EFFECTS OF MORDANTS ON THE MECHANICAL BEHAVIOUR OF DYED SILK FABRICS: PRELIMINARY TESTS ON COCHINEAL DYESTUFFS.

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ABSTRACT: *Failure of historic textiles is directly related to chemical, physical and mechanical degradation. Chemical processes that take place within the molecular structure of silk (hydrolysis, chain scission, cross-linking…) can be correlated to the loss of strength as well as the increased brittleness of textiles. This paper is the result of the early tests run on new silk samples. The objective is to characterize the effects of different dyestuffs on the structural stability of silk fabrics under specific environmental conditions. Comparisons to the behavior of weighted silks are also made.*

KEYWORDS: natural dyes, cochineal, silk, FTIR spectroscopy, UV-Vis spectrophotometry, mechanical properties

1.INTRODUCTION

Evidence of failure in historic textiles can be easily determined by simple observation. Tears, folding and drapes are common signs of both the lack of strength and elasticity of fabrics. The technical characteristics of the fabric itself (weight, density and chemical composition) contribute to increasing damage in the work of art as well. On the other hand, the exposure of silk fabrics to environmental factors such as relative humidity, heat, light and oxygen catalyze deterioration rates.

Several chemical analytical techniques have been widely used to determine changes in the molecular structure of silk as a consequence of ageing. However studies on the correlation of chemical degradation and changes in the structural behavior of historic silk textiles are scarce. This research is the first stage of a two-year project. This paper will show the early results of the study of changes evidenced in the mechanical properties of silk fabrics as a consequence of dyes present in their structure.

2.EXPERIMENTAL

2.1. Instrumentation

UV-Vis Spectrophotometer.
Spectra in the UV and visible region (200 – 1000nm) were measured using quartz microcells 50 µl HELLMA in a HITACHI U-2010 recording double beam spectrophotometer.

Fourier infrared spectrometer.
Vertex 70 Fourier infrared spectrometer (FTIR) with a FR-DGTS (fast recovery deuterated triglycine sulfate) temperature-stabilized coated detector made by BRUKER OPTICS® with a MKII Golden Gate Attenuated Total Reflectance (ATR) accessory. 32 scans were collected at a resolution of 4 cm^{-1} and spectra were processed using OPUS/IR software.

Mechanical tests
Tensile tests were conducted in the Mechanics Laboratory at the *Smithsonian Museum Conservation Institute* (Washington D.C.).

The equipment consists of a rectangular methacrylate box that contains several tensile testers. This box acts as a climatic chamber where relative humidity (RH) and temperature (T) can be controlled. The tensile testers are located in the upper part of the chamber whereas the light bulb and the tray are located on the lower level. A small fan makes the air circulate within the chamber. The fan accelerates the humidity absorption of the silica gel and creates stable and homogenous environmental conditions inside the chamber.

A high precision dew point hygrometer (General Eastern Hygro M4) is connected to the chamber and a small hygrometer is also located inside it. The tests were run at room temperature (23°C) and controlled relative humidity (45-50%).

2.2. Reagents and reference materials

2.2.1. Chemical reagents and solutions

Methanol, 96%, pa, Panreac; hydrochloric acid, 37%, pa, Carlo Erba; Potassium bromide KBr, 99+%, pa, Aldrich; De-ionised water grade HPLC, Medica Elga; Hydrochloric acid 3M:Methanol:Water (2:1:1) solution.

Colored compounds were obtained from ground cochineal insects by means of aqueous extraction.

2.2.2. Selection of fabrics

Experiments were performed on 100% silk known as *ponge textile* and supplied by Soditex, S.L. The characteristics of the fabric (Vicente-Palomino, 2006) were:

Name: Ponge
Composition: Silk
Number of yarns: 7 tex (warp), 4 tex (weft)
Density (taffeta): 60 (warp), 60(weft)
Fabric grammage: 0'00459g/m^2

2.2.3. Selection of dyestuffs

Anthraquinone dyestuffs were selected for all tests. Anthraquinone naturally occurs in plants (such as aloe, senna, rhubarb, and Cascara buckthorn) as well as fungi and lichens. Nevertheless, natural red dyes have commonly been obtained from cochineal insects.

