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The impact of natural ageing on the hydrothermal stability of new and artificially aged parchment and leather samples

Andrei Cucos*, Petru Budrugeac

National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 313, 030138 Bucharest, Romania

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ABSTRACT

The paper discusses the effects of a 4-year natural ageing on hydrothermal stability of new and previously accelerated aged parchments and leathers. It was observed that natural ageing generally lowers the denaturation temperature (measured using DSC), but in a different way for the two types of these collagen-based materials. Thus, for parchments the largest effect (up to 7 °C) was observed for the new samples, while for the strongly aged ones the temperature shift was negligible. For leathers, no relevant dependence of the denaturation temperature shift (3.0 ± 1.0 °C in average) with the previous accelerated ageing time was observed. For parchment, the enthalpy of denaturation decreases substantially following natural ageing, while for leathers no significant alteration was observed. It was also found that the 1-day accelerated ageing performed in 2013 had comparable effects on the denaturation temperature of these materials as the 4-year natural ageing, making the possibility of predicting the effects of natural ageing on patrimonial artifacts manufactured from parchment and leather.

1. Introduction

Parchments and leathers are support materials of many valuable patrimonial objects, such as scrolls, manuscripts, bookbindings, etc. The main constituent of these materials is collagen protein. The collagen molecule has a triple-helix structure, in which the three polypeptidic α chains are held together by hydrogen bonds [1,2]. In animal tissues including skin (from which leather and parchment are manufactured) its structure is hierarchical, so that the collagen molecules are progressively assembled into microfibrils, fibrils, fibers and bundles [3,4]. Parchment and leather retain this hierarchical supramolecular organization [5], which is responsible for their mechanical properties, such as stiffness (parchment) or elasticity and flexibility (leather).

Collagen within parchment and leather is sensitive to environmental factors, such as heat, humidity, light (UV, visible), air pollutants (SO_2, NO_x), as its triple helix structure can undergo several degradation processes under their action, such as partial denaturation (gelatinization), hydrolysis and oxidation [5]. Numerous accelerated ageing studies involving exposure of parchments and leathers to simulated environmental factors, followed by the assessment of the induced changes by various techniques, were performed [6–22]. The aim of these studies was to find the appropriate conditions for storage/exhibiting/conservation, but also to simulate and to gain insight into the natural ageing of these materials. The effects of accelerated ageing on hydrothermal stability are usually observed using Differential Scanning Calorimetry (DSC) [6–14] or Micro Hot Table (MHT) [15–19], by measuring the denaturation or shrinkage temperature. Generally, it was observed that ageing induces the decrease of this temperature, enhances the asymmetry (shoulder) and broadness of the DSC peak while reducing the enthalpy of denaturation [6–14]. These facts were explained by the dispersing of collagen populations with different thermal stabilities, the increase of structural disorder and the loss of fibrillar structure [13].

Still, there are no similar studies concerning the natural ageing of these materials, which would study the effect induced by natural ageing (on the order of several years) on the hydrothermal stability. Also, to our knowledge, no attempts were made to perform both natural and accelerated ageing on the same parchment/leather and to compare the impact of both on their hydrothermal stability.

In 2013 we have performed a study on several series of new and accelerated aged parchments and leathers under action of heat and moisture for progressively increasing time lengths [9] and observed the induced effects on DSC peaks and on DMA (dynamic mechanical analysis) curves. We found a progressive decrease of the temperature of denaturation in water with the accelerated ageing, and a good correlation of denaturation temperatures obtained by both techniques. After 4 years from this study, we questioned whether the corresponding samples had undergone significant changes in their hydrothermal

* Corresponding author.
E-mail address: andrei.cucos@icpe-ca.ro (A. Cucos).

