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ACCELERATED WEATHERING TESTS ON PROTEIN FIBERS

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Abstract: *Protein-based textiles, such as wool and silk, possess special properties and they are ranked higher on the hierarchical scale than the cellulosic ones (e.g., cotton, linen, hemp), in terms of quality. Wool is composed of keratin as the main protein component and silk consists of approx. 80% fibroin and 20% sericin. The degradation of protein-based fibers is a complex process and it is influenced by temperature, humidity and light. Also, these factors may favor a perfect environment for the development of certain microorganisms, which leads to further degradation. In the case of wool fibers, the mechanism of biodegradation involves keratinolysis (sulfitolysis, proteolysis and deamination) and for silk this mechanism is based on the proteolytic decomposition of sericin and fibroin. For the present work, protein-based fibers (wool and silk) were subjected to an accelerated aging process by using UV light, temperature and humidity. Samples from both types of fibers have been collected at a fixed time interval. The level of degradation was evaluated in terms of changes in fiber morphology, using Scanning Electron Microscopy. Also, an Energy Dispersive X-Ray spectrum was recorded in order to estimate the composition at different degrees of degradation of the samples. Moreover, chromatic parameters measurements were carried out in order to quantify the color modifications of the fibers.*

Key words: *protein fibers, wool, silk, textiles degradation*

1. INTRODUCTION

Natural fibers of animal provenience represent the elite of textiles, being considered a luxury [1]. They are divided into wool (from sheep, camel, cashmere goat, mohair, angora, alpaca), fur (rabbit, fox etc.) and silk (from silkworms) [2]. The main wool protein is keratin and it is a sulfur-rich protein which can form disulfide (bonds). These bonds are responsible for the cross-linked chains in the protein which give wool its high breaking strength [3]. Silk is biosynthesized as a cocoon by the larva of the silkworm *Bombyx mori* and consists of approx. 80% fibroin and 20% sericin [4,5]. Fibroin is a two-filament protein, i.e., heavy-fibroin (H-fibroin) and light-fibroin (L-fibroin) in a 1:1 ratio, linked together by a disulfide bridge. Fibroin has a high degree of crystallinity, while sericin presents a more amorphous structure, acting as a glue and coating the two filaments of fibroin [6]. Silk is also characterized by a high mechanical resistance, having application in various fields (clothing, industry, medicine etc.) [7].

Accelerated aging studies have been previously performed to identify the analytical markers for the degree of degradation of historic heritages [8]. Also, Mengüç studied the effects of sunlight

exposure on the performance of paragliding fabric [9]. The degradation of protein-based fibers is a complex process and it is influenced by temperature, humidity and light [10, 11]. For this study, wool and silk fibers were subjected to an accelerated aging process, in a UV chamber with controlled temperature and humidity. The degree of degradation was evaluated for the collected samples by using Scanning Electron Microscopy in order to analyze the morphology, Energy Dispersive X-Ray Spectroscopy, to estimate the composition at different stages of degradation and chromatic parameters analysis, to quantify the color change of the fabrics.

2. EXPERIMENTAL

2.1. Materials and methods

For this study, five samples of silk (60 g/m^2) and five samples of wool (198 g/m^2), all measuring 11×9 cm were exposed to accelerated aging conditions, in a UV chamber. For this, a QUV accelerated weathering tester device with the following working cycle was used: 8 hours of UV light exposure at a temperature of 70^{o}C, followed by 4 hours of humidity exposure (60%), at 50^{o}C. The instrument was equipped with fluorescent UV-B lamps (UVB-313), with a wavelength peak at around 313 nm, having nearly all their energy concentrated between 280 nm and 360 nm.

Both types of samples were collected every three days, having in the end five samples of each type at different degrees of degradation. These samples were characterized and compared to a reference sample (unexposed textile material).