Figure 1 shows the chemical structure of carminic acid ($C_{22}H_{20}O_{13}$), consisting of a core anthroquinone structure linked to a glucose sugar unit. Carminic acid is the coloring agent in carmine and occurs naturally in some scale insects, such as the cochineal.

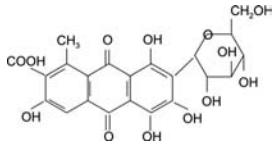


Figure 1. Chemical structure of Carminic Acid

Simple colorimetric tests have traditionally been used to identify the analytical chemistry of natural dyes [Masschelein-Kleiner, 1967]. This is the case of spectroscopic measurements such as infrared spectroscopy (IR) [Hofenk-de Graaff, 1969] as well as UV–Vis photometry [Hofenk-de Graaff and Roelofs, 1972 and Pall, 1994].

3. PROCEDURES

3.1. Preparation of samples

Control samples (not dyed) as well as cochineal dyed specimens as a function of different mordents and dyeing procedures were selected for this study. Tests were run on weft and warp yarns to evidence differences existing among them.

Ref.	*Sample*	*Dyes/mordants*	*Procedure*	*pH*
#0	Control silk	-	-	-
#9	T0016-07	Cochineal + alum	Hot dyeing solution -mordant: (1.9gr alum/ 200ml H_2O) -colorant (20 gr insect powder in 300ml water + 1ml NH_3)	6-7
#10	T0017-07	Cochineal + alum	Hot dyeing solution -mordant: (1.9gr alum/ 200ml H_2O) -colorant (20 gr insect powder in 300ml water +1ml acetic acid)	6
#11	T0018-07	Cochineal	Dyeing solution -no mordant -colorant (20 gr insect powder in 200ml water +2ml NH_3)	6

3.2. Chemical analysis

Samples (dyed silk fibers (T0016) (1.5-2.5mg)) were hydrolyzed for 15 minutes at 100ºC in an oven using 100µl HCl:MeOH:H_2O (2:1:1).100µl. MeOH 50% was added then and two phases were formed. The red extract was then analyzed by UV-Vis Spectrophotometry and FTIR-ATR spectroscopy.

a) UV-Vis Spectrophotometry

This colored solution was measured using quartz microcells 50 µl HELLMA in a spectrophotometer to obtain its Vis spectra. The absorbance measurements were carried out in the range 200nm e 1000nm.

b) FTIR-ATR Spectroetry

50 µl red extract was added (drop by drop) onto 0.1g of porphyrized and dried (at 100ºC for 2 hours) KBr. A red solid was obtained when the solvent had evaporated, and ATR-FTIR spectra was obtained from the dye using the FT-IR spectrometer with Golden Gate ATR attachment with diamond crystal. The IR spectrum were carried out in the range 600cm^{-1} e 4000cm^{-1}, with 32 scans and 4cm^{-1} resolution.

3.3. Mechanical tests

Testing conditions were established according to Hacke's report [Hacke ,2006, unpublished report]. 20 yarns width and 4 inches (10.16 cm) gage length were chosen for all tensile tests in order to shorten the overall testing time (through shorter gage length) and decrease the standard deviation (through maximum number of yarns). Accordingly 20-yarn specimens were obtained from each fabric both in the weft and warp directions. Additional fringed areas were retained at the edges. Typical sample measurements were: 0.44 cm (width) x 0.08 cm (thickness) for weft yarns and 0.305 cm (width) x 0.08 cm (thickness) for warp yarns. Two identical samples were tested for each specimen.

The specimens were mounted in the testing gages and conditioned in the chamber for 24 hours at 48+/-0.5 % RH and 24+/-0.5 °C prior to testing (Figure 4). Increments of strain 0.0025 were applied progressively at 30 second intervals.

Tensile test were run and force and strain curves were obtained. It was possible to determine the mechanical properties such as the strength and strain to failure of the silk samples from these curves. Restrained silk samples were tested in both the warp and fill direction.

In this specific case, the vertical scale indicates the **force per yarn** (expressed as Newton per yarn) of the specimen tested since it is not practical to calculate the tensile stresses as a function of unit cross-sectional areas in the case of fabrics.

