was attributed either to the removal of the sizing agents or to the oxidizing action of the alkaline deacidification solution.[5] In our research, we established that the reduction of the tensile strength was very real and occurred to both sized and unsized papers. We also found that the pH of the bath was irrelevant, since tensile strength decreased after both washing with deionized water and deacidification.[6]

Searching within the field of paper conservation did not yield any relevant explanation. However, we were aware of hornification, a phenomenon related with strength loss after drying, which has been widely investigated by the paper industry due to its importance to paper recycling. The term is used for the irreversible changes that occur after the first drying of cellulosic fibers, resulting in a decrease in the water retention value and tensile strength.[7] Hornification may also occur after rewetting and drying[8] and has been attributed to the formation of irreversible intra-fibre hydrogen bonds among cellulose microfibrils, a process that restricts cellulose swelling and decreases its absorption capacity. Occasionally other explanations have also been proposed.[9] The negative effect imparted by hornification to the flexibility of cellulose fibres is held responsible for the strength loss, but no evidence was found in the literature on hornification accounting for the increase in stretch at break. Nevertheless, we considered that the mechanism responsible for hornification may be relevant to the changes of strength properties after aqueous treatments. In both cases a strength loss occurs and in both cases this happens after the drying of paper.

5 Sistach (1996)

6 Moropoulou/Zervos (2003)

7 Nazhad (1994); Weise/Paulapuro (1996); Kato/Cameron (1999a); Hubbe et al. (2007); Sutjipto et al. (2008)

8 Sahin/Arslan (2008)

9 Fernandes Diniz et al. (2004); Hubbe et al. (2007)

In a previous publication[10], we speculated that strength loss may have been caused by mechanical damage and/or loss of bonding among cellulose fibres. Chemical damage was very unlikely to occur as a result of washing with deionized water. Previous investigations have shown that neither the degree of polymerization (DP) nor fibre strength is significantly affected by washing or recycling.[11] Besides, DP must decrease considerably in order to affect tensile strength. In an ageing experiment reported elsewhere[12], DP was seriously affected after 30 days of ageing, while tensile strength started to decrease after 120 days of ageing, when the DP of the samples had already dropped to the ⅓ of the original value. On the other hand, if mechanical damage and/or loss of bonding were the causes of the strength loss, microstructure changes were very likely to have occurred. Therefore, we decided to start the investigation of the possible causes of strength loss with the study of the changes in the microstructure of paper.

In this work, we investigate the effects of aqueous treatments on various microstructural properties of pure cellulose paper and examine the possible connection between the changes observed at the microscopic (microstructure) and the macroscopic level (strength properties). We also discuss any possible association with hornification.

2 Experimental

Various microstructural properties of a pure cellulose model paper (Whatman Nr. 2 filter paper) and occasionally of a number of historical rag paper samples were determined before and after the treatments. The samples have been extensively studied and their properties have been presented elsewhere[13], but are also summarized in Tab. 1. The two model conservation treatments, washing with deionized water and

10 Moropoulou/Zervos (2003)

11 Nazhad (1994), p. 65; Zervos (2007b)

12 Zervos (2007b), p. 265, Tab. 5

13 Zervos (2007b)

deacidification with semisaturated calcium hydroxide solution, are also described in detail in the same previous work.

Origin	Code	Fibre	Sizing	pH	Thickness [μm]	Grammage [g/m²]
Contemporary (Whatman Nr. 2)	U	Cotton	Unsized	7.06	190	103
ca. 1650	A	rag	Gelatin	8.61	139	70
ca. 1750	B	rag	Gelatin	4.40	213	180
ca. 1700	C	rag	Gelatin	6.74	152	68

Tab. 1: *Description of the samples*

Several methods have been used for the study of the microstructure of paper and pulp[14]: Nitrogen Adsorption (NA)[15], Water Vapour Adsorption[16], Mercury Porosimetry (MP)[17], Small Angle X-Ray Scattering (SAXS)[18], H NMR spin-lattice relaxation[19], Microscopy[20] and the Solute Exclusion technique[21]. MP is more suitable for the determination of larger pores than NA[22] and therefore it was preferred, since it would presumably offer an insight into the changes that occur in the larger pores between fibres and/or fibrils. A method based on water vapour sorption was also used, on the premise that using water as a probe would emulate the results of wetting, allowing for the effects of swelling of cellulose. Water vapour sorption presents also the advantage over MP and NA that it operates at nearly ambient conditions so that the determined values of the microstructure parameters would be

