Determination of the hydrothermal stability of leather and parchment

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LEATHER AND RELATED MATERIALS

Measuring the hydrothermal stability of leather and parchment – The significance of heating rate and shrinkage intervals

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ABSTRACT

The present paper evaluates the micro hot table technique used for measuring the hydrothermal stability of leather and parchment. It deals with the consequences of using a higher heating rate than the standard 2°C/minute. Measurements using heating rates at 1, 2, 4, 8 and 16°C/min were performed. The results show that an increased heating rate leads to an increased shrinkage temperature, but also that the shrinkage intervals increase drastically when increasing the heating rate. Furthermore, as the B1-interval in some cases seems so short that it can be questioned whether its presence is statically significant, the validity of the B1-interval was investigated. However, the statistical analysis shows that the B1-interval still remains valid.

INTRODUCTION

Since Fahrion (1908) published his method for measuring shrinkage temperature (Ts), determination of the hydrothermal stability of leather has developed into an industrial standard for quality control of leather (ISO 2002). Haines (1987) brought shrinkage temperature measurements to conservator-restorers, who, for example, use the results to select the most appropriate treatment for historical objects.

As summarised by several authors (Hobbs 1940, Borasky and Nutting 1949, Nayudamma 1958, Young 1990, Larsen et al. 1993, Rasmussen and Larsen 2002), various equipment, based on slightly different principles, have been developed over the years. The microscopical method was first published by Nageotte and Guyon (1930), Borrasky and Nutting (1949) and then refined by Larsen et al. (1993). Common to all methods is the heating of collagen fibres, in the form of leather, in an excess of water or in a water-based solution.

Over time, the heating rate has naturally been a topic for discussion and investigation. Heating rates between 0.5 and 10°C/min have been investigated (McLaughlin and Theis 1945, Borasky and Nutting 1949, Naghski et al. 1965, Kronick and Buechler 1986, Young 1990).

The ISO 2002 standard requires a heating rate of 2°C/min and, in combination with the number of analyses necessary per object to get a thorough picture of the state of degradation, determination of the hydrothermal stability is rather time-consuming. In practice, conservator-restorers sometimes use heating rates above the standard 2°C/min deliberately to save time and follow the guidelines of Young (1990), or accidently because it can be difficult to control the temperature rise using more simple equipment (Rasmussen and Larsen 2002).

The term shrinkage activity denotes any observable shrinkage in a fibre. Borasky and Nutting (1949) observed shrinkage in two stages; a 'slight gradual shrinkage' followed by a sudden pronounced shrinkage (the shrinkage temperature). Larsen et al. (1993) define five intervals: A1- and A2-intervals show distinct shrinkage activity in individual fibres; B1- and B2-intervals show shrinkage activity in an individual fibre immediately followed by shrinkage in another fibre, whereas more than two fibres are simultaneously and continuously moving in the C-interval.

The start of the main shrinkage interval (C-interval) is defined as the shrinkage temperature (Ts), where Tend is the last temperature in the main shrinkage interval. Tf represents the very first motion observed and Tl the very last.

Recently, Mühlen et al. (2012) have pointed out the importance of combining Ts with Tf when the degree of deterioration of parchment is determined. When the fibres in a sample are approximately in the same state of condition, the length of the intervals will be short, whereas incipient degradation results in longer intervals. When using simpler measuring equipment, it might be difficult to detect the presence of the B-interval (Rasmussen and Larsen 2002). Occasionally, not all intervals will be present (Badea et al. 2012).

The relatively simple micro hot table (MHT) method for measuring the hydrothermal stability of leather and parchment is generally cheaper and demands less specialised training than the more advanced systems available – differential thermal analysis (DTA) and differential scanning calorimetry (DSC) (Naghski et al. 1965, Fessas et al. 2006, Budrugeac et al. 2010, Badea et al. 2012). Compared to the latter, the MHT method is therefore more suitable for daily routine work. Furthermore, the MHT method offers the possibility of microscopic studies of the fibre morphology, which, especially in the case of parchment, provides additional supplementary information on the physical condition of the fibres (Mühlen Axelsson et al. 2012, Mühlen Axelsson 2014, Sommer et al. 2016).

MATERIALS

For the present study, a newly produced (Altenburg, Germany) calfskin parchment and historical vegetable-tanned upholstery calf leather were used. The exact age and tanning procedure of the leather was unknown.

METHODS

Shrinkage temperature measurements

The measurements were carried out using a FP82HT Hot Stage in connection with an FP90 Central Processor (Mettler Toledo) according to procedures previously described (Larsen et al. 1993, Larsen et al. 2002, Mühlen Axelsson et al. 2012). Each analysis was recorded using an Infinity-1 camera (Lumenera) and Studio Capture software (Studio86Designs).