In figures 6-9 the horizontal scale represents units of **strain** [1] which is the change in length of the specimen divided by its original length:

$$\varepsilon = \frac{L - L_o}{L_o} = \frac{\Delta L}{L_o} = \frac{\delta}{L_o} \qquad [1]$$

Where: L = current length of the sample
L_0 = original length of the sample
$\Delta L = \delta$ = change in length

The % elongation [2.3], of a material is an indication of the deformation a material is able to withstand before breaking. It is calculated as:

$$Elongation = \frac{L_o}{L_f} \cdot 100 \quad \text{or} \quad Elongation = \varepsilon \cdot 100 \qquad [2]$$

$$Elongation = \frac{\Delta L}{L_o} \cdot 100 \ (\%) \qquad [3]$$

Where: L_f = current length.
L_O = initial length.
$\Delta L = \delta$ = change in length

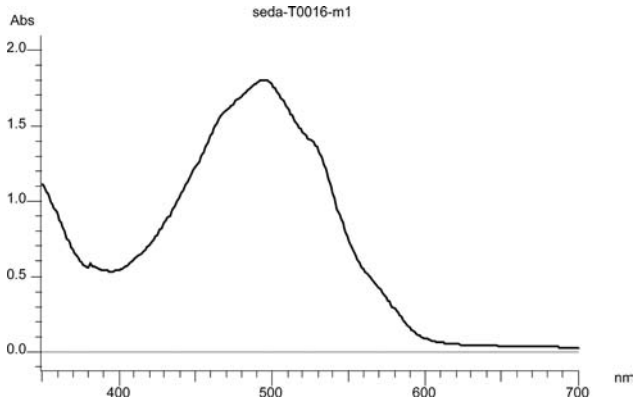


Figure 2. UV-Vis spectra of the dyed silk with mordant (0.0056g) (T0016-07) obtained by acid hydrolysis (HCl:MetOH:H2O (2:1:1)) and MeOH 50% extraction procedure

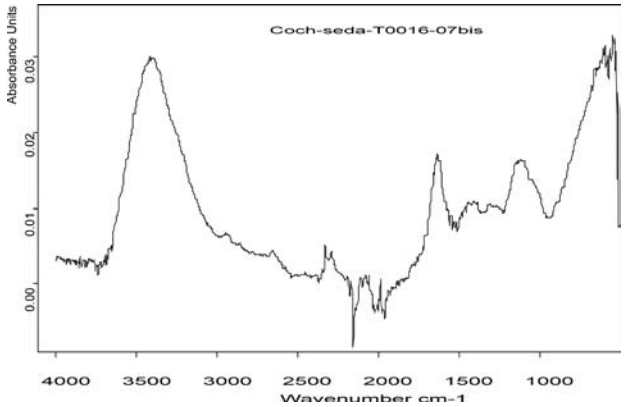
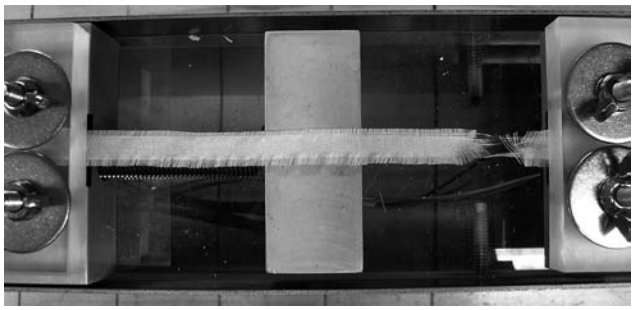
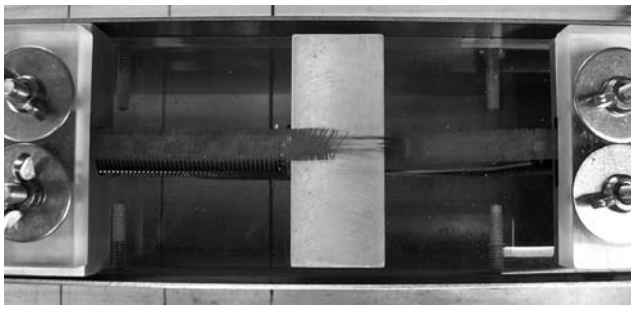


Figure 3. FTIR spectrum of the cochineal dyed silk (0.0013g) (T0016-07) obtained by acid hydrolysis (HCl:MetOH:H2O (2:1:1)) and MeOH 50% extraction procedure.





