PATRIMONY TEXTILE MATERIALS SHORT CHARACTERIZATION

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In this paper we aimed to characterize heritage samples through different analyses such as physicochemical and microbiological bioburden assessment analyses. The characterization was made on two types of textile materials coming from a private collection: the 1st was from the beginning and the second one from the end of the 20th century. Micro-destructive methods (such as SEM and optical microscopy) and macro-destructive methods (by use of chemical reagents for fibers solubilization) were used to identify and quantify the fibrous composition of the samples. The Differential Scanning Calorimetry (DSC) technique was successfully applied to confirm the fibrous composition. The microbiological bioburden of the samples was evaluated by isolation on two semi-synthetic media: Czapek-Dox and Potato-Dextrose-Agar supplemented with Chloramphenicol. Thus, we have realized a primary characterization of the samples with desire to continue the future studies with focusing on the evaluation of the classes of dyes used for dyeing the samples and the use of micro- or non-destructive methods to obtain more information that could give us a better view of the realization and application of archaeological textile materials. The results showed that the studied textiles were composed from natural yarns (wool and cellulose), unevenness damaged (holes, creases) due to conservation conditions and, in a lesser extent, to the microbiological activity of the specific strains present on the surface of the textiles.

Keywords: micro-destructive method, heritage sample, SEM, textile.

INTRODUCTION

Natural fibers such as cotton, wool, hemp, flax and silk are used since the beginning of human kind. In the 20th century there was a tendency to increase the production of synthetic fibers to the detriment of natural fibers, until highlighting of pollution impact that these synthetic fibers have on the human health and environment (Monteiro *et al.*, 2012). But, as we can see, there is a trend to go back in the past and learn about how the human lived healthier and without affecting the environment too much. Because of the amount of textile samples that can be found in different places of the world and the big impact that they have on our history, in recent years, there has been an increasing need for the development of micro and non-destructive analyses of historical samples characterization. These characterizations methods can provide useful information for improving the methods of preserving and restoring historical textiles and give us more information about how the people that didn't have so much technology, that exist in our days, were able to create so complex, resistant and beautiful textiles.

Unfortunately, the materials deterioration due to the storage conditions, the complex composition, the unknown dyeing and finishing processes make difficult an accurate analysis of heritage samples. More than that, the microbiological degradation due to enzymatic activity of various fungi strains or pests aggravates the problems.

This study aims to highlight some of the heritage materials characteristics through physical, chemical and microbiological methods.

MATERIALS AND METHODS

Samples

Two samples were evaluated in this study. First sample, abbreviated A, is from the beginning of the 20th century and it is a belt form Susag - Miercurea Sibiului area, while the second sample, abbreviated B, is a textile material from the end of the 20th century, both originating from a private collection.

Figure 1. Left: sample from the beginning of the 20th century (A); right: sample from the end of 20th century (B)

Methods

Two types of microscopes were used for evaluating the particularity of the samples, namely the Scanning Electron Microscopy (Quanta 200, FEI, Netherlands) and an Optical Microscope (Olympus BX41, Japan). SEM analysis is widely used for the examination of patrimony textiles because of its micro-destructive properties (Peceliunaite-Baziene, 2002). Optical microscopy gave us information about the type of fiber components and also a better view of the level of degradation of the two samples.

The fibrous composition was investigated based on SR 13231-95 and the UE Regulation 1007/2011 standardized methods. The main disadvantage of this method is its destructive character.

The thermal behavior of the samples was assessed by Differential Scanning Calorimetry - DSC (Perkin Elmer, USA) by using only a few milligrams of fibers. The fibers were placed in closed aluminum crucibles and a similar empty crucible was used as reference. The temperature program was started from 35°C (held for 1 minute) to 500°C (held for 1 minute) with a heating temperature of 10°C per minute. Nitrogen with a flow rate of 10mL/min⁻¹ was purged in the DSC oven. Beside SEM and optical microscopy analyzes, DSC is one of the most used techniques due to its advantages such as: any form and type of material may be tested, short time for investigations, small quantities of sample, micro-destructive analysis (Shafizadeh, 1985; Calamari *et al.*, 1990; Dong *et al.*, 2015; Ferrero *et al.*, 1998).

To deeply investigate the causes of deterioration, microbiological analyzes were carried out to isolate the eventually microorganisms present on the samples. Two different nutritive media were used in this procedure: Czapek-Dox –CD (Scharlau, Spain) a semi-synthetic media usually frequently used for isolation of fungal species such as *Aspergillus*, *Penicillium*, *Paecilomyces*, *Saccharomyces* etc. and a second nutritive media, Potato-Dextrose-Agar (Scharlau, Spain) supplemented with 250mg of Cloramfenicol antibiotic (250mg/400mL of PDA media) for inhibition of certain bacterial species (species of *Staphylococcus*, *Streptococcus*, *Escherichia* etc.). Chopped samples were put in sterile jars in 60 mL of sterile deionized water and agitated for 2h at 185 rpm. Afterwards, 300µL from each samples were plated in duplicates on each nutritive media and incubated for 7 days at 28°C.

RESULTS AND DISSCUSION

Physical-Chemical Evaluation

The fibrous composition of the samples is shown in Table 1. While the sample A is composed from a mixture of cotton and wool, the sample B is based on a complex mixture of cellulose yarns (cotton, flax, hemp).

