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THERMAL ANALYSIS OF MODEL AND HISTORIC TAPESTRIES

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Dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and thermogravimetry (TG) have been used to characterise model tapestries, especially woven for the EC-funded project (MODHT) and to historic tapestries in royal palaces and museums. Modulus values of woollen threads from model tapestries are reported and the effects of traditional dyeing and mordanting processes quantified. TG, particularly of black woollen threads showed alterations in thermal stability. Tests of creep on immersion in water and subsequent heating to 90°C and on exposure to a controlled relative humidity programme were also used to rank these effects. Modulus values of historic woollen samples were also obtained and DSC studies of model and historic silk samples are reported together with preliminary atomic force microscopy (AFM) images of silk fibres.

Keywords: *atomic force microscopy, DSC, damage, dynamic mechanical thermal analysis, silk, tapestry, TG, wool*

Introduction

This paper describes the work performed on characterisation of materials used in historical tapestries, in particular the silk and woollen threads of the woven structure. Tapestries belong to one of the most precious and yet the most vulnerable part of European cultural heritage. It is the aim of this project to assess the physicochemical state of the threads, and hence the damage. The ability to identify and assess damage to cultural heritage, in particular by indoor environments, is a major and growing concern for many curators and conservators. It is recognised that the quality of indoor environments is influenced by a number of factors which include the actual location of the museum or historic building, the level and type of illumination used, and the ever-increasing numbers of visitors. It is also recognised that it is the resulting synergistic action of this complex matrix of variables that produces damage to objects.

The aim is to demonstrate that it is possible to quantify changes which occur in model tapestries after dyeing and mordanting and also accelerated light ageing, and to compare these with the observed changes in historical threads. This approach will provide a set of risk assessment parameters to indicate when tapestries will no longer be able to support their mass and to be displayed, and will contribute to knowledge which would serve to modify their conditions of display, method of storage, proposed conservation treatment, and assist with decisions concerning their conditions of loan. The overall aim of the MODHT project (MODHT 'Monitoring of Damage to Historic Tapestries' http://www.hrp.org.uk) is to improve the care and protection of historic tapestries through a better understanding of both the materials and methods used in their construction and their mechanisms of degradation at the molecular level. The project takes an interdisciplinary approach and involves collaboration of experts in a number of disciplines: conservator-restorers and conservation scientists who work with major tapestry collections, analytical and textile chemists.

In this paper thermoanalytical techniques are used for the first time to evaluate the mechanical properties and thermal stability of threads from historic tapestries. To assist in this process and to provide samples of suitable size for the tests, model tapestries have been prepared according to traditional techniques of weaving, mordanting and dyeing, and the threads from these tapestries have been characterised. Dynamic mechanical thermal analysis (DMTA) together with thermogravimetry (TG) and differential scanning calorimetry (DSC) has been used for this study. Previous applications of DMTA by two of the authors focussed on unprimed and primed canvas [1] and it was found to be of great value for monitoring the effects of accelerated ageing. The glass transition temperature (T_g) was observed to shift to higher temperatures and there were changes in the modulus values. The effect of selected conservation treatment for use on canvas supported paintings was also evalu-

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Table 1 Model wool tapestry samples

Name	Abbreviation	Mordant
Undyed	CON W	–
Red/W1 Madder no lye	RW1	Alum $Al_2(SO_4)_3$
Red/W1 Madder with lye	RW1_wl	Alum $Al_2(SO_4)_3$
Red/W2 Madder no lye	RW2	Oak gall/alum
Red/W2 Madder with lye	RW2_wl	Oak gall/alum
Red/W3 Brazil no lye	RW3	Alum
Red/W3 Brazil with lye	RW3_wl	Alum
Red/W4 Cochineal	RW4	Alum
Red/W5 Cochineal	RW5	Alum
Black W1 $FeSO_4$	BLKW1	Oak gall
Black/W2 $FeSO_4$	BLKW2	Oak gall
Black/W3 $FeSO_4$	BLKW3	Alder bark
Black/W4 Cu+$FeSO_4$	BLKW4	Oak gall
Blue/W1 Woad	BW1	–
Green/W1 Weld+woad	GRW1	Alum
Green/W2 Woad+weld	GRW2	Alum
Alder bark tannin	Alder W	Alder bark
Alum mordant	Alum W	Alum
Oak Gall mordant	Oak gall W	Oak gall
Yellow/W1 Weld	YW1	Alum
Yellow/W2 dyers' Greenweed	YW2	Alum