Figures 4 and 5 show a control specimen and dyed one respectively when breaking under tensile stresses

The force-strain diagrams provide a history of the mechanical behavior of the silk samples.

4. RESULTS AND DISCUSSION

4.1. Chemical characterization

UV-Vis Spectrophotometry and FTIR Spectrometry were used to analyze dyestuffs present in T0016-07 samples. Acid hydrolysis (HCl: MetOH:H_2O (2:1:1)) and MeOH 50% extraction was performed prior to the analysis.

UV-Vis Spectrophotometry

The absorption spectra of the extracted dye are shown in Figure 2. Cochineal dyed silk (T0016-07) shows a 524 nm maximum absorption value.

After the chemical identification by UV-Vis spectrophotometric was accomplished, FTIR was used for the structural characterization of cochineal dyes.

FTIR Spectrometry

FTIR spectrum of cochineal extract from dyed silk is shown in Figure 3. FTIR absorption bands of the main component of caminic acid correspond to anthraquinone compounds. Theoretical values are: OH to 3400-2400 cm^{-1} (stretching, carboxylic acids), C=O to 1730-1700 cm^{-1} (stretching, carboxylic acids), C-O to 1320-1210 cm^{-1} (stretching, carboxylic acids), O-H to 1440-1400 cm^{-1} (bending, carboxylic acids); C=O to 1715 cm^{-1} (stretching, ketone), C-C to 1300-1100 cm^{-1} (stretching, ketone); C-O-C to 1715 cm^{-1} (stretching diaryl ether); C-H to 3020-3000 cm^{-1} (stretching, aromatic), C=C to 1600-1475 cm^{-1} (stretching, aromatic), C-H to 770-730 and 715-685 cm^{-1} (bending (mono), aromatic), C-H to 770-735 cm^{-1} (bending (ortho), aromatic), C-H to 880, 780 and 690 cm^{-1} (bending (meta), aromatic). These bands were found in the FTIR spectrum of the sample as well.

4.2. Tensile tests

Tensile tests were run for the control samples and the dyed specimens. Figure 6 shows the force-strain curves obtained for control silk samples.

The overlap of curves for both warp specimens and weft specimens in all tests demonstrates the repeatability of the testing procedure.

The force development around 1.8 N/yarn indicates that the silk is a strong material in the fill direction. Nevertheless, whereas all samples are developing similar forces and elongation before breaking, differences between warp and fill yarns can be observed.

As may be seen, the plots in the fill (weft) direction are steeper than the warp direction indicating a stiffer material or a higher modulus in that direction. Additionally, it may be observed that the elongation to failure is greater in the warp direction.

These effects and differences in strength to failure and percent elongation rates between weft and warp yarns are a result of the weave or crimp structure of the textile. As a rule, the fill yarns tend to be straighter than the warp yarns and, as a consequence, they tend to deform less than the warp yarns. That the warp yarns are weaker than the fill yarns suggests that they are lighter in weight and possibly lower in fiber content.

Given the geometry of the fabric structure and the fact that silk is hygroscopic, changes in both the dimensional response of textiles and their mechanical properties can also be expected when moderate oscillations in humidity in the environment take place.

Force-strain tests were also conducted on dyed specimens. This included specimens that had exposure to different dyes, dyeing procedures and mordents. Figures 7 and 8 correlate the force per yarn and the dimensional response of warp and weft yarns of control silk and cochineal dyed silk specimens (#9 and #10) at 23ºC and 48% RH. The mordant used in both cases was alum. NH_3 was contained in the dyeing solution in the case of #9, whereas acetic acid was used for #10.