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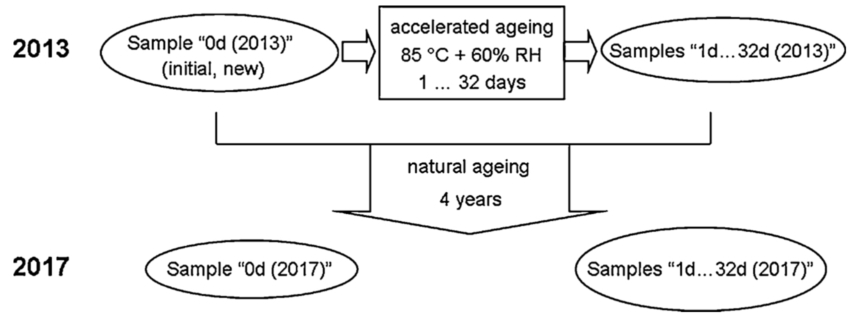

Scheme 1. Generic notations of samples within each of the parchment/leather series subjected to accelerated and natural ageing.

stability, so that in 2017 we measured again (using DSC only) some of the series of samples. We could thus observe the effect of natural ageing on the denaturation temperature of both new and accelerated aged samples, but also to compare the effects of both ageing types (natural and artificial) on these types of materials.

2. Materials

In this study we used two series of parchment and three series of leather from those used in the 2013 study [9], namely "Goat Kid 1″ and "Goat Kid 2″ parchments and "Goat Kid / Quebracho", "Goat Kid / Mimosa" and "Sheep / Mimosa" leathers. Within each series both the initial, "new" sample, noted as "0d (2013)", and the samples accelerated aged in 2013 from 1 to 32 days, noted as "1d…32d (2013)", were measured. The samples were kept in plastic sheet protectors, in the dark, in a drawer of a lab table for 4 years (from 2013 to 2017) and at room temperature, without being exposed to light, excessive heat, moisture or freezing temperatures. The naturally aged samples were noted as "0d…32d (2017)". Scheme 1 depicts the two types of ageing and the notations of the corresponding samples. Thus, the "0d (2017)" parchment and leather samples were naturally aged only, while the "1d…32d (2017)" samples have undergone both accelerated and natural ageing.

3. Methods

The DSC curves were recorded in 2017 using the same instrument and in the same experimental conditions [9]. Briefly, samples typically weighing 5–10 mg were placed in a stainless steel crucible filled with distilled water, closed with stainless steel lid with PTFE seal and heated from room temperature to 95 °C at a heating rate of 1 °C min^{-1}. As in the 2013 study, the samples were measured only once and no deconvolution of DSC peaks was performed. Also, the DSC peaks for the "16d (2017)" and "32d (2017)" parchments samples were very broad and hard to analyze, so these sample were not taken into account in this study. Generally, the area of the DSC peaks of parchments was difficult to assess, as these peaks didn't show a horizontal end baseline. So, for parchments the enthalpy values were only approximate. On that account, too, the halfwidth for these sample was not discussed in our work.

The DSC instrument was calibrated using the manufacturer-specified calibration procedures involving several pure substances (Hg, In, Sn, Bi, Zn, CsCl) to ensure correct temperature and enthalpy values.

4. Results and discussion

The DSC curves of the "Goat Kid 1" parchment samples, measured in 2013 and 2017 are presented in Fig. 1. It can be observed that compared to the series measured in 2013, the peaks of the samples measured in 2017 are smaller and shifted to lower temperatures, in an amount which depends on the accelerated ageing time, namely, the longer the ageing time, the slighter the shift. Thus, the value of T_d (the temperature of the minimum of denaturation endotherm) for the "new" sample (noted "0d" in Fig. 1) is shifted to a larger extent, by 7 °C, (from 67.1 to 60.1 °C), while for the "8d" sample the shift is only 1.5 °C (from 49.1 to 47.6 °C). This suggests that several days of accelerated ageing has already induced strong alterations in the collagen structure, decreasing the denaturation temperature much more significantly than the subsequent natural ageing.