ated [2]. Differences between untreated and treated material became increasingly apparent when subjecting the unprimed and primed canvas to varying conditions of relative humidity [3]. Recently a more robust arrangement has been developed which allows the sample to be subjected to controlled and programmable conditions of relative humidity [4].

Creep tests involving complete sample immersion in water have also been performed, particularly for parchment samples where they were heated through their shrinkage (denaturation) temperatures and the amount of shrinkage measured [5]. This test has also been used in this paper to study the effect of the various dyes on small pieces from model woven woollen tapestries, also light aged. Light ageing was performed in the Textile Conservation Department at Hampton Court Palace. Samples were aged for 400 h in the Xenotest (90 Megalux hours). This is equivalent to about 400 years exposure under normal museum lighting conditions. For model woollen tapestries 14 dyes and three mordants (alum, alder bark and oak gall) have been used (Table 1 lists the materials and gives the corresponding acronyms). The red dyes include madder, Brazil wood, cochineal (with and without lye), the yellow includes weld and dyers' greenweed, the blue is based on woad and green is made from their mixtures. The black dyes include iron sulphate and one of the black dyes uses additional copper sulphate. Table 2 lists the dyes used for the silk samples reported in this paper and the corresponding acronyms.

Table 2 Model silk tapestry samples

Name	Abbreviation	Mordant
Undyed	CON S	–
Alum	Alum S	Alum
Oak gall	Oak gall S	Oak gall
RS1a Brazil wood	RS1a	Alum
RS1b Brazil wood with lye	RS1b	Alum
Red/S2a Madder	RS2a	Alum
Red/S2b Madder with lye	RS2b	Alum
Red/S2c Madder with lye	RS2c	Alum
Red/S3 Cochineal	RS3	Alum
Blue/S1 Woad	BS1	–
Green/S1b Woad+weld	GS1b	Alum
Yellow/S1b Weld	YS1b	Alum

The aim of the thermoanalytical tests is to establish a database for model wool and silk tapestries, and to identify markers to assess the extent of damage in accelerated aged materials, and then historical materials. Testing of the threads and small woven pieces will also be described by thermogravimetry (TG) and differential scanning calorimetry (DSC). TG has been used by two of the authors to characterise historical parchments [5], and DSC has been used by one of the authors to distinguish between non-oil and oil based paint media in samples from paintings that were 500 years old [6]. More recently it has been used by two of the authors to study the effect of accelerated ageing of paint tempera and site ageing where the paint tempera strips were exposed as dosimeters for characterizing the quality of indoor environments in museums and galleries [7].

Methodology

Dynamic Mechanical Thermal Analysis (DMTA)

In DMTA testing was performed using a sinusoidal load over a range of temperature with controlled heating and a static load under isothermal conditions. The former option provided values for the glass transition temperatures (T_g) and the latter option gave values for Young's modulus and creep behaviour of materials under controlled environmental conditions.

A Rheometric Mark 3 Dynamic Mechanic Thermal Analyser was used in reverse configuration for measurement of stress/strain and for creep of samples either immersed in water or subjected to a controlled

relative humidity environment. The reverse configuration allows in situ monitoring of wetting and heating through to 90°C and was originally used for monitoring shrinkage in parchment [5].

