Thermochimica Acta 516 (2011) 19–28

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Dynamic mechanical analysis (DMA) of new and historical parchments and leathers: Correlations with DSC and XRD

A. Cucos [a,*], P. Budrugeac [a], L. Miu [b], S. Mitrea [a], G. Sbarcea [a]

[a] National Institute for Research and Development in Electrical Engineering ICPE-CA, Splaiul Unirii 313, 030138 Bucharest, Romania
[b] R&D Textile and Leather National Institute - Division Leather and Footwear Research Institute, 93 Ion Minulescu Street, 031215, Sector 3, Bucharest, Romania

ARTICLE INFO

Article history:
Received 15 September 2010
Received in revised form 3 December 2010
Accepted 11 January 2011
Available online 20 January 2011

Keywords:
DMA
DSC
XRD
Parchment
Leather

ABSTRACT

A sort of pure collagen, 22 sorts of new parchments, 35 sorts of old (14th–19th centuries) parchments, 19 sorts of new vegetable tanned leathers and 31 sorts of old (15th–19th centuries) leathers were investigated by DMA technique in tensile mode from room temperature to 260 °C. The obtained results were correlated with those determined by DSC measurements performed in N_2 flow in the same temperature range and by XRD. It was pointed out that all collagen-based materials contain a "crystalline" region exhibiting a phase transition ("melting") in the temperature range 210–260 °C, which is characterized by an endothermic peak in the DSC curve and an abrupt decrease of storage modulus in DMA. Differences in the parameters of this phase transition, related to various deterioration levels, were put in evidence and discussed.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Parchments and leathers are collagen-based materials constituent of many valuable patrimonial objects. The former have served as writing materials, while the latter have covered a wide range of utilizations, from clothing to decorative uses. Their preservation is a moral duty, but also a challenge for restaurators and conservators. The correct assessment of their degradation and preservation state is the cornerstone of the future conservation treatment.

There are many studies, especially published in the last two decades, concerning the application of various analytical methods in the characterization of these biomaterials [1]. These methods can be classified as non-destructive (optical, SEM, XRD, spectral methods: IR, UV–vis) and destructive (TG/DTG, DTA, DSC, DMA, TMA). The methods of thermal analysis were found to be very useful for assessment of the degradation degree of parchments and leathers, but also for autentification of patrimonial objects made from these materials [2–25].

In a previous work [23] the suitability of DSC technique in the characterization of patrimonial parchments and leathers was put in evidence. The changes of shrinkage temperature (determined by DSC analysis of wet samples) and of the "melting" temperature of the crystalline part of collagen-based materials (determined by DSC analysis in gas (N_2, O_2, synthetic air) flow as a result of natural ageing of parchments and leathers were determined and correlated with their degradation degree. In another previous paper [25], we have presented some preliminary results obtained by applying DMA method in tensile mode, involving heating of the sample from 20 °C to 260 °C. The results obtained for relative few sorts of new and old parchments and leathers have shown the suitability of this method for the characterization of these materials, as well as the possibility of correlation of changes in storage and loss moduli with the deterioration. We mention that till now there are only few DMA studies of some collagen-based materials, conducted in water [4], in wet state [5] or in dry state [6,7].

In this work, we expanded the DMA and DSC studies over a larger number of parchments and leathers, both new and old, and supplementary performed a qualitative XRD study, for verifying the conclusions drawn in previous papers [23,25]. Some new correlations between DSC and DMA results were put in evidence and discussed.

2. Experimental

2.1. Materials

- A sort of pure collagen ($\overline{M} \approx 130\,000$; produced by Riedel-de Haen AG);
- 22 sorts of new parchments manufactured from calf, sheep, goat, kid and lamb skins at The Leather and Footwear Institute (Bucharest, Romania);

* Corresponding author. Tel.: +40 21 3468298; fax: +40 21 3468299.
E-mail address: andreicucos@icpe-ca.ro (A. Cucos).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.01.006