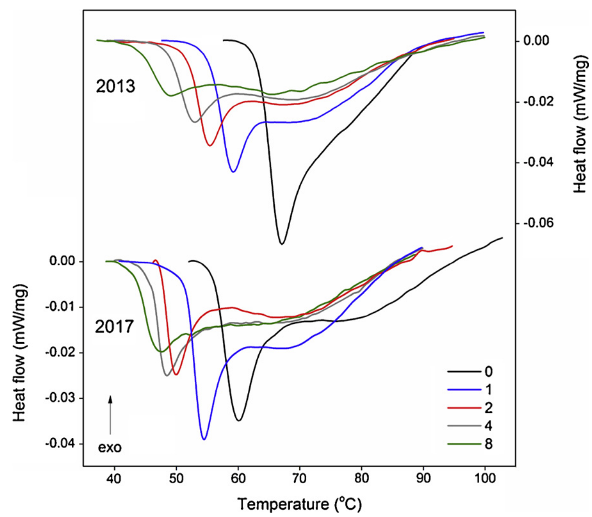

Fig. 1. The DSC curves for the "Goat Kid 1" series of parchments previously exposed to accelerated ageing in 2013 (time given in days), measured in 2013 and 2017. "0 days" stands for initial, "new" samples.

It is worth mentioning that the 1-day accelerated ageing and the 4-year natural ageing had very similar effects on the "0 d (2013)" sample, both shifting its DSC peak by nearly the same amount. Thus, the DSC peaks of the "1d (2013)" sample and of the "0d (2017)" sample have very close onset (55.2 and 56.0 °C, respectively) and denaturation temperatures (59.2 and 59.9 °C, respectively) (Table 1).

Significant changes are also observed concerning the shape of the "0d (2017)" sample's peak compared to that of the sample measured in 2013. Even if deconvolution was not performed, it is clearly seen that the sharp component of the peak is much smaller, while the shoulder is seen at higher temperature and is more pronounced. Overall, the peak is much broader. In [13], the asymmetry of the DSC peak is explained as follows: the sharp component of the peak is assigned to native collagen population, whereas the shoulder observed at higher temperatures is attributed to a more stable/stabilized collagen with a higher crosslinking degree. The peak broadness is explained by the presence of collagen populations with different hydrothermal stabilities. Thus, our results suggest a decrease of the native collagen and an increase in the stabilized collagen. It can be assumed that a fraction of the native collagen has had its stability reinforced by a crosslink formation, while the main fraction of the native collagen has significantly lost its stability, as evidenced by a reduced sharp component of the peak and its

Table 1
The values of T_d for the samples used in this study. The T_d values of the 1-day accelerated aged and 4-year naturally aged samples were bolded, in order to compare the effects of these two types of ageing on initial, "new" samples.

Sample	Accelerated ageing time (days)	T_d (°C) 2013	T_d (°C) 2017
Parchments			
Goat Kid 1	0	67.1	**60.1**
	1	**59.2**	54.5
	2	55.3	51.3
	4	52.9	48.7
	8	49.1	47.6
Goat Kid 2	0	66.2	**59.9**
	1	**58.1**	54.3
	2	54.9	52.1
	4	51.0	49.6
	8	47.9	47.4
Leathers			
Goat Kid / Quebracho	0	82.3	**79.9**
	1	**79.0**	75.7
	2	77.6	75.0
	4	75.7	72.4
	8	70.8	68.4
	16	65.5	63.2
	32	59.2	56.9
Goat Kid / Mimosa	0	83.8	**80.7**
	1	**80.1**	77.0
	2	79.8	75.6
	4	76.2	73.1
	8	72.6	69.3
	16	65.4	64.4
	32	57.7	55.9
Sheep / Mimosa	0	82.5	**77.8**
	1	**77.6**	73.2
	2	75.5	71.4
	4	70.9	69.1
	8	67.5	63.6
	16	58.9	56.7
	32	55.0	51.2

shift to lower temperatures. Also, the increase in broadness indicates a larger distribution of collagen populations with different thermal stabilities, that is, a diminution of structural order as a result of natural ageing.