14 Roberts (1996); Klemm et al. (1998)

15 Weatherwax (1977); Buschle-Diller et al. (1995); Westermarck et al. (1999)

16 Nazhad (1994); Haggkvist et al. (1998); Zervos (2007a)

17 Buschle-Diller et al. (1995); Vertommen et al. (1998); Westermarck et al. (1999); Westermarck (2000); Levis/Deasy (2001)

18 Kato/Cameron (1999b)

19 Haggkvist et al. (1998); Topgaard/Soderman (2002)

20 Weise/Paulapuro (1996)

21 Stone/Scallan (1967); Allen et al. (1991)

22 Westermarck et al. (1998)

as close to those occurring normally. X-Ray Diffraction (XRD) was used to study the effects of aqueous treatments on the crystallinity of paper cellulose.[23]

In this work, the following methods were used for the study of the microstructure of paper:

- Air resistance (Gurley method, TAPPI T 460[24]): The time needed for the passage of a specified quantity of air (100 ml) through a disk of the sample paper (6.4 cm^2) is determined. The shorter the time, the higher the open porosity of the sample. The reported values are the average of at least 10 determinations.
- Water Vapour Sorption: The method used for the determination of the Specific Surface Area (S_{BET}) of the paper samples has been presented in a previous paper[25]. In principle, it consists of a gravimetric system (CISorp Analyzer), which automatically records the water uptake of the samples (water uptake %), as the relative humidity in the sample chamber changes according to a predefined program.[26] The recording was performed at 23 °C and the dry sample mass was around 40 mg. Specifics of the procedure and the preparation of the samples have been described elsewhere[27].
  The Specific Surface Area of the samples in square meters per gram of dry paper is given by:

$$S_{BET} = \frac{a \cdot V_m \cdot N_A \cdot 10^{20}}{22400} \qquad (1)$$

  Where: $\alpha = 10.6$ Å^2 is the surface occupied by one water molecule[28], V_m is the water vapour volume in ml under normal conditions, corresponding to monomolecular layer and N_A is the Avogadro constant.

23 Segal et al. (1959); Daniels (1986); Zervos (2007a)

24 TAPPI T 460 om-88 (1988)

25 Zervos (2007a)

26 Mangel (1999)

27 Zervos (2007a)

28 Gregg/Sing (1982), p. 238

The determination of V_m is achieved by use of eq. (2) and the following treatment:

$$\frac{RH}{(1-RH)\cdot V_a} = A\cdot RH + B \qquad (2)$$

$\frac{RH}{(1-RH)\cdot V_a}$ 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. C and V_m are calculated from the values of A and B, according to the formulae:

$$C = 1 + \frac{A}{B} \quad \text{and} \quad V_m = \frac{1}{B\cdot C} \qquad (3)$$

The relative humidity (RH) is expressed as a decimal number (values between 0 and 1). Eq. (4) was used for the calculation of the volume of the adsorbed water vapour (V_a in ml under normal conditions) per g of paper from the CISorp results (water uptake %):

$$V_a = \frac{(\text{water uptake }\%)\cdot 22400}{18\cdot 100} \qquad (4)$$

- Changes in the volume of paper: They were determined from the changes in the dimensions of the sheets of paper (MD: machine direction, CD: cross direction, ZD: perpendicular to the surface of the paper leaves). The paper samples were preconditioned at 20 % RH and 23 °C and conditioned at 50 % RH and 23 °C prior to the determinations.[29] An increase in the paper volume indicates a corresponding increase in the porosity of the samples.
- Crystallinity: The Crystallinity Index proposed by Segal et al.[30] was determined from the diffraction spectra of the samples, as described in a previous paper.[31]
- Mercury Porosimetry: The method has been used extensively for the study of the microstructure of many materials, including paper and cellulose. It can be used for the determination of several

