e-PS, 2008, 5, 41-46
ISSN: 1581-9280 web edition
ISSN: 1854-3928 print edition

www.Morana-rtd.com

e-PRESERVATIONScience

published by M O R A N A RTD d.o.o.

FULL PAPER

THE INHERENT ACIDIC CHARACTERISTICS OF AGED SILK

Jeongjin Kim*[1], Xiaomei Zhang[2], Paul Wyeth[3]

1. Practical Arts Education, Jinju National University of Education, Kyungnam, 660-756 Korea
2. School of Archaeology and Museology, Peking University, 5 Yiheyuan Road, Haidian District, Beijing, P.R.China 100871
3. The Textile Conservation Centre, University of Southampton, Winchester Campus, Park Avenue, Winchester, Hampshire SO23 8DL, UK

corresponding author:
jin1827@yonsei.ac.kr

Silks are frequently a cause of concern for conservators and curators. Amongst other critical challenges, textile acidity is considered to pose a risk. Consequently, it is common practice to carry out pH measurements when assessing condition. Enhanced acidity is usually ascribed to previous processing treatments, adsorbed pollutants, and oxidative deterioration. However, the results of the detailed study reported in this paper suggest that increased acidity of silk is an expected consequence of ageing, irrespective of the effector of deterioration. Degummed *Bombyx mori* silk fabric was subjected to artificial ageing by light, heat and heat plus high humidity, in air. The tensile strength of the fabric gradually decreased under each of the ageing regimes, seeming to follow first order decay. The pH values of saline extracts of the silks similarly decreased. There was a correlation between the tensile strength and the apparent acidity of the aged silks, which was independent of the ageing factor, at least to a 50% drop in performance. While the tensile strength of silk was compromised to a similar degree by high temperature plus high humidity ageing in nitrogen, anoxic conditions generated a five-fold lower increase in apparent acidity.

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 deteriorate, significant amounts are in poor condition. When considering the most appropriate curatorial and conservation approaches, characterization of the condition of the silk together with an understanding of the material and its degradation processes is essential. In support of this, we are pursuing research aimed at developing suitable methodology and supplementing current knowledge.

The key structural element of degummed silk fibres is the protein fibroin. Ageing results in changes to the fibroin chemistry and

received: 30/10/2008
accepted: 05/12/2008

key words:
silk, acidity, pH, ageing

microstructure,[1] affecting the fibres mechanical performance, appearance etc. A surface pH test, frequently applied to historic fabrics by conservators, often produces a low pH value.[2] This is usually taken as an indication of contamination and enhanced risk to the silk and may lead to the decision for an interventive neutralising treatment. The possibility that such increased acidity may, at least in part, be an inherent property of deteriorated fibroin is generally not considered.

We set out to investigate the apparent changes to the acidity of silk that accompany ageing, and report our results in this paper. New silk fabric was artificially aged under four extremes (high temperature and low humidity, high temperature and high humidity, high temperature and high humidity under nitrogen, and sunlight equivalent irradiance) and the acidity of the fabrics determined. As surface measurements are not indicative of bulk acidity,[3,4] the pH values of extracts were measured. Saline rather than water was used as the extraction medium to better draw out the accessible acid. The data were compared with the changes in tensile strength of the fabrics, as a traditional measure of the state of deterioration.[eg 5-10] In this ideal case, we show that there is a direct correlation between the increased acidity and the decreased performance of the silk.

2 Experimental

2.1 Silk

Plain weave silk fabric (Whaleys habotai silk, 40 gm^{-2}; thread count per cm: warp 147, weft 122) was degummed in a 1% sodium dodecylsulfate + 1% sodium carbonate solution for 1 h at 98±2 °C, rinsed thoroughly in purified water and dried at room temperature. The fabric was then cut into 25 mm wide strips along the warp for artificial ageing.

2.2 Artificial Ageing

Accelerated ageing conditions were selected to degrade the test fabric to a range of strengths after reasonable exposure times.
Dry thermal ageing - The fabric strips were placed in a laboratory convection oven at 125 °C for up to 20 days.

