Journal of Molecular Structure 1075 (2014) 471–478

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

A vibrational approach for the study of historical weighted and dyed silks

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HIGHLIGHTS

- The present work is focused into obtain vibrational information of historical silk samples.
- The effects that the degumming and weighting processes have on the degradation of silk are inferred.
- The Raman data suggests that crystalline portions of silk are unaffected in historic samples.
- Spectral results indicate the presence of Prussian blue and Sudan Black B in samples dated from late 19th to early 20th century.

ARTICLE INFO

Article history:
Received 12 January 2014
Received in revised form 4 July 2014
Accepted 8 July 2014
Available online 15 July 2014

Keywords:
Weighted silk
Bombyx mori
Raman
ATR

ABSTRACT

Samples from six different historic silk objects were studied with the Raman and ATR-IR vibrational techniques. A set of degummed and weighted silks was prepared in order to recognize the vibrational signature associated with the processes used. The spectral information allowed the identification of the weighting process and the dyes used in some of the cases. The different spectra also allowed infer about the deterioration observed in the samples. The silk fibroin displays slight conformational modifications by the weighting process. The degumming process seems to have no chemical effect on the fibroin stability.

Introduction

Various works, as indicated by Li et al. [1], point to the fact that silk is easily affected by various environmental factors such as water, light, heat and microorganisms, which is probably due to its protein composition. Thus, some of the historic silk textiles and artefacts lost their mechanical strength and became more or less brittle after the exposure to those factors. In order to determine suitable approaches to the conservation of historic silk objects, it is important to be able to completely characterize the silk fibres and understand its degradation processes. Raw silk is composed by two filaments of the protein fibroin coated and held together by another protein called sericin; the later is also commonly known as "gum". In order to produce silk threads and fabrics, the gum (sericin) must be removed. Thus, the observed degradation process in historical textiles concerns the fibroin component; this protein is composed mostly by the amino acids glycine (G), alanine (A), serine (S) and tyrosine (Y). Two kinds of crystalline modifications, silk I and silk II, as well as the random-coil form, exist as dimorphs of silk fibroin from *Bombyx mori* in the solid state. X-ray diffraction studies determine that the conformation of silk II is an antiparallel β-sheet form. However, the conformation of silk I appear to be not well defined, as compared with that of silk II [2]. Works by Asakura et al. [3] and references cited therein, indicate that other conformations than -helix are verified for silk I. Studies on the amino acidic composition have been developed during the last years and the most repeating unit in the crystalline fraction seems to be the hexapeptide GAGAGS. G, A and S conform 85% of the fibroin. The crystallites are embedded in an amorphous matrix, which is mainly composed by tyrosine residues, thus adopting β-sheet, β-distorted turns and 3_1-helices structures which seem to confer the elastic property of the silk.

Few works on the degradation of natural fibroin fibres have been accomplished. A recent complete investigation to study the degradation mechanism of Chinese historic silk (*Bombyx mori*) for the purpose of conservation was carried out by Li et al. [1]; it

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http://dx.doi.org/10.1016/j.molstruc.2014.07.016
0022-2860/

was concluded that during the degradation process, the morphology of the cross-section of the silk fibre was found to change from stacking particles to lamellar sheets, with decreasing size of segments of silk fibroin. The degradation of both the crystalline and the amorphous region contributed to the loss of mechanical strength of aged silk. Zhang et al. [4] proposed that viscosity could be used as an indicator of residual tensile strength and more recently [5] concluded that the Asp/Gly molar ratio and tyrosine (Tyr) content was useful for gauging the conservation state of silk. Light microscope and scanning electron microscopies were used to determine the influence of soil burial and water on the morphology of archaeological silk fibres [6]. Spectroscopic, chromatographic and chemical data were analysed in order to infer about the physical deterioration of silk during the aging process [7]; it has been found that the amorphous region broke down and the crystallites progressively lost their strong alignment with the fibre axis but stayed intact until the ultimate stage. Samples of *Bombyx mori* silk fibroin, and its motif peptide component (GAGAGS) were already studied by using mainly Raman and surface enhanced Raman scattering (SERS) techniques [8]. A complete spectral analysis was performed and conformational modifications of the peptide by temperature and surface effect were inferred; the amorphous fragments are exposed to the Ag metal surface as indicated by the predominance of Tyr spectral signals.

The present work is focused to intend a molecular explanation of the observed degradation of six historical silk textiles belonging to the Textile Collection of the Museo Histórico Nacional de Chile; silk degumming, weighting and dyeing process effects on the degradation of *Bombyx mori* silk fibroin are investigated. To achieve this goal we propose to use vibrational spectroscopy through the infrared (ATR-IR) and Raman techniques along with SEM/EDS microscopy. The present spectroscopic results are thought to be helpful in other researches concerning silk degradation.

