

USE OF NEAR IR SPECTROSCOPY AND CHEMOMETRICS TO ASSESS THE TENSILE STRENGTH OF HISTORIC SILK

FULL PAPER

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Silk is a culturally important textile, found in many artefacts of historic significance including clothing, upholstery, banners and decorations. However, it is a fragile material and is prone to deterioration via a variety of mechanisms, particularly after certain historically common processing methods such as bleaching and weighting. Therefore it is important to be able to accurately characterise the material in order to inform the most appropriate strategies for conservation, display and storage. NIR spectroscopy allows the non-invasive, *in situ* investigation of these textiles, and when combined with chemometric (multivariate) analysis to draw correlations with data obtained by other methods, can provide a wide range of valuable information. Using these techniques, we have demonstrated that it is possible to gain information about the physical state and integrity of silk; although this is complicated by the range of degradative reactions which silk can undergo, it is possible to draw correlations between NIR spectra and mechanical properties derived from tensile testing. This will enable potential conservation treatments to be directed at those objects and areas in greatest need of intervention, and may also highlight aspects which may warrant additional investigation via other methods.

1 Introduction

Silk has long been regarded as one of the most luxurious and prestigious textiles, and is found in many artefacts of historic and cultural significance, including clothing, furnishings, banners and decorations. It was originally cultivated as a textile fibre in China (from roughly 3000 BC), and subsequently spread to the rest of Asia and then to Europe. The majority of commercial silk is derived from the cocoon of the domesticated silk worm, *Bombyx mori*, although some also comes from other species, yielding 'tussah' or wild silk.¹⁻⁴ The fibre is produced as a pair of proteinaceous fibroin filaments bound together by a second protein, sericin. Fibroin is largely formed of glycine, alanine and serine (comprising about 86 % of the protein) as the hexapeptide motif *-Gly-Ala-Gly-Ala-Gly-Ser-*, and is highly crystalline (approximately 70 %) with extensive anti-parallel β -sheet structures.^{2,3,5} This chemistry and microstructure gives fibroin a high

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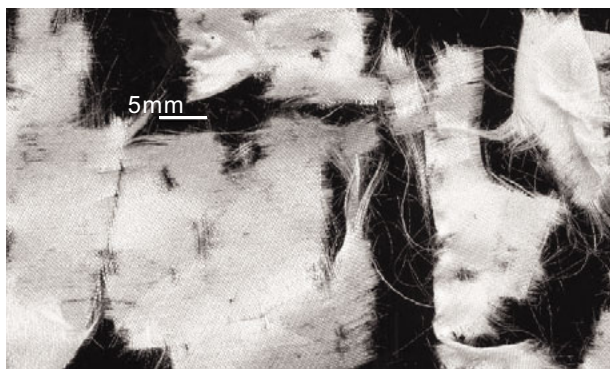


Figure 1: Light degraded silk, showing characteristic signs of "shattering".

strength, low extensibility and resistance to chemical attack. The second protein, sericin, is amorphous and hydrophilic, which allows the material to be readily removed, a process known as degumming. Degummed silk is prized for its strength, fineness, smoothness and lustre. However, it is also a fragile material and despite its chemical resistance is prone to deterioration by a variety of mechanisms, particularly through exposure to light (Figure 1); this may be further exacerbated by certain historically common methods of processing, such as bleaching and weighting.

Bleaching was historically achieved by a variety of methods, and although modern techniques have been developed which cause a minimum of damage, traditional methods were frequently much harsher,^{4,6} particularly 'sulphur stoving' (exposure to the fumes of burning sulphur) favoured in Europe from the late 18th to early 20th century.⁷ Metal salt weighting, a process also used in Europe from the late 18th century onwards to impart a specific texture and drape, is similarly associated with the long-term damage to silk textiles.^{4,7-11} Salts of tin, lead and iron were widely used, but are implicated in the destabilisation of the fibre, particularly with respect to photo-degradation.

