PRELIMINARY CHARACTERISATION OF VEGETABLE LEATHER USED IN HERITAGE BINDERY

LUCREŢIA MIU[1], ION BOGDAN LUNGU[2], MIHALIS CUTRUBINIS[2], ELENA BADEA[1,3], IOANA STĂNCULESCU[2,4]

[1]*INCDTP - Division Leather and Footwear Research Institute (ICPI), 93 Ion Minulescu, Bucharest, lucretia.miu@icpi.ro, elena.badea@icpi.ro*

[2]*Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), ion.lungu@nipne.ro, mcutrubinis@nipne.ro*

[3]*Faculty of Sciences, University of Craiova*

[4]*University of Bucharest, Physical Chemistry Department, ioana.stanculescu@gmail.com*

Leather heritage and art bindery require special performances regarding physical, chemical, mechanical, organoleptic and esthetics characteristics but also a good stability over a long period of time. unlike chrome tanned leather, vegetable tanned leather is ecological, and provides better firmness, fullness, malleability and dimensional stability as well as heat and moisture plasticity, resistance to light radiations and hydrothermal stability. The leather quality requirements for niche domains like heritage and art bindery cannot be satisfied by the standardized industrial processes. In order to obtain the most appropriate mix of qualities, the selection of both fresh leather (e.g. animal species and age) and technology is required from batch to batch. Since vegetable leather is intrinsically an inhomogeneous material, still it is necessary an improved knowledge on the relationship between fabrication technology and leather properties. This paper therefore focuses on the mechanical characterisation of vegetable leathers in relation to their thickness and anatomic topography.

Keywords: vegetable leather, mechanical properties, anatomic topography

INTRODUCTION

The study of leather processing throughout history has importance for technology and science but also for history and art (Higham, 1999). Raw hide processing methods were numerous: smoke tanning, fat tanning, fermented milk, eggs, volcanic earth, vegetable tanning using plants extracts from barks, fruits, leaves, etc. Various ingredients such as fermented milk, eggs, volcanic earth, urine, excrements or combinations thereof were used in various periods and geographic areas (Bravo, 1964; Deselnicu *et al*., 1984). Tanning with chrome salts came into use only by the end of the 19th century. Leather bookbinding originates in the East as a necessity, to protect the fragile paper. The most important types of leather used for bookbinding were made of goat and calf hides using sumac extracts. Leather processing for bookbinding up to the seventeenth century is described in the encyclopedias of Delalande and Diderot (Thomson, 2000). Bookbinding leather had to be fine, resistant to bending and compression, thin, vegetable tanned, with the characteristic book cover finishing. In the early 20th century many books from English and German heritage museums were found to be seriously degraded. The first investigation on leather degradation was conducted in 1842 by Atheneum Club in England in order to find the cause of damage to the bookbindings in their library (Thomson and Attenborrow, 2001; Haines, 1977; Cambras, 2004; Larsen, 1997). In 1911, the German authorities elaborated a series of regulations on the processing of leather for bookbinding: mineral acids, vegetable tanning agents such as spruce, birch, willow, chestnut, quebracho, and mirobolam, rapid tanning, bleaching agents, excessive leather stretching or thinning were banned.

Another issue, emerging in the early 20th century, was the unsuitableness of chrome leather for as new covers for valuable collections of books dating back several hundred years from the Hague library. Replacing of old vegetable leather with new chrome leather, later cataloged as totally wrong, led to the straining and contraction of the covers, including deformation of internal bindery and book within 10 years only (Thomson, 1983). This phenomenon was due to the ignorance of the chrome leather behavior over time. It is now well-known that chromium crosslink action continues long over the fabrication process and may cause significant surface shrinkage. To avoid further serious errors in conservation and restoration practice, an improved knowledge on the relationship between the fabrication technology and leather properties is still necessary. This study concerns with the relation between leather's mechanical (i.e. tensile stress, tensile strain, deformation) properties and anatomic topography (i.e. sampling position and direction).