Stress strain

Stress/strain mode measures the sample displacement (%) under the action of a linearly increasing force (0–10N) over 10 min, and identifies the region of linear viscoelastic behaviour from which Young's modulus values are calculated. Samples (20 mm× 10 mm) or single threads (weft/5 mm long) were supported in the tensile clamp. Threads were removed from the woven pieces from the weft direction, and measurements were made so that the applied force was along the weft direction, along which the tapestry experiences load on display. Traditionally in tapestries the pattern or scene is formed by the weft thread hand-woven into the warp. The warp which is usually linen or wool is entirely covered by the weft thread which can be wool, silk or metallic threads. Historical threads which were sampled from the tapestries by the conservators-restorers were mainly weft threads, and for our studies wool and silk. In the case of historical threads, where available, threads with a free length of 5 mm were used for the measurements. As this is a non-destructive form of testing measurements were made directly after sampling prior to destructive analysis.

Creep

The samples (woven wool, 20 mm×10 mm) supported in tensile mode were subjected to a small static load (0.1N) and the resulting displacement on (1) wetting and heating to 90°C (2) exposure to controlled RH programme monitored.

Creep in water

For testing in water conditions were as follows: (1) 10 min in air, (2) 10 min in water at room temperature, (3) 30 min as the temperature of the water was increased to 90°C, (4) 10 min in water at 90°C, (5) removal from water and drying in air at room temperature. Initial displacement of the samples gave an indication of the ease of sample wettability, and the amount of shrinkage on immersion in water gave an indication, when the samples were heated in water through the shrinkage temperature.

Creep in controlled RH

For testing under controlled conditions of relative humidity each sample was placed in a drying bottle containing silica gel for 24 h prior to testing. Test conditions were set up as follows:

10 min at 10% RH, relative humidity increase of 1% RH/min to 80% RH, 10 min at 80% RH. The change in displacement (%) was monitored as % RH increased.

The rate of moisture uptake was calculated from the slope of the displacement trace.

Thermal scans

Samples (5 mm threads) were clamped in the tensile mode and heated from 30 to 220°C at 3°C min^{-1} under the action of a sinusoidal load (frequency 1 Hz) and force of 2N. This measurement determines the viscoelastic parameters of wool and silk which include the glass transition temperatures.

Thermogravimetry (TG)

Thermogravimetry was performed on model wool tapestry (undyed and dyed, unaged and aged) samples under oxidising conditions. Samples were heated in a Shimadzu TGA-50 analyser to 750°C in a platinum crucible at 10°C min^{-1}. The flow rate of the purge gas (oxygen) was 40 mL min^{-1}.The resulting thermal degradation curves gave a measure of the change in thermal stability of the samples after the dyeing process and also on accelerated light ageing.

Differential Scanning Calorimetry (DSC)

Threads from model woven silk samples and some historical silk threads were measured using a Shimadzu DSC-50 analyser. Samples (0.4–0.6 mg) in the form of cut pieces of threads were placed into either standard aluminium crucibles (5 mm OD) or especially prepared micro-aluminium crucibles (3.5 mm OD) and heated to 500°C at 10°C min^{-1} in nitrogen purge gas or oxygen purge gas (60 mL min^{-1}) respectively. The resulting DSC curves in nitrogen provided information on the nature of transitions in the 230–250°C temperature range and DSC curves in oxygen provided information on the thermooxidative behaviour. The enthalpy of thermooxidative degradation was measured and compared to that of the control sample and the ratio used as a marker for change in chemical composition and hence damage assessment.

Atomic Force Microscopy (AFM)

A few silk fibres were carefully separated from the silk sample with a pair of tweezers and placed in the centre of a microscopy slide. With a pipette, a droplet (50 to 100 μL) of methanol (spectroscopic grade) was carefully deposited onto the fibres. After two minutes

the methanol evaporated, leading the silk fibre to bind to the glass substrate. This protocol ensured that the silk fibres were sufficiently fixed to the surface for the duration of the experiment (around 4 h). The glass slides were then transferred to the sample stage of an AFM (JPK, Berlin – Germany) mounted on an inverted optical microscope (Olympus - IX71). AFM images of the silk fibres were performed in contact mode (Microlever tip – C lever – Veeco Cambridge). The contact force between the tip and sample was estimated to be in the order of a few nano-newtons. The AFM tip was aligned on top of a silk fibre by adjusting the position of both the glass slide and AFM tip, using precision micrometers present on the AFM sample stage. For each sample, areas of 5 by 5 μm for different silk fibres were imaged at a resolution of 512 by 512 pixels at a scan rate of 1 Hz.

