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APPRAISAL OF THE OVERALL CONDITION OF ARCHAEOLOGICAL SILK FABRIC FRAGMENTS

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Abstract: *In order to preserve the cultural identity of a nation, it is imperious to take special care of the textile materials which are representative for a certain historical period. Environmental factors such as humidity, UV radiation, temperature, some enzymes and micro-organisms (bacteria and fungi) can cause serious damage to aged silk textiles, which could lead to the loss of the properties that make the said material historically valuable. To assess the level and type of degradation of archaeological silk samples, we used two types of analysis techniques. Scanning Electron Microscopy (SEM) was used to determine the morphological modifications of the fibers and also the types of impurities present on the materials' surface. Differential Scanning Calorimetry (DSC) was used to investigate the thermal behavior of the silk samples. The same analyzes were also performed on a reference unaged silk fabric sample for an easier and more accurate interpretation of the results from the archaeological samples. These methods are micro-destructive and do not require large amounts of sample, thus making them suitable for use especially in cases where very small amounts of sample are available or when the analyzed material is extracted from an important art piece. The evaluation of the state of deterioration of an archaeologic textile material is important for further restoration and determination of the optimum maintenance parameters.*

Key words: *SEM, DSC, silk, fiber, archaeology, textile, degradation*

1. INTRODUCTION

As a natural fiber, silk has played a significant role in humans' lives for over 5000 years [1] and continues to have great importance and uses in numerous domains. The main source of natural silk is a species of domesticated silkworm – *Bombyx Mori*, which is called mulberry silk [2]. Silk is a protein fiber which, in its natural, unmodified state, consists of a highly crystalline fibrillary protein – fibroin and an amorphous protein – sericin. The two fibroin filaments are encased in sericin, which acts as a cement for the fiber. Fibroin is the major protein component of silk fibers and contains glycine (45%), alanine (30%), and serine (12%) in a ratio of approximately 3:2:1, while sericin is composed mainly of glycine, serine and aspartic acid [3]. Aside from these two proteins, silk also contains wax, pigments and various inorganic compounds [4]. Degumming is the operation of removal of the sericin from the silk fibers and it is performed with the purpose of making them more lustruous and for improving their color and texture. In the case of archaeological silk, as in the case of any other material, it is imperative to determine the state of degradation in which it is found

due to the serious implications this has on the methods of restoration and preservation needed in order to maintain the material in proper conditions.

2. MATERIALS AND METHODS

2.1 Materials

With the purpose of developing our work, four archaeological silk samples from the 16th century from two different sites were investigated, as following in Table 1:

Table 1: *The samples, their provenance and the time frame they belong to*

Sample label	Sample appearance	Sample provenance
S1		Archaeological excavations, Mirăuți Monastery/ Suceava - Romania
S2		Căpriana Monastery/ Republic of Moldova
S3 (red arrow)		
S4 (green arrow)		

Samples S3 and S4 were collected from the same fragment of textile fabric, but they were approached as two distinct samples: the golden area – S3 and the brown area – S4.

For an increased accuracy in the interpretation of the results, a new 100% silk reference fabric was assessed in parallel with samples S1 – S4.

2.2 Methods

Scanning Electron Microscopy (SEM)

SEM investigations of the silk samples were performed using a FEI Quanta 200 Scanning Electron Microscope. Each sample was placed on a specimen stub using double sided conductive carbon tape and analyzed using the following parameters: HV: 20.00 kV; detector: GSED; vac. mode: Low Vacuum.

Differential Scanning Calorimetry (DSC)

The thermal behavior of the samples was determined with a Perkin Elmer Pyris Diamond DSC Differential Scanning Calorimeter. Samples weighing between 1.7 and 2.7 mg were encapsulated in aluminum pans and heated. The temperature program was performed as following: holding the sample at 50 ºC for 1 minute, then heating the samples up to 500 ºC at a heating rate of 10 ºC min^{-1} and finally holding the samples at 500 ºC for 2 minutes. The heating of the samples was carried out in a 20 mL min^{-1} nitrogen gas flow and the DSC was equipped with a refrigerated cooling system.

3. RESULTS AND DISCUSSION

Morphological characteristics

All samples were extremely brittle to touch and had to be handled carefully to avoid further damage. This high degree of degradation was confirmed by the SEM analyzes.