Table 1. Fibrous composition identification

Sample	Nature of raw material SR 13231:1995	Fibrous composition UE Regulation 1007/2011
A	Cotton + Wool	23.7% cotton + 76.3% wool
B	Cellulosic fibers (Cotton, Flax and Hemp)	100% cellulosic fibers

The results presented above are confirmed by SEM (Figure 2) and optical microscopy images (Figure 3). We can see in the pictures bellow the visual characteristics of the constituent fibers. The images give us information about the degradation of the fibers, as it can be seen that sample A is more degraded than sample B. The extended degradation of sample B is caused by longer exposure to environmental physical and chemical factors, like light, dust, organic and inorganic pollutants, temperature and humidity variations.

Figure 2. SEM images of: Sample A- a) cotton fibers (100 μ m); b) wool fibers (30 μ m); Sample B- c) cotton fibers (50 μ m); d) hemp and flax fibers (30 μ m);

Figure 3. Optical microscope images of: Sample A- a) cotton fibers(10x); b) wool fibers (10x); Sample B- c) cotton fibers (20x); d) hemp and flax fibers (20x)

Thermal behavior

In order to identify different textile fibers we have used DSC as an alternative qualitative method. DSC analysis is useful to distinguish different types of fibers and their differences after exposure to bleaching, descaling or other treatment processes (Tonetti *et al.*, 2015). Thermal behavior of samples A and B is presented in Table 2 and 3.

Table 2. Thermodynamic parameters for sample A and B

Thread	Weight sample [mg]	Onset temperature [°C]	Peak temperature [°C]	Delta H [J/g]
A: gray- transverse	5.9	350.78	357.43	13.1499
A: black	6.1	223.17	238.72	223.2328 J/g
B: white- peak 1	4.8	259.99	299.20	335.8923
B: white- peak 2		345.56	350.04	25.2335

Table 3. Thermogram for sample A and B

Thread	Thermogram	
A: gray- transverse
A: black
B: white

Sample A: The DSC results obtained for sample B are correlated with those obtained from the assessment of fibrous composition, namely 23.7% Cotton and 76.3% Wool. As can be seen in Table 3, the transverse gray yarn shows a broad endotherm peak at a temperature of 357.43°C, corresponding to the partially crystallized cellulose decomposition (Macsim *et al.*, 2011). In oxygen atmosphere, this peak is shifted to lower values (346.2°C) due to cotton pyrolysis followed by oxidation of the resulted compound by oxygen (Macsim *et al.*, 2011). Theoretically, cotton cellulose is characterized by three regions, located between 60-150°C, 150-250°C and 250-500°C, corresponding to water loss, non-cellulosic volatile components (waxes, acids, esters) and decomposition of cellulosic components (proteins, pectins and hemicellulose) and cellulose / chemical decomposition (cleavage of glycosidic linkages with levoglucose formation) (Ciolacu *et al.*, 2011).

In the case of the black thread, it is noticeable an endotherm peak that starts from 223°C with the maximum at 238°C. This peak is attributed to the cleavage of the crystal structure due to the melting and degradation of the various morphological components that form the complex hierarchical structure of the wool chain (Giuliano *et al.*, 2003; Jinan, 1997).

In the case of sample B, 2 peaks are detected: a large one with a maximum temperature of 299°C and a second small peak with maximum located at 350°C. As literature data show (Albano *et al.*, 1999) for the flax yarns, the thermal depolymerization of hemicellulose and glycosidic bonds takes place at about 340-370°C. At the same time, hemp shows a two-step degradation process: the first at 225-275°C corresponding to the decomposition of hemicellulose and the second at 325-360°C attributed to lignin decomposition (Pracella *et al.*, 2006). Under nitrogen atmosphere, an endothermic peak around 345°C is observed for the cellulose decomposition in cotton, the temperature being strongly affected by multiple factors as

contaminants, molecular weight, dyes, finishing agents etc. (Ibrahim, 2011; Ciolacu *et al.*, 2011; Xia *et al.*, 2016). Corroborating all the obtained data, we could affirm that the third component of sample B is cotton.

Bioburden

Microbial deterioration can affect historic and culturally important artefacts, by specific mechanisms, such as enzymatic activity on the substrate, biofilm formation attached to materials' surface (polymer matrix formation). After samples were placed in sterile jars (Figure 4), aliquots were plated on semi-synthetic nutritive media (spread with a Drigalski rod) (Figure 5).

Figure 4. Left- Sample A, Right- Sample B

Figure 5. Sample A and B on Czapek-Dox and Potato-Dextrose-Agar media

Following incubation period (28°C for 7 days), strains were visualized on an Olympus SZ 61 stereomicroscope, at magnification levels of 0.67x and 3x (Figure 6).

Figure 6. Sample A (left- 0.67x, right- 3x) (PDA media); Sample B (left- 0.67x, right- 3x) (Czapek-Dox media)

Microbial growth highlighting on Petri dishes show no biomass development on sample A plate, on Czapek-Dox media, compared to a filamentous structure developed on PDA media. Furthermore, sample B showed microbial development on Czapek-Dox plate, which can be highlighted as a yeast-like structure, and no development on the PDA plate. Also, it can be seen the lack of bacteria-like specific structures, both on Czapek-Dox media, which is a low nutritive value substrate, and on PDA media, that although it possesses high enough nutritive value for bacterial development, the presence of chloramphenicol in the media inhibited bacterial growth.

CONCLUSIONS

In the present work two different samples have been investigated using electronic and optical microscopy, standardized chemical methods, DSC and microbiological procedures. The used methods allowed the identification of the fibrous composition and the stage of the samples degradation. As the results demonstrated, the sample A is more degraded than sample B. Also we can correlate the obtained results with the ones existing in the literature. The future studies will be focused on the evaluating the classes of dyes or other type of compounds used in these samples manufacturing.

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