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Evaluation of parchment chemical degradation

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Long periods of exposure to noxious vapors can determine macromolecule splitting through hydrolysis and the emergence of new, hydrophilic functional groups. Thus, sulphur acid induces irreversible breakings down of collagen fibers, by splitting the polypeptide chains to amino acids and ammonium salts. All the above-mentioned phenomena lead to significant changes in the physical and mechanical properties of parchment. Mechanical properties of parchment are altered by sulphur acid, in the presence of oxygen, due to irreversible degradation that collagen fibers suffer, which consists of splitting up polypeptide chains in amino acids and ammonium salts, mainly ammonium sulphate, which renders the material brittle and fragile. Atmospheres rich in sulphur dioxide have a proven noxious influence upon the lastingness of ancient and new parchment. New parchment is less sensitive to the degrading agent than ancient parchment. This paper deals about parchment resistance to chemical degradation. Absorption of water vaporous vs. time exposure for different samples (exposed to 0.01M SO_2 during different periods of time) was studied.

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1. Introduction

The Parchment is an old support material for writing or/and painting. Records of writing on leather skins exist from the early Assysian civilisation period, and occasionally such rolls have also been found in Antic Egypt. The Dead Sea Scrolls found in Qumran (250 BC to 68 AD) are the oldest known parchments.

It replaced the use of papyrus during the ancient Roman period. Monastic scribes of the Middle Ages practically monopolized its use in Europe preceding the introduction of paper for writing [1].

Parchment is an animal skin specially prepared to provide a smooth, supple, and bright and regulate surface [2]. It is a clear difference between the preparation of leather and parchment. Both are washed, soaked, cleansed of flesh and hair and smoothed carefully, but after that leather proper is soaked in vegetable matter containing tannin, whereas parchment is dressed with alum and dusted with sifted chalk. Rarely, microscopic evaluation showed that when tannage agents are present, they are restricted to the outer grain and flesh layers [3].

Several terms – parchment, vellum, hide, and skin – are used to describe the same product "parchment" according to its animal provenance, its method of production, and its qualities. The skins of sheep and goats are the normal raw material of parchment; vellum is the technical expression for the finer skins of calf and kid [4].

Structurally, parchment consists of a protein fibre matrix, the main protein being collagen, which undergoes complex chemical changes during manufacture which cause partial degradations, with significant consequences upon the final product properties [5-7]. This material contains also water and a small amount of so called hide ground substances.

The physical and mechanical properties depend on the condition of the collagen and its moisture content. The new parchment contains the viscoelastic polymeric material collagen. Old parchment often loses the well-ordered triple helical conformation of the collagen to form random coils (gelatine).

Compared to paper, the most distinctive characteristic feature of this material is its durability. However, like all organic materials, parchment is supposed of different forms of degradation due to chemical, physical and biological factors.

The degradation occurs through various mechanism such a physical wear, stress from relative humidity cycling, mycological attack and chemical reaction with inks, metal fasteners and gases absorbed from the atmosphere. Collagen - based materials are particularly sensitive to sulphur dioxide [8].

Industrial towns' atmosphere contains sulphur dioxide traces, coming from the combustion of sulphur-containing coal. Sulphur dioxide, SO_2, directly reacts with oxygen in the presence of a catalyst, resulting in sulphur trioxide which in its turn reacts with water vapours and forms sulphuric acid [9].

Another studies deal about collagen material chemical degradation [10, 11].

The resistance to chemical degradation and the absorption of water vaporous vs. time exposure for different samples of ancient parchment and new parchment are comparatively studied in this paper.

2. Experimental

Experiments were carried out on ancient and new pieces of goat parchment. The degrading agent, sulphur dioxide was generated “in situ” in a sealed chamber. Samples were exposed to 0.01M SO_2 media during different periods of time: 0h, 2h, 4h, 6h, 8h. Experimental work was conducted as it follows: 2×2 cm parchment samples were first conditioned (dehydrated) in a $CaCl_2$ drying chamber and than introduced in the SO_2 – atmosphere chamber. The degrading atmosphere was created in a 5000 ml sealed chamber, through the *in situ* generation of 0,01M sulphur dioxide. After SO_2 exposure times (as established by the experimental design), a new drying process for water traces were performed. Than, the samples were supposed to water vapor absorption tests, for different periods of time (minutes): 20, 40, 60, 80, 100, 120, 180, 240, 300, 360, 420.