The susceptibility of silk means that accurate characterisation of its condition and state is important for the conservation, display and storage of these materials, as well as potentially providing information about provenance and usage. Furthermore, when faced with the common challenges of large collections and limited resources, this may help to direct efforts to those objects in greatest need of attention. Microsampling or, ideally, entirely non-invasive methods are favoured for conservation, as are techniques which allow *in situ* investigation and require minimal operator training. Light microscopy is the most widely used method of conservation assessment, but often requires sampling, relies on the operator expertise and is unlikely to reveal all features of interest, particularly those associated with subtle chemical alteration. Other techniques, such as infrared and Raman spectroscopy,¹²⁻¹⁴ pH measurement,^{15,16} electron microscopy,^{17,18} x-ray diffraction,¹⁹⁻²⁵ size-exclusion chromatography²⁶⁻²⁸ and mechanical testing,²⁹ may reveal more specific information, but have limitations of their own, often in terms of sampling requirements, time, cost or availability and do not provide a routine, non-invasive, *in situ* method of monitoring of artefacts. A technique which avoids many of these prob-

lems and allows a variety of properties to be derived from a single measurement would be of great value to conservators.

Near infra-red spectroscopy, with its ability to rapidly record good quality spectra via a simple fibre-optic probe fulfils these requirements, but the spectra, principally composed of overtones and combinations of vibrations observed in the mid-infrared region, are not necessarily readily interpreted. The method becomes particularly valuable, however, if it is combined with chemometric (multivariate) analysis, allowing specific experimental data derived from reference materials (characterised, for example, via the techniques noted above) to be correlated with NIR spectra, which then allows such properties to be predicted for unknown future specimens from their spectra.^{30,31} This, therefore, potentially allows condition assessment, as well as the derivation of a variety of other properties, to be made from a single NIR measurement. Approaches of this kind have already proven to be effective in the investigation of other organic materials in the context of conservation, allowing a range of characteristics to be derived from a single spectrum, as exemplified by the SurveNIR project.³²⁻³⁸

Multivariate analysis enables large, complex data sets (such as collections of spectra) to be reduced to a smaller, simpler set of components, which can reveal correlations to other variables (results derived from other experiments, for example), even if such co-dependency is not obvious in the original data.^{31,39} An initial matrix, X , is constructed of n rows (the number of spectra included in the model) by p columns (the number of data points per spectrum); matrix algebra is then employed to reduce X to smaller matrices and maps the samples onto a new coordinate system which describes the variance in the data, known as principal components (PC), thereby potentially revealing features of interest which were not apparent in the original spectrum. For the work presented in this paper, a partial least squares (PLS1) method was employed to derive correlations between the spectra and the experimental results, using X and a second matrix, Y , composed of a single column of n rows, each row containing the specific datum associated with corresponding spectrum in X . Once a chemometric model has been constructed it is possible to determine which spectral regions contribute the most information to it, thereby gaining a better understanding of the chemical and microstructural behaviours associated with the measured changes in the original material. One of the principal challenges of the method is the number of reference samples required to create a reliable chemometric model, particularly when the best source of representative materials is likely to be objects which themselves are of value. Carefully prepared surrogates can provide a partial solution to this problem, but artificially aged materials may not fully represent the properties of 'real' historical objects, therefore examples of such should also be included if possible.

We identified three particular characteristics of silk that would be of interest and value to a textile conservator, and demonstrated that it is possible to assess them via a NIR/chemometric method, using a reference set of historic materials and suitable surrogates to build the model: condition, in terms of degradation; metal salt weighting; and loading in a hanging

textile. Condition assessment, using the tensile strength of silk as a non-specific marker of degradation, is discussed in this paper. Investigation of the presence and nature of weighting treatments applied to the material⁴⁰ and the loading of a silk fabric, allowing potentially damaging forces at work in textiles hanging under their own weight to be assessed,⁴¹ have been published elsewhere. More broadly, the rôle of weighting and bleaching on the stability of historic silk and the behaviour of these materials have also been investigated.^{16,42}

2 Materials and Methods

2.1 Condition Assessment

Condition assessment provides information about the physical state of an object and is vital to conservation. In many cases an assessment of this kind can be carried out directly by a conservator or curator, but this approach requires a significant degree of expertise and experience and is often very time consuming, problems which may be exacerbated if the item itself is fragile or difficult to access. NIR spectroscopy in conjunction with chemometrics has the potential to allow a non-invasive, easily operated, *in situ* technique to be developed, but requires a reference technique which will provide the initial evaluation of condition on which the model can be based.

