Establishing the relation between degradation mechanisms and fibre morphology at microscopic level in order to improve damage diagnosis for parchments

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Establishing the relation between degradation mechanisms and fibre morphology at microscopic level in order to improve damage diagnosis for parchments – A preliminary study

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ABSTRACT

To clarify whether certain fibre morphologies can be used to diagnose specific degradation mechanisms, new and historical parchment was exposed to dry heat oxidation, humid oxidation, and acid hydrolysis. Degradation was examined by fibre assessment, measurement of hydrothermal stability and pH. All three degradation types lead to a lower hydrothermal stability. As also observed in natural degraded parchment, dry oxidation transforms the fibres into gel-like fragments with no main shrinkage activity detected. Whereas humid oxidation does not have any larger impacts on the fibre morphology, hydrolysis of the new parchment causes an unfolding of the fibre structure into flat fibres. Fibres from the historical parchment, on the other hand, tend to transform into pearls on a string structure. In the study, the new parchment displayed higher sensitivity to degradation at microscopic level than the historical parchment.

INTRODUCTION

With the objective of preserving parchment documents and objects collected in libraries, archives and museums all over the world, acquired knowledge about the deterioration pathways of collagenous material is needed. Furthermore, there is a specific need to develop diagnostic techniques for the daily assessment practices of conservator-restorers (Larsen et al. 2011). To clarify whether certain fibre morphologies can be used to diagnose specific degradation mechanisms, this paper looks at the relation between oxidative and hydrolytic degradation mechanisms and the changes in fibre characteristics and hydrothermal stability. The methods used are simple and micro-destructive and can easily be used as a routine practice in the conservation studio once the methods have been learnt.

Elevated temperature and light are factors that might lead to oxidative degradation of collagen, whereas hydrolysis may be caused by an acidic environment and high levels of humidity. In this study, heat-induced oxidation is examined both in the absence and in the presence of moisture as well as acid hydrolysis. Chosen parameters for the ageing methods are based on previous studies of accelerated aged and naturally aged collagenous material (Bowes and Raistrick 1964, Bowden and Brimblecombe 2002, Dif et al. 2002, Boghosian 2007, Della Gatta et al. 2007, Juchauld et al. 2007, Vest et al. 2007), as well as pickling practices in the leather production (Gnamm 1940, Wilson 1941, Aabye 1946, Bowes and Kenten 1950, Bowes and Raistrick 1967, Reed 1972, Thorstensen 1976, Sharphouse 1983).

MATERIAL

One new calf parchment (p) and one historical sheep parchment (hp) were used in the study. The supplier of (p) states that dehairing was performed with calcium hydroxide with an addition of sodium sulfide to speed up the process and that no other altering substances were used. The exact date of (hp) is unknown, but it has been kept in an archive for more than 150 years. Twelve samples, each with dimensions of 30 × 30 mm, were cut from each parchment. Three samples from each parchment were kept as unaged references and the remaining samples were subjected to different ageing methods.

METHODS

Ageing

Three samples from each parchment were aged in a ventilated oven (Memmert U, Strues KEBO Lab A/S) at 150°C and 0% RH for 96 hours. Three samples from each parchment were aged for 28 days in a temperature and humidity chamber (SH-240, Espec) set to 80°C and 60% RH. Three samples from each parchment were immersed in 0.01 M H_2SO_4 (95-97% w/w, J.T. Baker) for 2 hours at 25°C. The pH of the acid was measured at 1.82 (average of 5 measurements, performed with PHM240 pH/ION METER, MeterLab, SD 0.005, zero pH 6.57, sensitivity 99.8%).

Measurement of hydrothermal stability

The method used for measuring hydrothermal stability followed the procedure reported by Mühlen Axelsson et al. (2012), with a start temperature of 25°C and an end temperature of 100°C. Two measurements from each sample were performed with an acceptable tolerance of deviation of ±2°C for the main shrinkage temperature.

Assessment of fibre morphology and determination of amount of fibre damage

The method used followed the procedure described by Mühlen Axelsson et al. (2016). Although fibre thicknesses may vary according to age and species of animal as well as location in the layer (Haines 1999, Kite and Thomson 2006), separated corium fibres immersed in water show the same type of morphologies and behaviour at microscopic level (Larsen 2007, Mühlen Axelsson et al. 2012), as also seen in Figures 1 and 2. So far, nine different morphologies have been distinguished for parchment fibres at microscopic level: intact fibres, fraying, splitting, flat fibres, cracks, pearls on a string structured with swollen and twisted areas, bundles of fibres, gel-like fibres and dissolved structures (Larsen 2007, Mühlen Axelsson et al. 2012, Mühlen Axelsson et al. 2016). The full length of all the fibres visible in the photo as well as the individual length of each morphology represented in the fibres was measured in µm and the physical damage reported as a percentage.