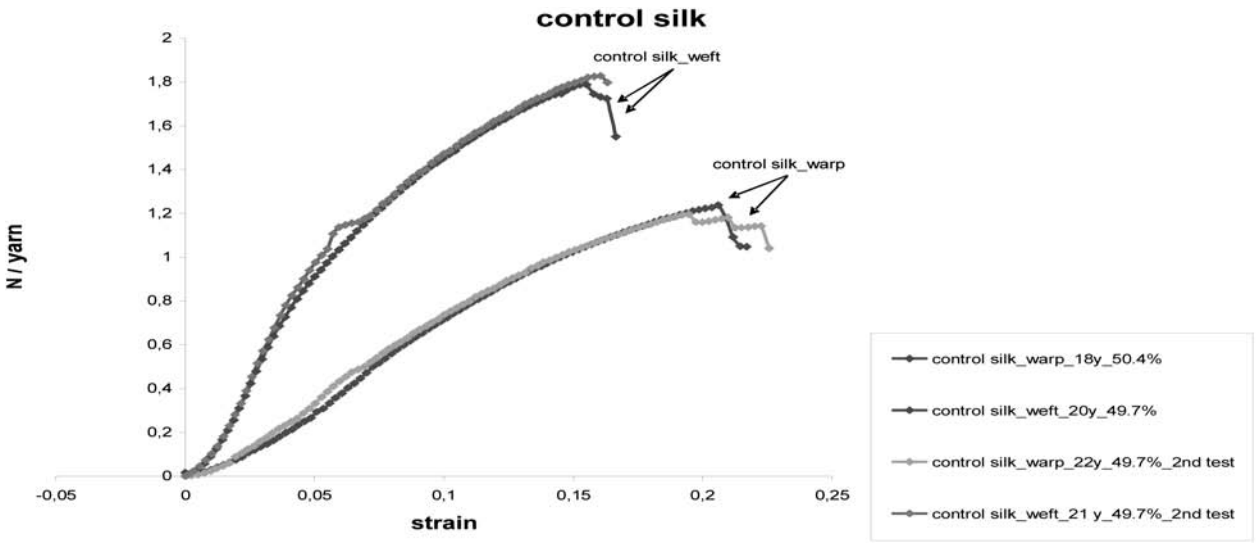


Figure 6 correlates the force and the dimensional response of control silk in the warp and weft directions (23ºC, 48% RH). Rigid control of the test environmental and the rate of load application insures repeatable results.

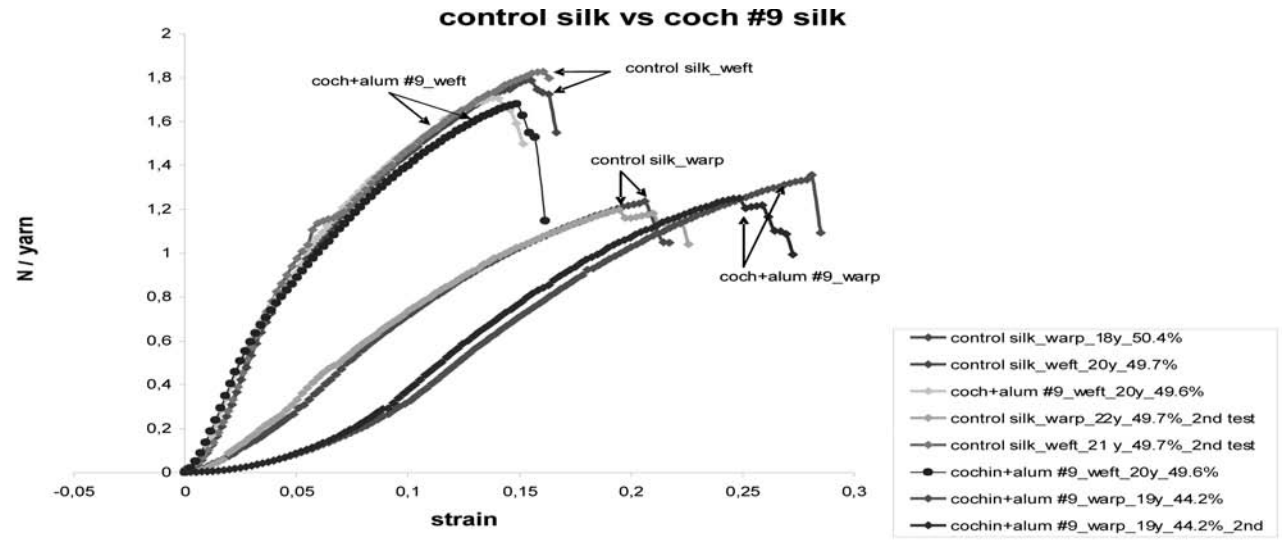


Figure 7. Correlates the force per yarn and the dimensional response of warp and weft yarns of control silk and cochineal dyed silk specimens (with alum and NH3) (#9) (23ºC, 48% RH)

