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EFFECT OF ACCELERATED THERMAL AGEING ON THE THERMAL BEHAVIOUR OF THE RECENTLY MADE PARCHMENTS

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To reveal the fire injuring of parchment, the changes in the thermal behaviour of some goat parchments, obtained from skins originating from different animals, as a result of thermal aging were determined by thermal analysis methods (DSC; simultaneous TG/DTG, DSC; micro hot table (MHT)). Thermal aging of parchments was revealed to bring about the decrease in shrinkage temperature, absolute value of enthalpy of denaturation in water and some changes in non-isothermal parameters characteristic for dehydration process in static air atmosphere.

The results obtained by DSC analysis performed in N_2 and O_2 flows as well as those obtained by simultaneous TG/DTG, DSC analyses have shown that both softening (melting) process parameters and parameters of thermo-oxidative processes have not been changed by thermal ageing. The results obtained by thermal analysis methods were correlated with those obtained by microscopic investigation of parchment samples immersed in water and scanning electron microscopy (SEM). The application of these microscopic techniques has revealed the morphology changes in the investigated parchments as a result of thermal degradation.

Keywords: *accelerated thermal degradation, parchment, SEM, thermal analysis*

Introduction

Among collagen-based materials, parchments contained in some heritage (historical and cultural) objects belong to the European culture. The investigation of deterioration as a result of environmental conditions under which the parchment is stored is important for damage identification and assessment in such objects. To this end, some destructive, micro-destructive and non-destructive analytical techniques were applied. From the data obtained by applying these techniques, actions to ensure the preservation of parchments in the form of manuscripts, scrolls, characters, book covers, and substrates for artwork can be taken. Among the analytical techniques, the thermal analysis methods (TG, DTG, DTA, DSC, DMA, methods for shrinkage temperature determination, thermo-microscopy, etc.) were used [1–18] to characterize the recently manufactured and old parchments and to reveal the changes in the parchment state occurring because of the natural or artificial aging.

Wild fire in libraries has produced not only the irreversible damage of some manuscripts and artwork made of parchment, but also a fire injuring of ancient parchments. In order to restore the damaged parchments, the investigation of the accelerated thermal ageing of parchments at relative high temperatures is required. The aim of the present study is to reveal the changes in the thermal behaviour of some goat parchments submitted to accelerate thermal ageing by applying the thermal analysis methods, and the correlation of the obtained results with the microscopic patterns of samples immersed in water and scanning electron microscopy (SEM) pictures.

Experimental

Materials

Our experiments were carried out on three parchments, P1, P2 and P3, which were obtained from goat skins originating from three animals.

Methods

Thermal aging

The air-accelerated aging was performed at 195°C and 1 atm within a chamber with air-forced circulation and temperature accuracy within the limits ±2°C. Thermal aging durations were: 0.5, 1 and 2 h for P1; 1.5 and 2 h for P2, 1 and 1.5 h for P3.

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DSC analysis

DSC curves were obtained by means of a DSC 204 F1 Phoenix apparatus produced by Netzsch – Germany. The following kinds of DSC measurements were performed:

- DSC analysis of the sample (1–5 mg) immersed in water (35 μL deionized water), hermetically sealed in an aluminum pan and stocked for 24 h. Each sample was heated from 25 to 110°C, at a heating rate of 10 K min^{-1}.
- DSC analysis of the sample (1–5 mg) in gas flow (nitrogen or oxygen; purity of each gas is higher than 99.999%; 20 mL min^{-1}), in an open aluminum pan, at the heating rate of 10 K min^{-1}, and in the temperature range of 25–280°C.

Simultaneous TG/DTG and DSC analysis

The heating curves (TG/DTG and DSC) of samples were obtained simultaneously by means of a STA 409 PC apparatus produced by Netzsch – Germany, in static air atmosphere, in the 25–650°C temperature range, at a heating rate of 10 K min^{-1}. The mass of the analyzed samples was in the range of 2.37–6.05 mg and the heating of each sample was performed in a cylinder shape Pt–Rh sample holder.