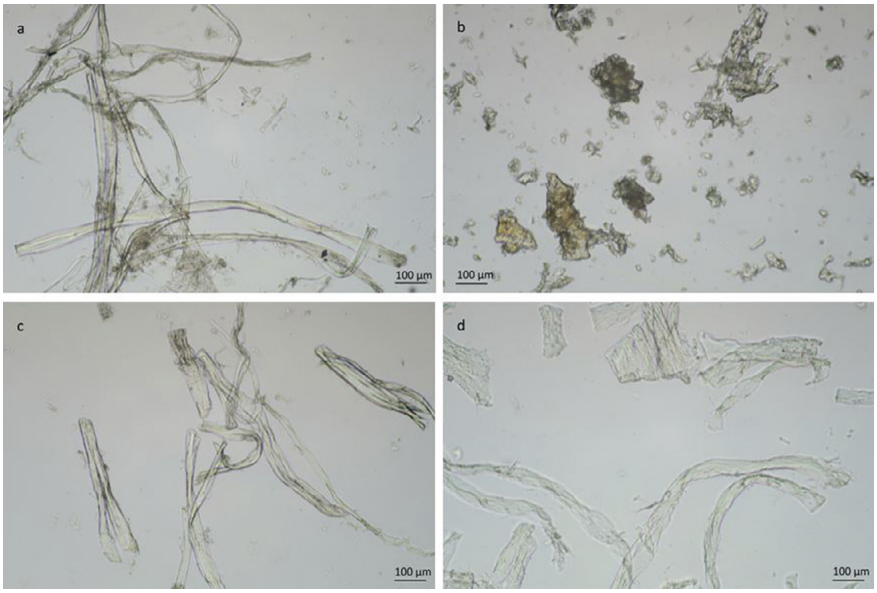

Figure 1. Fibres from new calf parchment: a) (p_ref); b) (p_dryoxid); c) (p_humoxid); d) (p_hydro)

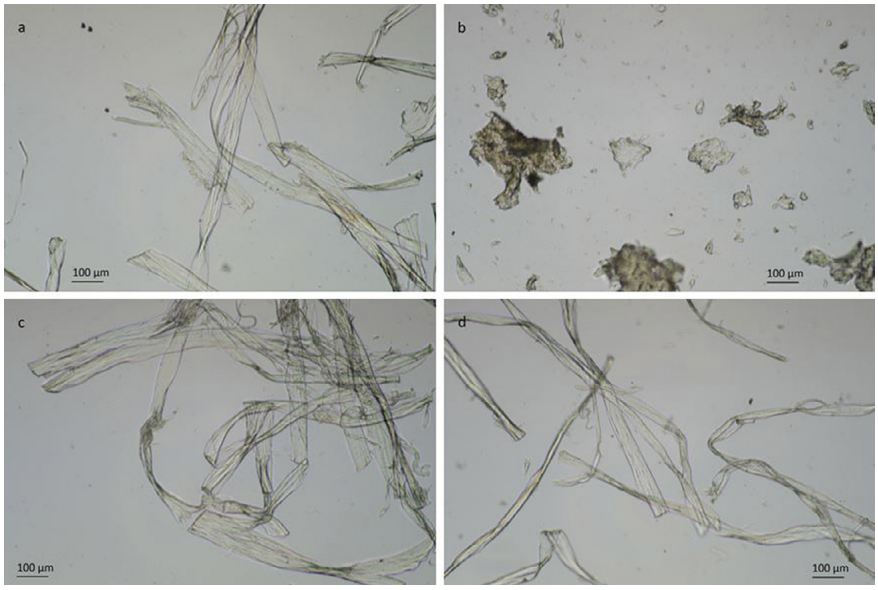

Figure 2. Fibres from historical sheep parchment: a) (hp_ref); b) (hp_dryoxid); c) (hp_humoxid); d) (hp_hydro)

pH measurement

Between 20 to 100 mg of each sample was cut into millimetre pieces and conditioned at 20°C and 65% RH for 48 hours in small glass beakers, after which time the pieces were weighed. The method for smaller samples was used and to each milligram of sample a volume of 0.05 ml of distilled water was added (Wouters 1994). The solutions were placed on a shaker board and gently agitated for 24 hours. pH measurements were performed on the extractions with a MeterLab PHM240 pH/Ion Meter (SD 0.005, zero pH 6.59, sensitivity 99.4%) with a Radiometer pHC2441-8 combined pH electrode calibrated with pH 4.0 and pH 1.0 buffer solutions. Each extraction was measured three times with the average reported.

