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THE INHERENT ACIDIC CHARACTERISTICS OF SILK, PART II – WEIGHTED SILKS

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Silk is found in many textiles of cultural and historic significance, but these fibres may deteriorate rapidly under adverse conditions, so are of particular concern to conservators and curators. Measurement of pH is common practice when assessing condition, as enhanced acidity is often ascribed to previous processing and treatment, adsorbed pollutants and oxidative deterioration, but recent research has demonstrated that the increased acidity of silk is an expected consequence of ageing, irrespective of the cause of deterioration. The study presented here builds on this earlier work to assess the role that common silk processing methods (bleaching and metal salt weighting) have on this phenomenon. Tensile strength was used as a marker of deterioration, independent of mechanism, and was compared with pH values of saline extracts of various silk samples. These samples included surrogates, prepared using historically accurate methods and subject to accelerated ageing, as well as a range of historic materials. It was seen that most samples followed the same correlation between pH and strength as seen in the previous work. However, silks weighted with tin salts appeared to be buffered (in the range pH 6.75-7.05), irrespective of their mechanical integrity.

1 Introduction

Archaeological and historic silk textiles form a valuable part of the collections in many museums, but as silk is a natural proteinaceous fibre, which is prone to deterioration, significant amounts are in poor condition. This problem is particularly acute for silk fabrics produced in Europe between the 18th and 20th centuries, and this is likely to be due to the particular processing techniques employed during this period. When considering the most appropriate curatorial and conservation approaches, characterisation of the condition of the silk together with an understanding of the material, its history and its degradation processes is essential. In support of this, we are pur-

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suing research aimed at developing suitable methodology and supplementing current knowledge.

In its native form, silk is found as a pair of filaments, formed of the highly crystalline protein fibroin, bound together by a second, largely amorphous protein, sericin.¹⁻⁸ In commercial usage, the sericin is generally removed by 'degumming'. Historically in Europe the fabric was sold on the basis of weight, so the material lost through degumming also represented a financial loss; therefore this weight was often fraudulently made up using organic agents such as protein glues, sugars, gums and resins. Subsequently this became an accepted processing method as it imparted a desirable drape and texture to the fabric. By the end of the 18th century these organic weighting agents had started to be replaced by more durable metal salts, which form insoluble complexes within the fibres.^{7,9,10} At the same time it was common practice to bleach silks by 'sulphur stoving', a process which involved exposing the material to the fumes of burning sulphur, yielding sulphur dioxide which formed sulphurous acid (the active bleaching agent) on contact with moisture in the fibres;^{7,11} sulphur may also be present in historic silks due to its use in clearing rinses.^{12,13} Both of these processes are implicated in the degradation of silk, and help to explain why European silk artefacts of this period are frequently in markedly worse condition than contemporaneous Asian silks.

Ageing results in changes to chemistry and microstructure of the fibroin filament, which will in turn affect bulk mechanical behaviour, appearance and other properties. Surface pH tests are often carried out by conservators as part of the initial assessment of an object, and frequently indicate significant acidity;^{4,14,15} however, although this is usually taken as an indication of contamination by acidic species, likely to enhance the degradation of the material, it has been shown in earlier work that this acidic character is in fact an inherent property of fibroin as it ages.¹⁶

This paper seeks to extend the results of this earlier work (hereafter referred to as the original data) by investigating the changes in the acidic properties of weighted and bleached silks. To this end surrogates were prepared from plain weave habutae silk using three historically common weighting regimes ('pink' tin, 'dynamite' tin and iron);⁷ a further set of samples were subjected to sulphur stoving, and some of these bleached materials were subsequently weighted by the 'pink' tin method. These specimens were then artificially aged, using elevated temperature and humidity, irradiation with

simulated sunlight or a combination of the two regimes. A comparison set of historic silks (between 50 and 200 years old) were also collected; although raw (un-degummed) silks are reported to absorb weighting agents more readily than degummed materials, due to the accessible, hydrophilic nature of sericin, the historic weighted examples included in this study were found to have been degummed.^{10,17}

It is known that surface measurements are not indicative of bulk pH,^{14,15} so the pH values of extracts were measured, using a saline extraction medium to better draw out the accessible acid (protons). These data were then compared with tensile strength measurements, a traditional measure of the state of deterioration of the material, and one which is independent of the precise mechanisms of degradation.