29 TAPPI T 402 om-88 (1988)

30 Segal et al. (1959)

31 Zervos (2007a)

microstructure parameters such as open porosity (%), mean pore radius, specific surface area, apparent and corrected density and pore size distribution. In this study, an instrument manufactured by Fisons Instruments and consisting of two parts was used. The first part (Macropores Unit 120) is used for the determination of large pores (7.5–100 μm radius) and the second (Porosimeter 2000) for the smaller pores (7.5–0.0037 μm radius). Both parts are connected through a control interface to a computer for data storage and processing. The instrument determines the volume of intruded mercury in relation to the exerted pressure and plots a histogram of the pore size distribution. The open porosity (P %) is calculated by the formula: $P\,\% = V \cdot d \cdot 100$, where V is the total volume of the intruded mercury and d the apparent density.
Sample preparation: 0.32 ± 0.02 g of paper (8 pieces of paper, approximately 2.0×1.2 cm) was weighted at ambient conditions. The paper sample was preconditioned and conditioned according to the appropriate standard (TAPPI T 402) and then weighted under controlled conditions (23 °C, 50 % RH) with 4th decimal digit accuracy. The sample was then predried in a dessicator. The last traces of moisture were removed in the instrument by degassing under vacuum for 20 minutes. The sample mass S_m entered in the program was calculated by the formula: $S_m = m - m \cdot W\,\%$, where m is the mass and W % the moisture content of the conditioned sample.

The determination of the strength properties reported here has been described elsewhere.[32]

32 Moropoulou/Zervos (2003); Zervos (2007b)

3 Results

The following table (Tab. 2) presents collectively the experimental results.

		TS [N/m]	SAB [%]	P % [MP]	Gurley Air Resist. [sec]	S BET [m^2/g]	V [mm^3]	CrI
Whatman U	R	1770	2.60	62.0	4.3	117.8	496	90.6
	C	1593	3.65	64.5	3.5	120.8	521	90.0
	H	1542	3.73	64.1				
Hist A	R	1842	4.43				107	
	C	1706	4.64				108	
	H	1734	5.12					
Hist B	R	4642	3.75			130.7	131	90.4
	C	3567	3.86			130.1	139	90.8
Hist C	R	1834	4.09				86	
	C	1491	4.20				88	

Tab. 2: *Results of the determinations of Tensile strength (TS), Stretch at Break (SAB), Porosity from Mercury Porosimetry (P %), Air Resistance (Gurley method), Specific Surface Area (S BET), Volume (V) and Crystallinity Index (CrI). R: Reference, C: Deacidified, H: Washed with deionized water.*

The next graphs (Fig. 1) and table (Tab. 3) illustrate the calculation of the Specific Surface Area (S BET) of the Whatman UC samples. The values of the water uptake in table 3 represent the mass of the adsorbed water vapour by 100 g of dry paper and are the means of 4 determinations. According to the BET treatment, the values of water uptake are plotted against RH, for RH values between 0.05 and 0.30. From the gradient A and the intercept B of the BET plot, the constant C and the water vapour volume corresponding to monolayer coverage (under normal conditions) V_m are calculated. S BET is then calculated from eq. 1. The same treatment was applied to the rest of the samples. The coefficients of determination (R^2) were in all cases very close to unity (better than 0.998), indicating the goodness of the fit and guaranteeing the reliability of the determined values.

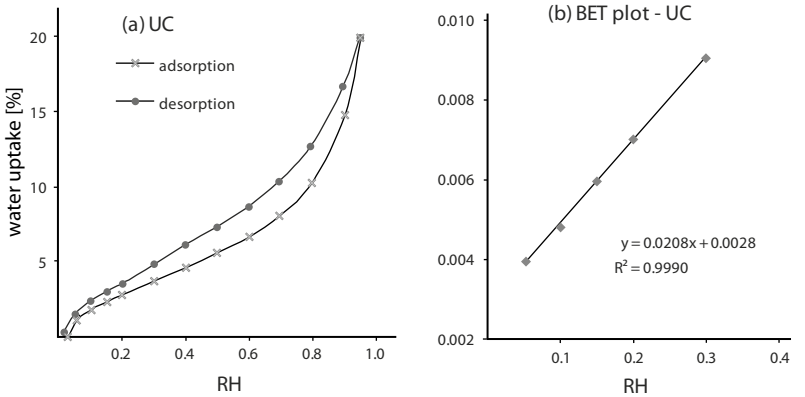

Fig. 1: *(a) Water vapour sorption isotherm of the sample UC (Whatman paper, deacidified). (b) BET plot of the same sample*

RH	Water uptake [%]	RH/[(1-RH)V_a]	Calculated BET parameters
0.026	0.00		A = 0.0208
0.053	1.13	0.00397	B = 0.0028
0.101	1.88	0.00479	R^2 = 0.9990
0.151	2.41	0.00594	C = 8.43
0.201	2.89	0.00700	V_m = 42.37 ml
0.300	3.81	0.00904	S_{BET} = 120.77 m^2/g

Tab. 3: *Water uptakes, corresponding RHs, and values of the calculated BET parameters of the sample UC (Whatman paper, deacidified).*