From the corium side of the samples, around 10 to 20 fibres were immersed in demineralised water in a well in a microscope slide. After the fibres had been thoroughly soaked for 10 minutes, the sample was inserted into the FP82 cell and the temperature was raised from ambient temperature by 1, 2, 4, 8 or 16°C/min. Ten measurements were performed for each heating rate.

Statistical analyses

To test the significance of differences in the measured Ts and Tb1 (subject measures) values at the different heating rates, a repeated measures analysis

of variance (ANOVA) for both material types was used (Badashah and Nath 2009). This analysis is based on the computed difference between each subject measure, the average of the differences calculated, the calculated standard deviation of the differences, and the calculation of the test statistic using this mean and standard deviation. The method makes use of the sum of squares, which represents a measure of variation or deviation from the mean calculated as a summation of the squares of the differences from the mean. The calculation of the total sum of squares considers both the sum of squares from the factors and from randomness or error. In ANOVA, the total sum of squares helps express the total variation attributed to various factors:

The total sum of squares = treatment sum of squares (SST) + sum of squares of the residual error (SSE)

In this case, the treatment sum of squares is the variation between the shrinkage measurements taken at different heating rates. The sum of squares of the residual error is the variation attributed to the error. The sum of squares is converted into mean squares by dividing it by the degrees of freedom. This makes it possible to compare these ratios and determine whether there is a significant difference due to heating rate. The larger this ratio, the more the heating rate affects the outcome.

An F-test is used to test the significance of variations between the measurement means, in this case to test the null hypothesis that all measurement means are equal regardless of the heating rate. Simply explained, the F-statistic is a ratio of two variances. Larger values represent a greater spread. In one-way ANOVA, the F-statistic is this ratio:

F = variation between sample means / variation within the samples

From the F-distribution is determined how consistent the results are with the null hypothesis and the probability (the p-value) of how common or rare the F-value is under the assumption that the null hypothesis is true. If the probability is low enough, the data is inconsistent with the null hypothesis and the evidence in the sample data is strong enough to reject the null hypothesis for the entire population.

In addition, the analysis-of-variance computations test changes across the repeated measures (within subjects) as well as differences between groups of subjects (between subjects.) Tests of the within-subjects values are called polynomial tests of order 1, 2, ..., up to k, where k is one less than the number of repeated measures (in this case the measurements at heating rates of 1°C, 2°C, …, 16°C). To test linear changes, the first polynomial is used. That is if the repeated responses increase (or decrease) around a line with a significant slope. The second polynomial tests if the responses follow a quadratic curve, and so on. In the present paper, the first and second polynomial tests are reported.

Moreover, two sample t-test were used to illustrate individual differences between the Ts measurements at a heating rate of 2°C and heating rates of 4°C/min, 8°C/min and 16°C/min for parchment and leather, respectively (Chakraborty et al. 2009, Dallal et al. 2009). In addition, a two-sample t-test to test for a significant difference between the calculated standard deviations for the Ts and Tb1 means was used.

RESULTS AND DISCUSSION

The results of the shrinkage temperature measurements are shown in Figure 1 and Table 1. As seen, the Ts and Tb1 increases by increasing heating rate in the case of both parchment and leather. For parchment, the Ts shifts upwards from 56.8 to 59.3°C. The shift upwards is a little lower for leather, from 49.6 to 51.4°C. The difference between the Ts observed at 2°C and 8°C is around 3°C for both leather and parchment. This tendency is in accordance with finds reported by other authors (Borasky and Nutting 1949, Young 1990, Chahine 2000). From their DSC study, Kronick and Buechler (1986) reported a 5°C decrease when lowering the heating rate from 10°C/min to 2.5°C/min. Comparing the MHT and

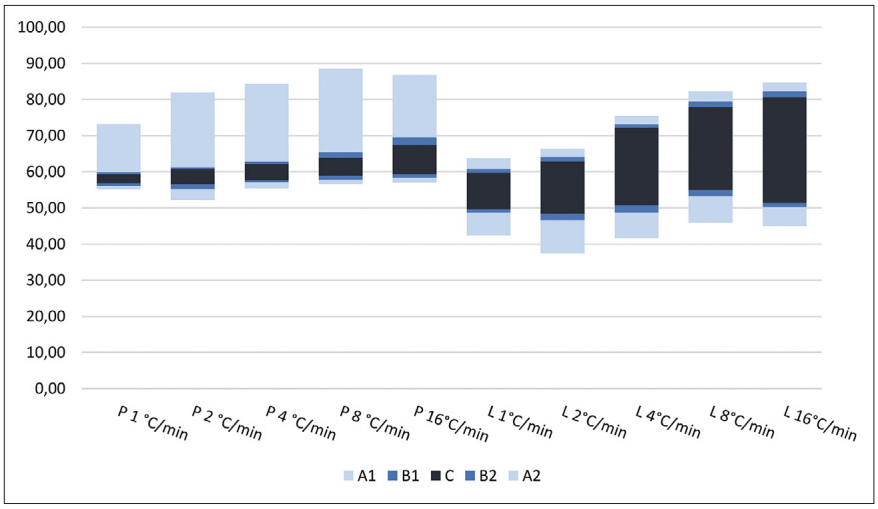

Figure 1. Lengths of the shrinkage intervals measured on parchment (P) and leather (L). The shrinkage temperature is the start of the C-interval