While the peaks of the samples within the series measured in 2013 underwent a continuous gradual change in terms of peak position, height and shape, for the 2017 series it is noted that the peaks do not show more smooth transitions. Thus, for example, the peak height for the "0d (2017)" sample is smaller than that for the "1d (2017)" sample; the peaks of "2d (2017)" and "4d (2017)" samples are quite close and similar, suggesting that natural ageing has acted in a different and even inhomogeneous way on accelerated aged samples.

Concerning the enthalpy of denaturation, ΔH, the 4-year natural ageing has induced a significant decrease for parchment samples (Fig. 3). Thus, for example, ΔH for the "0d" sample has dropped by ~23%, (from 47 to 37 J g^{-1}), while for the "8d" sample, the decrease was larger, ~35% (from 37 to 24 J g^{-1}).

The peak areas within the 2017 series show a similar trend with the accelerated ageing time, as for the 2013 series.

Opposed to parchments, the leathers were less affected by natural ageing. Thus, it can be seen in Fig. 4 that the denaturation profiles of "Goat Kid / Quebracho" leather in 2017 closely resemble those measured in 2013. The transitions are generally continuous and smooth in terms of peak height, position and shape.

Compared to 2013 samples, the peaks for 2017 samples are shifted to lower temperatures by about 3 °C irrespective of the initial accelerated ageing time. This is more clearly seen in the Fig. 2, where the two curves T_d variation in 2013 and 2017 for this series of leather are

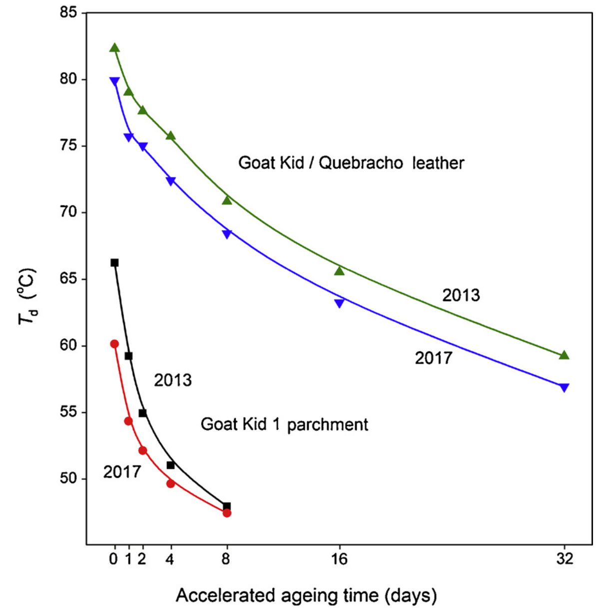

Fig. 2. Plots of T_d versus accelerated ageing time for the "Goat Kid 1" parchment series and "Goat Kid / Quebracho" leather series, measured in 2013 and 2017. Lines are guides for eye.