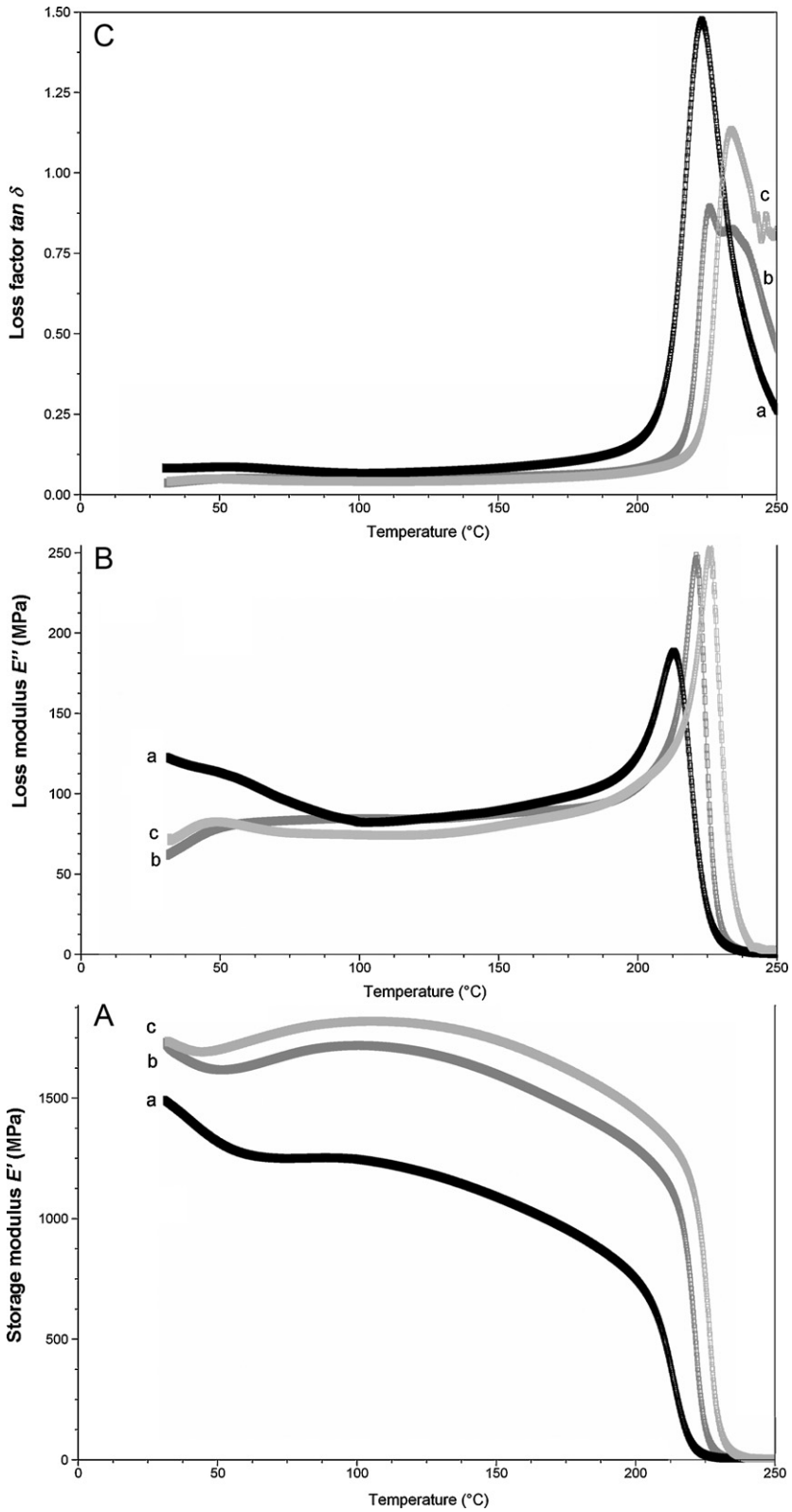

Fig. 1. (A) Storage modulus E' curves, (B) loss modulus E'' curves and (C) tan δ curves for (a) collagen, (b) new parchment made from goat skin, and (c) old parchment (14th century, Turin State Archives). Curves (b) and (c) are examples falling in the wide range of both E' and E'' for new and old parchments.

- 35 sorts of old parchments (14th–19th centuries) supplied by Turin State Archives (Turin, Italy), Moldova Museum (Iaşi, Romania) and Romanian National Museum of History (Bucharest);
- 19 sorts of new leathers manufactured from calf, sheep and goat skins vegetable tanned with quebracho, chestnut, oak and mimosa extracts at The Leather and Footwear Institute;
- 31 sorts of old leathers (15th–19th centuries, mostly covers of religious books, bookbinding leathers, chair tapestries, belts, etc.) supplied by Moldova Museum (Iaşi), Bucharest City Museum and Central Military Museum (Bucharest).

From each of the above-mentioned materials, three samples (for DMA, DSC and XRD, respectively) were cut next to each other and were measured once.

2.2. Methods

The DMA measurements were performed using a DMA Q800 (TA Instruments, USA) in tensile mode between room temperature and 260 °C at 3 K min^{-1}, under a controlled strain of 0.2% and 0.3 N static force, at 1 Hz frequency, in static air atmosphere. In order to measure its tensile properties, fibrous collagen had to be pressed into a rigid pellet. The applying of 10 tons load by means of a manual press afforded a 10-mm diameter, 0.3 mm-thick pellet, from which a rectangular sample was cut. For new parchments and new leathers, rectangle samples with typical dimensions of 5 mm × 20 mm were cut. Most samples from historical objects were smaller than those from new parchments and leathers. However, samples as small as 2 mm × 10 mm could be measured in DMA.

The DSC curves were recorded using a DSC 204 F1 Phoenix (Netzsch, Germany) in the same temperature range at 10 K min^{-1} in open aluminum pans and nitrogen flow (20 mL min^{-1}; nitrogen purity of 99.999%). The samples for DSC typically weighed 2–5 mg.

Both DMA and DSC were calibrated using the manufacturer-specified calibration procedures.

The X-ray powder diffraction patterns were collected on a Bruker D8 Advance diffractometer using an X-ray tube with Cu anode (with wavelength of the $K_{\alpha,Cu}$ radiation at 1.5406 Å). For all samples, the 2θ angle was scanned between 1.5° and 100°, with 0.040° step size and 1 s time per step. The samples were measured on the flesh side and were very different with regard to their available sizes, ranging from around 20 mm × 20 mm for new samples, to around 5 mm × 5 mm for old ones.

3. Results and discussion

3.1. Dynamical mechanical analysis (DMA)

The measured DMA parameters were the storage modulus E', which measures the stiffness of a viscoelastic material, the loss modulus E'', which represents the energy dissipated and the loss factor tan δ, which is the ratio of E'' to E' and represents the mechanical damping.

3.1.1. Collagen and parchments

The E' vs. T curve of the sample cut from the collagen pellet and examples of E' vs. T curves for new and old parchments are given in Fig. 1A. Similar curves were obtained for all parchment samples. At room temperature the collagen pellet has an initial E' value of ~1500 MPa, the new parchments' values are in the range 1000–3100 MPa, while old samples gave a similar range of values (1100–3300 MPa). It results that the stiffness of the parchments is very well preserved in time.

The following changes of E' occur at progressive heating: (1) an initial decrease of E' followed by a slight increase or a small plateau; (2) a continuous decrease up to around 200 °C and (3) a drop of modulus to a value close to zero for collagen and all parchment samples. The first part of the curves is due to moisture loss. Similar features of E' vs. T curves were previously observed by Nguyen et al. [26] for reconstituted collagen and by Odlyha et al. for a new parchment [6]. The abrupt decrease of modulus at temperatures above 200 °C, also observed by Nguyen et al. and Odlyha et al., is ascribed to melting of the crystalline fraction of collagen. A model of collagen-based materials consisting of a rigid-crystalline phase, a mobile-amorphous phase and an interphase was recently elaborated [27]. Within this model, the amorphous matrix embeds the crystalline collagen filaments and hinders the thermal denaturation of "dry" collagen on heating. As a result, this transition, called "melting of the collagen crystalline phase" [28,29], occurs at higher temperature (above 200 °C) than in a fully or partially hydrated parchment/collagen [30].

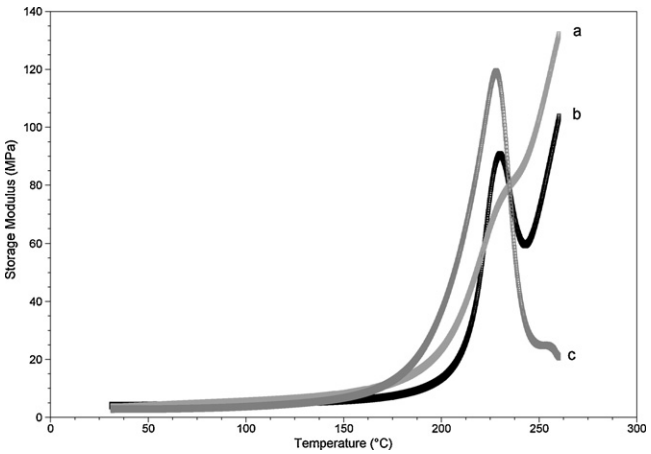

Fig. 2. Storage modulus E' curves of three new leathers made from: (a) sheepskin tanned with mimosa; (b) calfskin tanned with quebracho; (c) calfskin tanned with mimosa.