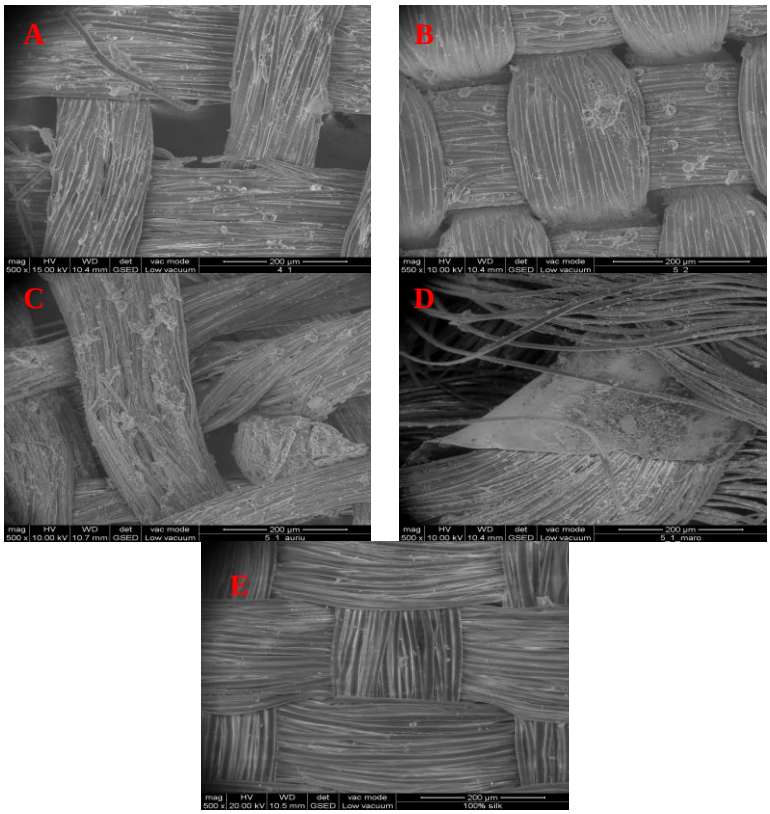

Fig. 1*: SEM micrographs of the silk samples, bar: 200 µm.* ***A*** *– S1;* ***B*** *– S2;* ***C*** *– S3;* ***D*** *– S4;* ***E*** *– reference silk*

As seen in Fig. 1 (A-D), all archaeological samples are soiled and deteriorated to some extent. The average diameter of the fibers from each sample is presented below, in Table 2:

Table 2: *Average diameter of the fibers*

Sample	Diameter, *μm*
S1	9.58
S2	8.84
S3	8.23
S4	9.31
Reference	9.48

In all cases, the diameters of the filament fibers indicate that all samples, including the reference, have *Bombyx mori* silkworm origin [5]. Most of the fibers from the archaeological samples presented signs of exfoliation along their length and some level of degumming.

Sample S1 was particularly deteriorated, taking in account that micro-fissures and cavities were present in the fibers' structure. These modifications of the surface characteristics determine the instability of the natural archaeologic silk filaments when mechanical stress is applied, resulting in the breakage of the filament [6]. In Fig. 2 (within the red circle) the fracture of the fiber reveals the fibroin microstructure [3].

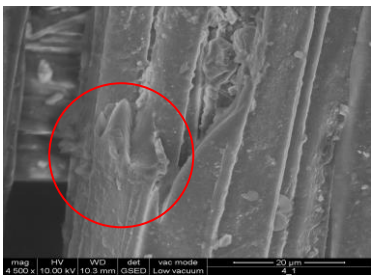

Fig. 2*: SEM micrograph of the fibroin microstructure in sample S1, bar: 20 μm*

The morphological assessment revealed in the case of all historic textile samples evidences of fungal infestation. These traces of infestation appeared as spherical shapes on the surface of the fibers either as individual fungal spores or as clusters [7], as shown in Fig. 3.

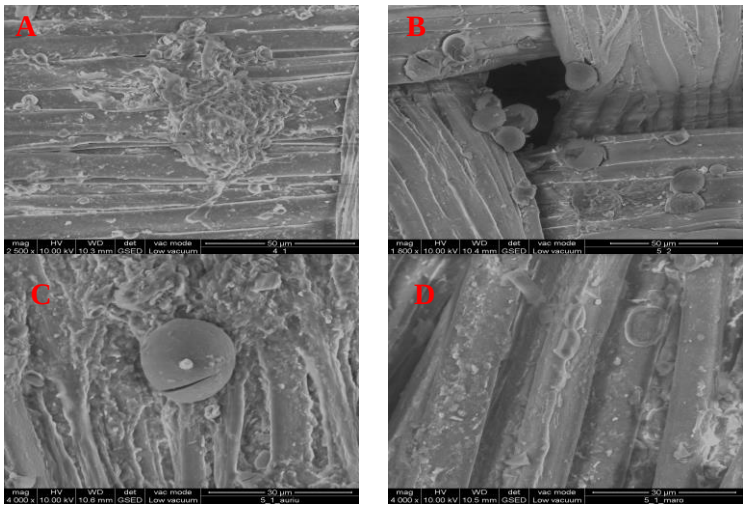

Fig. 3*: SEM micrographs of the fungal spores on the surface of the textile fabrics, bar: 50 μm for A and B; 30 μm for C and D.* ***A*** *– S1;* ***B*** *– S2;* ***C*** *– S3;* ***D*** *– S4*

Sample S4 stood out among the other samples due to the fact that some of the threads in its composition have metal strips twisted around the core represented by a bundle of silk filaments, as shown in Fig. 1 (D). The metal strips presented some depositions on their surface, possibly due to oxidation, among other impurities. Due to the fact that the metal strip was not tightly wrapped around the silk core, the core was still visible, this being called an 'open' metal thread [8].