RESULTS

Hydrothermal stability

When parchment fibres are heated in water, breakage of the bonds and thermal denaturation will eventually occur. Microscopically, this can be detected as different intervals. T_{first} is the temperature at which the first shrinkage activity is detected for a single fibre and T_{last} is the temperature at which the last shrinkage activity occurs in the process. T_s is the main shrinkage temperature and T_{end} is the end temperature of the main shrinkage interval. ΔT is defined as T_{end} minus T_s and ΔT_{total} is defined as T_{last} minus T_{first} (Larsen et al. 1993). Table 1 presents the result for hydrothermal stability with *n* indicating the number of measurements.

Assessment of fibre morphology and determination of amount of fibre damage

In Table 2, the visual assessment of the fibre morphology is reported. *n* indicates the number of photos used in the assessment, with around ten fibres from each photo being assessed. Figures 1 and 2 present fibre examples before and after ageing.

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Table 3. Average pH for each sample

Sample	pH		*n*
p_ref	5.9	±0.08	9
p_dryoxid	5.5	±0.11	9
p_humoxid	6.0	±0.21	9
p_hydro	3.0	±0.15	9
hp_ref	6.5	±0.12	9
hp_dryoxid	6.3	±0.15	9
hp_humoxid	6.2	±0.18	9
hp_hydro	2.8	±0.17	9

Table 1. T_{first}, T_s, T_{end}, ΔT, T_{last} and T_{total} for all samples

Sample	T_{first}	T_s	T_{end}	ΔT	T_{last}	ΔT_{total}	n
p_ref	42.9	54.9 ±0.70	63.7	8.8	89.7	46.8	6
p_dryoxid	28.7	-	-	-	64.9		6
p_humoxid	32.2	39.2 ±0.44	49.0	9.8	88.5	56.3	6
p_hydro	34.0	39.2 ±0.84	49.6	10.3	89.1	55.1	6
hp_ref	28.5	33.4 ±0.77	49.5	16.1	78.1	49.6	6
hp_dryoxid	45.2	-	-	-	61.4		6
hp_humoxid	27.5	31.7 ±0.97	44.0	12.3	83.6	56.1	6
hp_hydro	28.5	31.8 ±1.11	45.9	14.1	87.1	58.6	6

Table 2. Visual assessment of fibre damage and type of fibre morphology for all samples

		Amount of damage in %											
Sample	*n*	Flat		Pearls		Bundles		Gel-like		Fragments		Total	
p_ref	6	31	±27.6	42	±14.1	-	-	7	±4.4	-	-	80	±12.8
p_dryoxid	6	-	-	-	-	-	-	50	±0.0	50	±0.0	100	±0.0
p_humoxid	6	38	±17.1	51	±17.7	-	-	2	±2.1	-	-	91	±4.0
p_hydro	6	53	±16.4	37	±14.2	2	±4.3	3	±3.4	-	-	96	±3.5
hp_ref	6	46	±21.5	45	±16.1	-	-	-	-	-	-	91	±5.6
hp_dryoxid	6	-	-	-	-	-	-	50	±0.0	50	±0.0	100	±0.0
hp_humoxid	6	49	±16.0	45	±16.1	-	-	0	±1.0	-	-	94	±1.5
hp_hydro	6	33	±23.4	61	±23.4	-	-	0	±0.4	-	-	94	±3.0

pH measurement

The results for the pH measurements in Table 3 are reported as the average of three measurements for each sample.

DISCUSSION

Hydrothermal stability

In line with a recent study (Mühlen Axelsson et al. 2016), it is also possible to conclude here that the decrease in hydrothermal stability after ageing is more significant for (p) than for (hp), regardless of the ageing method. This can be explained by the natural and commenced degradation for (hp_ref) before the accelerated ageing begins. This is also reflected in the low T_{first} of 28.5°C and T_s of 33.4°C for (hp_ref) compared to T_{first} of 42.9°C and T_s of 54.9°C for (p_ref). ΔT, expressing the homogeneity of the fibre mass, furthermore confirms the high deterioration of (hp_ref) with an uneven spread in hydrothermal stability with a ΔT of 16.1°C compared to (p_ref) with a ΔT of 8.8°C.

