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Preserving silk: Reassessing deterioration factors for historic silk artefacts

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Abstract. The results of preliminary experiments in which we have investigated the effects of RH, as well as light, on the deterioration of new silk are reported. Relative humidities were chosen to reflect a variety of typical display conditions. The temperature and RH dependent kinetics of silk ageing were determined, by assessing the changes in mechanical properties and silk fibroin molecular weight. Initial results confirm that light (with the UV component excluded) is not necessarily the critical factor causing damage to silk objects. This has implications for the collections management and display of historic silks, leading to a reassessment of the most appropriate environmental parameters for the preservation of silk objects.

Keywords: silk, activation energy, deterioration rates, tensile testing, molecular weight

1. Introduction

Silk can be found in numerous examples of costume, flags and banners, tapestries, upholstery, etc., in collections worldwide. These objects are unique records, offering invaluable evidence of political, economic, and social histories. However, silk is susceptible to ageing, and the preservation of such artefacts is of significant concern.

The deterioration of silk causes embrittlement of the textile leading to splits and tears, and eventually a powdery and very friable fabric. Interventive conservation treatments, to consolidate silks, may radically alter their appearance, dramatically affecting the way in which visitors see and interpret the objects. Alternative preventive conservation methods are being sought to improve the longevity of silks in cultural heritage collections, by optimising the display parameters.

Light has long been considered the major cause of damage to silk objects, which has led to lower light levels for displays. However, recent research on historic tapestries casts doubt on this. Historic samples were in a severely degraded state despite being taken from the reverse of the tapestries where the dyes remained bright (Hallett and Howell, 2005a). Modern tapestries, artificially light aged equivalent to 400 years on display, were less deteriorated than historic samples. This suggests other environmental factors are important, and circumstantial evidence implicates raised humidity (RH), although there has been little research on this factor, with one notable exception (Hansen and Sobel 1994).

We have therefore begun to investigate the ageing of silk under a variety of conditions, including low and high RH, relevant to open display in English Heritage properties. The kinetics work presented here is a preliminary study, designed to supplement current data with rates of silk deterioration and the associated activation energies obtained from accelerated ageing. The results will be used to put further accelerated ageing experiments into context, allowing estimation of the equivalent display intervals under particular environmental regimes.

2. Experimental

To represent the plain silks which make up the majority of the English Heritage collection, medium weight habotai silk was used. Three pieces of silk, 25 x 100 mm (warp in the longest direction) provided replicates for each ageing condition. The replicates were placed in hybridisation tubes (Figure 1) and artificially aged for up to 6 weeks; one tube being removed from each set weekly.

The problem of relating the results of accelerated ageing experiments to real conditions are well documented (Feller, 1994; Erhardt and Mecklenburg, 1995). The assumption is made that the reactions occurring at elevated temperatures are the same, and proceed at proportionally the same rates to each other, as those occurring at room temperature. In this initial study a limited number of accelerated ageing parameters were selected. To induce measurable changes in a reasonable time, while not using extreme conditions which could invalidate the above assumption, temperatures of 50, 60, 70, 80 and 90 ºC were chosen. Saturated salt solutions were used to produce environments of approximately 30% RH ($MgCl_2$), 50% RH (NaBr) and 75% RH (NaCl) at each temperature. The individual RH levels are reported to vary by less than 6% over the temperature range (Greenspan, 1977).

Additional samples were placed in a daylight ageing chamber to study the effect of light on silk deterioration. The irradiation level is 7000 lux,

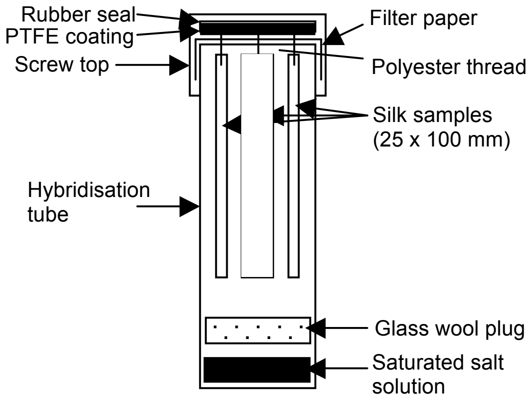

FIGURE 2. Kinetics ageing experimental set up

provided by a bank of 12 F20W/AD artificial daylight fluorescent bulbs. Measurements inside the hybridisation tubes show the illumination level was reduced to 1900 lux. UV was excluded by a polycarbonate filter. In terms of display this is approximately equivalent to 13 months at 200 lux or 4.3 years at 50 lux. For comparison, samples were also aged in the dark by wrapping the hybridisation tubes in aluminium foil and placing in the light box alongside the light ageing samples.