2.2. Characterization techniques

The fiber morphology and elemental composition of the samples were evaluated with a FEI Quanta 200 Scanning Electron Microscope (SEM), equipped with an ET detector, as well as with an Element Energy-Dispersive X-ray Spectroscopy System (EDX) from EDAX-AMETEK.

The chromatic parameters L*, a*, b* C*, H* have been measured for each sample, using a Datacolor spectrophotometer (with a D65/10 lamp).

3. RESULTS AND DISCUSSIONS

3.1. Visual observation

The visual effect of the weathering process of the samples is their increasing yellowing after every time interval. Moreover, in the case of silk, the change of color is accompanied by an aggressive disruption of the fabric, as presented in Table 1.

Table 1: *Images of silk and wool fabrics at different times of exposure*

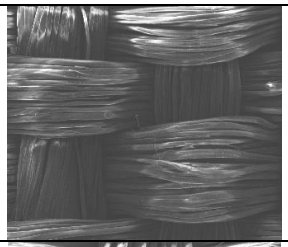
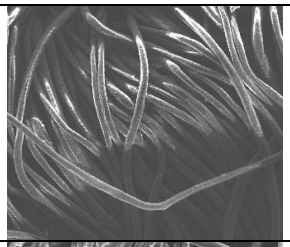
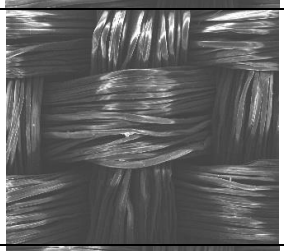
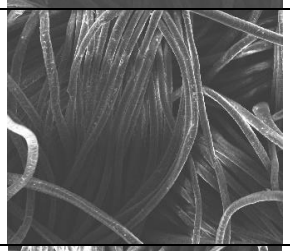
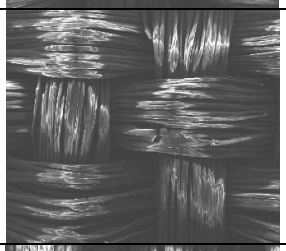
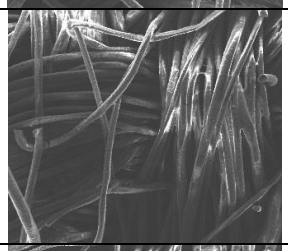
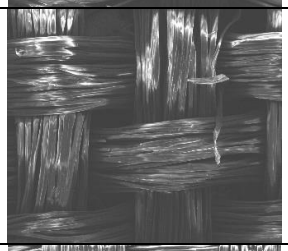
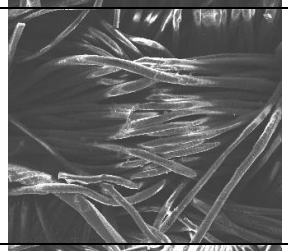
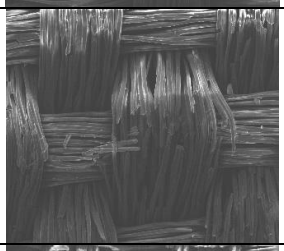
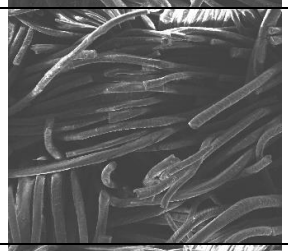
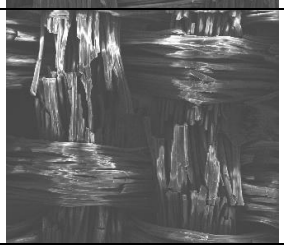
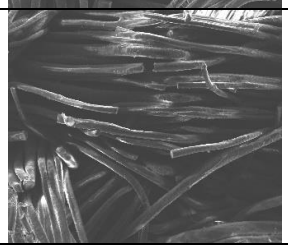
Exposure time	t_0	t_1	t_2	t_3	t_4	t_5
Silk						
Wool						

3.2. Scanning Electron Microscopy characterization

Table 2 contains the SEM micrographs of the samples, collected every three days, where t_0 represents the start of the experiment (unexposed fabric). All images were collected at 500X

magnification and an accelerating voltage of 10 kV, in high vacuum mode.