Results and discussion

Stress/strain

Wool

- Model tapestry: Figure 1 shows the Young's modulus values of woollen model tapestry threads (5 mm). The dark bars correspond to the unaged wool threads (undyed, dyed and mordanted) and the lighter grey coloured bars to the corresponding light aged threads. These measurements indicate that dyeing and mordanting processes in most cases reduce the stiffness of the threads to varying degrees. Unaged wool woven threads have values of Young's Modulus in a range 5000–2000 MN m^{-2} (Fig. 1). All dyes except yellow/W2 (Table 1) show a decrease in the values of Young's Modulus (range between 3500–2000 MN m^{-2}), among which blue/W1, yellow/W1, black/W1 and Red/W2 with lye undergo the most reduction. The light aged samples in most cases demonstrate a further reduction in stiffness and have lower values of Young's modulus, in particular Red/W3 with lye which has a value for the unaged sample of 4446 MN m^{-2} (*SD*=147), while the aged one has a value of 2385 MN m^{-2} (*SD*=141). Values were recorded as an average of at least 5 measurements.
- Historical tapestry: Young's modulus values for historical threads range between 1500–500 MN m^{-2} (Fig. 2). This is considerably less than the lowest values for the accelerated aged threads and indicates that a significant loss in stiffness has occurred. Figure 2 shows threads from Royal Palace in Madrid (PNM1-2), museums in Bruges (BRU2-3) and Hampton Court Palace tapestries (HRP1-3). The names of the historical tapestries are listed in Table 3. Four samples measured from tapestries from the Royal Palace Madrid (PNM1) and (PNM2) gave values in the range 1666–1114 MN m^{-2}. Two samples were measured from tapestries from Bruges (BRU2) and (BRU3) gave values of 1900–1720 MN m^{-2} . In one of the tapestries from Hampton Court Palace (HRP1) most of the threads were below 1000 MN m^{-2}, and these included green, blue and beige. In the case (HRP2) over half the threads tested were above 1500 MN m^{-2}, and included pink, black and blue threads. For the Hampton Court Palace (HRP3) values were on the whole below 1500 MN m^{-2} and the threads were mainly red in colour. Conservation records show that some of these tapestries have undergone previous restoration namely PNM2, BRU2 and BRU3. Characterisation of the dye used in the threads is being performed by other partners in the project.

Silk

- Model tapestry*:* Measurements on threads from woven silk model tapestries have been made on Red/S3 cochineal, BS1/woad, and YS1b/weld. Young's

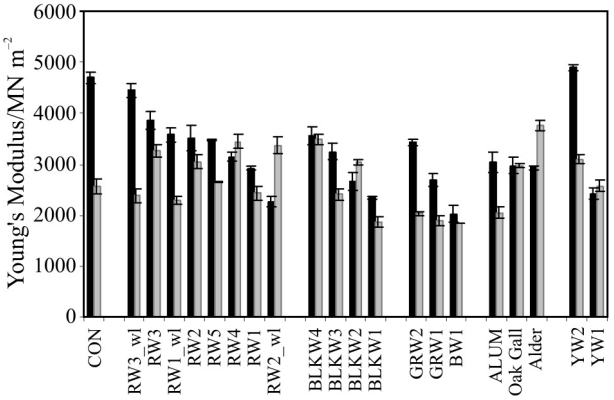

Fig. 1 Young's modulus for model woollen threads: dark bars correspond to unaged and the lighter grey coloured bars to the light aged threads