The inflexion point of this decrease of storage modulus, $T_{Storage}$, was used to estimate the temperature of melting of the samples. In our study $T_{Storage}$ was found to be 213 °C for collagen, 215 ± 6 °C for new parchments and 224 ± 7 °C for historical parchments.

The loss modulus dependence on temperature for parchments showed the following features (Fig. 1B): a broad and weak peak at 50–90 °C, a continuous increase to about 200 °C, and a very sharp maximum/peak at T_{Loss} = 215 ± 6 °C for new parchments and 222 ± 4 °C for old parchments. These features resemble quite well those of collagen, for which the peak appears at 213 °C. A good agreement between the T_{Loss} and $T_{Storage}$ values was obtained for these samples.

The tan δ curves (Fig. 1C) show a broad and weak peak at 50–90 °C, a slight increase up to about 200 °C, followed by a large peak, which is split in some cases and appears at temperatures exceeding the $T_{Storage}$ and T_{Loss} by few degrees. The average position of this peak, $T_{Tan\delta}$, is 223 ± 5 °C for new parchments and 238 ± 8 °C for old parchments. The corresponding peak for collagen appears sharply at 223 °C.

The comparison of the obtained results shows the following:

(1) the parchments exhibit a DMA behavior similar to collagen;
(2) the ranges of initial values of moduli and the shapes of E' vs. T curves for new and old parchments are practically identical.
(3) surprisingly, most historical parchments have a higher melting temperature than new parchments; this could due to either crosslinking occurring by natural ageing or peculiarities of manufacturing procedures used some centuries ago.

The last two statements confirm the observation according to which the parchment is a material of outstanding stability that can survive for many centuries without loosing its characteristics.

3.1.2. New leathers

The initial values of storage modulus for new leathers are low (3–45 MPa) and slightly increase on heating up to about 180–200 °C (Fig. 2). Above this temperature, a rapid increase is seen, and the behaviors of new leathers become different, namely: (a) a continuous increase of modulus with a shoulder at around 230–240 °C (4 samples), (b) a peak at 225–240 °C followed by a minimum and

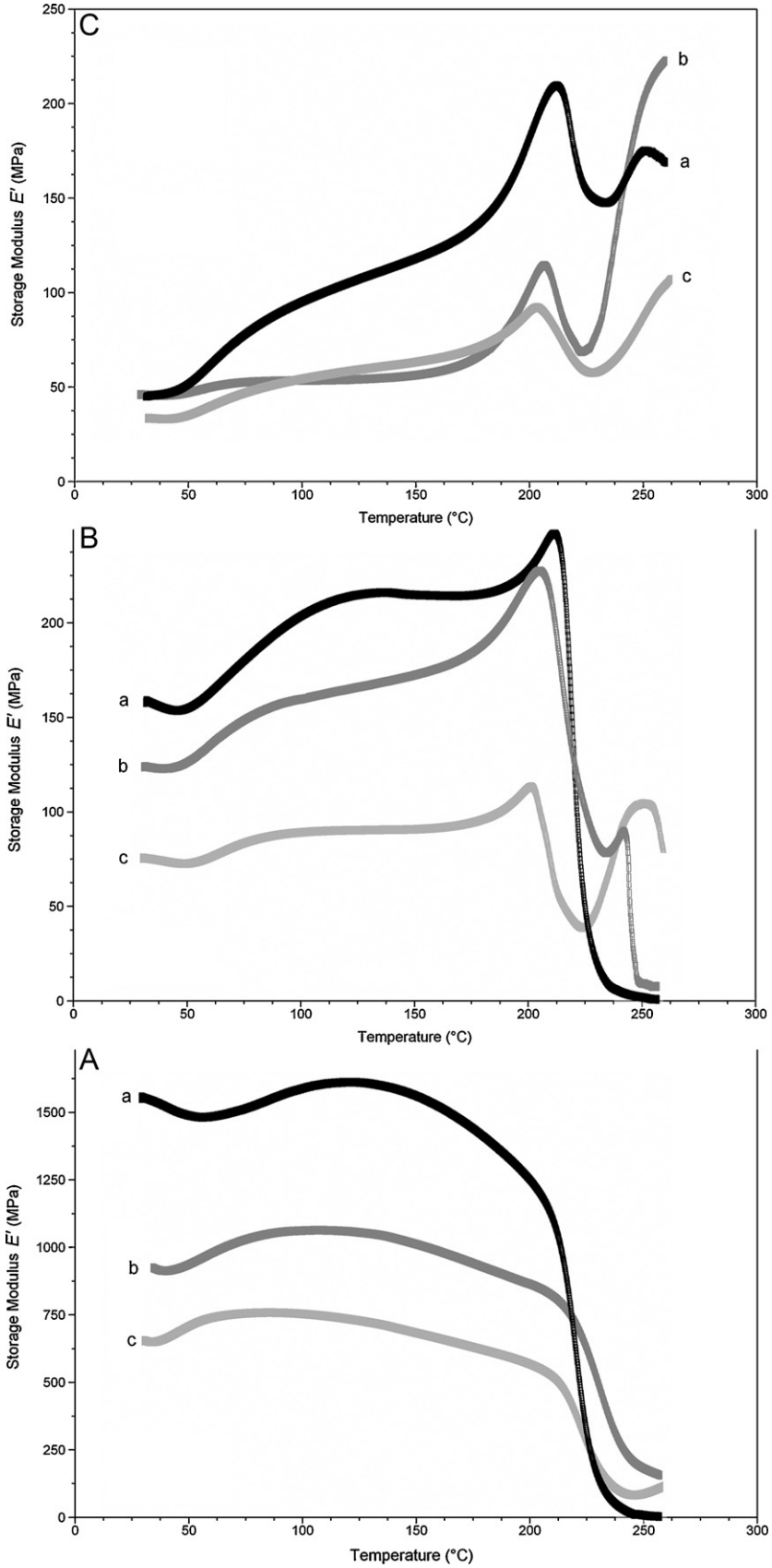

Fig. 3. Storage modulus curves of some old leathers. (A) (a) Sbornic (religious book), Putna monastery, 1474, (b) bookbinding leather, 17th century, (c) gospel, edited in Bucharest in 1765. (B) (a) Sheath of medieval rapier, (b) bookbinding leather, 1818, (c) bookbinding leather, 1808. (C) (a) Minei (religious book), 15th century, (b) bookbinding leather, 17th century, (c) slavonic manuscript, 18th century.