4 Discussion

The following table summarizes qualitatively the determined changes in the paper properties after aqueous treatments:

TS	SAB	P % [MP]	Air Perm. [G]	S BET	V	CrI
↓	↑	↑	↑	↑	↑	-

Tab. 4: *Trends of the changes of paper properties after aqueous treatments. Abbreviations are explained in Table 3. ↑: increase, ↓: decrease, -: no changes.*

Tensile strength and stretch at break universally decreased and increased respectively, with the changes being statistically significant in most cases. As discussed in the introduction, all evidence suggests that chemical damage is very unlikely to occur and points towards mechanical damage and/or loss of bonding strength. The porosity of the samples increased, as indicated by both MP results and volume changes. The increase in the volume of the samples indicates a decrease in density with a corresponding increase in the porosity. In almost all cases, the paper samples exhibited slight in-plane shrinkage, while at the same time their thickness increased. The in-plane shrinkage may be due to drying under strain when manufactured. The air permeability of the Whatman samples, as determined by the Gurley method, also increased. The results of the Gurley test indicate that deacidification alters the paper structure in ways that facilitate the passage of air through the sample. It seems that the size and/or the quantity of the pores connecting the two sides of the paper must have increased. Concerning the changes in the crystallinity of cellulose, our results verified those of Daniels[33], that aqueous treatments have no statistically significant impact on it.

According to the results of the water adsorption measurements, the S BET of cellulose of the Whatman samples increased after the aqueous treatments. The student t-test (assuming non-equal variances) indicated that the increase is statistically significant at the 95 % confidence level. The change in the S BET of the historical samples B was not statistically significant. The most important and indicative data were expected to be acquired by MP and concerned the mean pore radius. Unfortunately the effect of aqueous treatments on the mean pore radius and the pore size distribution could not be quantified, because the results of MP were inconsistent. It is believed that the very high pressures exerted during the experiments (up to 2000 bars) may have caused unexpected changes to the microstructure of paper (probably partial compression and/or collapse of the paper structure[34]), thus rendering the results unreliable.

33 Daniels (1986)

34 Vertommen et al. (1998)

Still, the water sorption results by means of the f-plots offer some insight into the trends of the changes that occur to the pore sizes.

The f-plot is a comparison plot.[35] It compares the sorption isotherms of two samples or those of the same sample before and after a treatment and assists in the visualization of their differences. In an f-plot, the ratio f of the two ordinates of the sorption isotherms of the treated and the reference sample at the same RH is plotted against RH. If the treatment has no effect at all on the sorption behavior of the sample, the f-plot is a horizontal straight line at y = 1. If the shape of the isotherms remains the same, the f-plot is still a horizontal straight line that shifts above or below 1, depending on whether the overall adsorption increased or decreased. Any other change in the sorption behaviour of the sample is manifested as a deviation of the f-plot from the horizontal. In figure 2, the f-plots of the treated Whatman and Historical B samples with the untreated as reference are presented. In both cases, a reduction and an increase of the sorption capacity of the samples after the treatment is observed at low and high RHs respectively, indicating that the surface area corresponding to the smaller and the larger pores decreased and increased respectively. It seems that the size and/or the quantity of the smaller pores (most probably pores inside the cell wall) decreased, while those of the larger pores (pores between the fibres and/or fibrils) increased. Exact values of the pore sizes cannot be specified since the CISorp instrument is not optimized for such determination, but the exhibited trends are also important.

35 Gregg/Sing (1982); Zervos (2007a)

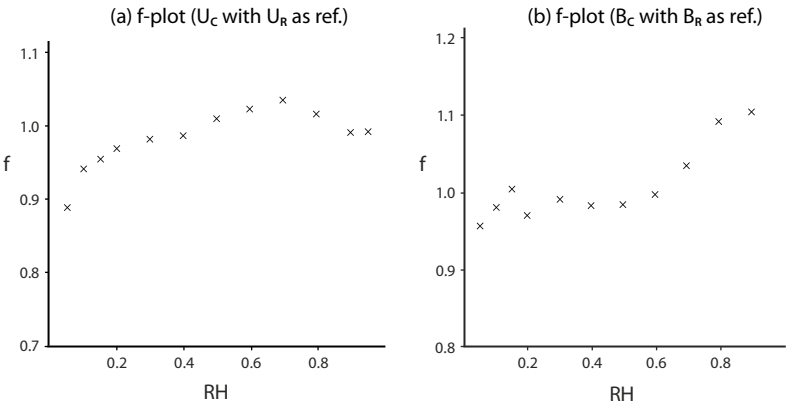

Fig. 2: *f-plots of the treated Whatman (a) and Historical B (b) samples with the untreated as reference.*