Table 1. Average values (n = 10) of the lengths of the shrinkage intervals measured on parchment (P) and leather (L), as well as the temperatures Tf, Ts, Te and Tl. Standard deviations (SD) are given in grey

	°C/min	Tf	Ts	Te	Tl	ΔA1	ΔB1	ΔC	ΔB2	ΔA2	ΔTt
Parchment	1	55.1	56.8	59.3	73.2	0.9	0.8	2.5	0.6	13.3	18.1
	SD	0.96	1.00	0.70	10.70	0.59	0.46	0.68	0.38	10.85	10.92
	2	52.1	56.5	60.7	81.9	3.1	1.2	4.2	0.5	20.7	29.8
	SD	3.31	1.40	1.00	12.20	2.81	1.55	0.97	0.45	12.43	13.74
	4	55.4	57.7	62.1	84.3	1.8	0.6	4.4	0.7	21.6	29.0
	SD	1.86	1.70	1.10	8.30	1.57	1.67	1.05	1.27	8.30	8.81
	8	56.5	59.5	63.9	88.5	1.2	1.1	5.1	1.6	23.0	32.0
	SD	1.58	2.10	1.90	10.30	1.64	2.08	1.92	2.62	10.34	10.46
	16	57.1	59.3	67.4	86.8	1.2	1.0	8.1	2.1	17.3	29.7
	SD	1.80	1.40	3.90	8.80	1.39	1.38	3.86	3.44	8.82	8.23
Leather	1	42.4	49.6	59.7	63.7	6.2	1.0	10.1	1.0	3.0	21.3
	SD	4.40	1.10	4.10	4.30	3.40	0.70	3.60	0.60	1.90	4.49
	2	37.4	48.4	62.8	66.3	9.2	1.8	14.4	1.3	2.3	28.9
	SD	4.30	2.60	4.60	3.90	2.00	1.70	4.00	0.80	1.60	4.35
	4	41.7	50.9	72.2	75.5	6.9	2.2	21.4	1.0	2.3	33.8
	SD	4.00	2.10	5.50	5.80	2.80	1.50	4.80	1.00	1.90	5.82
	8	45.9	54.8	78.0	82.1	7.4	1.6	23.1	1.5	2.7	36.2
	SD	4.80	1.50	3.00	3.90	3.50	1.70	3.00	0.80	1.50	6.47
	16	45.0	51.4	80.6	84.7	5.2	1.2	29.2	1.6	2.5	39.1
	SD	3.30	3.20	4.00	4.60	3.50	0.50	5.60	0.90	2.10	7.57

DSC methods, Budrugeac et al. (2015) show a mean difference of 4.8°C between their measured Ts (2°C) and its equivalent Td (10°C). Chahine and Rottier (1992) found a mean difference of 4.7°C when comparing Td measurements of leather at 2 and 10°C/min, respectively.

The most likely explanation for the significantly higher Ts and Tb1 values measured at the heating rates of 4°C/min, 8°C/min and 16°C/min is that the rate of uptake of heat energy in the parchment fibres is slower than the heat rate of the equipment. Therefore, the actual temperature of shrinkage is lower than measured by the system.

In Figure 1, it is clear that the B-intervals are short compared to the length of both A-intervals and the C-interval. However, the lengths of the main shrinkage interval (ΔC) and the total interval of shrinkage (ΔTt) increase dramatically by increasing the heating rate. For parchment, ΔC was prolonged by 5.6°C, while the ΔTt shifted from 18.1 to 29.7 °C. For leather, the ΔC increased from 10.1 to 29.2°C, and the ΔTt almost doubled, rising from 21.3 to 39.1°C. In the authors' opinion, this extension might also be observed as wider peaks in the DSC thermograms.

Shown in Table 2 are the results for the repeated measures analyses of variance. As it appears, the test for the linear component is significant and the quadratic component not significant in all cases. Thus, the increase in Ts and Tb1 with an increasing heating rate is predominantly linear for both parchment and leather. Although relatively short (1.0–2.2°C for leather and 0.6–1.2°C for parchment), the starting temperature of the B1-interval (Tb1) is very accurate, measured with a standard deviation close to that of the measured Ts.