After ageing each sample was subjected to tensile testing to determine the maximum load at break and the tensile extension at maximum load. Data was acquired at 22±2ºC, 52±5% RH on an Instron 5544 instrument, adapting the standard method for fabric strips BS EN ISO 13934-1:1999, with gauge lengths of 50 mm and a crosshead speed of 10 mm/min. Results for strips which broke close to the jaws were discarded and average values calculated.

The weight-average molecular weight (Mw) for the silk fibroin of the samples was determined using High Performance Size Exclusion Chromatography (HPSEC). The method developed by Howell and Hallett (2005b) was used, with 1.5 mg of silk dissolved in 0.6ml of 21.5M lithium thiocyanate. The greater concentration and volume allowed three repeated runs to be performed. Eluate absorbance readings were taken at 280 nm and the data were recorded and processed with EZChrom software.

3. Results

3.1 Tensile testing

The tensile strength (measured as the maximum load at break) and tensile extension at break showed comparable changes. Figure 2 shows the maximum load at break results for samples aged at 75% RH and over the range of temperatures; similar trends were observed at 30% and 50% RH. There was a gradual reduction in the results over the length of each set of heat and humidity ageing conditions, with the most marked effects at higher temperature and high humidity. For example, at 75% RH and 90 ºC the maximum load was halved after just one to two weeks. There was also a noticeable increase in the yellowing of the samples at higher temperatures and humidities.

The ageing dependence on relative humidity is illustrated with the extension at maximum load for samples treated at 60 ºC (Figure 3). Perhaps surprisingly, at all temperatures the smallest change was observed for the samples kept at 50% RH. Although this is a tentative conclusion requiring confirmation, given the relatively small decrease in values coupled with the data scatter and size of the experimental error, it was confirmed by the maximum load results. Ageing at 75% RH caused the most deterioration.

For samples aged in the light box at room temperature (20 ºC light and 20 ºC dark) there was a small change after 6 weeks with little significant difference between the two sets of samples (Figure 2).

3.2 Molecular weight results

Silk fibroin is a semi-crystalline fibrous protein. Upon ageing the chain is cleaved, initially in the intercrystalline amorphous regions. It has been suggested previously that the fibroin HPSEC-determined weight-average molecular weight, Mw, might provide a marker of the state of deterioration.

Resource constraints have limited the analysis of the aged silk samples by HPSEC. However, the results so far appear to parallel the tensile data. Those samples aged at 20 ºC in the light box, whether exposed to light or not, show quite limited changes in Mw. On the other hand, high temperatures and high humidity seem to effect significant reductions in Mw (Figure 4).

3.3 Activation energy determination

Knowledge of the activation energy for silk deterioration will allow prediction of the ageing rate under particular temperature and RH levels. This can be used to estimate the proportional deterioration that can be expected over a specific display period and under defined environmental conditions. Literature data is limited to activation energies extracted from thermal analyses (Bora, et al., 1993; Garside and Wyeth, 2002), which may not be relevant to silk deterioration occurring on open display.