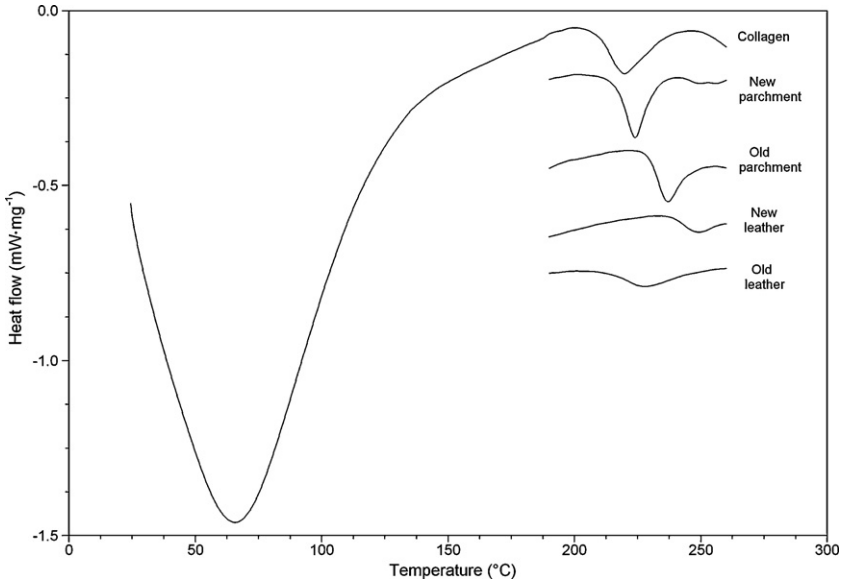

Fig. 4. Examples of DSC curves of the studied materials. The full-scale curve of collagen only is shown. For parchments and leathers, only the region of melting is pictured. The curves are normalized on the 190–260 °C domain and are shifted vertically for clarity.

a new increase (12 samples), or (c) a maximum at around 230 °C, then a drop of modulus to finite values (3 samples).

The stiffening at high temperatures could be due to the presence of both bound and excess tannins (not entirely removed in the washing step of procedure used for manufacturing of leather), which could generate an additional cross-linking of the collagen fibrils, and to the loss of oils and fats (added to leather in order to give softness and flexibility). The melting of crystalline fraction of leather causes a decrease or only a shoulder in modulus. After the crystalline (rigid) part has melted, the reinforcement of material continues, except for case c, where the modulus decreases to finite values.

3.1.3. Old leathers

The most intriguing results were obtained for historical leathers. Various shapes of E' vs. T curves were observed, as follows:

- For 16 samples of old leathers the storage modulus curves were found to be quite similar to those for parchments (Fig. 3A). Two rigid samples from 15th and 19th centuries exhibited large initial values for modulus (1550 and 1020 MPa, respectively), which decreased to zero on melting. Other leathers of this group showed lower initial moduli (220–920 MPa) which decreased to finite values (50–200 MPa) at high temperatures.
- The shapes of other leathers exhibited a peak of E' at around 200 °C, just before the drop in modulus (Fig. 3B). A decrease of E' to zero, to finite values or a second peak could be observed.
- Some old leathers were quite soft (the initial values of E': 20–80 MPa) and showed E' vs. T curves with an ascending shape (Fig. 3C), resembling that of new leathers. The dominant process on heating is also the stiffening of the sample, which is interrupted by the melting process, put in evidence as a slight decrease of storage modulus.

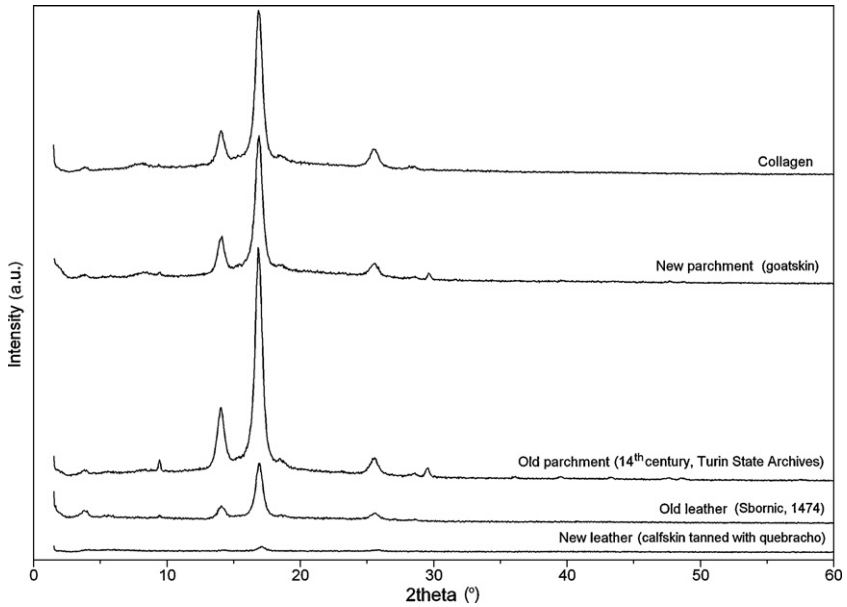

Fig. 5. Examples of XRD patterns of the studied materials. Data above 60° are not shown, as no peak is observed.