Humid oxidation and hydrolysis led to drastic decreases in the hydrothermal stability for (p), with a lowering of T_s to 39.2°C after both ageing methods, while the decrease in hydrothermal stability for the hydrolysed samples compared to their references is more evident for (p) than (hp).

Dry heat oxidation led to such a reduction in hydrothermal stability that no main shrinkage interval could be detected. Only a few individual shrinkage movements were recorded for the dry oxidised samples. This is fully in line with previous research on parchment treated with dry heat at 150°C for 48 hours (Hassel 2002) and it is to be expected that the main

shrinkage interval in the heavily deteriorated collagen occurred below ambient room temperature. In the shrinkage process, it is common that fragmented fibres show little activity with few movements. But when it occurs, the shrinkage most often takes place at high temperatures, probably as a reflection of crosslinks in the structure and the fact that fragments mainly consist of hydrophobic parts with higher hydrothermal stability.

Fibre morphology and assessment of amount of fibre damage

The natural degradation of (hp) was reflected in the high amount of physically damaged fibres (91%), with all ageing treatments for (hp) increasing the physical damage. Despite good hydrothermal stability, (p_ref) had a large amount of physically damaged fibres (80%). The reason for this is unknown, but could be a reflection of a harsh liming process where stabilising agents during production may have increased the hydrothermal stability. The suspicion of the existence of added unknown chemicals in the manufacturing process is enhanced by the fact that (p_ref) has quite a high number of gel-like fibres (7%) along with fibres with a 'shaggy' appearance (Figure 3). The reference for (hp) does not show this type of morphology and it is our experience that this is not a common morphology for parchment fibres. As the appearance is quite similar to that of tanned collagen fibres, it could indicate that strengthening substances and/or other modern substances were added to the manufacturing process.

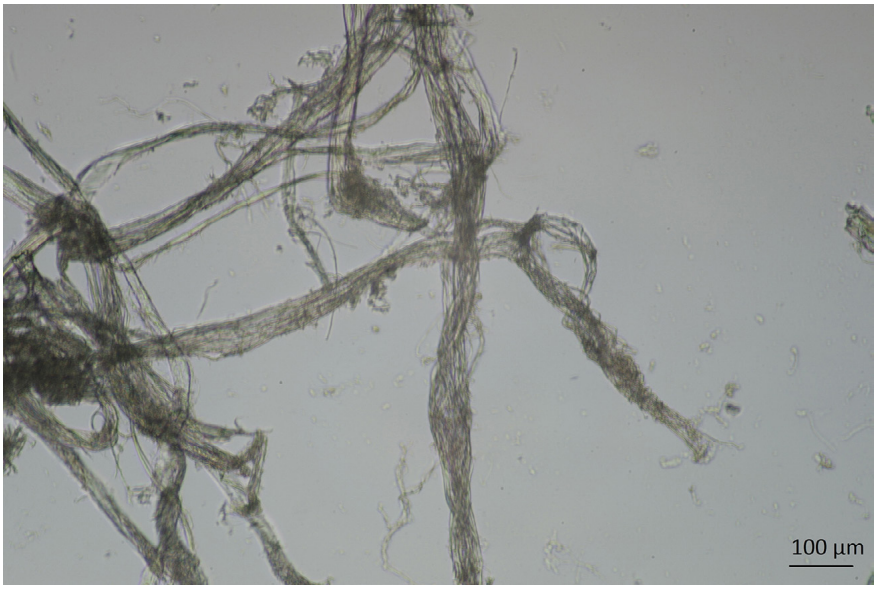

Figure 3. Fibres from the new parchment reference

Dry oxidation generated a total deterioration of the fibre mass with the formation of small gel-like fragments. The morphology of the fibres from the study's dry oxidised parchment samples was very similar to that reported in a previous study on heat-damaged parchment (Hassel 2002).