Determination of the shrinkage temperature (T_s)

The shrinkage temperature was determined by the following methods:

- Micro hot table (MHT) method, using a MHT apparatus produced by Caloris – Romania.
- DSC analysis of each sample, immersed in water, under the above mentioned conditions. The extrapolated onset temperature of the endothermic peak, revealing the parchment damage, was recorded as the shrinkage temperature [4, 19, 20].

Scanning electron microscopy (SEM)

SEM observations were made for gilt parchment samples by means of a TESLA BS 301 apparatus.

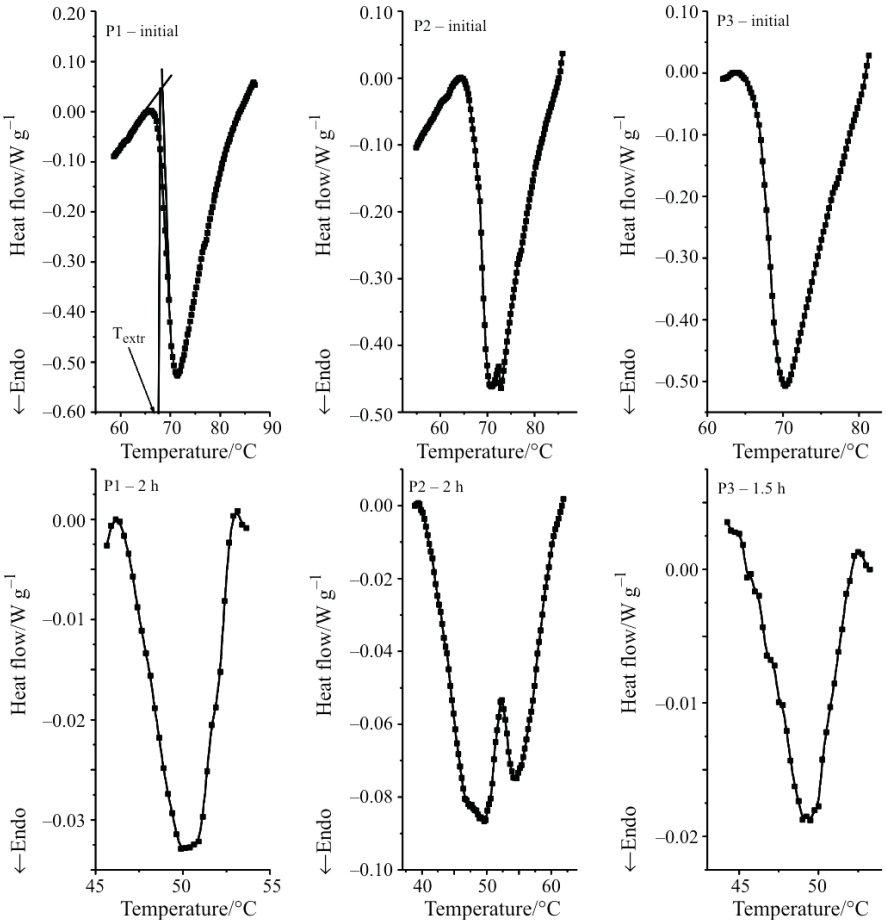

Fig. 1 DSC curves for the non-aged (initial) and aged parchments immersed in water

Results and discussion

Changes in hydrothermal stability of parchments as a result of thermal aging

Figure 1 shows some DSC curves obtained for non-aged (initial) and aged parchments. Each parchment is characterized by extrapolated onset temperature (T_{extr}), temperature corresponding to the minimum of DSC curve (T_{min}), and the enthalpy change (ΔH). The inspection of the DSC curves obtained for initial parchments has shown some differences in the hydrothermal behaviour of these materials obtained from skins origination from three different animals. For example, unlike endothermic peaks of parchments P1 and P3, the DSC peak of parchment P2 is split in two. The split of DSC curves also has been revealed for thermal aged samples of P2. This shows that parchment P2 has a higher heterogeneity than parchments P1 and P3.