High temperature and humidity ageing – Silk strips were put in 150 ml glass hybridisation bottles (Sigma-Aldrich) with a tube containing 5 ml water, to provide 100% humidity (Fig. 1). The bottles were sealed using a screw-top with an underlying PTFE-faced rubber septum and placed in a fan-assisted convection oven at 100 °C. Ageing was continued for up to 20 days.

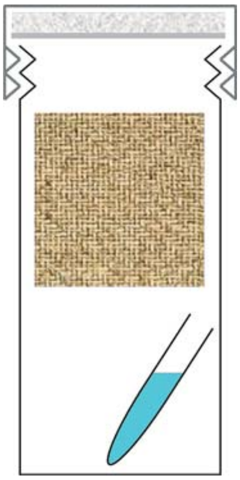

Figure 1: The set up for high temperature and humidity ageing of silk. Silk strips were arranged around the inside of 150 ml glass hybridisation bottles. A small glass tube containing 5 ml water was inserted at the bottom, and the bottles sealed using a screw-top with an underlying PTFE-faced rubber septum.

High temperature and humidity ageing under nitrogen– Samples were placed in glass hybridization bottles and aged as above. However, prior to sealing each bottle an oxygen absorber (Ageless, Mitsubishi Gas Chemical Co.) together with an indicator tablet (Ageless Eye) was added and the bottle flushed with nitrogen. The tablets, which turn blue in the presence of oxygen, remained pink during the ageing time course suggesting that anaerobic conditions, with oxygen levels of 0.1% or less, were maintained throughout.

Light ageing – Samples were exposed to simulated sunlight in a Q-Sun Xenon Test Chamber model Xe1 for up to 20 days. The temperature was maintained at 40 °C during the light exposure, and the system was programmed to deliver 0.4 W/m^2 of light energy at the wavelength 340 nm (equivalent to a total dose of 25 MJ/m^2 over one day). The positions of the samples were rotated regularly to ensure even exposure.

2.3 Tensile Tests

Test strips, measuring 2.5×5 cm, were conditioned for at least 72 h at 20±2 °C, 55±5% RH. Data were then acquired under the same ambient conditions on an Instron 5544 instrument, adapting the standard method for fabric strips BS EN ISO 13934-1:1999, with gauge lengths of 3.0 cm and a crosshead speed of 2 mm/min. Six replicates from each sample were analyzed. Data for replicates which broke close to the jaws were discarded and average values calculated for the remainder; there were four or more valid replicates in each case.

The tensile strength was taken as the load (N) at break.

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.[3,11] A small amount of each silk (20.0 mg) was soaked in 1.0 ml degassed 0.1 mol/l NaCl solution at 20±2 ºC and the pH of the extract measured using a BDH Glass+ combination microelectrode, following two point calibration (pH 4.00 and 7.00). Extraction was carried out in a capped 1.5 ml polypropylene vial for 30 min to allow complete equilibration. Saline was selected for the extraction to enable sodium ions to displace protons in the Donnan equilibrium,[12,13] effectively allowing equilibration of immobile, fibroin-associated acids and the solution, and a truer measure of acidity. The extractions were repeated in triplicate and averages 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. For convenience and consistency we chose simply to monitor the changing strength in the direction of the warp. The full numerical data are tabulated in Appendix 1. The results are presented as the proportional drop in performance (Fig. 2). In each case the data fit an exponential decay, following a linear trend in the semi-logarithmic plot, despite the variety of degradative mechanisms that may be operative, including hydrolysis and heat and light promoted oxidation. The slopes of the lines allows calculation of the rate constants for the apparent first order ageing processes (Table 1).