Table 2: *SEM micrographs of silk and wool fibers at different times of exposure*

Exposure time	Silk	Wool
t_0		
t_1		
t_2		
t_3		
t_4		
t_5		

The SEM results for silk at different stages of degradation show that the fibers are strongly affected starting with t_2. At t_4 and t_5, the disruptions of the fibers become significantly visible. On the other hand, wool fibers seem to keep their integrity up to t_3. This enhanced resistance might be due to the presence of sulfur bonds in the keratin structure, the main constituent protein of wool.

3.3. Energy-Dispersive X-Ray Spectroscopy analysis

The EDX measurements were performed in order to study the composition of the materials. For silk, the results show that it contains only the specific elements of the constituent amino acids: carbon, nitrogen and oxygen, dispersed in a uniform manner on the entire surface (Fig. 1). In contrast, besides these elements, wool also contains sulfur (from the disulfide bonds) and fluorine, which might come from the dye used in the case of this sample (Fig. 2). For both materials, multiple measurements were performed, at different exposure times, but no considerable difference in composition and distribution on the elements was observed.

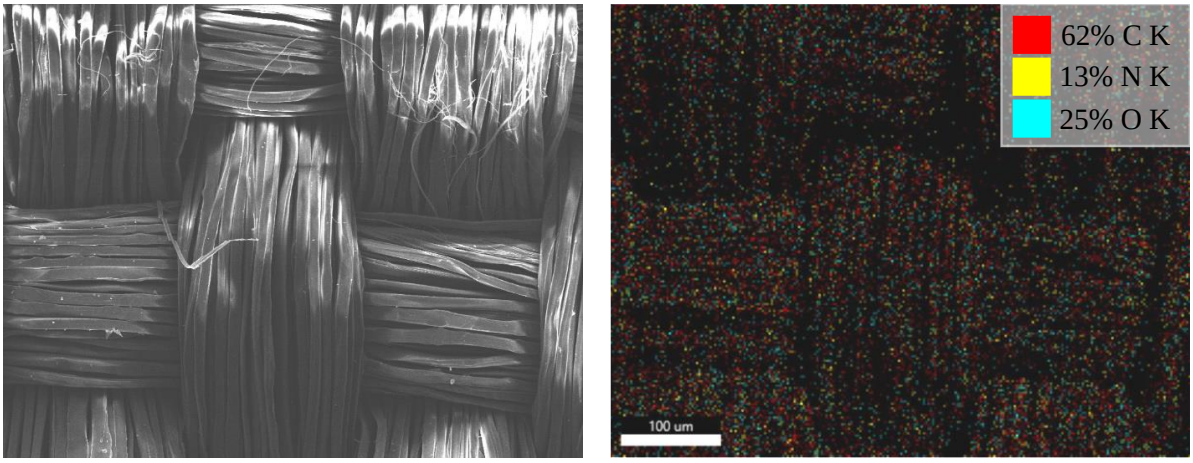


***Fig. 1**: SEM micrograph for the silk sample at t_0 (left) and its elemental mapping (right)*

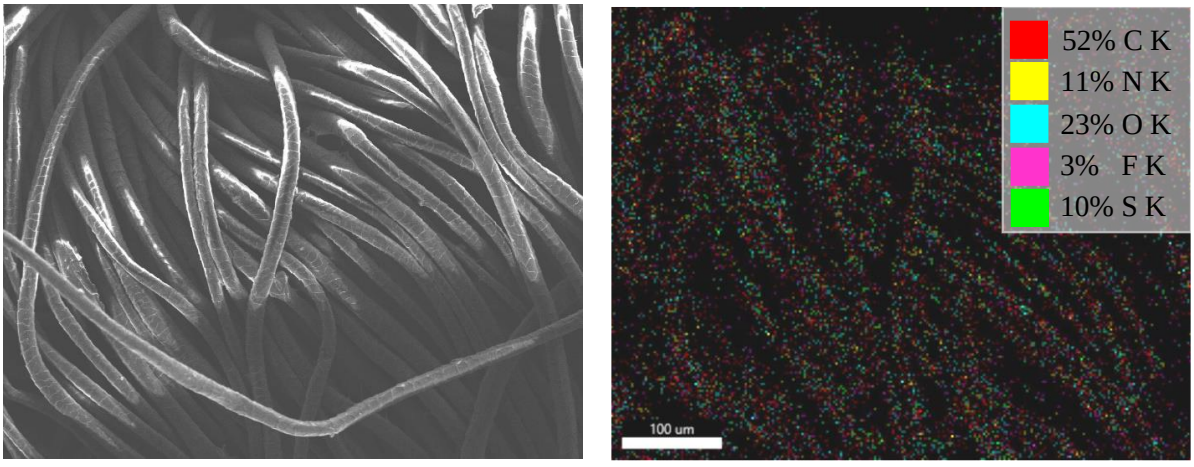


***Fig. 2**: SEM micrograph for the wool sample at t_0 (left) and its elemental mapping (right)*

3.4. Chromatic parameters measurements

The chromatic parameters measured for each sample are listed in Table 3, for silk and Table 4, for wool. In both cases, the color has considerably changed. The values suggest a strong modification of the color, up to t_2. In the further stages of the experiment, the color change slightly varies.

Table 3: *The chromatic parameters and white indices of silk samples*

Exposure time	L*	C*	DL*	DC*	DE*	White index Berger	White index CIE	T	Remarks
t_0	90.95	6.80	-	-	-	45.84	46.94	-4.20	-
t_1	84.85	23.52	-6.09	16.72	17.0	-25.54	-49.20	-15.18	Darker More saturated Greener