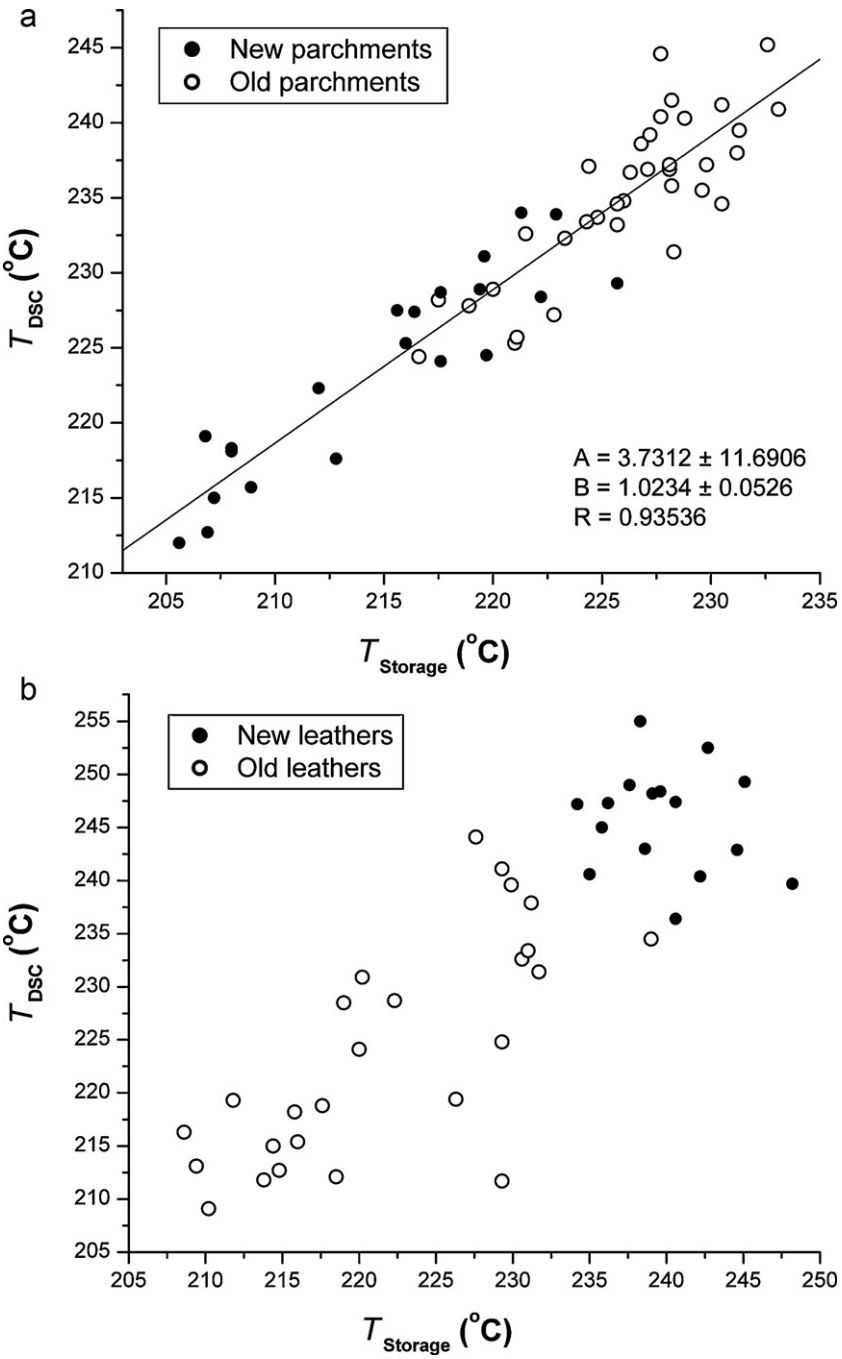

Fig. 6. T_{DSC} vs. $T_{Storage}$ plots for new and old parchments (a) and leathers (b).

The explanation of the DMA behaviors of old leathers is difficult, due to the complexity of the degradation processes, the heterogeneity of the samples and different preservation states. According to our results, the shapes of E' vs. T curves of old leathers represent various levels of their deterioration and are not related to their actual age. The most important observation is that on natural ageing some leathers reach a DMA behavior similar to parchment/collagen. The cause could be that on ageing the non-collagen components of leathers (tannins, oils, etc.) are altered due to their oxidative and hydrolytic degradation, as shown, for example, by the decrease of tannin extracts for old leathers comparative to the new samples [31]. We can thus suppose that, deprived of the large tannin molecules and aggregates, as well as of the oils and other components, the collagen fibrils and bundles come closer, resulting in a more compact and rigid network. On the other hand, some old leathers exhibit a DMA behavior similar to new leathers, which means a low degradation and a good preservation state. As will be seen in Section 3.3, the XRD of old leathers also showed them to be intermediate between new leathers and parchments/collagen.

3.2. Differential scanning calorimetry (DSC)

The typical DSC curves for the studied materials have been discussed previously [23] and are schematically represented in Fig. 4. The first and large endothermal peak below 100 °C corresponds to the loss of moisture. Above 200 °C these materials show a smaller endothermal peak which is due to the