Experimental

Samples

Two sets of samples were selected from the costume collection of the Museo Histórico Nacional of Chile, comprising a group of textiles that exhibit worrying levels of deterioration (Fig. 1). The first group includes samples of light color weighted silk that are highly friable and whose degradation has continued over time despite being stored under controlled conditions. This group consists of three samples: cream color lining of a dress from the late nineteenth century, HWS1; a pink lining of a dress from 1910 to 1911 HWS2 and a purse from *ca.*1920, with highly deteriorated and fragile fabric HWS3, see Table 1.

A second group includes samples of dark silk from the same period as the light samples, which are differentiated from the others by presenting a lesser degree of degradation with respect to the stability of the textiles. In this group there are three samples: a black/purple dress from early 1900 HDS1, a black Manila mantle dated to the late nineteenth or early twentieth century HDS2 and a black mantle likely associated with mourning, from the first half of the 20th century HDS3.

The Sudan Black B dye, as well as all the chemicals used in the degumming and weighting processes, were supplied by Aldrich and used without further purification.

Silk degumming and weighting

Sericin from the *Bombyx mori* silk (CS) sample (obtained from worm's cocoon) was eliminated following traditional procedures [9], that is, by using 4 g/L soap and 1 g/L soda ash (Na_2CO_3) and adjusting the pH to the 8.5–10 range. The bath/silk ratio was 30/1 in weight. In a first case (D1) the process was carried out at pH 10, at constant boiling temperature for 1 h; in a second case (D2) the process was performed at pH 8.5, at constant 85 °C for 2 h. The final product was washed in water just heated at 80–90 °C by 15 min and, at the end, washed with water at 20 °C.

The weighting processes were carried out following the methodologies described by Garside et al. [10]; from an unweighted white silk sample UWS, Pongée 7 from France. In the case of the pink weighting process, developed in 1892–93, the silk is deposited and left in a $SnClO_4{\cdot}5H_2O$ aqueous solution at pH = 1 for 6 h at room temperature. Then, the silk is changed to a Na_3PO_4 aqueous solution bath at pH = 10 and leave it for 1 h at 60 °C. This process is repeated 2 times. The Neuhaus weighting process (1897), or tin-phosphate-silicate method (dynamite I), has the same steps of the pink weighting process but with successive addition of phosphate baths and concluding with a silicate bath. The dynamite II process follows the same method of the dynamite I procedure, but includes between the phosphate and silicate baths, the addition of $Al_2(SO_4)_3$ aqueous solutions before the final silicate bath. Neither dynamite I nor dynamite II weighting processes were performed in this work. Before starting the tannin weighting the silk is partially rinsed in a bath of diluted HCl acid; then, the sample is introduced in a gallic acid solution during 1 h at 85 °C. Finally, the silk is maintained during 1 h at 85 °C in a bath composed by $FeSO_4{\cdot}7H_2O$, concentrated acetic acid and metallic iron.

Instrumentation

The Raman and surface enhanced Raman scattering (SERS) spectra of the historical samples were measured with a Renishaw micro-Raman system (RM1000) using as excitation the 633 and the 785 nm laser lines. This instrument is equipped with a Leica microscope, and an electrically cooled CCD camera. The signal was calibrated by using the 520 cm^{-1} line of a Si wafer and a 50x objective. The laser power on the sample was not higher than 1 mW. The resolution was set to 2 cm^{-1} and 5–40 scans of 10–30 s each were averaged. Spectra were recorded in the 100–1800 cm^{-1} region. The laser power at the sample was chosen to avoid sample degradation, ranging from 0.36 to 6.35 mW. FTIR attenuated total reflectance (ATR-IR) spectra were acquired with a Bruker alpha FTIR spectrometer over the range 4000–370 cm^{-1}, accumulating 128 scans at a spectral resolution of 4 cm^{-1}. Fabric samples were placed on the surface of the diamond ATR window. Complementary ATR-IR spectra were performed using a Thermo Nicolet iZ10 apparatus over a Ge ATR window. This spectroscopy is an efficient technique to quantitatively determine the orientation and conformation of proteins in single silk fibres [11]; however, this work doesn't deal with polarization measurements. All spectra are presented as obtained since only relative intensities are compared.

Preparation of silver nanoparticles

Silver nanoparticles were prepared by chemical reduction of silver nitrate with hydroxylamine [12]. The size distribution of the nanoparticles is in the range 60–150 nm, with the most probable size around 80 nm [12]; the FWHM of the silver colloids is 90 nm. The aqueous solutions utilized for the Ag-NPs formation were prepared by using nanopure water. The colloid shows a milky grey color and its extinction spectrum showed a maximum *ca.* 411 nm. For the extinction spectra a diode array spectrophotometer Hewlett Packard 8452 A was used. A control of the purity of the colloidal solution was carried out by measuring the Raman spectrum from aggregates dried over a quartz slide at room temperature; only bands due to νAg-Cl at *ca.* 236 cm^{-1} were observed.