Analytical condition assessments may be carried out in a variety of ways, but most such techniques have limitations: It is possible to focus on the effects of specific modes of deterioration (photo-degradation, oxidation, hydrolysis, physical wear-and-tear, etc.), by following characteristic changes in analytical data linked to chemical or microstructural alterations,¹²⁻²⁵ and this is important when considering the particular causal mechanisms by which materials deteriorate, but is often too limited to provide a synoptic overview of an object's condition. Techniques such as size exclusion chromatography (allowing changes in degree of polymerisation to be investigated)²⁶⁻²⁸ and mechanical testing (to study the ways in which the physical properties of the material have altered with ageing, regardless of the precise cause of damage)²⁹ give a better overview of general condition, but both require sampling and cannot be carried out *in situ*.

We decided to use tensile strength as a non-specific marker of degradation, and so build a chemometric model based on the breaking load of a set of silk samples (both historic materials and surrogates) intended to represent the range of properties and characteristics commonly encountered in silk artefacts. The reference set initially included undyed, untreated fabrics from a variety of sources, as well as a range of materials treated with weighting agents to different levels (as weighting is known to influence spectra).⁴⁰ This group was then expanded to include additional samples as limitations of models based on the original set became apparent: A number of dyed silks, of a variety of hues and depths of shade, were included in this as the strong absorbance of such coloured materials can often lead to irregular base-lines in the NIR spectrum (even though the dyes themselves are often present in quantities too small to yield specific spectral peaks). Silk samples under tension were also

incorporated as other investigations had demonstrated that NIR spectra of these materials undergo measurable changes on loading,⁴¹ so it was necessary to exclude this effect from the model. Similarly, as water is an important structural component and plasticiser of most natural organic polymers, their spectra are influenced by variations in humidity, so samples held under elevated or reduced humidities were added to the model.

2.2 Methods

NIR spectra were recorded from samples using a *Perkin Elmer 'Spectrum One NTS'* spectrometer, via an *'Axiom'* fibre optic probe, over the range 10,000 - 4100 cm^{-1} , with a resolution of 4 cm^{-1} and 50 accumulations. Spectra were recorded from a single thickness of fabric, and from samples suspended in air; although better quality spectra may generally be recorded using a *Spectralon* backing plate, this would often be impossible to achieve for *in situ* analysis of historic fabrics, but gently separating fabric layers of such objects to provide a suitable air-gap is more likely to be practicable and acceptable. The samples included both historic materials and surrogates (prepared using historically accurate methods and subjected to a variety of ageing regimes)⁷, a number of which were strongly coloured; furthermore some of the specimens were also recorded under moderate tension (loaded to 5 and 10 N across a 10 mm wide fabric strip, to mimic the effect of an object hanging under its own weight), and at elevated and lowered humidities (80 and 30 % RH, respectively, achieved using saturated salt solutions). This provided a reference set of 153 spectra, an overview of which is provided in Table 1.

Subsequently, the physical properties (specifically tensile strength, measured as breaking load) of these materials were assessed using an *Instron '5544'* mechanical tester, using 10 mm wide strips of fabric, with a gauge length of 50 mm and an extension rate of 10 mm/min, recording data using a load interval of 1 N and a time interval of 0.1 s; values were averaged over six repetitions per sample.

These data were then investigated using *CAMO Unscrambler 9.7*; the spectra were normalised via extended multiplicative scatter correction (EMSC) and then correlations drawn with tensile strength

Samples	No.
Modern silks, untreated	6
Modern silks, artificially aged	8
Weighted and/or bleached surrogates	20
Weighted and/or bleached surrogates, artificially aged	52
Weighted surrogates, 10 years old (natural ageing)	18
Weighted and/or dyed historical silks	23
Selection of above silks, loaded to 5 or 10 N	12
Selection of above silks, at 30 or 80 % RH	14

Table 1: Overview of the silk samples (153) used to generate the chemometric model.

using a partial least squares (PLS1) regression model. The best results were achieved when the spectral range included in the calculation was limited to 4100-5550 and 6490-7310 cm^{-1} .

This model was then applied to spectra recorded from a set of previously uncharacterised material to derive predicted breaking strengths; this set of sixteen specimens included modern untreated silks, dyed materials and historic specimens. Subsequently the actual mechanical properties of the samples were determined, and the results compared with the chemometric predictions.