MATERIALS AND METHOD

The mechanical tests were conducted on calf leather (fig. 1) manufactured at the INCDTP-ICPI through traditional methods. Commercial extracts from quebracho wood were used for tanning. The mechanical tests were performed with a Tinius Olsen Testing Machine with a 5 kN cell force accredited by the RENAR Romanian Authority. Determination of tensile strength and measurement of the percentage extension performed following the EN ISO 3376: 2011 – Leather – "Physical and mechanical tests". The constant load speed was 100 mm/min. The samples were cut in a bone shape specimen (ISO 527-2 type 5B - ISO 37 type 4, DIN 53504 type S3) of 35 mm in length, 6 mm shoulder width, 12 mm gage length, 2 mm specimen width. Using such small samples enabled us to obtain a high number of samples for a better characterisation of each leather, an especially of the thickness variation. A much bigger cutting device, specimen number 5 of ISO 527-3 (6 mm in width and 80 mm the testing length), was used in a previous study reported by some of us (Lungu, 2014) that resulted in only 11 samples per leather and not very clear results.

One of the major problems when working with natural materials is their intrinsic inhomogeneity. This is partly due to the animal anatomy and partly to the manufacturing process. In Figure 1a, it is shown the position of the sampling area which represents the spine area of the calf leather. The neck/head and tail directions are indicated. To avoid the scattering of results due to the mentioned topographical inhomogeneity, all samples were cut from the spine area, close to the back bone of the animal. The direction of sampling was perpendicular on the backbone (batch 1 being the closest and batch 4 the furthest) (Fig. 1b). The sampling area was: 120 mm wide and 370 mm long. Four batches were used for measurements (10 samples were collected per each batch).

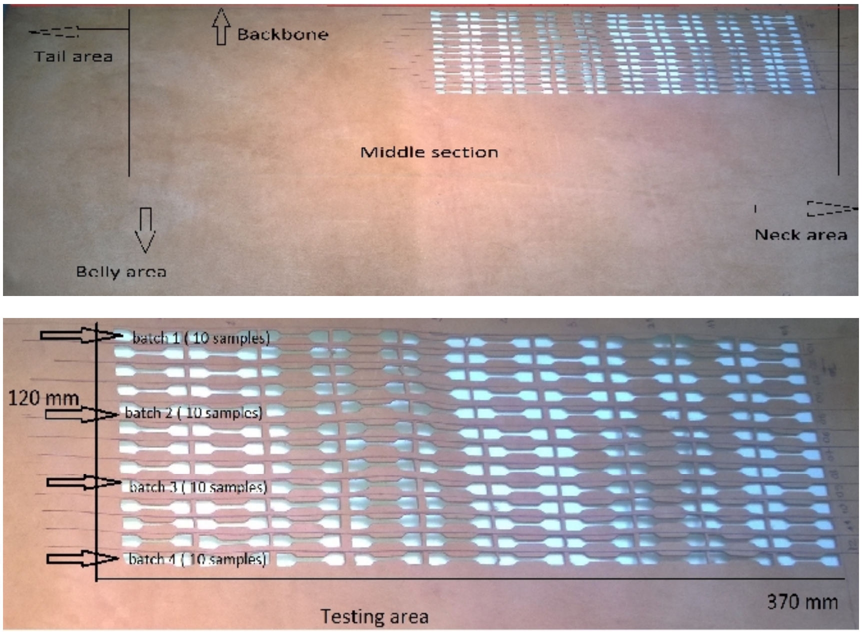

Figure 1. (a) Sampling area of the calf leather; (b) Detail of the sampling area

RESULTS AND DISCUSSIONS

The results obtained for each batch are shown in Tables 1-5. Due to the samples small dimensions, the leather's thickness non-uniformity impact was diminished, thus affecting in a small proportion the measurements. This is confirmed by the small values of the standard error of the mean and also by the small differences between the mean values for all 4 batches. Also, the standard deviation values are very low indicating that thickness variation is very close to the mean. The total variation of thickness along the tested area was 0.01 mm. The thickness and its coefficient of variation for all batches are listed in Table 1.

