ABSTRACT  Decisions on the conservation and display of a textile, including prioritisation for treatment, should be informed by objective knowledge of its current physical state. Measuring the tenacity and elasticity of yarns and fabric, however, generally requires sampling and is necessarily destructive. Bearing in mind the need to maintain the integrity of the artifact, an indirect approach requiring at most the removal of just microsamples is preferred. On ageing, the performance of a natural fibre such as silk or linen is compromised as the components within the fibre deteriorate. There is a reasonable correlation between the reduced tenacity of silk upon ageing and both the shortening of the silk fibroin polymer and the disorientation of the fibroin crystallites. These two parameters can be measured from just a short length of a silk thread using size exclusion chromatography (SEC) and polarized infrared (IR) spectroscopy, respectively. Other destructive microanalyses, e.g. X-ray diffraction (XRD), X-ray microtomography (XRM) and thermomechanical studies, can also offer characteristic chemical and microstructural identifiers. More recent technological advances and applied research suggest the potential for non-destructive approaches to condition assessment; with techniques such as near-infrared spectroscopy (NIR), the sampling constraint is circumvented by monitoring a dependent physical effect such as moisture sorption.

Keywords: linen, silk, condition monitoring, fibre microstructure, ageing, non-destructive analysis

Introduction

In September 1921, the British explorer, Sir Ernest Shackleton, set off for the Antarctic. His planned final expedition was short-lived; on reaching South Georgia he was taken ill and died on 5 January 1922. His body was sewn in canvas and covered with the white ensign, which as a member of the Royal Yacht Squadron he had the privilege of flying. The squadron, which was eventually presented with the ensign by Shackleton's son, recently commissioned Conservation Services at the Textile Conservation Centre to stabilise the flag and improve its display. When it arrived at the centre the ensign was in an extremely weak state, especially areas of cream-white silk where significant sections were missing. Handling of the stiff, fragile fabric proved to be a problem and this influenced the choice of treatment.

Decisions on the conservation and display of a textile, including prioritisation for treatment among other items in a collection, should be informed by knowledge of its current physical state. It was clear from the outset that the majority of the ensign silk had suffered significant deterioration and appeared mechanically weak and brittle. Frequently though, we may rely too much on such simple visual and tactile clues, and perhaps the object’s recent history. Such a subjective assessment in the light of our own experience is necessary, but may not be sufficient. A more reliable objective approach defining the precise physical condition at the outset could contribute to a better informed choice and perhaps outcome.

In this paper, the ways in which this can be achieved while maintaining the integrity of the textile are explored. Earlier results are reviewed that show a link between mechanical properties, which will define the condition of a textile, and some measurable indirect markers. To develop this approach further, it is important to understand these relationships in terms of the microstructural modifications that can occur on natural fibre ageing, so these changes are highlighted to rationalise these data for silk and to suggest further indicators for linen which might be interrogated. While characterisation of the chemical state is equally important in determining the longer term preservation protocol, I focus simply on these microstructural parameters and finally suggest techniques that might be applied to microsamples or to the intact textile in situ to extract these signatures of deterioration and hence indirectly evidence the condition of a textile.

Correlating mechanical properties and microanalytical markers

Occasionally it is possible to determine the mechanical properties of a textile in situ; such an approach proved crucial to improved understanding of the behaviour of the 200-year-old HMS Victory fore topsail (Garside and Wyeth in this volume, pp. 118–25). Generally though, measuring the tenacity and elasticity of yarns and fabric requires sampling and is necessarily destructive.

Practical and ethical considerations dictate the application of indirect analytical methods which require only small specimens consisting of no more than a few short fibres. The most useful methods will show unique signatures for degraded material that correlate with the physical properties of the aged threads. For assessing the ageing of silk, high-performance liquid chromatography (HPLC) and Fourier transform infrared
(FTIR) spectroscopy have been applied (Garside and Wyeth 2002).