The dependencies of T_{extr}, T_{min}, T_s (determined by MHT method), and ΔH on the accelerated aging time are shown in Figs 2–4. The analysis of data presented in these figures has revealed the following:

(a) a good agreement between T_{extr} and T_s (determined by MHT method) that also was reported in our previous works [14, 16, 17]

(b) a decrease in all mentioned characteristics of parchments with the thermal aging time

The statement (b) could be explained by the changes in the fibre morphology as a result of thermal aging, revealed for all parchments immersed in water by microscopic examination performed in MHT experiments. The changes in microscopic patterns of parchment P1 immersed in water as a consequence of

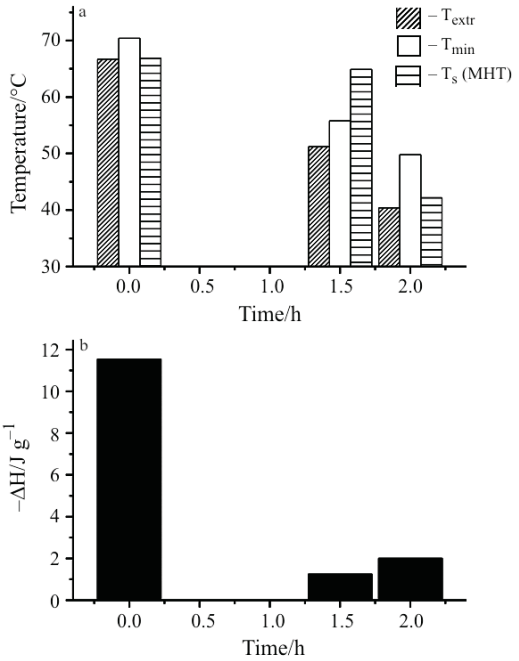

Fig. 3 a – The shrinkage temperature values (T_s) determined by DSC and MHT methods, temperature corresponding to the minimum of DSC curve (T_{min}) and b – ΔH *vs*. the accelerated aging time for parchment P2

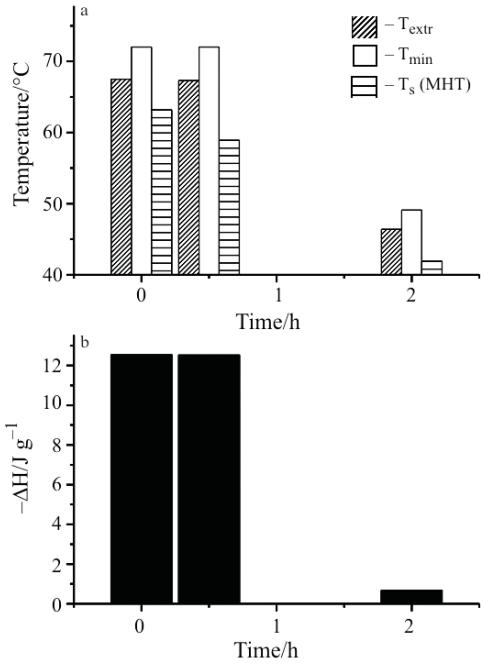

Fig. 2 a – The shrinkage temperature values (T_s) determined by DSC and MHT methods, temperature corresponding to the minimum of DSC curve (T_{min}) and b – ΔH *vs*. the accelerated aging time for parchment P1

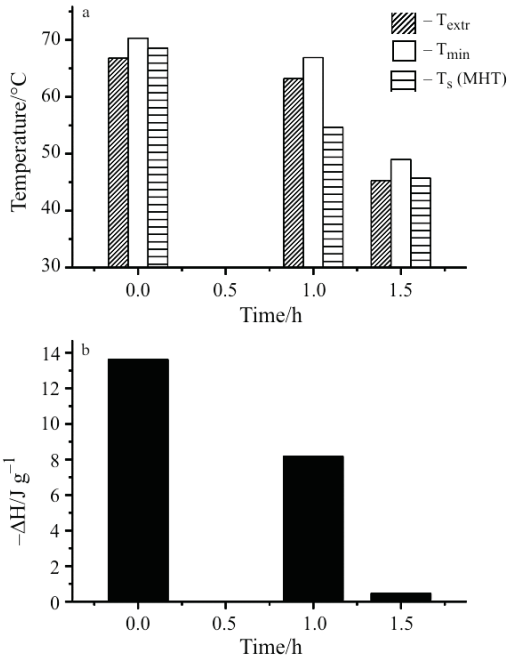

Fig. 4 a – The shrinkage temperature values (T_s) determined by DSC and MHT methods, temperature corresponding to the minimum of DSC curve (T_{min}) and b – ΔH *vs*. the accelerated aging time for parchment P3

