THE SUITABILITY OF THE DMA METHOD FOR THE CHARACTERIZATION OF RECENT AND HISTORICAL PARCHMENTS AND LEATHERS

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Abstract

The dynamical mechanical analysis (DMA) technique was used for the characterization of some recently manufactured and historical parchments and leathers. The obtained results were correlated with the DSC measurements performed for these biomaterials. We point out the suitability of the DMA method for distinguishing qualitatively between a recently manufactured leather and a patrimonial one, as well as for assessing the deterioration of the parchments and leathers as a result of natural ageing.

Keywords: parchment, leather, DMA, DSC

Introduction

The use of the thermal analysis methods (TG, DTA, DSC, DMA etc.) to characterize materials belonging to the cultural heritage is well documented [1-22]. From those techniques, the dynamic mechanical analysis (DMA) can provide very useful information about the subtle changes of the sample structure, that occur with heat, based on the mechanical effects that accompany them. However, there are only few papers on the DMTA. They are studies of collagen-based materials that serve as support for historical objects: parchments and leathers [3, 5]. Moreover, these measurements were conducted either in water, in order to study the shrinkage behavior of these materials [3], or in dry state and a temperature range not exceeding $220^{o}C$, probably because the samples were starting to decompose [5]. In this work we will demonstrate that heating at even higher temperatures (up to $260^{o}C$) reveals interesting details about the melting (softening) of the crystalline (rigid) region of collagen-based materials (parchments, leathers) and about cross-linking, which sometimes overlaps with the decomposition process.

The DSC was proved to be a very suitable method for the characterization of this type of material [22]. For this study, we also performed DSC measurements of the samples in the attempt to correlate the DMA and DSC data and to have a clearer image of the processes mentioned above.

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Experimental

Materials

The following collagen-based materials were investigated: a new parchment manufactured from calfskin (NP), a historical parchment (Legislative Document of Principality of Moldova, 1820) (HP), a new leather item, manufactured from calfskin, tanned with quebracho (NL) and a historical leather item (book cover of Gospel, Bucharest, 1760) (HL). The recent samples (NP, NL) were manufactured by The Leather and Footwear Institute, Bucharest, Romania, while the historical samples were supplied by the Moldova Museum, Iasi, Romania (HP) and by the Bucharest City Museum (HL).

Methods

The DMA measurements were performed using DMA Q800 equipment (TA Instruments, USA) in the tensile mode between room temperature and 260^0C 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 environment.

The DSC curves were recorded using DSC 204 F1 Phoenix equipment, (Netzsch, Germany) at the same temperature range, at 10 K. min^{-1} in open aluminum pans and with nitrogen flow (20 mL.min^{-1}; nitrogen purity of 99.999%).

Results and discussion

The DMA curve of the storage modulus for the new parchment is shown in Figure 1.
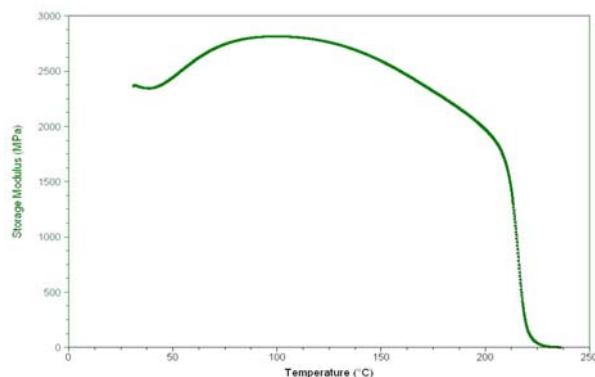

Fig. 1. The DMA curve of new parchment NP.

The E' curve has the following features: an initial value of 2400 MPa, a weak minimum at $40 – 50^oC$, a slight increase up to about 100^oC, then a continuous decrease and, finally, an abrupt drop, with an inflexion at 216^oC.

In order to identify the processes responsible for this behavior, a DSC measurement of the sample was performed (Fig. 2).