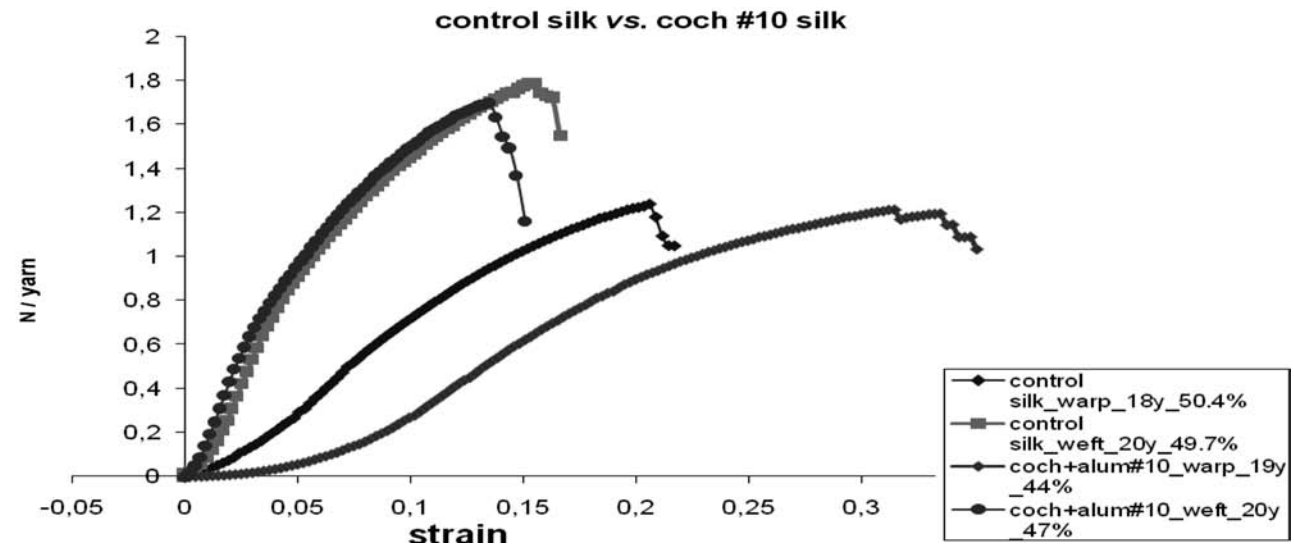


Figure 8. Correlates the force per yarn and the dimensional response of warp and weft yarns of control silk and cochineal dyed silk specimens (with alum and acetic acid) (#10) (23ºC, 48% RH).