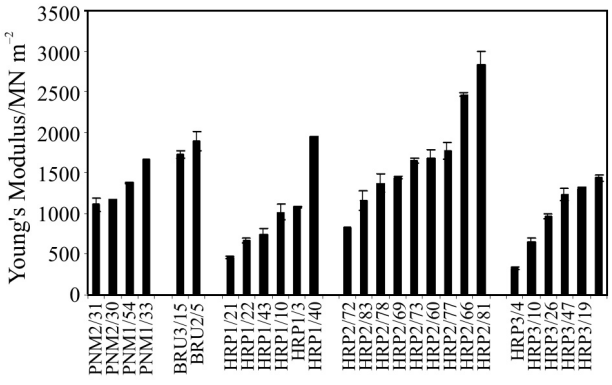

Fig. 2 Young's modulus for historical woollen threads (Royal Palace Madrid (PNM1–2), Bruges (BRU2–3) and Hampton Court Palace (HRP1–3))

Table 3 Name and period of the historical tapestries tested

Abbreviation	Name of tapestries	Date
PMN1	Dedalo e Icaro	Brussels, 1545
PMN2	Jupiter y Ganimedes	Brussels, 1545
PNM5	Neoptolemo y Polixena	Brussels, 1545
PMN7	Rafael y Tobius	Brussels, 1550
PNM8	Atalanta y el jabali de Calidonia	Brussels, 1620
BXL1	Justitia disarmed by Misericordia	1519–1524, Brussels
BXL2	Christ before Pilate	c. 1520, Brussels
BXL3	The Legend of Herkenbald	1513, Brussels
BXL4	Man and the seven sins	1519–1524, Brussels
BRU1	Verdure with the coats of arms of the Brugse Vrije (fragments)	c.1530, Bruges
BRU2	Mary's Dedication in the Temple	1639, Bruges
BRU3	Miracles of Holy Mary of the Potterie series	c.1630, Bruges
HRP1	The Triumph of Time over Fame	Flemish C1500–1530
HRP2	History of Tobias	Flemish C16
HRP3	Triumph of Death Over Chastity	Flemish C1500–1530

Modulus values were between 20000–15000 MN m^{-2} where the lower values were for the dyed samples, in particular cochineal. Light ageing reduced the stiffness of the samples except for cochineal dyed samples where the dye and mordanting processes had already caused a significant decrease before light ageing. The mordanting and dyeing process for the cochineal samples involved the use of copper turnings which could account for the more significant changes. The mordanting procedure involved the following: the bath contained alum and salt in water heated to boiling and to which copper turnings were added. The pH was 3.15. When the heat was turned off the silk was immersed and left for 24 hrs while cooling to 22°C and pH of 3.97. This was rinsed until pH of waste water was 6. The dyeing procedure involved the preparation of a solution of gum arabic containing oak galls, copper turnings, cochineal and tumeric. This was boiled for 2 h and then made up to 50 dm^3 at 70°C and pH of 4.8. The silk was immersed for 10 min and removed. The liquor was then boiled and the silk immersed and boiled for 2 h [8].

- Historical tapestry: Samples from selected tapestries from Hampton Court Palace (HRP1, HRP2, and HRP3) were measured, in which all from HRP1, and a number from HRP2, and all from HRP3 broke during measurement. Samples from HRP2 gave values considerably lower than those for the accelerated aged samples, and samples from the Royal Palace of Madrid (PNM1-2) gave slightly higher values than for HRP2 samples but still lower than for the accelerated aged samples. Further testing using smaller loads is in progress to enable majority of historic samples to be measured. In addition single fibres are also being measured.

Creep

Creep in water (wool; woven piece)

Figure 3 gives the displacement (%) (left hand Y-axis) curve *vs.* time and the temperature profile (right hand Y axis) of the creep test for control and dyed samples (BLKW1-3). The negative displacement represents shrinkage and positive displacement expansion. On the displacement curve the numbers refer to (1) contraction on immersion in cold water (2) further shrinkage on heating to 90°C (3) time taken for onset of expansion on drying in air and (4) the maximum expansion on drying in air. The time at which the sample is removed from water is indicated by the drop in the temperature profile. The results of the complete set of woollen samples are listed in Table 4. All showed varying amount of shrinkage on immersion in water at 20°C, followed by further shrinkage with increasing temperature. On removal from water at 90°C an expansion (partial recovery) occurred after varying periods of time in air for the different samples. Different dyes and mordants showed varying degrees of maximum shrinkage in water at 90°C and varying recovery times. Maximum shrinkage in water at 90°C occurred for Red/W2 and the