Scanning Electronic Microscopy (SEM) images was performed by TESLA BS 800 microscope.

The water uptake by samples was mesured with a Partner Model XA 60/220 electronic balance with a 0.01mg.

The ratio [12]:

$$Q = \frac{m_w}{m_s} \tag{1}$$

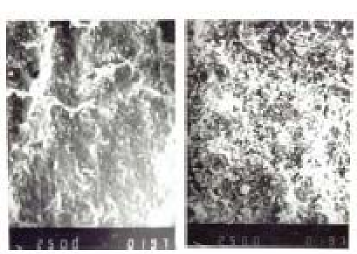
between the absorbed water mass, m_w, and the sample mass, m_s, were fitted with a polynomial 5th order approximation:

$$Y = A + B_1 \cdot x + B_2 \cdot x^2 + B_3 \cdot x^3 + B_4 \cdot x^4 + B_5 \cdot x^5 , \tag{2}$$

and then graphically represented.

3. Results

In Fig. 1 are presented the SEM images of old parchment trated with 0.06 mg/l SO_2 vapor concentration (a) comparatively with untreated old parchment. It cam be seen that the treated samples present surface modifications especially crashes.



(a) (b)

Fig. 1. SEM images of old parchment treated (a) and untreated (b).

Polynomial coefficients of 5th order approximation are given in Table 1 for ancient parchment and in Table 2 for new parchment, when the concentration of SO_2 in the exposure atmosphere was 0.01M.

Correlation coefficients between variables (τ - exposure duration to noxious atmosphere, min; t - duration of water vapors absorption test, min; Q - mass fraction of absorbed water vapors) were also computed.

The dependence between the amount of absorbed water vapors, Q and time, τ is given in Fig. 2 for ancient parchment and in Fig. 3 for new parchment respectively, for different exposure times to SO_2 - containing atmosphere, t.

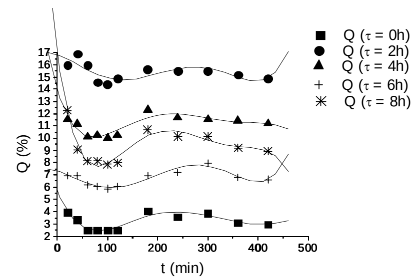


Fig. 2. Absorption of water vapors vs. time for ancient parchment.

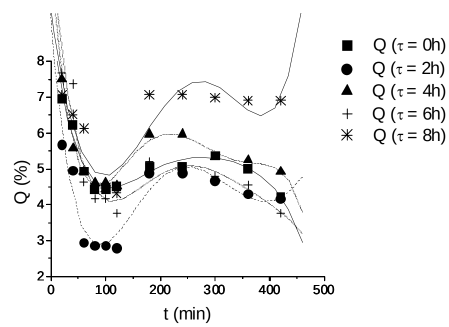


Fig. 3. Absorption of water vapors vs. time for new parchment.

4. Discussions

The minimum degrading action of SO_2 is obtained after τ = 80 min contact with water vapor for ancient parchment, while new parchment exhibits this minimum value after τ = 90 min. When this period is exceeded, the sensitivity to dioxide action increases. A variation of polynomial coefficients with the exposure time to contaminated atmosphere can be noticed. This phenomenon is a result of the degrading action of SO_2 upon the collagen protein, which determines macromolecule splitting and alteration of functional groups (acidic carboxylic groups and basic amino groups), which finally results in collagen macromolecule disarrangement.