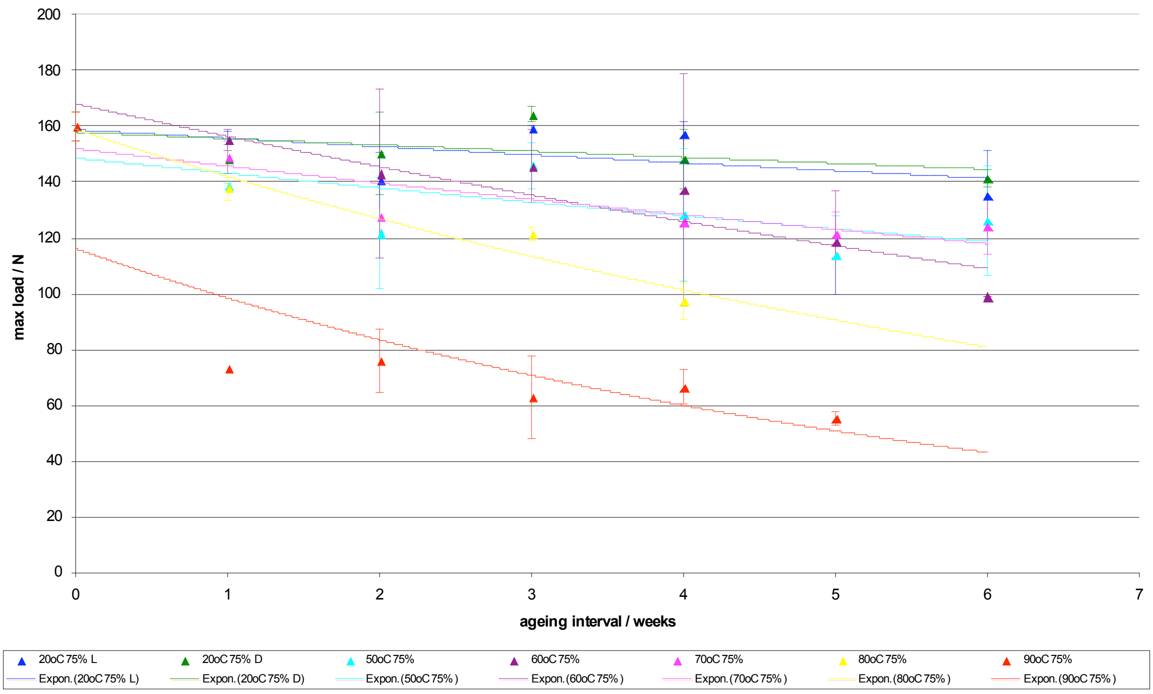

FIGURE 3. Maximum load results for samples aged at 75% RH. (Figures 2-4 show best fit exponential trend lines)