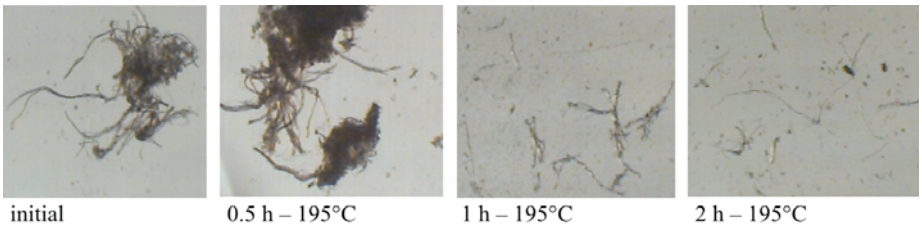

Fig. 5 The patterns of parchment P1 immersed in water (25°C)

thermal aging are shown in Fig. 5; similar patterns were obtained for all parchments. The fibre sizes, adhesion and coherence have shown to be decreased with the increase in the aging time. The fibres of the initial parchment are long with a high structural coherence, while after 0.5 h of aging, the fibers have become tight and made ball like clusters. After 1 h of heating at 195°C, the relative length of fibres decrease by about 50%, and after 2 h of aging an emphasized fragmentation of fibres was observed.

DSC analysis in N_2 and O_2 flow

Figure 6 shows the DSC curve obtained by analysis of parchment P3 – initial in N_2 flow; similar DSC curves were obtained for all investigated parchments, initial and aged, both in N_2 and O_2 flow. At a relative low temperature, each investigated parchment has exhibited an endothermic peak, denoted by I, corresponding to the loss in material humidity. This process is followed by an endothermic process, denoted by II. The process II, earlier detected by Okamoto and Saeki [21] and recently [16–18] put in evidence for collagen based materials, could be explained by the biphasic amorphous-crystalline structure of collagen-based materials according to which the crystalline triple-helix is embedded into an amorphous matrix [17, 21]. Very recently [18], the data from Proton solid-state NMR obtained for collagen-based materials (pure collagen, parchment, leather) have led to a three-phase model

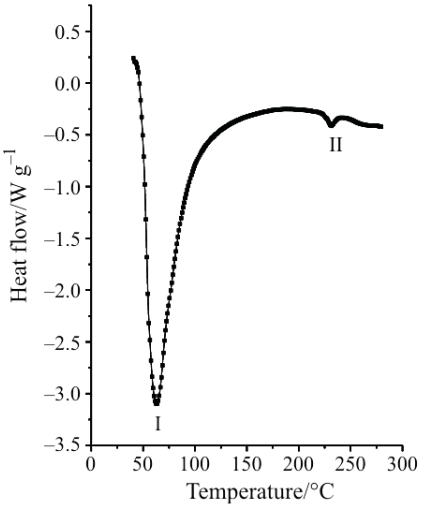

Fig. 6 DSC curve for initial P3 parchment, obtained in N_2 flow

(rigid, inter-face and mobile phase). Consequently, the process II might be related to softening (melting) of rigid (crystalline) part of parchment.

Table 1 lists the results obtained by DSC analysis in N_2 and O_2 flows for the initial and thermal aged parchments P1, P2 and P3. The analysis of these results has revealed the following:

(a) some of the dehydration peaks I from DSC curves obtained in N_2 and O_2 flows have exhibited one or two shoulders

(b) for some parchments, the softening (melting) peaks have exhibited splits

Table 1 DSC data obtained by analysis of investigated parchments in N_2 and O_2 flows