Table 1. Polynomial coefficients for ancient parchment

τ (ore)	A	B_1	B_2	B_3	B_4	B_5
0	5.6909	-0.10021	0.00104	-4.18355E-6	7.20192E-9	-4.43406E-12
2	16.84922	-0.01463	-2.61546E-4	3.05676E-6	-9.93113E-9	1.017E-11
4	13.90942	-0.13175	0.00152	-6.94109E-6	1.38996E-8	-1.02639E-11
6	7.35195	-0.01308	-2.08294E-4	2.89513E-6	-9.92052E-9	1.03832E-11
8	16.89266	-0.2966	0.00329	-1.49743E-5	3.03908E-8	-2.29013E-11

Table 2. Polynomial coefficients for new parchment

τ (ore)	A	B_1	B_2	B_3	B_4	B_5
0	9.0623	-0.11616	0.00105	-4.16423E-6	7.80976E-9	-5.76138E-12
2	8.88041	-0.17526	0.00173	-6.81031E-6	1.1686E-8	-7.2278E-12
4	10.5789	-0.19195	0.00209	-9.57858E-6	1.96116E-8	-1.49293E-11
6	11.04462	-0.17094	0.00149	-5.65488E-6	9.80912E-9	-6.47568E-12
8	9.30864	-0.1076	7.74508E-4	-1.37452E-6	-1.63304E-9	4.50563E-7

The action of degrading atmospheric media changes the electric charge of the collagen macromolecules and determines a shift of the iso-electric pH point, which affects the material properties. Under acidic conditions, the increasing of the exposure time results in a large amount of releasing of carboxylic functional groups, leading to a lower iso-electric pH value; moreover, numerous hydrophilic functional groups determines the swelling of collagen matrix up to a point to which it becomes compact and water vapor absorption ceases.
Long periods of exposure to noxious vapors can determine macromolecule splitting through hydrolysis and the emergence of new, hydrophilic functional groups. Thus, sulphur acid induces irreversible breakings down of collagen fibers, by splitting the polypeptide chains to amino acids and ammonium salts.

5. Conclusions

All the above-mentioned phenomena lead to significant changes in the physical and mechanical properties of parchment. Mechanical properties of parchment are altered by sulphur acid, in the presence of oxygen, due to irreversible degradation that collagen fibers suffer, which consists of splitting up polypeptide chains in amino acids and ammonium salts, mainly ammonium sulphate, which renders the material brittle and fragile. Atmospheres rich in sulphur dioxide have a proven noxious influence upon the lastingness of ancient and new parchment. New parchment is less sensitive to the degrading agent than ancient parchment.

Reducing further degradation of old parchment is difficult because the damage has in effect already occurred. Conservators and restorators will have to whether the storage of this material in an inert atmosphere and/or in air with a special absorbent would be beneficial and prevent further sulphur dioxide accumulation, reducing further damage to the remaining collagen structure.

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References

[1] G. H. Bravo, J. Trumpke, 100 000 Jahre Leder, Basel, 15 (1970).
[2] H. J. Plendereith, Probleme de patologie a cărții, **XI**, Bucureşti, 118 (1975)
[3] R. Reed, Ancient Skins, Parchments and Leathers, London - New York, 172 (1972)
[4] M. Avi-Yonah, Ancient Scroll*s*, Palphot Ltd, Jerusalem, 18 (1994)
[5] G. Chiriță, C. Ionescu-Boeru, Fundamentals of leather fabrication, Technical Publ. House, Bucharest, 82 (1975).
[6] R. Larsen, Proceedings 5th EC Conference Cultural Heritage Research: a Pan – European Challenge, Cracow, 76 (2002).
[7] A. B. Quandt, The Book and Paper Group Annual, **15**, 22 (1996)
[8] R. Larsen , Microanalysis of Parchment, Archetype Publications Ltd., London, 45 (2002).
[9] E. Beral, M. Zapan, Chimie anorganică, Ed. Tehnică, Bucureşti, 714 (1977).

[10] N. Melniciuc-Puică, R. Apetrei and D. O. Dorohoi, An. St. Univ. "Al. I. Cuza" Iaşi, Chim., **XIII**, 85 (2005).

[11] N. Melniciuc- Puică, E. Ardelean, Proceedings of International Conference „Disaster and Pollution Monitoring", Universitatea Tehnică „Gh. Asachi", Iaşi, 209 (2005).

[12] N. Melniciuc-Puică, L. Vereştiuc and D. O. Dorohoi, An. St. Univ. "Al. I. Cuza" Iaşi, Chim., **VIII** (2), 314 (2000).

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