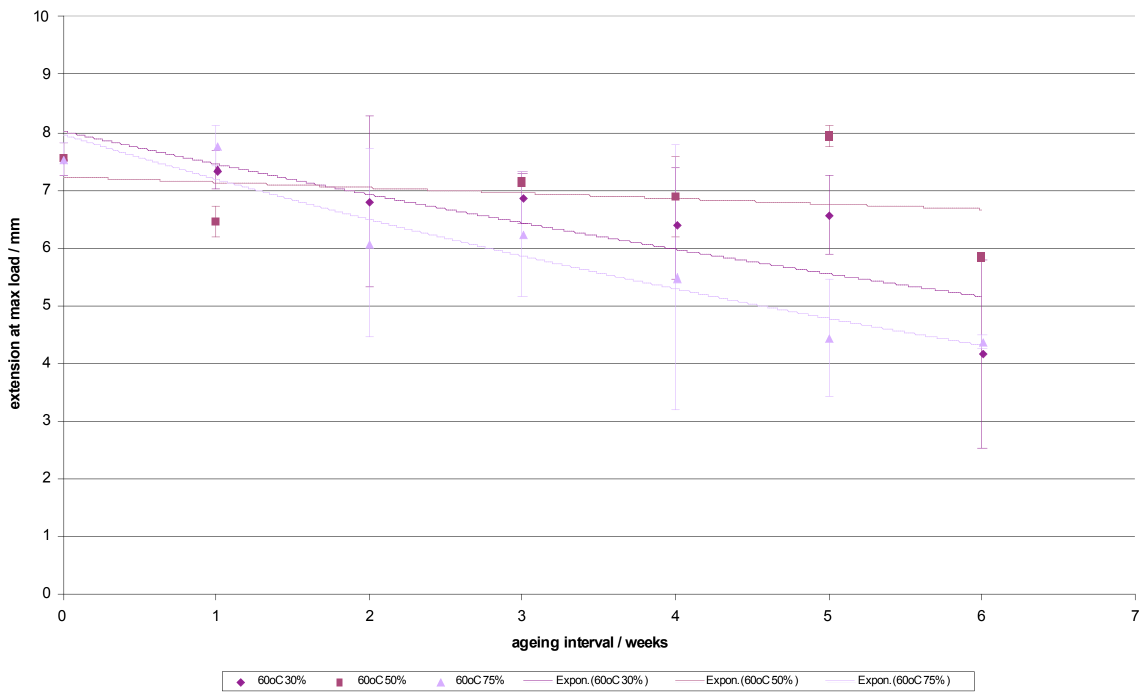

FIGURE 3. Extension at maximum load results for samples aged at 60 ºC

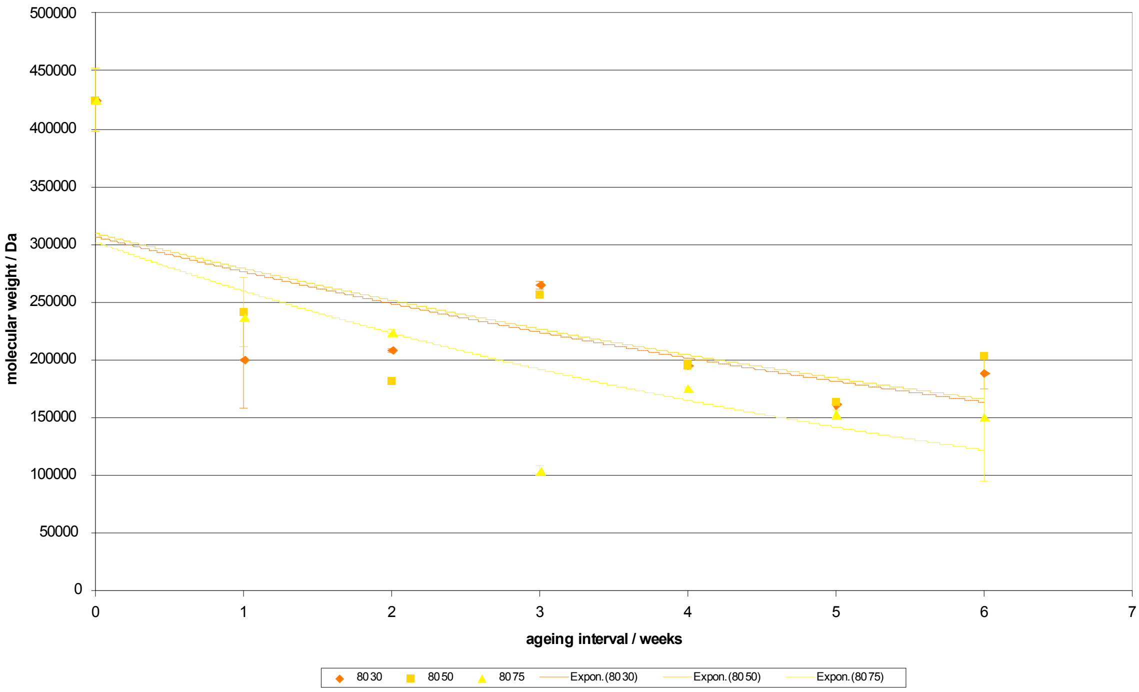

FIGURE 4. Changes in weight-average molecular weight after ageing at 80 ºC

In previous silk accelerated ageing studies, at 0 and 100% RH, we have found that tensile properties show an exponential decrease over time (Kim, et al., 2008). For the present data, the apparent first order rate constants of deterioration, k, were determined from the slopes of plots of the log (load or extension) versus time, following linear regression. The Arrhenius equation (equation 1) was then applied to determine the activation energy for deterioration at each RH level.

$$k = Ae^{-Ea/RT} \qquad (1)$$

In equation 1 k is the rate constant, A the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature (in K). E_a values were estimated from the slopes of graphs of ln(k) against the reciprocal temperature (Figure 5). Although the analyses of the extension and load data produce somewhat different activation energies (Table 1), the trend is consistent. For the three RH levels studied, E_a is highest at 50% RH and around half this value for 30% and 75% RH. This may arise from two competing mechanisms for ageing. Thermally promoted fibroin chain scission may predominate at low RH; whereas hydrolytic cleavage may become important at high RH. At intermediate RH silk-bound moisture may inhibit the former process. Of course, this interpretation must be treated with caution, bearing in mind the caveats suggested above concerning the significance of the data. Nonetheless, it is clear that the current outcomes have profound implications for the long term preservation of collections.

4. Conclusions

The results from this initial study show that UV-filtered light ageing caused little damage to silk. However, at elevated temperatures and relative humidity there is significantly enhanced deterioration.