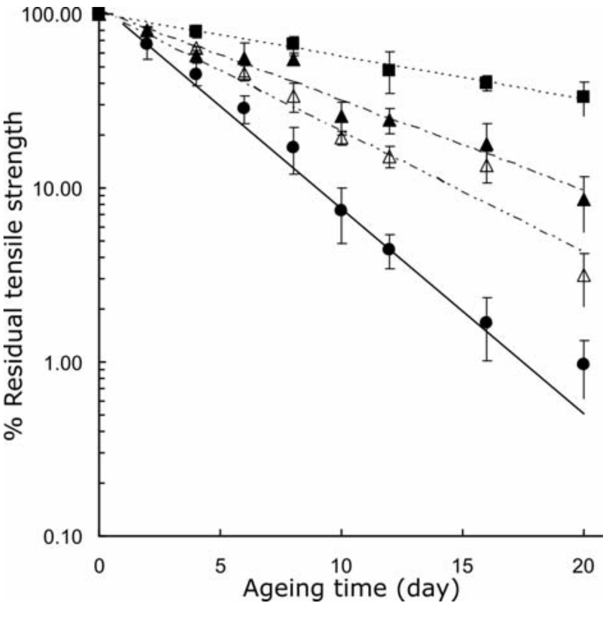

Figure 2. Plots of the percentage residual tensile strengths of the silk samples (logarithmic scale) versus ageing time for dry thermal ageing (■), high temperature and humidity ageing (▲), high temperature and humidity ageing under nitrogen (Δ), and sunlight equivalent ageing (●). The data points represent the averages for up to six replicates (error bars show the standard deviations). Linear regression best fits to around 10% residual tensile strength are drawn for first order exponential decay models.

	first order rate constant, k (days^{-1})			
	T	T+M	T+M (N2)	L
ts	0.056±0.003	0.12±0.01	0.14±0.01	0.25±0.02
pH	0.16±0.01	0.21±0.07	0.12±0.03	0.41±0.14

Table 1. First order rate constants (k) estimated for the initial parts of the four ageing time courses from the changes in tensile strength (ts) and the pH of extracts. [The slopes of the plots are –k/2.3]. T, dry thermal ageing; T+M, high temperature and humidity ageing; T+M (N_2), high temperature and humidity ageing under nitrogen; L, sunlight equivalent ageing.

The light ageing data confirm the significant damaging effect of sunlight with a UV component. Comparison of the rates for dry thermal ageing and high temperature and humidity ageing in air shows a markedly enhanced rate of deterioration caused by elevated humidity. Swelling of the silk consequent upon moisture uptake could account for the altered reactivity. However, maintenance of the rate increase under nitrogen further implicates hydrolysis rather than oxidation as the dominant degradative process affecting performance.

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. The numerical data is again given in the Appendix. Over the initial parts of the time courses the data (Fig. 3) seem to reflect the trends seen for the tensile strength semi-logarithmic plots. For each time course, the first order rate constant for the initial increase in apparent acidity of the aged silks was calculated by applying linear regression; the values are tabulated (Table 1). Only data points for those samples which had residual tensile strengths of 50% or more were included in the regressions. While for high temperature and high humidity ageing under nitrogen the value of the rate constant is similar to that for the change in tensile strength, for all the ageing regimes in air the rate constants for acid increase are nearly double those for the tensile strength reduction.

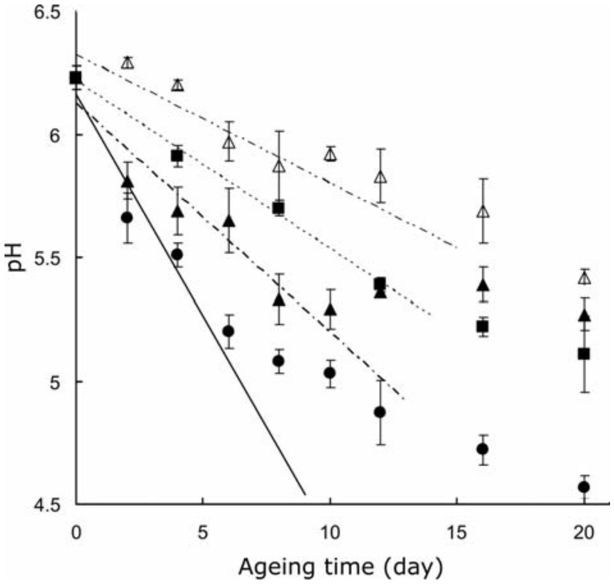

Figure 3: pH of silk extracts plotted against ageing time (data point symbols as for Fig. 2); bars show the standard experimental errors. The lines show best fits to the data points for those samples which had residual tensile strengths of 50% or more.