Table 1. Variation of thickness

Batch	Thickness (mm)	Coefficient of variation
1	1.003	0.027
2	0.999	0.041
3	0.012	0.038
4	1.003	0.039

These coefficients indicate the magnitude of variation for different means obtained from the 4 batches. It can be observed that the batch no 1 has the lowest variation, 0.027, while the other 3 batches have higher but close values, around 0.039. This indicates that thickness is more uniform closer it is to the backbone. Consequently, as the intrinsic variation of thickness is excluded, the mechanical tests results will indicate the behaviour of leather when exposed to stress, furthering from the backbone to the belly region.

In Table 2 are reported the results of the mechanical tests for the batch closest to the backbone. There are low values of standard deviation and standard error implying that the values are close to the mean and the mean is relatively accurate. This aspect is confirmed by the results obtained for the other 3 batches.

Table 2. Mechanical test and thickness results for batch no. 1

	Thickness (mm)	F_{break} (N)	F_{max} (N/mm^2)	Strain (%)
Mean	1.021	26.52	12.98	46.91
Standard deviation	0.028	3.038	1.433	9.660
Std error to the mean	0.009	0.961	0.453	3.055

Higher values for standard deviation and standard error are obtained for the values of deformation as illustrated in Fig. 2. They indicate a greater spread of the results from the mean. The deformation values indicate that the material is inhomogenous, which in our case represents an intrinsic characteristic of vegetable leather. Nevertheless, for batch no. 1 the values are lower than for the other 3 batches, indicating that the inhomogeneity increases as the distance from the backbone increases. In summary, for batch no.1 we found small variation in thickness and higher variation in deformation.

Comparing the variation of thickness and deformation it can be observed that the inhomogeneity of leather does not impact its thickness but rather its mechanical behaviour.

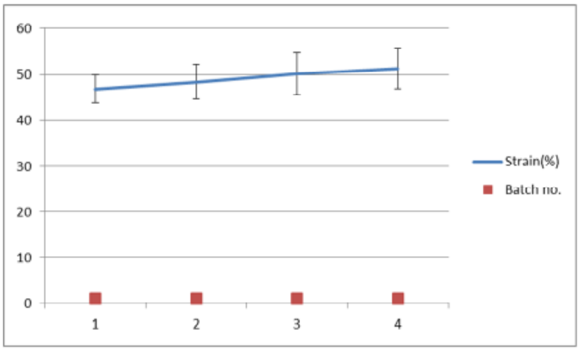

Figure 2. Variation of mean strain values

From the values reported in Tables 3-5 it can be observed that both the breaking force and tensile stress have a clear downtrend slope. This indicates a clear decrease of leather's mechanical resistance. In the same time, the deformation has an uptrend slope while distancing from the backbone, showing an increase in inhomogeneity. We can therefore state that leather's mechanical resistance is affected by the anatomical inhomogeneity which increases when moving from backbone to belly area.

Table 3. Mechanical test and thickness results for batch no. 2

	Thickness (mm)	F_{break} (N)	F_{max} (N/mm^2)	Strain (%)
Mean	0.999	23.72	11.87	48.45
Standard deviation	0.041	1.892	0.973	11.680
Std error to the mean	0.013	0.598	0.308	3.693

Table 4. Mechanical test and thickness results for batch no. 3

	Thickness (mm)	F_{break} (N)	F_{max} (N/mm^2)	Strain (%)
Mean	1.002	23.32	11.63	50.2
Standard deviation	0.038	2.891	1.390	14.335
Std error to the mean	0.012	0.914	0.439	4.533

Table 5. Mechanical test and thickness results for batch no. 4

	Thickness (mm)	F_{break} (N)	F_{max} (N/mm^2)	Strain (%)
Mean	1.003	21.45	10.673	51.4
Standard deviation	0.039	2.797	1.249	14.107
Std error to the mean	0.012	0.884	0.395	4.461

Figure 3 reports the values of the tensile stress (N/mm^2) in function of thickness for each batch. It can be observed that the tensile stress decreases as the distance from backbone increases (e.g. from batch no. 1 to batch no. 4) while the thickness remains almoust constant. This means that the material is becoming less hard as the distance from the backbone increases.