Material	T_a/°C	t_a/h	N_2			O_2		
			T_m(I)/°C	T_m(II)°C	$-\Delta H$/J g^{-1}	T_m(I)/°C	T_m(II)°C	$-\Delta H$/J g^{-1}
P1	initial	0	79.6	228.9, 232.9	6.22**	51.6, 81.1*	227.6	6.61
	195	0.5	66.6, 83.0*	230.4, 232.6	4.78**	79.3	226.3	5.05
	195	1	80.8*, 88.5	230.4	4.85	55.0, 71.3*	228.4	5.95
	195	2	86.2	230.1	5.18	58.7	229.6	5.66
P2	initial	0	54.0, 58.0*, 72.3*	230.0	6.24	50.6, 82.0*	228.3	6.86
	195	1.5	54.0, 58.0	230.9, 232.5	4.79**	60.4	226.9	3.28
	195	2	66.9, 88.0*	230.4	6.42	85.4	227.5	10.18
P3	initial	0	63.0	231.5	4.47	52.9, 77.4*	225.7	4.21
	195	1	51.7, 53.3, 69.3*	230.7	6.92	54.9, 68.2*	229.0	7.44
	195	1.5	58.4, 61.0, 76.4*	227.9	6.78	58.3, 62.8*	225.6	5.59

T_a=accelerated aging temperature; t_a=aging time; T_m(I)=temperature corresponding to the DSC peak of process I;
T_m(II)=temperature corresponding to the DSC peak of process II; ΔH=change in the entalpy in the considered process.
*Temperature corresponding to a shoulder of the DSC peak, **value corresponds to the global process including both processes

(c) T_m(II) and ΔH values have not been dependent practically on the gas in which DSC analysis was performed, and are not affected by thermal aging

The statements (a) and (b) could be explained by heterogeneity of the investigated parchments that is characteristic for the initial material and/or that resulted from thermal aging. The statement (c) shows that the amorphous-crystalline or three-phase structure is not changed by thermal aging of parchments.

Simultaneous TG/DTG and DSC analysis

Figure 7 shows the TG, DTG and DSC curves for the parchment P3 – initial; similar plots have been obtained for all analyzed samples. They are qualitatively in agreement with the results previously reported for some collagen-based materials [7, 9, 10, 14, 22–25].

The non-isothermal thermo-oxidative degradation of a sort of parchment occurs through three successive processes accompanied by mass losses. In the first endothermic process (denoted by I in Fig. 7), the water was completely lost. The next two steps (denoted by II and III in Fig. 7) are exothermal ones and consist in the pyrolytic decomposition and thermo-oxidation of the parchment. Between the end of the process I and the beginning of process II, in a temperature range where the mass loss is very low, the softening (melting) process (denoted by I' in Fig. 7) characterized by an endothermic peak in DSC curve occurs. Between processes II and III, an exothermic process (denoted by II' in Fig. 7) with a small change of sample mass occurs. The later process could be caused by the oxidation of the solid products resulting in process II to solid compounds, which will be decomposed and/or oxidized with release of volatile compounds.

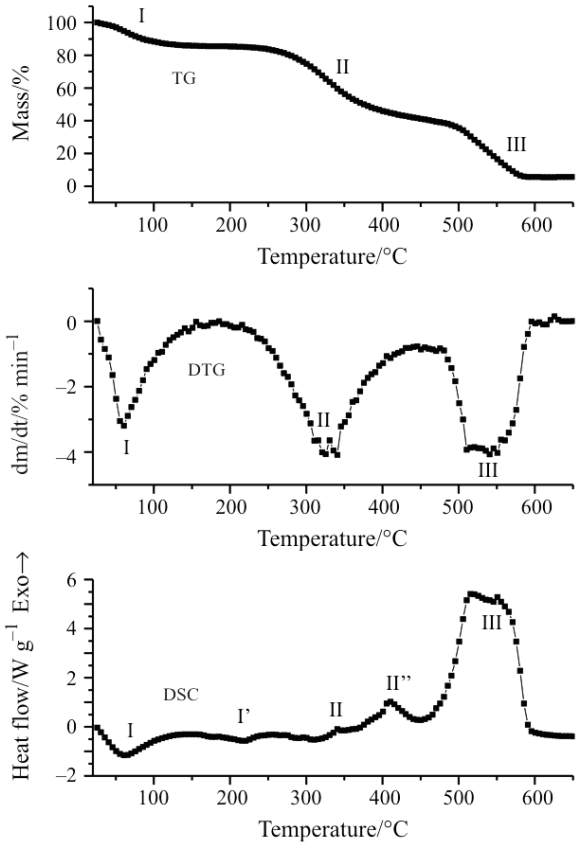

Fig. 7 TG, DTG and DSC curves for the parchment P3 – initial, analyzed in static air atmosphere