Chromatographic procedures that reveal the relative fibre polymer chain length are becoming routine and have advantages over traditional viscometric methods in terms of the smaller quantity of material required. A variety of tin and iron weighted silks was analyzed by high-performance size exclusion chromatography (HPSEC) according to the method developed by David Howell, and a simple relationship was noted between the strength of the silk and the silk fibroin peak retention time, i.e. the time it takes to wash the dissolved sample through the chromatography column. The silk fabrics sampled were artificially thermally and photo-aged; the results suggest effective shortening of the fibroin polymer on ageing. Kathryn Hallett and David Howell have further refined their methodology (Hallett and Howell in this volume, pp. 143–50), which also presents a more robust approach to the correlation between mechanical properties and SEC-derived fibroin molecular weights.

In an alternative approach, advantage was taken of the fact that the characteristic highly ordered microstructure of fibroin, with β-sheet crystallites, leads to a typical FTIR spectrum, as illustrated in another paper in this volume (Sato and Sasaki, pp. 44–7). This is dominated by peaks arising from the vibrations of the peptide links in the backbone. The amide I band arises mainly from the C=O stretching vibration of the peptide group with a small contribution from N–H in-plane bending. The ratio of the IR peak intensities at 1615 and 1655 cm\(^{-1}\) has been taken as a crystallinity index for silk fibroin, since this reflects the relative proportion of the polymer in an organised β-pleated sheet relative to α-helix or random coil arrangement. By polarizing the IR radiation so that the electric vector is restricted to one direction and recording the IR spectrum with silk fibres aligned parallel and then perpendicular to the electric vector, the fibroin crystallite orientation can also be monitored. The 1615 cm\(^{-1}\) amide I carbonyl absorption is strong when the fibre is perpendicular to the electric vector, reflecting not only a high degree of crystallinity but also preferential alignment of the crystallites along the silk fibre axis. It has been noted that although the overall crystallinity may not change much on ageing, nonetheless the orientation parameter, the ratio of the apparent crystallinities measured from the polarized IR spectra of the fibres in the two alignments, drops as the fibre ages, and again there seems to be a reasonable correlation with the breaking strength of a variety of aged silks (Fig. 1).

Rationalising the relationship for silk

Microstructural modifications are the key to the change in behaviour of textile fibres on ageing, and the link with the chromatographic and spectroscopic data. Typical of natural structural materials, silk is a hierarchical composite. It is produced by the silkworm from the nematic-liquid-crystalline fibroin precursor, emerging from the spinneret as twin fibres (or brins) encased in a sericin gum. In commercial processing, this gum is washed off in water to leave the fibroin protein fibres. Fibroin is a fibrous polyamide with a MWt ~ 350 kDa and degree of polymerisation ~ 3000.

Typically, polypeptide chains are arranged in particular ways, as dictated by bonding across the peptide backbone; higher order structure results from further interactions between amino acid side groups. The long fibrous peptide chain of silk folds back on itself and hydrogen bonding then occurs across the chain to form a β-pleated sheet. The sheets stack to form crystalline regions with shear between the sheet layers being possible as the intersheet bonding is simply via van der Waals interactions. About five pleated sheets each with 12 chains make up a nanocrystallite, which runs along the fibre axis.

About two-thirds of silk fibroin is crystalline. The ordered β-sheet regions are separated by hydrophilic blocks in a block copolymer. Amino acids with larger side chains, such as tyrosine, are found within these intercrystalline zones. The picture is that of a typical thermoplastic fringed micelle or semi-crystalline polymer aggregate with crystallites embedded in an amorphous matrix, though for silk the crystallites are highly oriented (Fig. 2).

Moving up the hierarchical microstructure of the fibre, the nanocrystalline fringed micelles (2 × 6 nm lateral dimensions) make up the silk microfibrils. Aggregates of 1000 or so microfibrils then form the higher order fibrils which are about 1 μm in diameter, and so on to the fibre which is a wedge in cross-section, 15–25 μm across. At each level, the ordered elements are embedded within amorphous matrices derived from the non-crystalline components of fibroin.