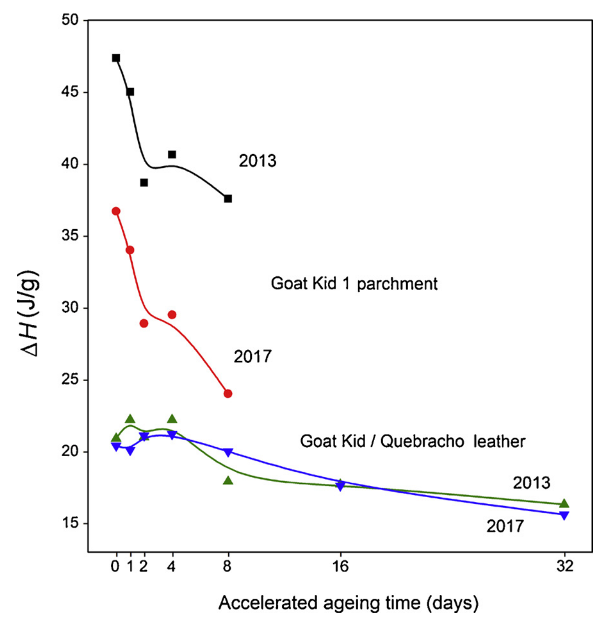

Fig. 3. Plots of ΔH versus time of accelerated ageing (performed in 2013) for the "Goat Kid 1" parchment series and "Goat Kid / Quebracho" leather series, measured in 2013 and 2017. Lines are guides for eye.

almost parallel and separated by this value.

The shapes of the peaks generally match the ones found in the 2013 series, However, at a closer look, the 2017 peaks show some slight shoulders on both sides, indicating, as for parchments, that an inhomogeneous effect on collagen populations has occurred following natural ageing.

The peak areas didn't show a significant alteration following natural ageing (Fig. 3), retaining the slight decreasing trend with the accelerated ageing time performed in 2013. For one specific sample, "8d (2017)", the measured enthalpy was found to be even larger than in 2013. A stabilization effect is highly unlikely, this result is most probably due to the inhomogeneity of leather. In average, for all leather samples used in this study, the natural ageing has induced an

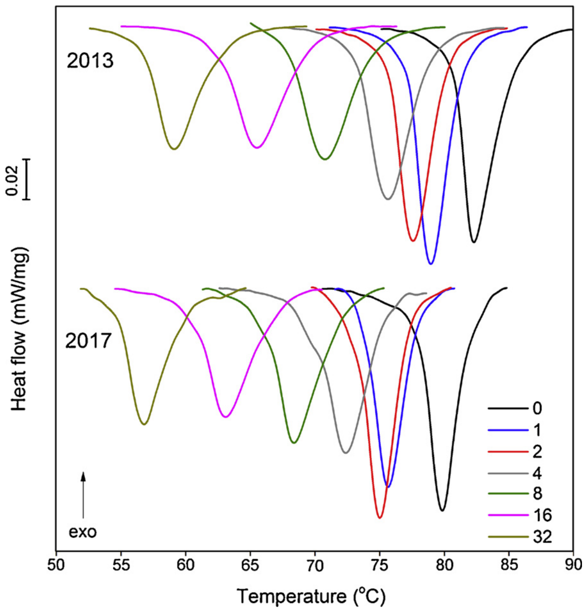

Fig. 4. The DSC curves for the "Goat Kid / Quebracho" series of leathers previously exposed to accelerated ageing in 2013 (time given in days), measured in 2013 and 2017. "0 days" stands for initial, "new" samples, unexposed to accelerated ageing.

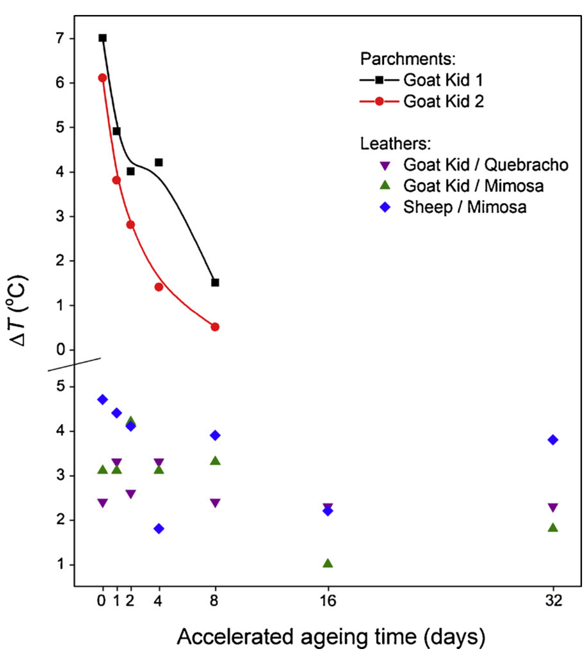

Fig. 5. Plots of ΔT, the difference between the denaturation temperatures measured in 2013 and 2017, versus the accelerated ageing time (in 2013) for the studied materials. Lines are guides for eye.

insignificant ~5% decrease in enthalpy.