2 Experimental

2.1 Silk

Plain weave, degummed, undyed silk samples (yarn count approximately 50 (warp) × 40 (weft), 36 g/m²) were weighted using three methods – 'pink' tin (Sn(IV) chloride and sodium phosphate; three repetitions; weight gain 54 %), 'dynamite' tin (Sn(IV) chloride, sodium phosphate, sodium silicate and aluminium sulphate; two repetitions; weight gain 98 %) and iron (iron sulphate; three repetitions; weight gain 17 %).⁷ A further sample was bleached by exposure to the fumes of burning sulphur in a contained environment (4-5 g sulphur per 100 g silk, followed by thorough washing);¹¹ some of this bleached material was then weighted using the 'pink' tin method, as before.

A set of twelve historic silk samples were also collected to provide a set of comparison data, two of which had previously been identified as being tin weighted.

2.2 Artificial Ageing

The surrogate materials were subjected to accelerated ageing, using thermal, light or combined conditions. Thermal ageing was achieved by sealing the samples in separate hybridisation tubes, with a small vial of an appropriate saturated salt solution, to achieve an internal relative humidity of 75 % when placed in an oven at 70 °C; this was maintained for four weeks. Light ageing was carried out in a Q-Sun 'Xe1 Xenon Test Chamber' for one week; the temperature was maintained at 28 °C, and the system was programmed to deliver 0.4 W/m² of light energy at the wavelength 340 nm

(equivalent to a total dose of 25 MJ/m² over one day). The positions of the samples were rotated regularly to ensure even exposure. For the final set of samples a combined ageing regime consisting of one week in the light ageing chamber followed by one week's thermal ageing (both using the same conditions as above) was employed.

2.3 Tensile Tests

Mechanical testing was carried out on test strips of dimension 2.5×5 cm, using an Instron '5544' instrument controlled by 'Bluehill' software; a gauge length of 3 cm and extension rate of 2 mm/min were employed, and the samples tested to breaking point. Six replicates for each sample were assessed (those which broke at the jaw were excluded, and it was ensured that there were at least four valid replicates in every group); average values (and standard deviations) were calculated for each set. Samples were equilibrated at 20±2 °C and 55±5% RH for at least 72 h prior to testing, and these conditions were also maintained throughout the experiment.

2.4 Determination of Acidity

To obtain estimates of acidity microextractions were carried out in saline; the advantages of such an approach have been outlined by others.^{14,18} A small amount of each silk (20.0 mg of silk; the actual amount of sample was varied to take into account the additional mass of weighting agent; for the historic samples with unknown weighting levels, this was based on measurements of yarn count and fibres per yarn) was soaked in 1.0 ml degassed 0.1 mol/l NaCl solution at 20±2 °C and the pH of the extract measured using a BDH 'Glass+' combination microelectrode, following two point calibration (pH 4.00 and 7.00). The initial pH of the saline solution was 7.02. Extraction was carried out in a capped 1.5 ml polypropylene vial for 30 min to allow complete equilibration.¹⁶ Saline was selected for the extraction to enable sodium ions to displace protons in the Donnan equilibrium, effectively allowing equilibration of immobile, fibroin-associated acids and the solution, and a truer measure of acidity.^{19,20} The extractions were repeated in triplicate; averages and standard deviations were calculated.

3 Results and Discussion

3.1 Tensile Strengths of Aged Silks

Degradation of silk results in a loss of strength in both the warp and weft (Tables 1 and 2). For convenience and consistency we chose simply to monitor the changing strength in the direction of the warp. The susceptibility of the surrogates to ageing depended on the methods of initial treatment (while 'dynamite' weighted specimens showed behaviour similar to untreated silk, pink tin weighted samples displayed a greater susceptibility to light ageing, but a reduced rate of thermal