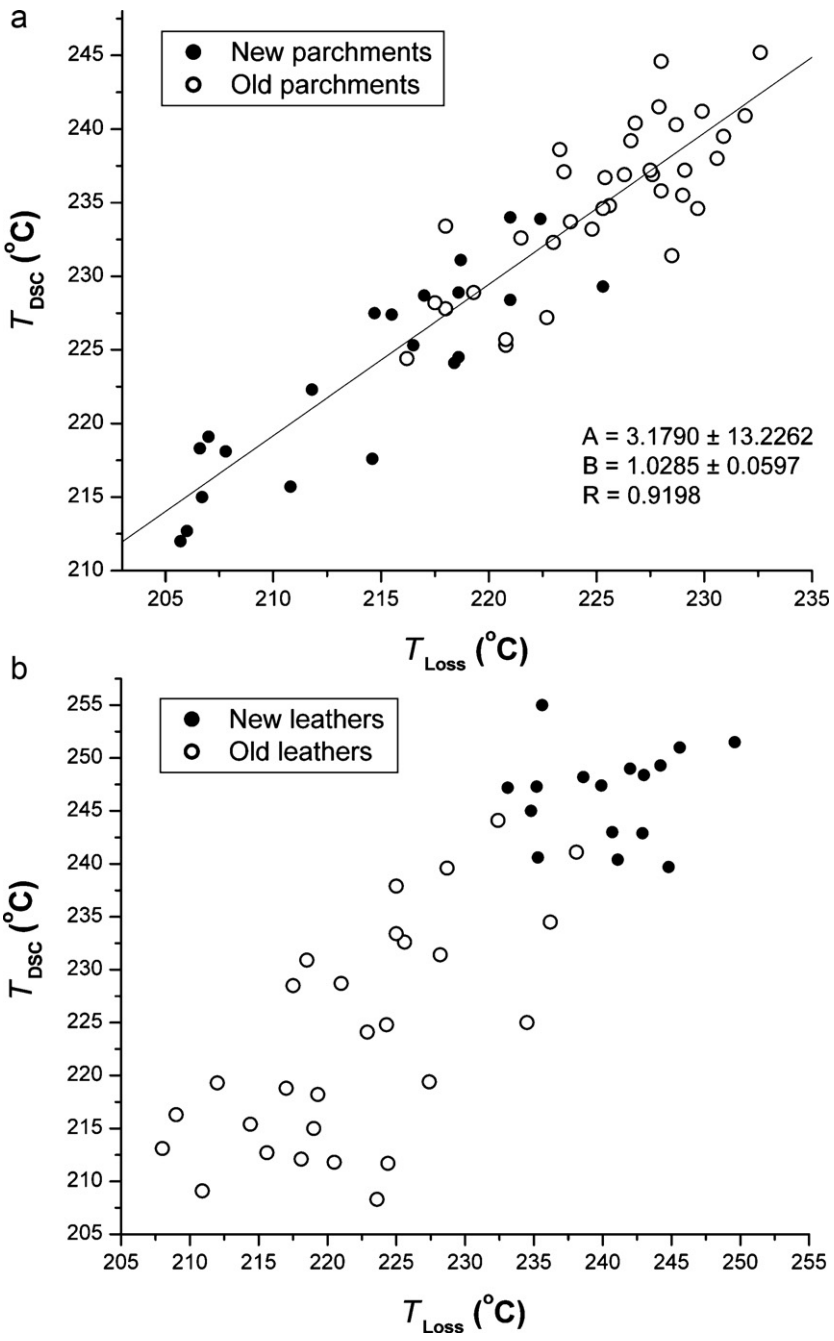

Fig. 7. T_{DSC} vs. T_{Loss} plots for new and old parchments (a) and leathers (b).

melting of the collagen crystalline phase, earlier detected by Okamoto and Saeki [28]. This peak is generally distinct for collagen, new and old parchments, broader and smaller for new leathers, while for old leathers it can be of various shapes: distinct, broad, small or even undetectable for some samples. The observed differences are most probably related to various deterioration levels. The positions of these peaks, T_{DSC}, and the corresponding enthalpies, ΔH, were found as follows: 220 °C ($-13\,J\,g^{-1}$) for collagen, 224 ± 7 °C ($-9 \pm 3\,J\,g^{-1}$) for new parchments, 235 ± 5 °C ($-8 \pm 3\,J\,g^{-1}$) for historical parchments, 246 ± 5 °C ($-2 \pm 1\,J\,g^{-1}$) for new leathers and 224 ± 11 °C ($-4 \pm 2\,J\,g^{-1}$) for historical leathers. As one can note, there are high uncertainties for enthalpy data, which are probably due to the fact that measurements were made on a wide variety of samples.

3.3. X-ray diffraction (XRD)

Fig. 5 shows typical XRD patterns obtained for pure collagen, new and old parchments and leathers. All investigated collagen-based materials exhibit XRD patterns similar to that of pure collagen, in which the main diffraction peaks appear very distinctly at 2θ values of 14.1, 16.9 and 25.5°. The presence of these peaks directly confirms the existence of a crystalline region in these materials. As can be seen in Fig. 5, high differences among the intensities of peaks corresponding to different collagen-based materials were observed. However, we can make only some qualitative considerations on the crystallinity of the investigated materials, as the intensity value depends also on the sample size and morphology. Thus, the intensities of the peaks for new parchments are comparable to those of collagen sample. That means that new parchments

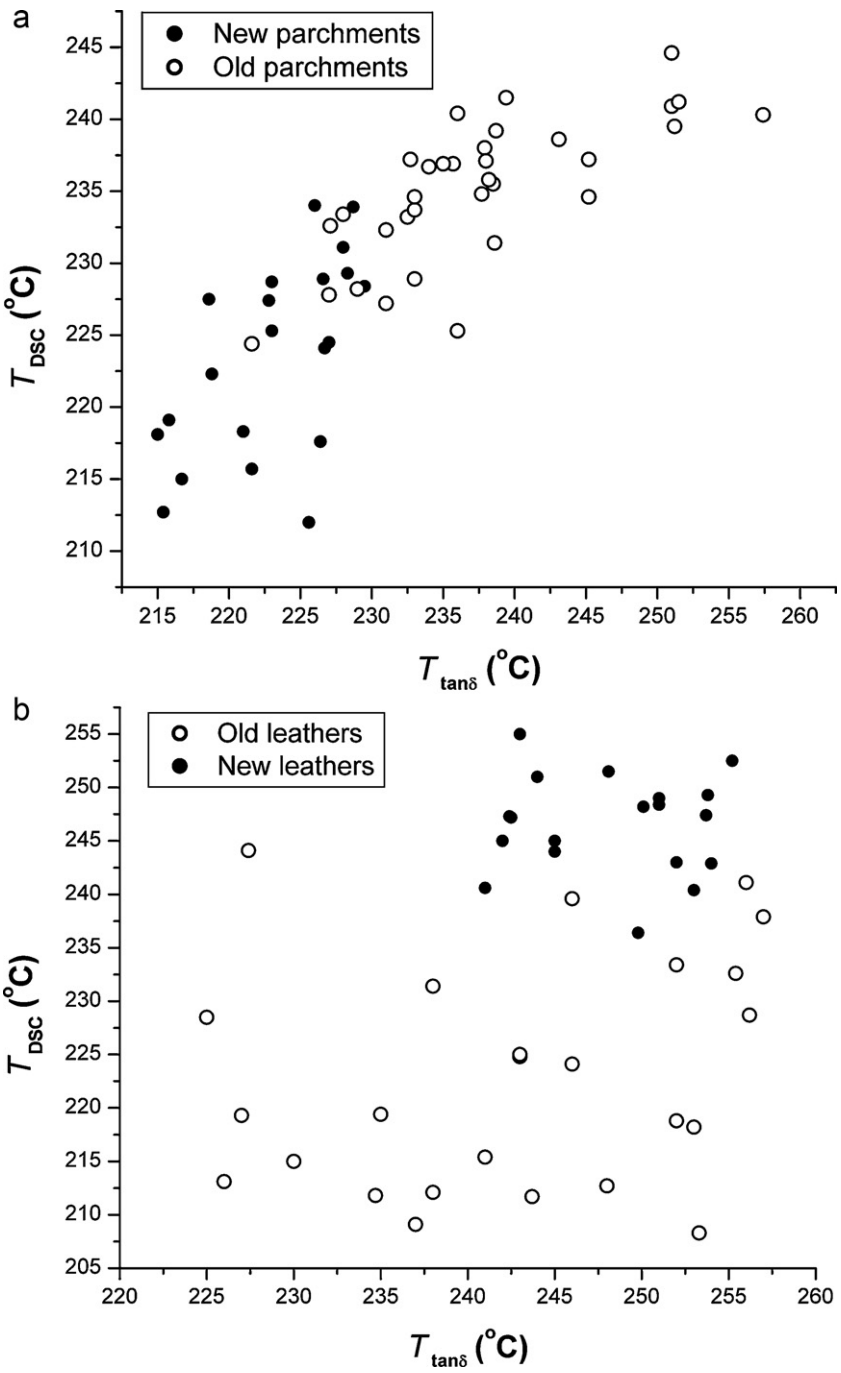

Fig. 8. T_{DSC} vs. $T_{Tan\delta}$ plots for new and old parchments (a) and leathers (b).