t_2	82.26	27.15	-8.69	20.36	22.13	-36.42	-74.12	-19.28	Darker More saturated Greener
t_3	82.47	25.54	-8.47	18.74	20.57	-31.67	-65.59	-18.28	Darker More saturated Greener
t_4	81.73	27.30	-922	20.51	22.48	-36.96	-76.29	-19.93	Darker More saturated Redder
t_5	83.44	28.56	-7.51	21.76	23.03	-39.95	-77.86	-18.31	Darker More saturated Greener

Table 4: *The chromatic parameters and white indices of wool samples*

Exposure time	L*	C*	DL*	DC*	DE*	White index Berger	White index CIE	T	Remarks
t_0	74.57	8.64	-	-	-	The textile used was dyed in a shade of pink			-
t_1	73.49	20.05	-1.08	11.41	13.69				Darker More saturated More yellow
t_2	71.49	27.79	-3.08	19.15	21.35				Darker More saturated More yellow
t_3	70.72	31.11	-3.85	22.47	24.69				Darker More saturated More yellow
t_4	70.27	32.66	-4.31	24.02	26.23				Darker More saturated More yellow
t_5	68.82	35.18	-5.76	26.54	28.83				Darker More saturated More yellow

4. CONCLUSIONS

Accelerated weathering test have been performed on silk and wool fibers, in order to evaluate the degree of degradation of protein-based textiles. The weathering process consisted of UV exposure, accompanied by temperature and humidity. The samples were collected every three days,

in order to observe the stages of degradation. The samples were characterized in terms of morphology and composition, using a Scanning Electron Microscope coupled with an EDX detector. The SEM results revealed an early degradation of the silk samples, occurring from stage t_2 of the experiment and a relatively better resistance of the wool fibers compared to the silk ones, which showed discontinuities of the fibers starting with stage t_4. EDX analysis did not show any significant changes in the elemental composition of any of the two fiber types. The chromatic parameters measurements indicated significant color changes starting with t_2. This kind of experiments might be a starting point for investigating the degradation processes occurring in heritage textiles and for testing potential conservation treatments for heritage textiles.

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