The two most common degradation morphologies, namely flat fibres and pearls on a string, were almost evenly represented in all samples except after dry oxidation. There was a trend towards fibres unwinding into flat fibres after hydrolysis in the case of (p), but the opposite trend applied for (hp). However, this deviation could be explained by standard

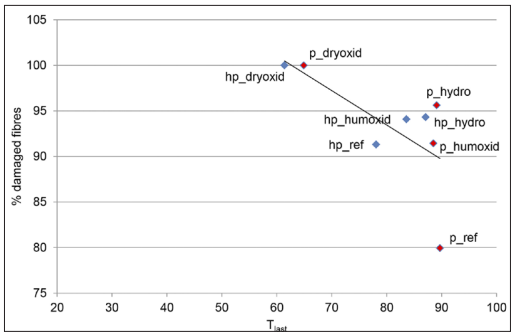

Figure 4. Amount of damaged fibres plotted against T_{last}. Correlation coefficient of the two variables R = 0.67

deviations. Nonetheless, as seen in Figure 1, hydrolysis clearly led to more flat and somewhat more transparent fibres for (p). Both humid oxidation and hydrolysis reduced the amount of gel-like fibre structure for (p), probably because of dissolving reactions. Apart from this, humid oxidation did not seem to cause any significant changes to the fibre morphology for any of the two parchments.

pH measurement

The pH for new parchment is normally around 7 (Hallebeek 1989, Chahine 1991, Kennedy and Wess 2003), but values over 9 have been reported (Larsen et al. 2002). Previous studies presented pH values of between 4 and 9 for historical parchments (Larsen et al. 2002).

In addition to breakage of the peptide and amide bonds in the structure, acid brings the collagen away from its isoelectric point (pI) and such altering of the charge balance leads to a swelling of the structure. The least swelling is found at a pI of around 5 and the greatest swelling in the acid region starts rapidly at pH 0.5 and reaches a maximum at pH 2–3 (Bowes and Kenten 1950, Thorstensen 1976). In this study, it was noteworthy that the pH for (p_ref) was lower than the pH for (hp_ref). The treatment with H_2SO_4 caused a drastic decrease in pH to around 3 for both parchment types, results that are very comparable to the pH of 2.9 for new parchment accelerated aged at 95% RH for 12 weeks (Chahine 1991). Acid swelling gradually increases until a pH of 3 is reached where nearly all carboxylic groups of the collagen are ionized (Thorstensen 1976). This well-defined swelling effect is also clearly visualised in the result of the fibre morphology for the hydrolysed samples, with more flat and unwound fibres. On the other hand, the expected fragmentation of the fibres due to a hydrolytic breakage of the peptide bonds in the collagen was not visible after hydrolysis.

Correlation

In Figure 4, the amount of damaged fibres is plotted against hydrothermal stability. As no main shrinkage interval was detected for any of the dry oxidised samples, the hydrothermal stability is expressed by T_{last} rather than the more customary T_s. As seen, dry oxidation had the largest degradation effect on both damage markers. Dry oxidation of (p) even pushed the level of both degradation indicators beyond (hp_ref), (hp_humoxid) and (hp_hydro). The outlier causing the low correlation coefficient of 0.67 was (p_ref) with its surprisingly high number of damaged fibres. In conclusion, the amount of damaged fibres versus T_{last} accurately expresses what has been discussed in the paper, namely that a high hydrothermal stability may very well be combined with a high number of physically damaged fibres.

CONCLUSION

Out of the two parchment types used in the study, the most sensitive for degradation at microscopic level was the new parchment. This can most likely be explained by the natural degradation that has already taken place in the historical parchment before the accelerated ageing starts.

While humid oxidation does not seem to have any large degradation effect on the fibre characteristics, it is evident that long-term acidic storage may lead to irreversible changes in the fibre morphology with an unfolding of the structure together with breakages of vital bonds as reflected in a decrease in hydrothermal stability.

It is possible to conclude from the study that oxidation caused by heat in the absence of water causes severe damage at microscopic level. Dry oxidation at 150°C led to a full degradation of the fibre mass, transforming it into gel-like fragments. As also observed in natural aged parchment, such fragmented pieces showed no typical main shrinkage interval in the hydrothermal measurement, indicating an almost total denaturation caused by the dry heat.

Moreover, the study showed the importance of a proper manufacturing process for new parchment, especially if the intention is to use it for the restoration of historical objects. Parchment with good hydrothermal stability may very well be combined with a high level of degraded fibres. As both analyses are reflections of the physical and chemical degradation of the material, it is therefore highly recommended that the measurement of hydrothermal stability is always combined with studies of the fibre morphology. Both methods are simple and require only smaller amounts of fibres.

Finally, to improve the diagnoses of historical parchment in daily conservation practice, the authors' observations call for further investigations to establish an even closer relationship between the different morphologies and specific natural degradation mechanisms.

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MATERIALS LIST

New calf parchment produced by Pergamena (www.pergamena.net).

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