and collagen have close values of crystallinity degree. Quite surprisingly, the old parchments gave in general higher intensities than new parchments, although these samples were much smaller. Except two samples, all new leathers exhibited very faint or even no diffraction peaks of collagen. As far as the old leathers are concerned, they exhibited patterns with very different intensities, from very low to comparable to that of collagen, indicating a crystalline degree intermediate between those of parchments and new leathers.

3.4. Correlations between DMA, DSC and XRD results

In order to find a correlation between the DSC and DMA results, the positions of the melting peaks, T_{DSC}, were plotted against the DMA data, namely: (a) temperature of inflexion point of storage modulus, $T_{Storage}$, (b) temperature of the main peak of loss modulus, T_{Loss}, (c) temperature of the main peak of loss factor, $T_{Tan\delta}$.

The plotting of the T_{DSC} data against the $T_{Storage}$ for both new and old parchments shows a quite linear dependence (Fig. 6a). These points can be reasonably fitted by a straight line of slope 1.023 ± 0.053, thus very close to unit. This confirms that both methods measure the same process. The plot also clearly shows that both groups overlap in a small region, but most of points for old parchments are at higher temperatures.

As far as the leathers are concerned, the data for both new and old samples are very scattered (Fig. 6b). This is due to a higher heterogeneity of leather samples compared to the parchment samples. Scattering may also be due to the broad shape of DSC melting

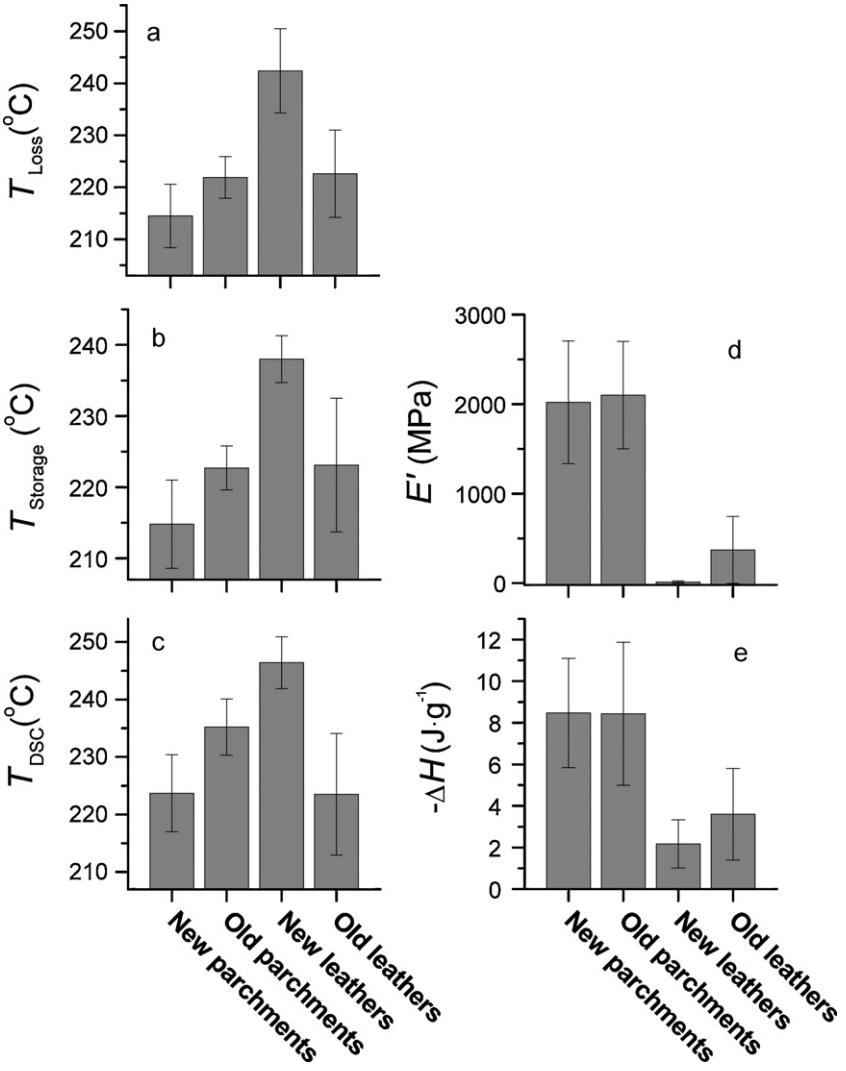

Fig. 9. Average T_{Loss} (a), $T_{Storage}$ (b), T_{DSC} (c), initial E' (d) and $-\Delta H$ (e) values for the studied collagen-based materials.

peaks. It can be seen also that, unlike the new parchments, the new leathers form a distinct group of points at higher temperatures.

The T_{DSC} vs. T_{Loss} plot was found to be similar to the T_{DSC} vs. $T_{Storage}$ plot (Fig. 7). This is especially true for parchments, where the T_{Loss} and $T_{Storage}$ points are very close, as mentioned above.

The tan δ data showed poor correlation with the DSC data, even for parchments (Fig. 8). Therefore the peak of tan δ does not express the real melting of these biomaterials.

The average data and the corresponding errors for melting temperature measured in DSC and DMA, the enthalpy of melting and the initial values of E' are represented in Fig. 9. Both methods show that:

(a) The old parchments have a higher average melting temperature than the new samples;
(b) The new vegetable tanned leathers exhibit the highest values of T_m;
(c) The data for old leathers are intermediate between those for new parchments and new leathers, but also have the highest error, due to the heterogeneity of these samples.