Sample	Ageing Regime	Average pH	Breaking Load / N
Silk, unweighted	Unaged	6.10 (0.11)	71.16 (1.22)
	Thermal	6.03 (0.14)	55.27 (3.23)
	Light	5.77 (0.16)	29.42 (4.85)
	Light/Thermal	5.79 (0.09)	12.24 (3.09)
Pink weighted	Unaged	6.78 (0.03)	64.14 (1.81)
	Thermal	7.05 (0.07)	54.11 (0.47)
	Light	6.93 (0.09)	9.22 (1.66)
	Light/Thermal	6.89 (0.17)	3.23 (0.40)
Dynamite weighted	Unaged	7.03 (0.20)	59.68 (1.95)
	Thermal	6.76 (0.07)	35.70 (5.55)
	Light	6.96 (0.17)	17.52 (6.36)
	Light/Thermal	6.86 (0.12)	6.87 (1.02)
Iron weighted	Unaged	5.97 (0.14)	41.68 (2.45)
	Thermal	4.82 (0.01)	6.44 (2.63)
	Light	5.53 (0.11)	7.37 (1.00)
	Light/Thermal	5.13 (0.13)	3.78 (0.56)
Bleached	Unaged	6.05 (0.21)	57.98 (1.75)
	Thermal	5.51 (0.09)	31.72 (7.17)
	Light	5.59 (0.13)	19.36 (4.78)
	Light/Thermal	5.34 (0.04)	5.36 (0.49)

Table 1: Acidity and breaking loads of weighted and artificially aged silk samples (standard deviations are given in parentheses).

Sample	Average pH	Breaking Load / N
1	5.02 (0.09)	5.68 (1.58)
2	5.04 (0.04)	6.42 (0.94)
3	5.21 (0.11)	3.33 (0.61)
4	5.46 (0.06)	4.3 (0.25)
5	4.89 (0.08)	3.98 (0.6)
6	5.66 (0.38)	20.48 (1.58)
7	3.90 (0.04)	2.9 (1.65)
8	4.88 (0.03)	4.06 (0.54)
9	4.85 (0.03)	3.78 (1.75)
10	4.83 (0.03)	3.48 (0.98)
11	6.91 (0.08)	15.65 (0.86)
12	6.75 (0.09)	9.81 (1.84)

Table 2: Acidity and breaking loads of historic silk samples (standard deviations are given in parentheses).

ageing; iron weighted samples were more vulnerable to both light and thermal ageing; bleached silk was particularly prone to thermal ageing but light ageing was not significantly exacerbated; bleached and tin weighted silk appeared to be protected from the enhanced thermal ageing observed with the purely bleached material), as reported elsewhere.⁸

3.2 Acidity

Since the same quantity of silk was used for each extraction, the pH values of the saline extracts may be taken as indicative of the acid contents of the samples, assuming the weighting agents or any residual bleaching agent do not directly contribute. Numerical data is given in Table 1 (and with breaking loads), and it can be seen that the acidity of the unweighted, iron weighted and bleached samples increases with ageing. However, for both of the tin ('pink' and 'dynamite') weighted materials, acidity appears to fall in the range pH 6.75-7.05, regardless of ageing; it should be noted that this is considerably less acidic than untreated, unaged silk (pH 6.10).

Similar data for the historic silk samples is presented in Table 2.

3.3 The Correlation Between Acidity and Tensile Strength

If tensile strength is plotted against pH (Figure 1), it can be seen that the data points fall into two distinct domains. The unweighted, iron weighted and bleached samples, along with the majority of the historic specimens, follow the behaviour previously observed with the untreated but aged habutae silks,¹⁶ with a good correlation between the two properties, although by including these new data the distinction between the ageing regimes (specifically oxic and anoxic conditions) that had been observed in the earlier work is no longer seen.¹⁶ However, for the two sets of tin samples, a mar-

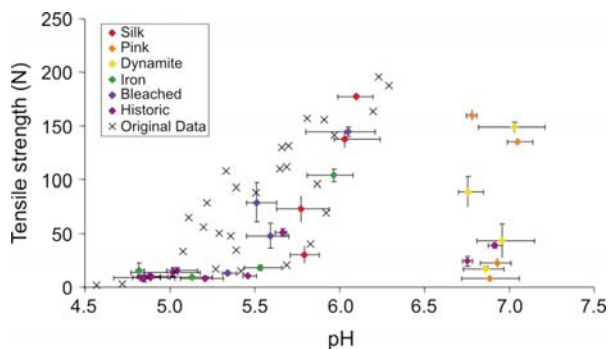


Figure 1: Plot of pH against tensile strength for various surrogate and historic silk samples, including data from previous experiments.¹⁶

kedly different behaviour is seen, with acidity remaining constant (and almost neutral), even as the fibres lose mechanical integrity; two of the historic samples also behave in this manner; therefore, for tin weighted silks, pH cannot be used as a reliable indicator of condition.