The experimental evidence presented so far indicates that aqueous treatments actually have an impact on the microstructure of paper, but does not allow for a straightforward explanation of how the observed changes in the microstructure are related to the changes in the mechanical properties of paper. The strength loss could be associated with hornification. The relevant literature indicates that the recycling of paper may not be necessary for hornification to occur and that simple wetting and drying may trigger this process.[36] In hornification, the creation of new irreversible hydrogen bonds between microfibrils inside the fibre wall is assumed.[37] This assumption offers a straightforward explanation for the decrease of the water retention value. The explanation of the strength loss is less straightforward: the formation of new irreversible hydrogen bonds inside the fibre wall is believed to render the cellulose fibres more compact, imparting stiffness and rigidity to them. According to Hubbe et al.[38], "more flexible fibers should better conform to the shape of adjacent fibers, developing higher proportion of bonded area", and consequently rigid fibers develop less bonded area and therefore lower tensile strength. In line with that, reduction

36 Kato/Cameron (1999a); Sahin/Arslan (2008)

37 Kato/Cameron (1999a)

38 Hubbe et al. (2007), p. 752

of bonding or bond strength has been reported as the cause of strength loss.[39] Nevertheless, even if hornification can account for the strength loss, the increase in stretch at break would still remain unexplained. There is no hint in the relevant literature that hornification could be responsible for it, and the proposed mechanism of hornification cannot explain it. In fact, a decrease at stretch at break is reported as a result of hornification after paper recycling.[40] Certainly, the slight in-plane contraction of the samples after drying could allow for some increase in stretch at break, but the latter is disproportionate to the former, since for the Whatman paper the contraction was less than half the increase in stretch (both measured in the CD direction).

A plausible but tentative mechanism that can account for both the tensile strength loss and the increase in stretch at break and is compatible with the experimental results is presented in figure 3 and discussed here. According to it, the wetting of the paper does not occur instantly. As the sheet of paper is immersed in the aqueous bath, one or more fronts of water are created and advance in it, depending on the number of points of initial contact of the sheet with the surface of the water. As the front propagates, the surface tension of water exerts a force on the cellulose fibers and fibrils, and assisted by swelling, pulls them partially out of the matrix. Water penetrates into the network of cellulose fibres and destroys most of the hydrogen bonds between them, thus facilitating their shifting. The result is illustrated in an idealized and exaggerated fashion in figure 3, where the fibres and the fibrils of the initially dry paper (Fig. 3a) have been shifted by the action of water, and in the wet paper end up further apart and with less overlap (Fig. 3b). On drying, two processes occur simultaneously: On the one hand, the paper matrix contracts, bringing the fibres and fibrils closer to each other, and on the other, hydrogen bonds start to form between them at the areas of contact. As a result, a number of fibres and fibrils that in the initial dry stage were more or less straight end up bent and with less overlap with adjacent fibres (Fig. 3c). In addition, the initial distance among fibres is not completely restored and therefore, the voids among fibers and/or

39 Nazhad/Paszner (1994)

40 Nazhad (1994), p. 37

fibrils are enlarged. Less fibre overlapping means less bonded area and therefore lower tensile strength. On the other hand, the bent fibres and fibrils allow for more stretch before failure, explaining thus the higher stretch at break. Inside the fibres and among microfibrils, irreversible hydrogen bonds are formed as expected because of hornification, resulting in pore diminution and/or closure[41], but between fibres and fibrils the bonding is attenuated and the voids are enlarged.

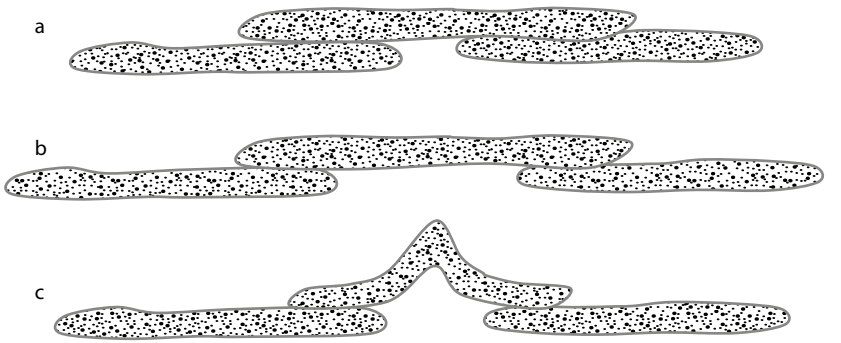

Fig. 3: *Idealized and exaggerated schematic, illustrating the stages of the proposed mechanism. Fibres (or fibrils): (a) in initially dry paper (b) in wet paper (c) after drying. This illustration does not imply that the position shifting of the fibres/fibrils occurs lengthwise. On the contrary, most of the sifting has to occur laterally, which is the direction of the fibre expansion and shrinkage.*