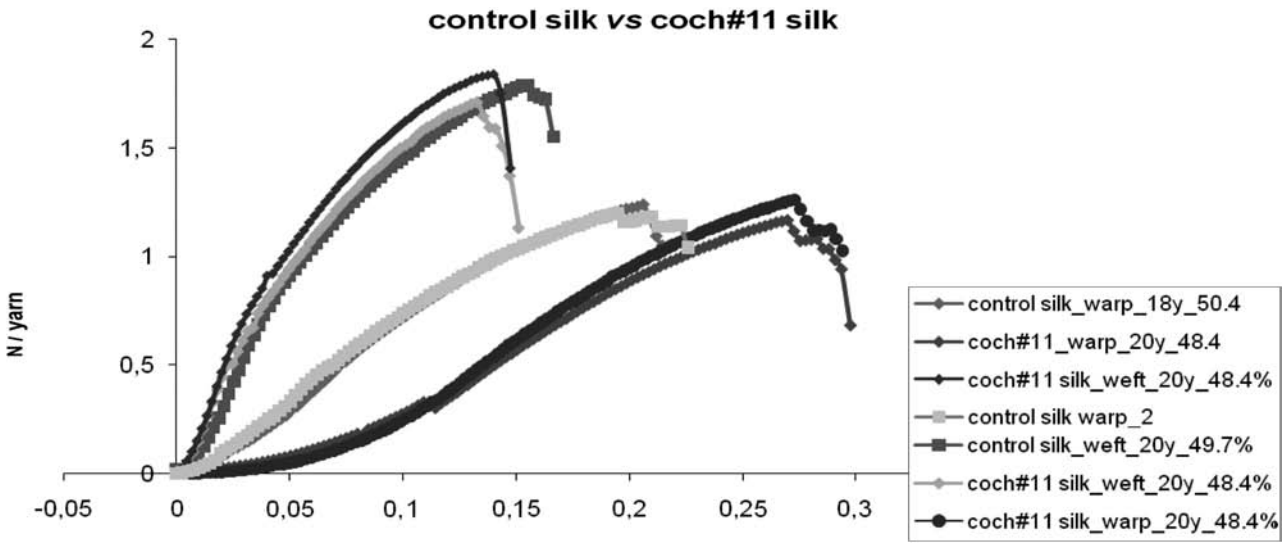


Figure 9. Correlates the force per yarn and the dimensional response of warp and weft yarns of control silk and cochineal dyed silk specimens (non mordanted) (#11) (23ºC, 48% RH).

Again, the overlapping of the plots demonstrates the consistency of the tests and, as before, differences between the warp and fill directions are observed. It can also be seen that the cochineal dyestuffs warp silk samples experience a significantly higher elongation and strength to failure than the control samples. On the other hand, the dyed samples tested in the weft (fill) direction failed at a lower force and elongation than the controls.

Additional tests were conducted with dyed samples containing non mordant. This is what is called a 'direct dyeing'. Differences between control silk samples and the dyed specimens are almost inexistent. Only a slight increase in the breaking strength and the modulus can be observed for samples tested in either the weft (fill) and warp yarns. The elongation to failure stayed the same in all cases.

Early tests indicate that the addition of metallic substances as mordants such as alum clearly induce changes in the mechanical properties of dyed silk textiles.

5. CONCLUSIONS

Preliminary results of the analytical characterization and the study of the mechanical properties of new silk fabrics have been shown and differences between control samples and cochineal dyed specimens were observed. Initial test results show that different dyeing procedures with mordants clearly determine different mechanical properties.

Silk samples dyed with cochineal were characterized with UV-Vis Spectrophotometry and FTIR Spectrometry. The analytical signal at visible spectrum corresponds to typical cochineal red tones. FTIR was used to identify the chemical structure of the extracted caminic acid commonly found in anthraquinone compounds.

The next stage is to determine how strength to failure and percent elongation are affected in each case and how specific environments contribute to modify such behavior. It is also necessary to check which dyestuffs (and dyeing procedures) induce the most significant effects on the durability of silk textiles.

Additional tests must be conducted on artificially aged samples in order to check for degradation induced by relative humidity, temperature and light.

To conclude, further research is needed to correlate chemical reactions catalyzed by metallic particles present in weighted silks and their implications in changes observed in their mechanical properties.

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Versión española

TITULO: ***Efectos de los mordientes en el comportamiento mecánico de tejidos de seda teñidos. Ensayos preliminares con tintes elaborados a partir de cochinilla.***

RESUMEN: *La degradación de los tejidos antiguos implica cambios químicos, fisicos y mecánicos en su estructura.*

Las reacciones químicas que tienen lugar en la estructura molecular de la seda (hidrolisis ácida, ruptura de enlaces, entrecruzamientos…) están directamente relacionados con la pérdida de resistencia y el aumento de la fiabilidad de los tejidos.

Este artículo es el resultado de ensayos preliminares realizados en muestras de seda nuevas (no envejecidas). El objetivo es caracterizar los efectos que tiene las sustancias colorantes en la estabilidad estructural de los tejidos de seda en diferentes condiciones medioambientales. También se incluyen referencias al comportamiento de sedas mordentadas.

PALABRAS CLAVES: *tintes naturales, cochinilla, seda, espectroscopia FTIR, espectrofotometría UV-Vis , propiedades mecánicas*