Accelerated ageing periods are often difficult to relate to lengths of time on display in real conditions. However, the activation energies provide a means to do this. The average temperature in historic houses forming part of our wider study is 20 ºC. Using the activation energies we can calculate equivalent periods of display at 20 ºC, which produce the same extent of deterioration as accelerated ageing at highest temperatures. For example, using averages calculated from the values in Table 1, the same level of deterioration caused by one year's ageing at 80 ºC (the temperature used in long term ageing experiments) would be expected for around 167 years on display at 50% RH, but 11 years at 30% or 75% RH. After ageing at 80 ºC for one year the samples at 50% RH are predicted to have 45% remaining strength, whereas those aged at 75% RH are predicted to have no residual strength. Hallett and Howell (2005a) correlated weight–averaged molecular weight with the per cent

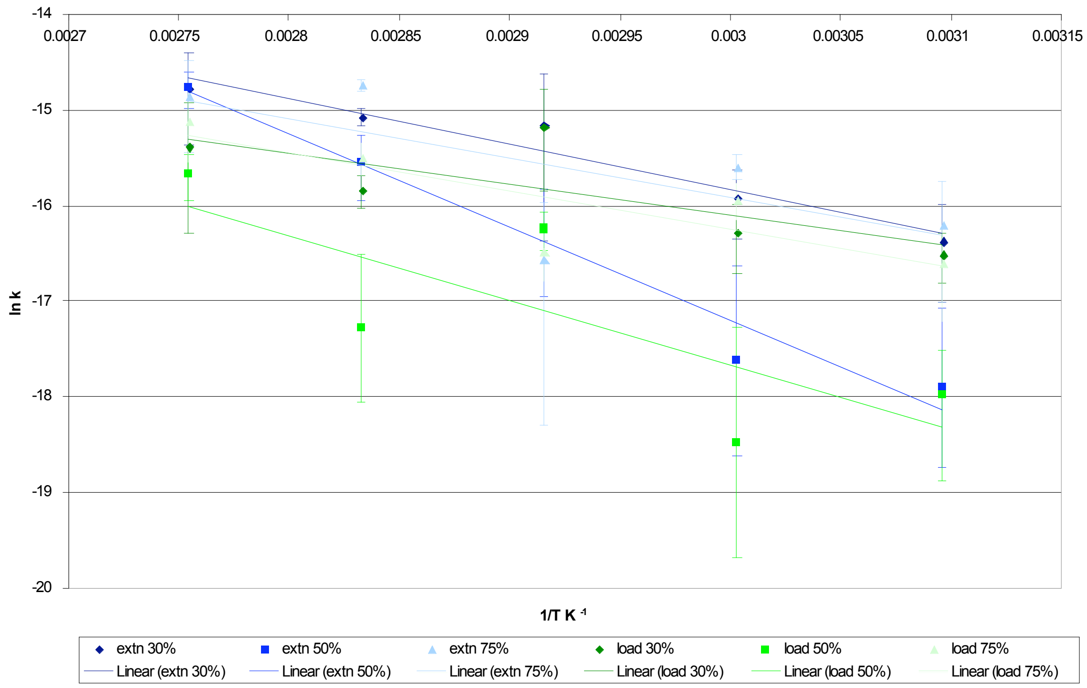

FIGURE 5. Arrhenius plot for tensile testing results

TABLE 1. Activation energies based on tensile testing results (in $kJmol^{-1}$)

	30% RH	50% RH	75% RH
Extension	40 ± 6	81 ± 9	34 ± 21
Max load	27 ± 13	56 ± 26	33 ± 12

elongation at maximum load, which gave 0-10% elongation for historic tapestry samples analysed by HPSEC. The results presented here are in this range which indicates the accelerated ageing regimes create deterioration approximate to that seen in the historic materials.

These results also emphasise the heightened risk that may be associated with display at the extremes of RH which are encountered in historic houses. The outcomes therefore indicate that it would be best to maintain an intermediate RH to enhance the long term preservation of silk collections. However, more detailed experiments are required to confirm these preliminary findings and to determine the extent, in terms of RH, of the safer display region. Further work is now in progress which includes studies at more RH levels, as well as considering possible synergistic effects between light and humidity and the influence of UV light. From the longer term accelerated ageing experiments it is hoped to better understand the causes of silk deterioration in historic houses, firmly establishing the key detrimental environmental factors and so identifying the optimum conditions for display.

This preliminary study confirms that light is not necessarily the critical factor in the deterioration of silk.

5. Acknowledgements

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