Thermal properties

The characteristics determined by calorimetry confirmed the modification of the chemical structure of the archaeological silk samples.

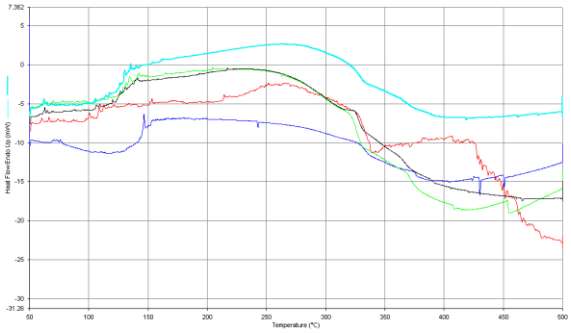

Fig. 4*: DSC MultiCurve thermogram of the samples, endotherms upwards. Red curve – reference silk; Dark blue curve – S1; Green curve – S2; Light blue – S3; Black curve – S4*

All of the samples have roughly the same allure, yet the DSC curve corresponding to the reference silk slightly differs from the others.

Table 3: *DSC temperatures and enthalpies*

Sample	Peak max. temp., ºC	ΔH, J/g
S1	336.99	-15.1249
S2	330.84	-36.3692
S3	332.84	-29.6721
S4	331.83	-26.7411
Reference	338.66	-77.1736

According to Table 3 above, the main exothermic event corresponding to the thermal decomposition of the materials occurred between 330 and 340 ºC. In the case of the reference sample, the maximum temperature of the peak is higher than in the case of any of the archaeological samples. This fact, along with the highest negative enthalpy among the samples, suggests the difference of the state of degradation of the samples S1-S4, in comparison to the reference sample [9]. The high negative enthalpy of thermal decomposition for the reference curve is caused by the fact that the undamaged protein structure of the unaged silk requires more energy to be thermally decomposed due to the stronger intramolecular bonds.

5. CONCLUSIONS

The morphological and thermal assessments of the archaeological silk samples were performed using two micro-destructive techniques – Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC). The SEM characterization revealed a high level of damage of the silk fibers and also a fungal contamination, possibly due to improper storage

conditions. DSC analysis confirmed the SEM assessment of the silk samples. The damage of the protein structure was highlighted via DSC.

All these characteristics of the archaeological silk fragments that were determined can be useful for the development of decontamination and restoration methods.

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REFERENCES

[1] Badillo-Sanchez, D., Chelazzi, D., Giorgi, R., Cincinelli, A., & Baglioni, P. (2018). *Characterization of the secondary structure of degummed Bombyx mori silk in modern and historical samples*. Polymer Degradation and Stability, 157, pp. 53-62.

[2] Gogoi, S. (2016). *Assam Silk: Sericulture*. Research & Reviews: Journal of Agriculture and Allied Sciences, 5(2), pp. 50-54.

[3] Shen, Y., Johnson, M. A., and Martin, D. C. (1998). *Microstructural Characterization of Bombyx mori Silk Fibers*. Macromolecules, 31(25), pp. 8857-8864.

[4] Yukseloglu, S.M., Canoglu, S. (2016). *Silk fibre degradation and analysis by proteomics.* Annals of the University of Oradea – Fascicle of textiles, leatherwork, 17(1), pp. 137-142.

[5] Andersson, M., Johansson, J., and Rising, A. (2016). *Silk Spinning in Silkworms and Spiders*. International Journal of Molecular Sciences, 17(8), 1290.

[6] Marian, C. (2001). *Repere ale restaurarii textilelor arheologice din matase naturala.* Tehnopress, pp. 76-79.

[7] Abdel-Kareem, O. (2010). *Monitoring, Controlling And Prevention Of The Fungal Deterioration Of Textile Artifacts In The Museum Of Jordanian Heritage.* Mediterranean Archaeology and Archaeometry, 10(2), pp. 85-96.

[8] Gleba, M. (2008). *Auratae vestes: Gold textiles in the ancient Mediterranean*. Publicacions de la Universitat de Valencia, Purpureae Vestes II, pp. 61-77.

[9] Prasong, S., Yaowalak, S., Wilaiwan, S. (2009). *Characteristics of Silk Fiber with and without Sericin Component: A Comparison between Bombyx mori and Philosamia ricini Silks.* Pakistan Journal of Biological Sciences, 12, pp. 872-876.