The results obtained by simultaneous TG/DTG and DSC analysis of the parchments listed in Table 2 in air have revealed the following:

(a) for each parchment and process I (dehydration), T_{min}^{DTG}, T_{min}^{DSC} and ΔT have exhibited maximum values for the maximum thermal aging time, while $\%\Delta m$ is not practically influenced by aging

(b) in the limits of inherent experimental errors, the values for softening (melting) temperature are practically equal with those determined by DSC analysis in N_2 and O_2 flows

(c) for the thermo-oxidative processes, the changes in the characteristic parameters are not significant and cannot be correlated with the thermal aging time (for process II: $\overline{\%\Delta m}$=45.6±1.9%; $\overline{T}_{min}^{DTG}$=331±13°C; $\overline{\nu}_{max}$=4.21±0.20 min^{-1}; for process III: $\overline{\%\Delta m}$= 38.1±2.1%; $\overline{T}_{min}^{DTG}$=539±10°C; $\overline{\nu}_{max}$=4.99±0.75 min^{-1}).

These results have confirmed that the thermal aging of all parchments had caused some morphology changes in these without any changes in the amorphous-crystalline or three-phase structure.

Scanning electron microscopy

The morphology changes in parchments due to the thermal aging resulting indirectly from the above presented results, was confirmed by SEM determinations. SEM technique enables general features of the sample surfaces, the fibre shapes and their packing to be inspected [11, 14, 15].

Figure 8 shows the SEM pictures of the initial parchment P1, corresponding to the papillary layer, reticular layer and cross-section. The papillary layer has a compacted structure, and some pores corresponding to hair follicles. The reticular layer also has a compact structure with randomly disposed fibres. In the cross-section both papillary and reticular layers are observed.

Figure 9 shows the SEM pictures of the parchment P1, subjected to accelerated aging at 195°C for 2 h. The comparison of the SEM pictures in Figs 8 and 9 has revealed the following:

- the structure of the papillary layer in the aged parchment is similar with that corresponding to initial one

Table 2 The parameters of non-isothermal degradation of the investigated materials in static air atmosphere

Material	T_a/°C	t_a/h	Process I dehydration				Process I' melting	Process II thermo-oxidation				Process II'	Process III thermo-oxidation				
			ΔT/ °C	Δm/ %	T_{min}^{DTG}/ °C	T_{min}^{DSC}/ °C	T_{min}^{DSC}/ °C	ΔT/ °C	Δm/ %	T_{min}^{DTG}/ °C	V_{max}/ min^{-1}	T_{max}^{DSC}/ °C	ΔT/ °C	Δm/ %	T_{min}^{DTG}/ °C	T_{max}^{DSC}/ °C	V_{max}/ min^{-1}
P1	initial	0	25–181	15.3	61	67	222	181–444	45.5	322	3.87	–	444–601	36.9	534	523	5.30
	195	0.5	25–187	16.6	59	64	222	187–421	45.0	341	4.34	402	421–600	42.6	522	526	5.71
	195	1	25–188	10.4	78	77	226	188–443	45.9	342	4.22	426	443–602	38.5	545	546	5.89
	195	2	25–192	12.4	82	84	220	192–431	44.4	352	7.22	399	431–601	39.8	537	535	5.97
P2	initial	0	25–201	16.1	60	73	231	201–440	45.1	309	4.58	434	440–600	36.3	526	523	4.74
	195	1.5	25–192	14.2	59	64	224	192–423	43.1	325	4.13	421	423–602	39.3	543	536	4.39
	195	2	25–217	14.2	70	78	229	217–449	50.1	322	4.01	418	449–603	38.1	544	530	5.41
P3	initial	0	25–190	14.5	59	62	218	190–449	44.2	339	4.30	411	449–596	35.8	538	517	4.15
	195	1	25–199	14.7	62	67	226	199–449	46.5	330	4.22	344	449–604	36.4	551	542	4.15
	195	1.5	25–212	14.1	73	76	221	212–454	46.5	327	4.22	418	454–608	37.0	551	540	4.21