3 Results and Discussion

The PLS plot of measured and predicted values is shown in Figure 2, demonstrating that a strong correlation can be drawn between the spectra and the physical strength of the material. A good chemometric model is one that will reliably predict the behaviour or properties of an unknown sample. The quality of the model can be assessed by its precision and accuracy, the former denoting the difference between repeated measurements and the latter the difference between the predicted and the true values.^{43,44} The standard error of calibration (SEC) is a measure of precision, based on standard deviation of the differences between the predicted and measured values, whilst the root mean squared error of calibration (RMSEC) measures accuracy of the model on the

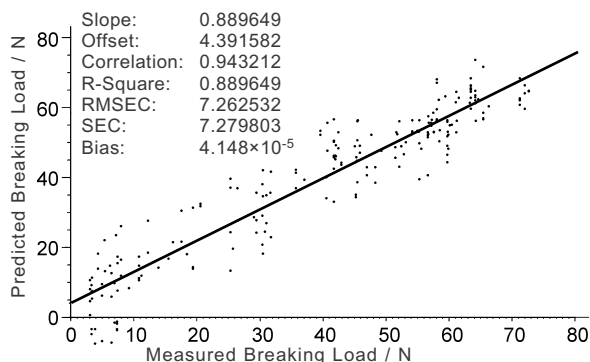


Figure 2: Correlation between measured and predicted breaking loads silk fabrics, generated using PLS regression.

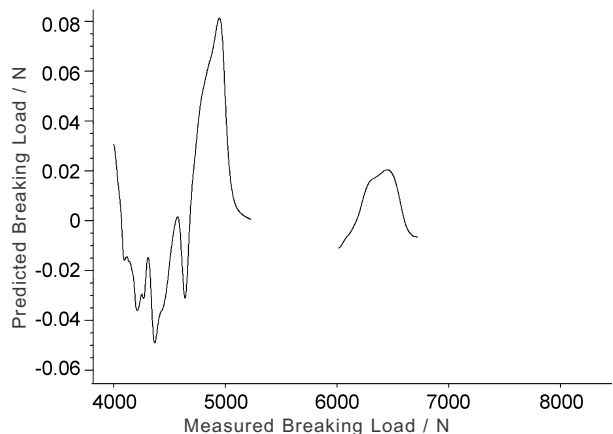


Figure 3: Predicted and measured breaking loads for previously uncharacterised silk samples, using the PLS regression model, with 95% prediction interval.

RMS of these differences; bias is the mean of the differences. Lower SEC and RMSEC values indicate a better model. The validity of the final model for assessing 'real' samples was then investigated by applying it to a set of samples which had not previously been investigated; when the tensile strengths of these materials were measured, and the predicted and actual values compared (Figure 3) it can be seen that this model then provides a good prediction of the state of the material, with the exception of the two black dyed samples, which is probably due to the strong, broad absorbance of these materials.

If earlier versions of the model are considered (Figures 4.a and 4.b),⁴⁵ it is apparent that as the sample size and variety increases, the accuracy (i.e., RMSEC) of the model decreases slightly, but conversely it is able to provide more accurate predictions for the range of materials typically encountered when dealing with items of cultural heritage; for example, the initial study, using only uncoloured silk, yielded a stronger predictive model when dealing only with these types of material, but gave poor results with dyed or discoloured fabrics.

The regression co-efficient plot for the model is presented in Figure 5. This gives an indication of the extent to which different variables (i.e., spectral intensities at specific wavenumbers) influence the principal component: the greater the distance from zero (either positive or negative), the greater the contribution to the model from that region of the spectrum, and values close to zero indicate little or no contribution. Therefore, it is apparent that the majority of the information is derived from range 4600-5000 cm^{-1} ; this has been shown to be associated with the 'amide