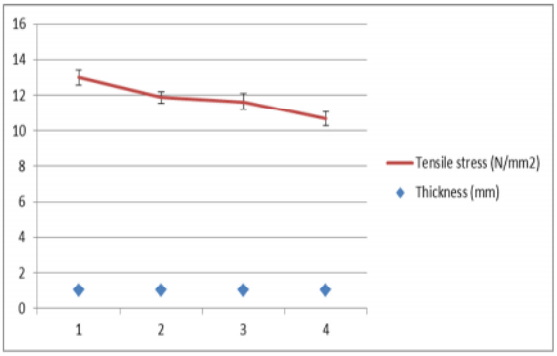

Figure 3. Mean tensile stress values related to thickness

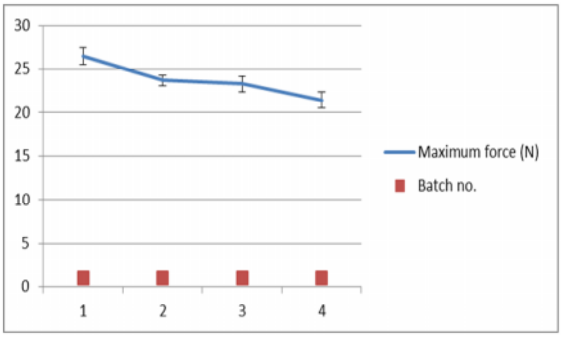

Figure 4. Mean maximum force values for 4 batches

The value of maximum force (N) (Fig. 4) is also decreasing as the distance from the backbone increases.

The accuracy of our results is supported by the low standard error and standard deviation values reported in Tables 1-4.

CONCLUSIONS

One of the major problems when working with natural materials concerns with their topographic inhomogeneity. The use of a big number of very small samples enabled us to eliminate the effect of thickness on leather mechanical properties and evaluate the influence of topography only. We found high values for standard deviation and standard error for the deformation values confirming the topographic inhomogeneity of leather and its increase as the distance from backbone increases. Moreover, the breaking force and tensile stress showed a clear downtrend slope indicating a decrease of leather's resistance supported by the increase of its inhomogeneity and distance from the backbone area.

Acknowledgement

The authors wish to thank the Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI) for support to TEXLECONS project (PNCDI II 213/2012).

REFERENCES

Bravo, A.G. (1964), *Storia del cuoio e dell'arte conciaria*, Assoc. Ital. del Cuoio, Torino.

Cambras, J. (2004), *The Complete Book of Bookbinding*, New York: Lark Books.

Deselnicu, M., Olteanu, Ş. and Teodorescu, V. (1984), History of leather processing in Romania, Technical Press, Bucharest.

Haines, B.M. (1977), "Deterioration in leather bookbindings – our present state of knowledge", *British Library Journal*, http://www.bl.uk/eblj/1977articles/article9.html.

Higham, R.D. (1999), "The Tanner's Privilege – A Historical Review of the Tanner's Status in Different Societies", *Journal of the Society of Leather Technologists and Chemists*, 83, 25.

Larsen, R. (1997), *Environment Leather Project Deterioration and Conservation of Vegetable Tanned Leathers*, Final Report, Copenhagen.

Lungu, B.I., Moise, V.I., Cutrubinis, M. and Stanculescu I. (2014), "Study on mechanical proprieties of gamma irradiated leather and parchment", *Proceedings of the 5th International Conference on Advanced Materials and Systems - ICAMS 2014*, Bucharest.

Thomson, R. (1983), *The Nineteenth Century Revolution in the Leather Industries in Leather Manufacture Through the Ages*, Northampton, East Midlands Industrial Archaeology Group.

Thomson, R. (2000), "Bookbinding leather; yesterday, today and perhaps tomorrow", *Journal of the Society of Leather Technologists and Chemists*, 85, 66.

Thomson, R. and Attenborrow, G. (2001), "A Survey of Current Bookbinding Leathers", *Journal of the Society of Leather Technologists and Chemists*, 86, 163.