T_a=accelerated aging temperature; t_a=aging time; ΔT=the temperature range where the process occurs; Δm=mass loss; T_{min}^{DTG}=temperature corresponding to the least reaction rate; T_{min}^{DSC}=temperature corresponding to the endothermic DSC peak; T_{max}^{DSC}=temperature corresponding to the exothermic DSC peak; $V_{max}=-d\%\Delta m/dt$ at T_{min}^{DTG}

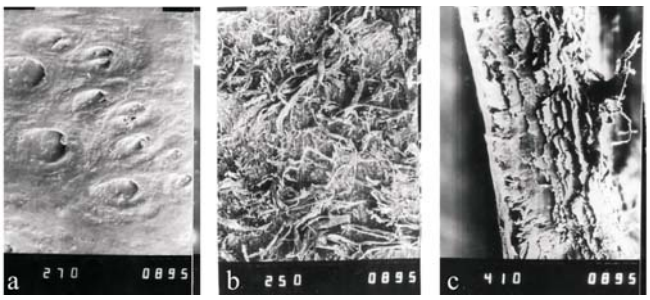

Fig. 8 SEM pictures for the parchment P1 – initial; a – papillary layer, b – reticular layer, c – cross-section

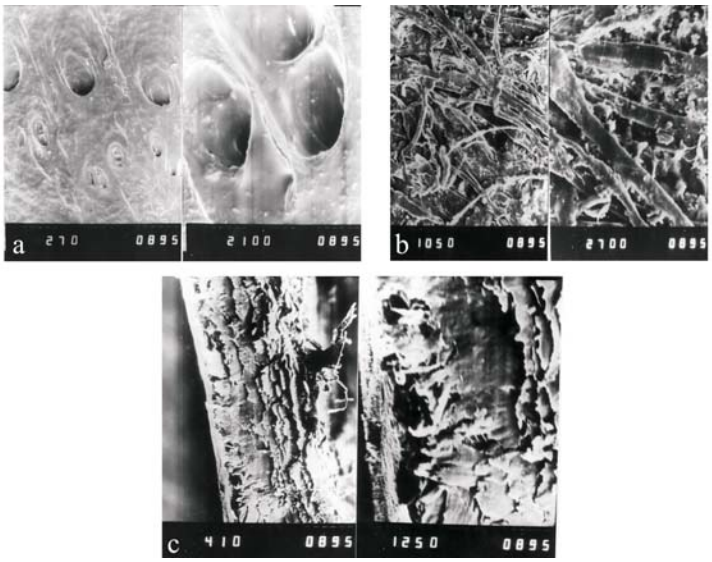

Fig. 9 SEM pictures for the parchment P1 aged at 195°C for 2 h; a – papillary layer, b – reticular layer, c – cross-section

- the aged and initial parchments exhibit different structures of the reticular layer; unlike the initial parchment, the aged parchment has more spaced fibres with broken ends
- for both parchments, the papillary and reticular layers are observed in cross-section, but the aged parchment exhibit some additional cracks, delaminated and porous areas

Similar observations have resulted from observing of SEM pictures obtained for all investigated parchments.

Conclusions

- The changes in the thermal behaviour of three goat parchments, obtained from skins originating from three animals, as the result of thermal aging at 195°C were revealed by using the the thermal analysis methods (DSC; simultaneous TG/DTG, DSC; MHT) and microscopic (optic and SEM) observation.
- The DSC analysis of samples immersed in water and MHT determinations have shown a decrease in shrinkage temperature and absolute value of denaturation enthalpy in water with the increase in the thermal aging time. The changes in the hydrothermal stability by thermal aging were also confirmed by simultaneous TG/DTG, DSC analyses performed in static air atmosphere.
- The DSC analysis in N_2 and O_2 flows and simultaneous TG/DTG, DSC analyses performed in static air atmosphere have shown that both softening (melting) temperature and corresponding, and parameters characteristic for thermo-oxidative processes are not changed by thermal aging. A relative high thermal stability of amorphous-crystalline or the three phased structure of the investigated parchments has resulted.
- The results obtained by thermal analysis methods were correlated with the changes in the parchment morphology determined by microscopic observation of parchments immersed in water and application of the SEM technique.

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