Such a mechanism would result in an increase of the size of the larger pores, with a simultaneous decrease in the size and/or number of the smaller pores. In order to verify this mechanism, reliable data on the changes of the mean pore radius and the pore size distribution would be necessary. As discussed previously, such results were unreliable and are not shown here. Nevertheless, the f-plots presented above indicate that such changes actually occur: the water sorption decreased at low RHs and increased at higher RHs, thus indicating that the surface area corresponding to the smaller pores decreased and that corresponding to the larger pores increased. The increase of the specific surface area (S BET) of the Whatman paper sheets after aqueous treatments also supports the speculation that the strength loss may have been caused

41 Nazhad (1994); Hubbe et al. (2007)

by loss of bonded area. It has been found that hornification results in a decrease of the specific surface area after recycling.[42] The specific surface area measured by adsorption is in fact the free (non-bonded) area of paper. Since we found an increase in the specific surface area, there must be another mechanism which overcompensated for the decrease caused by hornification. This overcompensation could have been caused by the decrease in bonded area. Surface area that does not take part in bonding anymore, becomes free surface area, and is added to the measurable by adsorption surface area.

This study showed that there are similarities between the effects of aqueous treatments and the effects of recycling. In both cases tensile strength decreases and the microstructure of paper is altered. Nevertheless, there are also important differences. Washing causes an increase in stretch at break, while recycling causes a decrease. The specific surface area increases slightly with washing, but decreases considerably with recycling[43]. Crystallinity has been reported to increase with recycling[44], but is not affected by washing. These differences are not surprising, since recycling requires the disintegration and reformation of a paper sheet, while washing exposes an already formed sheet to the effects of wetting and drying. As discussed above, hornification must contribute to the effects of washing, but other processes must also participate.

Further research is necessary for the elucidation of the mechanisms responsible for the observed effects, and for the verification of the tentative model presented above. The following tests could help to either verify or reject it, and in any case could offer a better insight into the causes of strength loss:

- Zero span tensile strength determination[45]: It would verify that the fibre strength is not affected.[46] The stretch at break should also be determined.

42 Hubbe et al. (2007)

43 Nazhad (1994)

44 Nazhad (1994)

45 TAPPI T 231 cm-85 (1985)

46 Nazhad (1994)

- Light scattering coefficient (LSC) determination[47]: An increase in LSC would indicate loss in surface bonding.[48]
- Mercury porosimetry: A second attempt to gather information about the changes in the mean pore radius and the pore size distribution.
- Water retention value determination: It would verify that hornification actually occurs.
- Nitrogen adsorption: It could probably detect changes in the smaller pores, verifying the hypothesis that hornification occurs inside the fibres.
- Microscopy (either optical or scanning electron microscopy), followed by digital image processing: If applied on the same area of the sample before and after the treatment, it might provide direct evidence concerning the changes in the voids between fibres and fibrils, but also in fibre shape and conformation.

5 Conclusions

We have shown that aqueous treatments affect the microstructure of pure cellulose paper:

- The porosity increases, as shown by the results of mercury porosimetry and volume measurements.
- The water adsorption tests showed that the specific surface area of the samples also increases.
- The Gurley tests showed that the air permeability is enhanced.

The experimental evidence presented here indicates that changes in the microstructure of paper occur simultaneously and are related to the strength loss and the increase at stretch at break after aqueous treatments. Nevertheless, the details of the process remain obscure. A tentative mechanism accounting for the observed changes is proposed that assumes the compaction of cellulose inside the fibres due to hornifica-

47 TAPPI T 425 om-06 (2006)

48 Hubbe et al. (2007), p. 753

tion, the increase of the size of the voids between fibres and/or fibrils, and the attenuation of bonding. The mechanism could be further elucidated by use of the zero span tensile test, mercury porosimetry and nitrogen adsorption, the determination of the water retention value, and microscopy (either optical or scanning electron), followed by digital image processing.

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