The DSC curve shows two endothermic peaks. The first larger peak, exhibiting a broad minimum at around 70^oC, that was due to the loss of water naturally absorbed by the material from the atmosphere. The effect revealed by DMA was an increase in modulus, that is, a stiffening of the sample, as previously observed by Odlyha et al. for a new parchment [5] and by Nguyen et al. in a collagen sample reconstituted from bovine tendon [23].
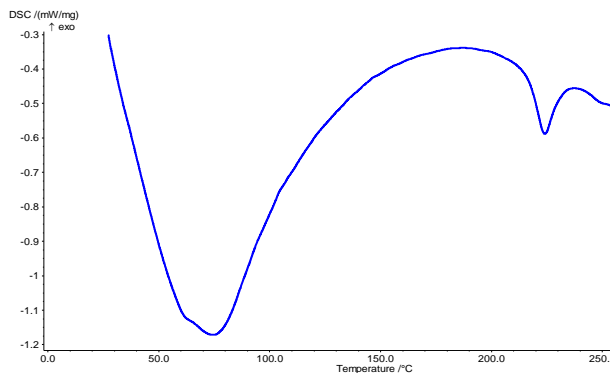
Fig. 2. The DSC curve of new parchment NP.

The smaller and sharp peak at 225.3^{o}C, was due to the melting (softening) of the crystalline (rigid) fraction of the material, corresponding to the denaturation of the collagen triple helix, previously detected by Okamoto and Saeki [24]. This caused a drop of modulus to a value close to zero. Previous studies [20] demonstrated that the decomposition with formation of volatile compounds of the collagen in parchments became dominant after the melting process was over. Therefore this final decrease in modulus obviously occurred due to the melting process. The small difference between the temperatures corresponding to the DSC peak and the inflexion point in DMA could be attributed to the heterogeneity of the sample and to the different heating rates. A progressive decrease of E' in the interval 120 – 200°C was also observed by Odlyha et al. [5] and was probably caused by a kind of melting of less ordered regions of the collagen fibrils.

The DMA behavior of the old parchment is shown in Figure 3 and is similar to that of the new sample. This fact confirmed once more that the old parchments preserve their mechanical properties very well through natural aging. The initial modulus had a value (2900 MPa), close to that for the new sample. One may identify the occurrence of the same processes and that the only difference is the slightly higher melting temperature for the historical sample in comparison to that of the recent parchment (the temperatures corresponding to the inflexion point of E' are: 230.0^{o}C for the old parchment and 216°C for the new parchment).

The DSC curve recorded for the historical sample is also similar to that of the new sample. The application of DMA and DSC techniques led to similar melting temperature values (230.0^{0}C and 234.6^{0}C, respectively).

Unlike parchments, which are relatively simple biomaterials, leather involves more complex systems, because it is composed of a matrix of collagen fibrils, which includes molecules of tanning agents, either bound to fibrils or free. The effect of these tannins is expected to be revealed by DMA patterns of the leather items.
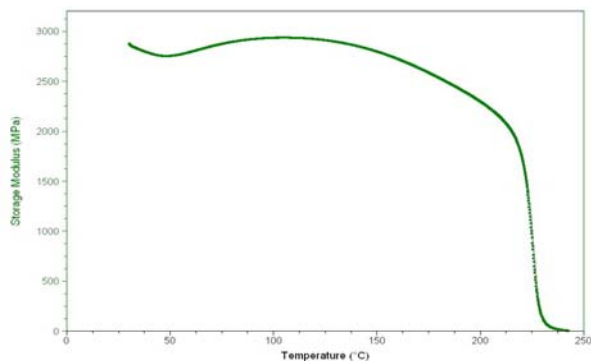

Fig. 3. The DMA curve of historical parchment HP.

The E' curve for the new leather is shown in Figure 4. The initial modulus has a value of 4 MPa. It increases continuously up to a temperature of about 200°C, then sharply and reaches a maximum of 90 MPa at 229.8^{o}C. After a drop in modulus and a minimum at 242.6^{o}C, the increase of E' is resumed.
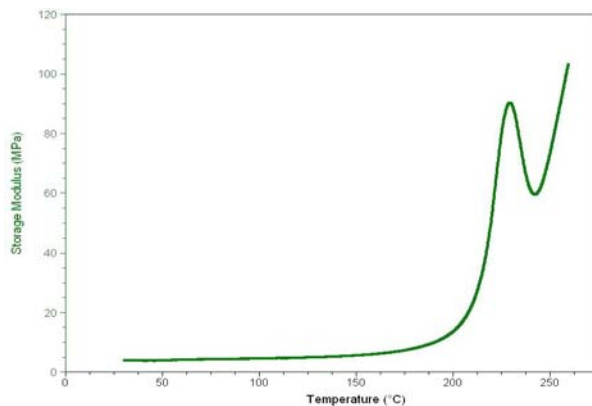

Fig. 4. The DMA curve of new leather NL.