In such a composite, the crystallites are key load bearers at the molecular and nano-level. The amorphous zones linking the crystallites affect the viscoelasticity of the material. This is reflected in part in an initial linear portion of a stress-strain curve. The matrix components serve to distribute the load among the microfibrils and crystallites, affecting the fibre tenacity or breaking strength. The matrix and the matrix-crystallite and matrix-microfibril interactions will also influence the toughness of the material (i.e. the energy represented by the area under the stress-strain curve).

Figure 1 The correlation between the measured breaking load and a polarized-FTIR-derived crystallite orientational order parameter for a variety of processed and aged silks (Garside and Wyeth 2002). For the purpose of illustrating the relationship, the identity of the particular silks is not significant.
Ageing will of course change all of this through alterations to the microstructure consequent upon modifications to the fibroin chemistry. Light and heat promote hydrolytic and oxidative degradation, reactions occurring the more readily in the open, amorphous intercrystalline matrix:

- Here the fibroin chain can be cleaved, compromising the tenacity as load transfer becomes unevenly distributed.
- The amorphous zones can eventually be cut into a number of small fragments which can then assemble into new nano-crystallites, but these will add little to the strength of the fibre.
- Some covalent cross-links can form between chains, generating a type of rigid network polymer. This would create a more brittle, less tough material.
- Further modifications of the amino acid residues will also result in reduced performance through effects on the secondary bonding interactions.

The correlations between the SEC and IR spectroscopy data and the breaking strength of the aged silks can then be rationalised. For chromatography, small silk fibres were immersed in a concentrated lithium thiocyanate solution. This disrupts the hydrogen bonds that hold the protein chains together, allowing the fibroin polymer to dissolve, but without cleaving the chains. On applying to the chromatography column, smaller polymer chains are washed through more slowly. The degraded silk samples had a much greater retention time (the time that the polymer fragments stay on the column) than pristine silk, demonstrating the prominent degradation of the polymer chains on ageing.

The polarized IR results suggested a link between fibroin crystallite disorientation and fibre tenacity. This is understandable since both can be considered a consequence of disruption of the amorphous regions. The constraint which dictates the exquisite organisation of the β-sheet crystallites is relaxed once the intercrystalline fibroin becomes broken, allowing the crystallites to reorient.

In both these instances, the analytical techniques are effectively measuring an amplified signal from the polymer molecules or crystallites compared to the relatively minor chemical modifications wrought to the polymer chains.

**Other microstructural parameters for interrogation**

Having confirmed that assessing aspects of the structural state of a fibre is a valid means of indirectly assessing its physical condition, we can ask what other microstructural parameters could usefully be investigated, and by what means, with the aim of estimating the condition of a historic natural fibre textile such as the proteinaceous silk ensign or the cellulosic linen Victory sailcloth; ideally non-destructively and certainly by using at most just microsamples.

Linen exhibits the same fringed micelle organisation of the fibrous polymer, in this case cellulose. The nanocrystalline micelles act as the building blocks for construction of the elementary fibrils, microfibrils and macrofibrils (Fig. 3). These are cemented with matrix materials, now hemicelluloses, pectin and lignin. Beyond the microstructural organisation (which

Figure 2 Crystalline (dark) and amorphous (light) regions in a semi-crystalline polymer aggregate. For silk, such nanocrystallites are exquisitely aligned along the fibre axis.

Figure 3 The hierarchical microstructure contained within a linen fibre.
can be seen for silk), in linen the fibrils are arranged in layers in the plant cell wall, wrapping around the fibre axis; furthermore, tens of individual short ultimate cells stick together to create the medium-length fibre. The same general results of ageing as noted for a semi-crystalline polymer aggregate will apply, but there will be extra changes in the microstructure due to the complexity of this cellulose fibre composite.