The deviation of data points below pH 5.4 from the first order trends may indicate that the pK_a values of the accessible weak acids of the aged fibroins are 4.4 or less, resulting in near complete ionization in the extracts at pH values above 5.4, and partial ionization below this.

3.3 The Correlation Between Acidity and Tensile Strength

A relationship between the apparent acid content of the bulk silk and performance is confirmed in the correlation plot (Fig. 4). Curves are drawn for easier visualization of the trends in the data; these were generated by regression using exponential fits to the data points for moist thermal ageing under nitrogen and for light ageing. For the anoxic ageing, the acid content of silk doubles as the tensile strength halves. The correlations for dry and moist thermal ageing in air and light ageing seem to be very similar, certainly to a reduction in performance of 50% with a concomitant five-fold rise in apparent acid content.

Similar relationships have been observed between the tensile strength of aged silk and the decrease in fibroin molecular weight[14] and fibroin crystallite disorientation.[15] Both of these latter parameters are directly affected by the cleavage of the peptide chain. The ageing-dependent increase in the apparent acidity of the bulk silk is also indicative of peptide disruption.

The consequences of thermal, heat, humidity and light promoted deterioration on fibroin at the molecular and microstructural levels are suggested in some detail in reference 1. Silk is a highly crystalline fibre, and it is the intercrystalline regions which are particularly subject to degradation. Here the bulkier and acidic and basic amino acid residues reside. Fibroin is somewhat richer in acidic amino acids (aspartic acid and glutamic acid).[16] In its native state the side chains of these acids may be involved in secondary bonding (hydrogen-bonding, salt linkages), helping to maintain some secondary structure. However, as the fibres deteriorate the polymer here is broken down. Consequent enhanced access may then allow a truer measure of the acid content of the protein. This may account for the increasing acidity of the silk extracts, with progressive deterioration during moist thermal treatment under nitrogen. Though, based on the molar ratios estimated from amino acid analysis of degummed *Bombyx mori* silk,[16] even for the most highly degraded samples, just a small fraction of the carboxylic acidic side chains contribute, presumably some having been neutralized in the original fabric processing, some being involved in salt bridges and others remaining inaccessible.

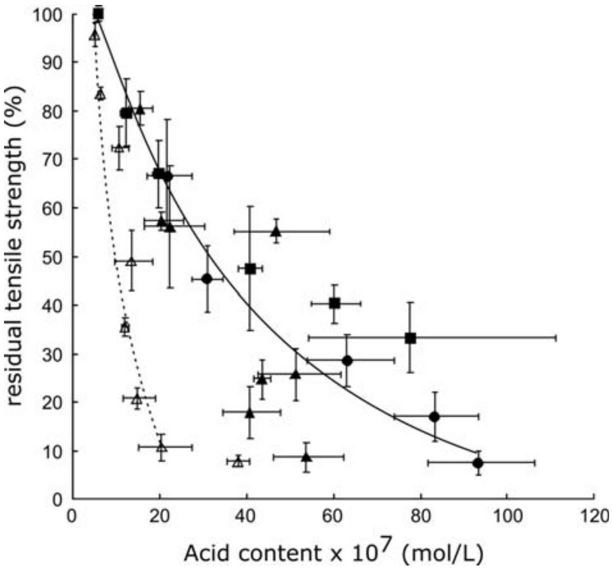

Figure 4: Correlation plot of apparent acid content of the silks versus % residual tensile strength (symbols as in Fig. 2). The acid content is simply taken as the average value of $10^7[H^+]$ for the extracts. Error bars reflect the standard deviations for the residual tensile strengths and the acid ranges of the extracts. The three data points for extreme light ageing have been omitted to allow expansion of the graph. Curves are drawn for easier visualisation of the trends.

In air the rate of loss of tensile strength afforded by moist thermal ageing parallels that for tensile strength reduction and acid generation under equivalent anoxic conditions. The straightforward conclusion is that both these parameters are directly dependent on cleavage of the fibroin chain. The acidity changes accompanying fibroin degradation in air appear somewhat more involved, with oxygen (which was in large excess in all three cases) effecting a five-fold enhancement in acid generation (and now on the order of the silk fibroin molar content).