A good correlation between the initial E' value of the materials (Fig. 9d) and the enthalpy of the melting process recorded in DSC (Fig. 9e) was also found. Thus, the new and old parchments show high and close values of the enthalpy and modulus. The new leathers exhibit low average values of these parameters, while the old leathers have intermediate values. Interestingly, the same variation was seen in the intensities of the XRD patterns of these materials (new and old parchments—high, new leathers—low and old leathers—intermediate). The explanation could be that the value of modulus is related to the content of crystalline collagen, which is in turn put in evidence by the enthalpy of melting measured in DSC, and to the crystallinity degree measured in XRD.

From the above presented results, it appears that both the temperature related to melting process and the shapes of E' vs. T curves could be used as qualitative criteria to discriminate between new undamaged and old damaged leather samples.

4. Conclusions

1. A large number of new (recent manufactured) and old (historical and/or cultural) parchments and leathers has been studied by means of DMA in tensile mode, DSC and XRD.
2. The basic evaluated DMA parameter was the storage modulus, which reflected more perceptibly the viscoelastic changes on heating, especially the decrease of it as a result of melting of crystalline part of collagen-based materials, the existence of which was confirmed by XRD measurements.

3. It was obtained that on progressive heating in the range 25–260 °C, all the collagen-based materials exhibit two main successive processes, namely dehydration and melting of the "crystalline" part of material.
4. The employment of DMA and DSC methods leads to close values of "melting" temperature. Both DMA and DSC lead to the following sequence order of melting temperatures: collagen ≈ new parchments ≤ old parchments ≈ old leathers < new leathers.
5. It was put in evidence that old leathers exhibit a DMA behavior intermediate between that of parchment/collagen and that of new leathers.
6. Our results strongly confirm that DMA is a very useful method for characterising parchments and leathers, both recently manufactured and historical/patrimonial.
7. It was pointed out that DMA measurements could be used for qualitative distinction between new undamaged and old damaged leather samples. However, these data must be correlated with other criteria, as those mentioned in previous papers [20–22].

Acknowledgements

The research was financed by Romanian Ministry of Education and Research, Program PNII, Contracts 91-012/2007 and 92-089/2008.

References

[1] B. Dolgin, V. Bulatov, I. Schechter, Rev. Anal. Chem. 28 (2009) 151–307.
[2] R. Larsen, Thermochim. Acta 365 (2000) 85–99.
[3] C. Chahine, Thermochim. Acta 365 (2000) 101–110.
[4] N.S. Cohen, M. Odlyha, G. Foster, Thermochim. Acta 365 (2000) 111–117.
[5] M. Odlyha, G.M. Foster, N.S. Cohen, R. Larsen, J. Therm. Anal. Calorim. 59 (2000) 587–600.
[6] M. Odlyha, N.S. Cohen, G.M. Foster, A. Aliev, E. Verdonck, D. Grady, J. Therm. Anal. Calorim. 71 (2003) 939–951.
[7] G. Della Gatta, E. Badea, R. Ceccarelli, T. Usacheva, A. Mašić, S. Coluccia, J. Therm. Anal. Calorim. 82 (2005) 637–649.
[8] B. Roduit, M. Odlyha, J. Therm. Anal. Calorim. 85 (2006) 157–164.
[9] S. Prati, G. Chiavari, D. Cam, J. Therm. Anal. Calorim. 66 (76) (2001) 315–327.
[10] C. Genestar, J. Cifre, Thermochim. Acta 385 (2002) 117–126.
[11] G.M. Foster, S. Ritchie, C. Lowe, J. Therm. Anal. Calorim. 73 (2003) 119–126.
[12] K. Heide, E. Hartmann, K. Gert, H.G. Wiedemann, Thermochim. Acta 365 (2000) 147–156.
[13] V.A. Drebushchak, L.N. Mylnikova, T.N. Drebushchak, V.V. Boldyrev, J. Therm. Anal. Calorim. 82 (2005) 617–626.
[14] S. Shoval, P. Beck, J. Therm. Anal. Calorim. 80 (2005) 609–616.
[15] Q. Wang, M. Odlyha, N.S. Cohen, Thermochim. Acta 365 (2000) 189–195.
[16] I.C.A. Sandu, M. Brebu, C. Luca, I. Sandu, C. Vasile, Polym. Degrad. Stab. 80 (2003) 83–91.
[17] H. Anastasiou, Th. Hasapis, T. Zorba, K. Pavlidou, E. Chrissafis, K.M. Paraskevopoulos, J. Therm. Anal. Calorim. 84 (2006) 27–32.
[18] M. Odlyha, Q. Wang, G.M. Foster, J. de Groot, M. Horton, L. Bozek, J. Therm. Anal. Calorim. 82 (2005) 627–636.
[19] K.H. Friolo, A.S. Ray, B.H. Stuart, P.S. Thomas, J. Therm. Anal. Calorim. 80 (2005) 559–563.
[20] P. Budrugeac, L. Miu, V. Bocu, F.J. Wortmann, C. Popescu, J. Therm. Anal. Calorim. 72 (2003) 1057–1064.
[21] P. Budrugeac, L. Miu, C. Popescu, F.J. Wortmann, J. Therm. Anal. Calorim. 79 (2004) 975–985.
[22] P. Budrugeac, L. Miu, M. Souckova, J. Therm. Anal. Calorim. 88 (2007) 693–698.
[23] P. Budrugeac, L. Miu, J. Cult. Herit. 9 (2008) 146–153.
[24] D. Fessas, A. Schiraldi, R. Tenni, L.V. Zuccarello, A. Bairati, A. Facchini, Thermochim. Acta 348 (2000) 129–137.
[25] A. Cucos, P. Budrugeac, Int. J. Conserv. Sci. 1 (2010) 13–18.
[26] A.-L. Nguyen, B. The Vu, G.L. Wilkes, Biopolymers 13 (1974) 1023–1037.
[27] C. Popescu, P. Budrugeac, F.J. Wortmann, L. Miu, D. Demco, M. Baias, Polym. Degrad. Stab. 93 (2008) 976–982.
[28] Y. Okamoto, K. Saeki, Kolloid-Z. Z. Polym. 194 (1964) 124–135.
[29] E. Badea, L. Miu, P. Budrugeac, M. Giurginca, A. Mašić, N. Badea, G. Della Gatta, J. Therm. Anal. Calorim. 91 (2008) 17–27.
[30] P. Budrugeac, E. Badea, G. Della Gatta, L. Miu, A. Comănescu, Thermochim. Acta 500 (2010) 51–62.
[31] M.E. Florian, The mechanism of deterioration in leather, in: M. Kite, R. Thomson (Eds.), Conservation of Leather and Related Material, Elsevier, Bruxelles, 2006, pp. 36–57.