Proceeding up the fibre hierarchy from the molecular level, with ageing we can expect:

- Cellulose chain cleavage in the amorphous zones effecting fibre weakening and resulting in a lowered degree of polymerisation, increased crystallinity, a reduced average crystallite size, and some disorientation of the cellulose crystallites. There will be ensuing altered accessibility to the amorphous regions as the nature of these regions change through loss of material, crystallisation and some covalent cross-linking. Besides loss in tenacity, the viscoelasticity will be affected adversely, so permanent deformation will occur more readily.
- At the intermediate levels as a result of breakdown and embrittlement of the intracellular matrix we will see more facile cleavage of elementary fibrils and microfibrils. For example, there is evidence for brittle failure in the scanning electron micrographs (SEMs) of the Victory sail fibres after tensile testing (Garside and Wyeth in this volume, pp. 118–25). This compares with the ductile fracture observed in new sailcloth fibres.
- At the upper level of the hierarchy, the fibres will disintegrate through separation of the ultimate cells as the intracellular glue fails. This is beautifully highlighted by X-ray microtomography (XRM) of a short section of yarn (Fig. 4). This will result in facile slippage and uneven load distribution and hence reduced overall strength.
- Finally, as the cuticle fragments (as suggested in the micrograph of another Victory sail fibre), the bulk of the fibres reduce due to material loss from washing out and gaseous emission (the area density of a well-degraded area of the Victory sail appears to be about 80% of its original value) and the weave loosens. The fibres themselves may slip irrecoverably under lower forces with undue consequences on the strength of the yarn.

### Microanalytical methodology for condition monitoring

The question then arises as to whether these age-dependent microstructural changes are measurable, i.e. if there are related recordable signatures of ageing. A variety of primary techniques could be used to probe the microstructure directly (Table 1). SEC and electrochromatography perhaps also coupled with mass spectrometry (MS) can reveal alterations in the degree of polymerisation of a polymer chain.

Besides offering insight into the current physical state of an artifact, spectrometric and spectroscopic signatures could also be invaluable in highlighting the current chemical state of the object and predicting susceptibility to further deteriora-

### Table 1 Primary analytical techniques that are able to determine the changes in age-dependent microstructural parameters directly.

<table>
<thead>
<tr>
<th>Microstructural change</th>
<th>Primary technique</th>
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<tbody>
<tr>
<td>Altered degree of polymerisation</td>
<td>SE–HPLC/EC, SE–HPLC–MS</td>
</tr>
<tr>
<td>Change in crystallinity (degree and size)</td>
<td>XRD, FTIR, Raman</td>
</tr>
<tr>
<td>Crystallite disorientation</td>
<td>LM, XRD, pol-FTIR mic, Raman</td>
</tr>
<tr>
<td>Intracellular matrix failure (nano-micro scale)</td>
<td>SEM fractography</td>
</tr>
<tr>
<td>Ultimate cell separation</td>
<td>XRM, SEM</td>
</tr>
<tr>
<td>Looser weave, fibre thinning, cuticle fragmentation</td>
<td>XRM (density), SEM</td>
</tr>
</tbody>
</table>

While this list of techniques seems limited and perhaps limiting, there are other secondary methods able to probe a dependent physical effect, which should be equally valid in assessing condition. For example, Odlyha et al. have made good use of dynamic thermomechanical analysis (in this vol-

![Figure 4](https://example.com/figure4.png)
Moisture uptake is another age-related parameter that could be measured to reveal a textile's physical condition.

Water will probe the accessibility of the amorphous intermicellar matrix. Experiments designed to follow moisture absorption will also track changes in the higher level intracellular matrices and any disruption to the pores and channels within the ultimate cells. (The matrix of the middle lamella, the intercellular space, might be expected to be less hydrophilic in the first place.)

Moisture sorption can be determined by simple gravimetry, weighing fabric samples kept under controlled humidity conditions. It has been found possible to generate reproducible sorption data on microsamples as well using just a milligram or less of linen yarn, weighing the sample under conditions of varying relative humidity (RH) in custom apparatus. The data shown here for linen threads were acquired in trials using the IGAsorp instrument from Hiden Isochema (Table 2). As anticipated, moisture sorption reflects the relative ageing of the samples. Adsorption-desorption isotherms (25 °C) were recorded between 0 and 90% RH, and a kinetic determination of a 20–80% RH step was also made.