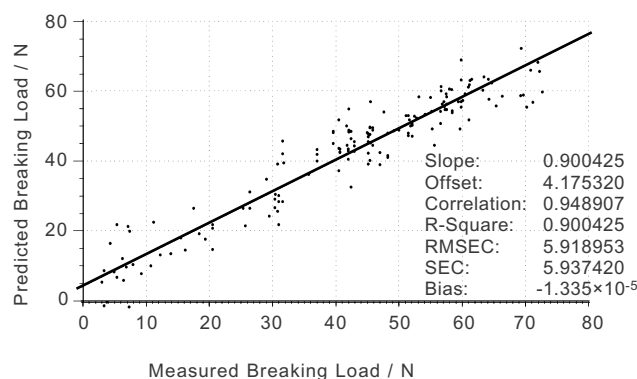
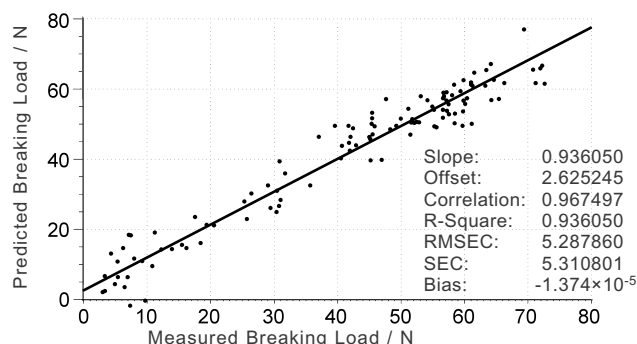


Figure 4: Previous versions of the predictive model, demonstrating its development; (a) using only undyed materials, under 'museum' conditions (22 °C, 55% RH); (b) using dyed and undyed fabrics, under 'museum' conditions.

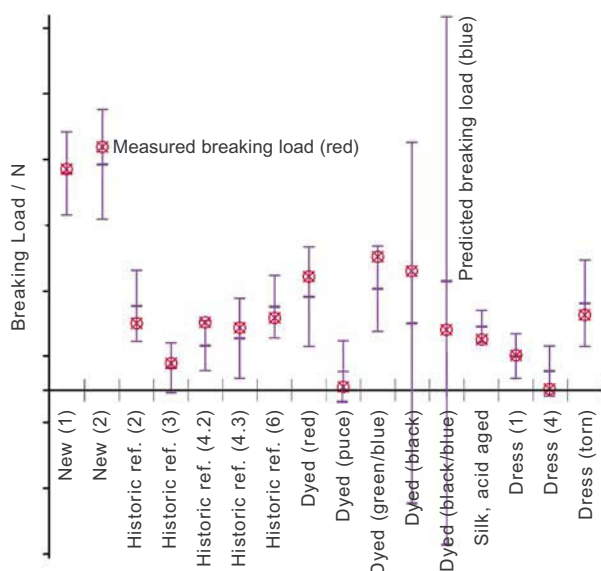


Figure 5: Regression co-efficient plot for the PLS regression model of breaking loads.

Red - Measured breaking load,

Blue - Predicted breaking load, with prediction interval.

A+II' and 'amide B+II' combination vibrational modes,⁴⁶ suggesting that the principal contribution to the analysis arises from subtle changes in the secondary structure of the protein as it degrades. These kinds of changes have previously been observed using X-ray diffraction^{19,20} and polarised infrared spectroscopy.^{21,22} In the final model, the best predictions were achieved by limiting the spectral range to those regions richest in information (specifically 4100-5550 and 6490-7310 cm^{-1} , as noted above and as can be seen in Figure 5). However, with earlier versions, better results were achieved using the full spectrum, possibly due to base-line variations encountered with more strongly coloured samples which had not been included in the reference sets used to construct the model.

Therefore it can be seen that a predictive model built using a representative set of samples can provide a powerful tool to assess the state of silk fabrics, and one that is able to cope with a wide range of different sample types and conditions; the exceptions are samples from which a good quality NIR spectrum cannot be recorded (the black samples in this case).

4 Conclusion

We have demonstrated that by using NIR spectroscopy in combination with suitable chemometric models, it is possible to assess general condition of silk as measured by its breaking strength, information which will inform possible conservation, display and storage strategies; this complements other outcomes of the research project in which it has also been shown that the presence and nature of weighting agents (important when considering the provenance of European silks),⁴⁰ and the extent of localised loading within the fabric,⁴¹ can be measured using similar approaches (and, indeed, these factors can be derived from the same spectra used for the condition assessment). The NIR/chemometric approach has numerous advantages over conventional methods of assess-

ment, as it permits the non-invasive, rapid and *in situ* interrogation of objects, factors which are of particular importance when dealing with fragile and valuable historic objects for which any direct intervention should ideally be kept to a minimum, and allows a broad range of properties to be derived from a single spectrum.

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