Nonetheless, this suggests that for most silk samples, the behaviour characterised previously still pertains, with acidity increasing as a function of degradation, largely independent of the precise degradation mechanism.¹⁶ The highly crystalline regions that comprise the majority of the fibroin protein are largely resistant to damage, which instead predominantly affects the amorphous, intercrystalline components.^{3,4} These latter regions contain bulkier and acidic residues, particularly aspartic and glutamic acid; in the native state, these may be involved in secondary bonding (hydrogen bonding and salt-linkages), helping to maintain some secondary structure. Deterioration allows enhanced access to these components of the polymer, thus permitting a truer measure of its acidic content. However, based on the molar ratios estimated from amino acid analysis of degummed *Bombyx mori* silk, even with the most highly degraded samples just a small fraction of the carboxylic acidic side chains contribute to the measured pH. It is assumed that the remainder have been neutralised during processing, still contribute to secondary bonding or remain inaccessible within the polymer structure.

This still appears to hold true for the iron weighted and bleached samples, even though they contain species (metal salts or sulphur residues) which may be expected to influence the acidic properties of the fibre. However, for the tin weighted materials, this relationship between inherent acidity and tensile strength is not observed; the mechanical properties of the silk fibres are still impaired by degradation, but this is not accompanied by an increase in acidity. Indeed, the tin weighted materials have a lower acidity, regardless of their state of degradation, than even those silk samples which had not been subjected to weighting, bleaching or accelerated ageing. The preferential degradation of the amorphous region of the polymer (with a resulting increase in accessibility of acidic residues) is well characterised as the main deterioration path for silk,^{1,3} and there is no evidence that tin weighted silk behaves in a significantly different manner. Even if acidic residues are still exposed during ageing, it appears that the tin complexes are able to act as buffers, constraining the silk to a roughly neutral pH.

This buffering effect may help to explain why tin weighted silks appear to degrade no more rapidly

than unweighted silks when exposed to ageing conditions likely to promote hydrolytic reactions, despite the initial damage caused by the weighting process. It may also give an insight into the discrepancy observed between the bleached materials, which degrade rapidly under hydrolytic ageing conditions, and those which have been bleached and subsequently tin weighted, which conversely deteriorate at a rate comparable to that of the untreated silk.

4 Conclusion

As the fibroin protein which comprises silk deteriorates it undergoes an inherent increase in acidity, due to the scission of the polymer in the amorphous regions with the resultant increase in accessibility of the bulky acidic amino acid residues found here. This had been observed in previous research,¹⁶ and was found to also occur with silk treated by certain historically common processes (iron weighting and sulphur bleaching). However, another widespread weighting regime (tin weighting, either by the 'pink' or 'dynamite' processes) was found to dramatically alter this behaviour: it appears that the metal complex acts as a buffer, limiting the pH of the material to roughly 6.75-7.05, irrespective of the degree of degradation, and suggests that under conditions where hydrolytic attack is the principal degradative pathway, tin weighting may in fact offer a degree of protection to the fabric (highlighted by the difference in behaviour of bleached fabrics, which degrade rapidly when exposed to conditions likely to promote hydrolysis, and bleached then tin weighted fabric which do not). This may further suggest why tin weighted historic fabrics which have not been exposed to light are often in surprisingly good condition.

Samples for which an indication of degradation cannot be determined by pH measurement due to this effect (i.e., those in which tin weighting agents act to buffer acidity) are readily identified, as the measured pH is significantly higher (in the range 6.75-7.05) than that of even new (untreated and unaged) silk (typically around 6.10).

This work emphasises the necessity of understanding the properties and behaviour not only of constituent materials but also of historic processing methods when dealing with objects of cultural heritage, in order to adequately inform conservation treatments, and suggest the most suitable methods of display and storage by highlighting the stability or susceptibility of materials with respect to particular degradative processes.

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