The adsorption-desorption isotherm shapes were subtly different for the three specimens, though showing hysteresis and reflecting Type IV behaviour in each case, i.e. suggesting relatively strong interaction with water followed by condensation within fibre pores (Fig. 5). The behaviour of the historic linen tended towards type V, with not only less excess water in the pores but also reduced structural (monolayer) and bound (multilayer) water, consistent with poorer access to amorphous regions and the composite matrices. In addition, the historic linen had a significantly shorter equilibration time in the kinetic experiment (1003 s) compared to the modern linen (1127 s) and heat-aged modern linen (1137 s). The results suggest that aged linen is characterised not only by the extent of moisture sorption but also by other related parameters such as the hysteresis and the sorption kinetics. Moisture sorption appears to be a valuable indicator of condition.

Our particular interest in moisture sorption as a potential signature of condition is connected to the fact that vibrational spectroscopy is able to report on the water content of organic materials. Water absorbs in the mid-IR region, but recording spectra on unprocessed fibres under conditions of varying RH is not straightforward. Slightly higher in frequency, in the near-infrared (NIR), spectral recording is much simpler. For the NIR, fabric samples laid against a probe readily acquire a reflection spectrum; the technique offers much potential for direct studies on textiles.

NIR spectra are the result of the excitation of overtones and combinations of molecular vibrational modes and so are rather more involved than mid-IR spectra, and are more commonly used to estimate concentrations for components of known spectral characteristics, but this is precisely what is required. The water absorption in the NIR is seen around 7000 and 5200 cm⁻¹ (Fig. 6). While these absorption peaks are overlapped by those arising from other hydroxyl containing species, such as cellulose, nonetheless it should be possible to estimate the relative contribution from water. Indeed moisture determination by NIR spectroscopy is routine for other applications in industry. The technique can, however, offer more than just moisture content. Since spectral acquisition takes only a minute (or less) even kinetic studies are feasible as the RH above the fabric is varied. On-site condition monitoring may not be so fanciful a notion.

**Table 2** The measured moisture sorption at 90% RH for three linen samples determined by microgravimetry on a 2 cm thread from each specimen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% moisture sorption ± 0.5</th>
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<tbody>
<tr>
<td>Modern linen</td>
<td>17.7</td>
</tr>
<tr>
<td>Heat-aged modern linen</td>
<td>15.6</td>
</tr>
<tr>
<td>16th-century linen</td>
<td>13.1</td>
</tr>
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</table>

![Figure 5](image) Absorption-desorption moisture isotherms for a modern linen yarn (● ■) and a naturally aged 16th-century linen yarn (◇ □). Diamonds denote absorption (the lower trace in each pair), while squares indicate desorption (upper traces).

![Figure 6](image) The NIR spectrum of a linen cloth recorded on a PerkinElmer Spectrum One instrument using an integrating sphere accessory under ambient conditions (RH 52%). Water absorbs at around 7000 and 5200 cm⁻¹.
Conclusions

The conservation and display of a textile should be informed by objective knowledge of its current condition. Through an appreciation of the make-up of natural textile fibres from the fibrous polymer molecule to the macrofibrils and fibre cells, and an understanding of the modifications that ensue on deterioration, it is possible to specify the microstructural changes that will affect fibre performance and could act as age-dependent markers. Some of these, such as the disorientation of silk crystallites or the breakdown of the intracellular cement in linen, can be followed directly, but by techniques that demand microsampling. Indirect methods that could probe microstructural parameters through the measurement of other dependent physical effects, however, might offer truly non-destructive interrogation. Gravimetric analysis of linen moisture sorption suggests that this is one such age-related parameter that bears investigation. Preliminary studies indicate that NIR spectroscopy should offer a versatile approach to the in situ measurement of the moisture sorption signature, hence revealing the condition of a historic textile.

Acknowledgements

I am indebted to Nell Hoare and colleagues at the Textile Conservation Centre for their support, and especially to Paul Garside for his invaluable input, both intellectual and practical. I would also like to acknowledge the encouragement given by the late Nigel Seeley, then at the National Trust, for our pilot studies on aged linen.

Reference


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