4 Conclusions

Our results establish that the acid content of fibroin increases upon ageing. It is unlikely though that acidity could serve as a practical indicator of degradation. Even if sampling were possible, extraneous factors such as adsorbed pollutants would vitiate the condition assessment of historic silks by simple pH measurement of extracts.

Nonetheless, there are further valuable outcomes. The similar behaviour observed under the three different aerobic ageing regimes is striking. This suggests that fibroin chain rupture alone can account for the reduced performance of silk (at least to a 50% reduction), following dry and moist thermal ageing and light ageing. So, in the earlier critical stages (perhaps representing up to a few hundred years under standard museum conditions for degummed but otherwise unprocessed silk), any technique which can indirectly monitor the cleavage of the fibroin chain should enable effective condition monitoring, with reference to a standard model, irrespective of the particular environmental challenges which have effected ageing.

Another incidental outcome is confirmation that humidity is an important concern when considering the display and storage environment for silk. This is the topic of ongoing research.

In the context of conservation, it is worthwhile emphasizing that a lowered apparent acidity seems to be an intrinsic property of degraded silk and parallels compromised performance. Neutralising the acid, eg by washing in a buffered solution, may relieve concerns about acid-promoted peptide hydrolysis, but will not repair the fragmented polymer.

5 Acknowledgements

This research was completed while XZ and JK were Research Fellows in the AHRC Research Centre for Textile Conservation and Textile Studies, at the Textile Conservation Centre. We gratefully acknowledge the University of Peking for granting study leave to XZ. The work was supported by the Korean Research Foundation Grant funded by the Korean Government(MOEHRD), KRF-2006-214-C00104, awarded to JK. We are indebted to Maria Hayward, Director of the Research Centre, and Nell Hoare, Director of the TCC. The work would not have been possible without the support of all our colleagues at the TCC, especially Paul Garside.

6 References

1. P. Garside, P. Wyeth, *Chp. 4 Textiles*, in: E. May, M. Jones, Eds., *Conservation Science: Heritage Materials*, Royal Society of Chemistry, Cambridge 2006, pp. 56-91.

2. A. Tímár-Balászy, D. Eastop, *Chemical Principles of Textile Conservation*, Butterworth-Heinemann, London, 1998.

3. J. Vuori, S. Tse, *Preliminary study of a microextraction method for measuring the pH of textiles*, in: K. MacKay, B. Suzhay, J. Thompson, Eds., *Textile Speciality Group Postprints*, American Institute for Conservation, Washington 2005, pp. 63-73.

4. M. Montague, *pH testing methods in textile conservation*, in: P. Ewer, B. McLaughlin, Eds., *AIC Textile Speciality Group Postprints, 23rd Annual Meeting, St Paul, Minnesota, 1-4 June 1995*, American Institute for Conservation, Washington, 1995, 20-23.

5. X. Zhang, S. Yuan, *Research on the evaluation of the deterioration degree of silk fabrics*, Sci. Conserv. Arch., 2003, **28**, 31-37.

6. R.R. Bresee, G.E. Goodyear, *Fractography of historic silk fibers*, Adv. Chem. Ser., 1986, **212**, 95-109.

7. S.P. Hersh, P.A. Tucker, M.A. Becker, *Characterization of historical and artificially aged silk fabrics*, Adv. Chem. Ser., 1989, **220**, 429-449.

8. K. Hirabayashi, *The deterioration and preservation of silk fabrics*, Sci. Pap. Jap. Antiq. Art Crafts, 1981, **26**, 24-34.

9. M.A. Becker, N. Tuross, *Initial degradative changes found in Bombyx mori silk fibroin*, ACS Symposium Series, 1994, **544**, 252-269.

10. M.A. Becker, Y. Magoshi, T. Sakai, N.C. Tuross, *Chemical and physical properties of old silk fabrics + Biochemical analysis of 17 Japanese silk kimono lining fabrics*, Stud. Conserv., 1997, **42**, 27-37.