When plotting ΔT, the difference between T_d(2013) and T_d(2017) the denaturation temperature (maximum of the DSC peak) within each series, measured in 2013 and 2017, versus the accelerated ageing time (Fig. 5), some observations can be made:

1) for parchments, there is a strong dependence of ΔT on the accelerated ageing time. Thus, the maximum temperature difference is noted for the "0d" samples for which a decrease of 6–7 °C is recorded after 4 years of natural ageing. Then, ΔT decreases with the accelerated ageing time, reaching the lowest value for the "8d" samples (1.5 and 0.5 °C for "Goat Kid 1" and "Goat Kid 2", respectively) meaning that the 4-year natural ageing didn't practically affect their denaturation temperature. Longer accelerated ageing times have thus induced strong alterations of collagen's structure, that were further less affected by the subsequent natural ageing.

2) for leathers, no dependence of ΔT with the accelerated ageing time was observed. The ΔT data are scattered between 1.0 °C ("16d" "Goat Kid / Mimosa" sample) and 4.7 °C ("0d" "Sheep / Mimosa" sample). Within the "Goat Kid / Quebracho" series, the variation of ΔT was the smallest. The average ΔT for the 24 measured leather samples was found to be 3.0 ± 1.0 °C.

To our knowledge, there is no reported study concerning the comparison of both accelerated and natural ageing effect on parchment and leather. Our study shows that the 1-day accelerated ageing at 85 °C and 60% RH performed in 2013 has a comparable effect on the T_d values as the 4-year natural ageing. This is especially true for leathers, where differences less than 1 °C were observed (Table 1). For Sheep Mimosa, the values of T_d are almost identical, but the shapes of the peaks are different. For parchments the 1-day accelerated ageing had a slightly stronger effect on the T_d values, the decrease of T_d exceeding that caused by natural ageing by about 2 °C.

In our work, the accelerated ageing could reproduce quite closely the changes in hydrothermal stability of these materials caused by the natural ageing, even though there were some differences concerning the area and the shape of the denaturation peaks. These differences can be attributed to the different mechanisms of the two ageing types and to the inherent inhomogeneity of such samples. Surely, many more studies are needed to find the proper parameters and the relationship between accelerated ageing time and natural ageing.

5. Conclusions

Two series of parchments and three series of vegetable-tanned leathers previously accelerated aged and measured by DSC in 2013, were measured again after 4 years for observing the effect of natural ageing on the denaturation temperature which reflects their hydrothermal stability. The natural ageing lowers the denaturation temperature in a different way for the two types of these collagen-based materials. For parchment the largest effect was observed for the initial, "new" samples, while for the strongly aged ones the temperature shift was negligible. For leather, no relevant dependence of the denaturation temperature shift with the previous accelerated ageing time was observed, the peak temperature decreasing in average by 3.0 ± 1.0 °C. Following natural ageing, the enthalpy of denaturation diminishes substantially for parchment, while for leather no significant alteration was observed. Thus, in this study, it was found that parchment is more susceptible to the effects of natural ageing than leather. The latter is less affected as confirmed by the smaller temperature decrease and the preservation of peak shape and area. In our study it was found that the 1-day accelerated ageing performed in 2013 had comparable impact on the denaturation temperature of these materials as the 4-year natural ageing. These studies can be useful for assessing and forecasting the effects of natural ageing on patrimonial artifacts manufactured from parchment and leather.

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