Table 2. Variance repeated measures analysis of Ts and Tb1 for parchment. Error denotes an error in the sum of squares (SS) and cross-products matrix. Df denotes the degree of freedom

		Polynomial Test of Order 1 (Linear)		Polynomial Test of Order 2 (Quadratic)		Polynomial Test of Order 1 (Linear)		Polynomial Test of Order 2 (Quadratic)	
	Source	Ts	Error	Ts	Error	Tb1	Error	Tb1	Error
Parchment	SS	54.022	10.184	1.586	18.836	48.164	8.25	1.36	19.993
	df	1	9	1	9	1	9	1	9
	Mean Squares	54.022	1.132	1.586	2.093	48.164	0.917	1.36	2.221
	F-Ratio	47.739		0.758		52.54		0.612	
	p-Value	0.000		0.407		0.000		0.454	
Leather	SS	102.414	60.548	5.761	50.903	96.629	68.068	0.098	70.877
	df	1	9	1	9	1	9	1	9
	Mean Squares	102.414	6.728	5.761	5.656	96.629	7.563	0.098	7.875
	F-Ratio	15.223		1.019		12.776		0.012	
	p-Value	0.004		0.339		0.006		0.914	

Table 3 shows the results of the two sample t-tests for parchment and leather. As seen for the parchment, the mean Ts obtained by measuring at 8°C/min and 16°C/min differ highly significantly from the mean obtained by measuring at 2°C/min. Interestingly, the mean difference between the measurement at a heating rate of 2°C/min and 8°C/min is 2.4°C, and close to the accuracy of the method which is ± 2°C. On the other hand,

the difference from the mean Ts obtained by heating at 4°C/min is only 1.2°C and not significant at the 95% level.

However, for leather, the mean Ts values obtained at 4°C/min and 16°C/min all differ significantly from that obtained at 2°C/min. For a heating rate of 8°C/min, the difference is even highly significant. This deviation from the expected picture of a higher difference at the 16°C/min heating rate is probably due to a subsample variation. The mean values for Ts and Tb1 for leather are 0.6°C and 0.9°C higher, respectively, than for parchment. Furthermore, the standard deviations are double for leather in both cases. This shows a higher spread in the measurement observations and thus indicates a greater variation in hydrothermal stability for the leather subsample. As mentioned, this could be due to uneven distribution of tannins and/or greater variation in the degree of deterioration.

Table 3. Results of the two sample t-tests between the Ts measurements at a heating rate of 2°C versus heating rates of 4°C/min, 8°C/min and 16°C/min for parchment and leather, respectively

	Heating rate (°C/min)	4	8	16
Parchment	Mean difference	1.22	2.37	2.82
	t-Value	-1.760	-2.981	-4.513
	p-Value	0.096	0.009	0.000
Leather	Mean difference	2.48	6.46	3.06
	t-Value	-2.352	-6.867	-2.375
	p-Value	0.031	0.000	0.029

Furthermore, the two-sample t-tests show that there are no significant differences between the standard deviations obtained by the measured Ts and Tb1 at the different heating rates, neither for leather nor for parchment (Table 4). This strongly indicates the existence of the B1-interval and that particular cases, where the B1-interval is not observed, may be linked to deterioration, which has altered the distribution of the hydrothermal stability of fibres in the parchment. The absence of the B1-interval has only been observed in deteriorated parchment; never in new or slightly deteriorated parchment.

Table 4. Two sample t-tests for the difference between standard deviations (Ts vs. Tb1)

	Mean difference	t-Value	p-Value
Parchment	0.078	0.313	0.763
Leather	0.0396	0.778	0.459

CONCLUSION

It is evident that the Ts value shifts significantly upwards by increasing the heating rate. This is highly problematic, as the value is used as a measure of deterioration and as a factor for deciding upon the right conservation treatment. Furthermore, our results show a significant relation between dramatically increased ΔC and ΔTt with an increased heating rate. It thus gives the wrong impression of a larger spread in the hydrothermal stability of the parchment or leather fibres. When dealing with cultural heritage objects, one is always interested in knowing the worst-case scenario, as well

as obtaining as correct a picture as possible of the actual condition of the objects. Solely for this reason, deviation from the standard 2°C/min cannot be recommended. With respect to the extended length of the shrinkage intervals, it is suggested that an examination be performed as to whether the width of the peaks in the DSC thermograms correspondingly increase as the heating rate increases.

With respect to the B1-interval, our studies have shown that even though it can be very short, it can be measured with the same accuracy as the Ts. Therefore, it is highly important not to leave out this interval from the measurements, as it represents fibres with lower hydrothermal stability and a relatively high shrinkage activity, and thus gives an indication of the initial deterioration. In cases with long B1-intervals, permanent damage of a large population of fibres may take place at temperatures relatively far below Ts even at storage conditions that are considered acceptable.

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