11. S. Saverwyns, V. Sizaire, J. Wouters, *The acidity of paper. Evaluation of methods to measure the pH of paper samples*, in: R. Vontobel, Ed., *Preprints 13th Triennial ICOM Meeting of the ICOM Committee for Conservation, Rio de Janeiro, 22-27 September 2002,* Vol. II, James and James, London, 2002, pp. 628-634.

12. J.H. Flynn, L.E. Smith, *Comparative pH measurements on papers by water extraction and glass electrode spot tests*, Tappi, 1961, **44**, 223-227.

13. A.M. Scallan, *The pH inside the fibre wall*, in: J.F. Kennedy, G.O. Phillips, P.A. Williams, Eds., *Cellulose Sources and Exploitation, Industrial Utliization, Biotechnology and Physico-Chemical Properties*, Ellis Horwood, Chichester, 1990, pp. 211-215.

14. K. Hallett, D. Howell, *Size exclusion chromatography as a tool for monitoring silk degradation in historic tapestries*, in: R. Janaway, P. Wyeth, Eds., *First annual conference of the AHRC Research Centre for Textile Conservation and Textile Studies, Scientific Analysis of Ancient and Historic Textiles: Informing Preservation, Display and Interpretation, Winchester, 13-15 July 2004*, Archetype Publications, London, 2005, pp. 143-150.

15. P. Garside, P. Wyeth, *Characterization of historic silk by polarized attenuated total reflectance Fourier transform infrared spectroscopy for informed conservation*, Appl. Spectrosc., 2005, **59**, 1242-1247.

16. I. Vanden Berghe, J. Wouters, *Identification and condition evaluation of deteriorated protein fibres at the sub-microgram level by calibrated amino acid analysis*, in: R. Janaway, P. Wyeth, Eds., *First annual conference of the AHRC Research Centre for Textile*

Conservation and Textile Studies, Scientific Analysis of Ancient and Historic Textiles: Informing Preservation, Display and Interpretation, *Winchester, 13-15 July 2004*, Archetype Publications, London, 2005, pp. 151-158.

7 Appendix

Mean percent residual tensile strength (%rts) and extract pH values (pH) for the aged silks. Standard errors (se) are also given. Denotation: Ap: ageing period (day), T: dry thermal ageing, T+M: high temperature and humidity ageing, T+M (N_2): high temperature and humidity ageing under nitrogen, L: sunlight equivalent ageing.

T				
Ap	% rts	se	pH	se
0	100.00	3.0	6.23	0.05
4	79.56	13.9	5.91	0.04
8	67.02	13.6	5.7	0.03
12	47.50	25.0	5.39	0.03
16	40.27	7.7	5.22	0.04
20	33.28	14.2	5.11	0.16

L				
Ap	% rts	se	pH	se
0	100.00	3.0	6.23	0.05
2	66.56	23.0	5.66	0.10
4	45.21	13.2	5.51	0.05
6	28.64	10.5	5.2	0.07
8	17.02	10.0	5.08	0.05
10	7.39	5.1	5.03	0.06
12	4.38	1.9	4.87	0.13
16	1.68	1.3	4.72	0.06
20	0.97	0.7	4.57	0.05

T+M				
Ap	% rts	se	pH	se
0	100.00	3.0	6.23	0.05
2	80.48	6.8	5.81	0.08
4	57.19	3.8	5.69	0.10
6	56.07	24.6	5.65	0.13
8	55.10	5.0	5.33	0.10
10	25.69	10.7	5.29	0.08
12	24.67	8.0	5.36	0.02
16	17.89	10.6	5.39	0.07
20	8.61	6.0	5.27	0.06

T+M (N_2)				
Ap	%rts	se	pH	se
0	100.00	3.0	6.23	0.05
2	95.72	4.9	6.29	0.02
4	83.59	2.6	6.2	0.02
6	72.27	8.9	5.97	0.08
8	49.03	12.4	5.87	0.14
10	35.42	3.5	5.92	0.03
12	20.64	4.3	5.83	0.11
16	10.70	5.5	5.69	0.13
20	7.75	2.1	5.42	0.03