The DSC curve shows a distinct melting peak at 241.0^{o}C, which falls in the same range observed for new leathers [22].

The initial increase of E' could be caused by the excess tannins content that was not entirely removed in the washing step of the procedure used for leather manufacturing. At relative high temperatures these tannins can generate additional cross-linking of the collagen fibrils, leading to the reinforcement of the sample. The melting of the crystalline (rigid) fraction of leather causes the drop in modulus on the DMA curve and a corresponding peak on the DSC curve. After the crystalline (rigid) part melts, the reinforcement of the material continues.

The DMA E' curve for the historical leather (Fig. 5) is completely different from that for the new sample. Surprisingly, it resembles more the E' curve of the parchments, as it shows almost the same variation of modulus: a broad peak at 90^{0}C, a progressive and almost linear decrease up to 200°C, then a sharp one, with an inflexion at 222.3^{o}C. However, at high temperatures the modulus does not reach a zero value, but a minimum of about 75 MPa, after which it slightly increases. Also, the initial modulus (650 MPa) is very high compared to that of the new leather, and it is closer to that of the parchment samples.
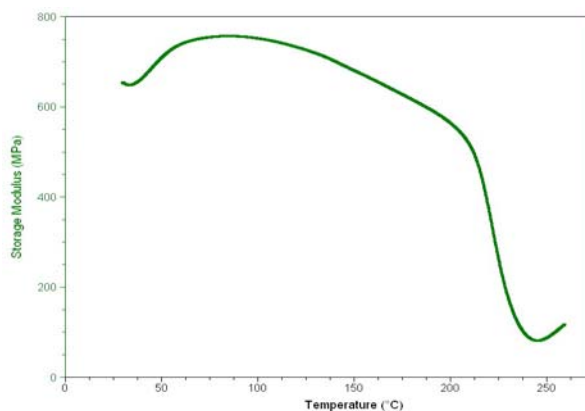

Fig. 5. The DMA curve of historical leather HL.

The E' behavior of the old leather may mainly rest in the crystalline part of collagen, that is not cross-linked by the tannins, as in the case of parchments. From this point of view, the processes occurring during heating of the investigated old leather and that of parchments are similar. However, unlike parchments, the old leather exhibits a finite value of the modulus after melting. That could be explained by the lower proportion of collagen in the old leather. The corresponding DSC curve is similar to that shown in Figure 2, but with a broad peak for the melting (softening) process, which suggests a high heterogeneity and fragmentation of the collagen matrix, caused by natural aging. The final slight increase of E' at temperatures higher than 240^0C could be explained by the presence of a small amount of excess tannins, that remained after aging, and that determined a minor cross-linking.

Conclusions

Historical samples of parchment and leather, as well as more recent similar items, were analyzed by DMA and DSC methods. While the DSC provided raw information about the dehydration and melting processes, the DMA method revealed more details about the subtle changes in those materials under heating. Thus, a very distinct melting process is observed in the DMA curves of the parchment samples as a sharp decrease in modulus, while for the new leather, the dominant process was the additional cross-linking caused by the excess tannins. Interestingly, the behavior of the old leather was closer to that of the parchments than to the new leather items. It exhibited a major melting (softening) of the crystalline (rigid) part and a minor cross-linking process. Moreover, there was no significant difference in thermo-mechanical properties between the new and the old parchment items, which explained why that material can last for centuries without altering its characteristics.

The obtained results show that both the DMA and the DSC techniques may be used for qualitative distinction between recently manufactured leather and heritage items, as well as for assessing the deterioration degree of parchments and leathers as a result of natural aging.

Work is in progress to apply the DMA technique in association with other analytic methods for a better understanding of the natural deterioration mechanisms for parchments and leathers.

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