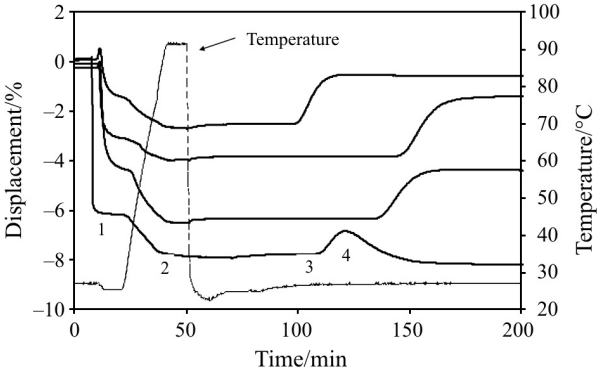

Fig. 3 Displacement (%) *vs.* time with temperature profile for black model wool tapestries. From top to bottom: BLKW2, BLKW3, BLKW1 and control

minimum for woven pieces treated with oak gall mordant. Unaged samples had a greater shrinkage than aged ones in 12 out of the 16 measured pairs (Table 4). Recovery time of unaged after wetting and heating to 90°C relative to control revealed that a large difference from the control occurred in the case of Red/W5 and alum mordant. In 12 out of the 16 measured pairs the unaged samples have a longer recovery time than their corresponding light aged samples (Table 4). The largest difference occurred in the undyed sample where drying time is much greater for the aged than the unaged.

In Fig. 3 all three black samples show differences in behaviour relative to the undyed unaged sample in terms of initial shrinkage, maximum shrinkage, time for recovery (Table 4). Black/W2 shows a much smaller contraction and shorter time for recovery than BLKW1. The smaller contraction may be due to reduced elasticity due to reduced α-helical content in the wool. This is confirmed by DSC measurements in nitrogen of these samples (Fig. 4) which show reduction in the transition observed between 235–240°C. Transitions in this temperature range have previously been described as markers for the α-helical content in wool [9]. BLKW2 contains more iron sulphate than BLKW1 and this may be the reason for the difference in behaviour in creep test. All the black samples except Black/W3 contain oak gall as the mordant. Black/W3 was prepared using alder bark tannin. Black/W4 in the creep test behaves similarly to Black/W3 but shows significant differences when measured by DSC (Fig. 4) and TG which is discussed later in this paper.

Creep during RH ramp (10–80% RH)

- Wool (woven piece): Generally it was found that samples showed an initial expansion and that after 60% RH this was followed by a pronounced shrinkage. It was also found that the slope of the expansion curve varied with the dye and mordant used and with light ageing. To further distinguish between the samples the rate of moisture uptake relative to the control was calculated and expressed as a percentage. Figure 5 summarises the data for the samples tested; the positive side refers to samples where moisture uptake was faster than the control and the negative side slower than the control. In the case of mordants, alum appears to retard moisture uptake more than oak gall. In the latter this is enhanced on light ageing. In the case of dyes, red madder (RW1/RW2) and cochineal (RW4/RW5), the black dyes (BLKW1/BLKW2), and the light aged green dyes (GRW1/GRW2) retard moisture uptake. Dyes such as weld, Brazil wood, and woad, particularly the light aged samples enhance moisture sorption.
- Silk (woven piece): In situ monitoring of increasing RH (10–80%) showed that the displacement (%D) of silk increased. This continued until 70% RH when a small shrinkage was observed. The behaviour of unaged undyed control sample, together with the cochineal dyed sample RS3, woad

Table 4 Creep test in water for woollen pieces

Sample	%D in cold water	%D at 90°C	Time for recovery/ min
CON W	–6.16	–7.74	38.9
CON W 400	–4.10	–6.06	84.9
BW1	–2.66	–3.20	95.4
BW1 400	–3.38	–3.85	68.8
GRW1	–3.34	–4.11	53.0
GRW1 400	–2.63	–2.83	44.7
YW1	–2.86	–3.55	77.5
YW1 400	–2.76	–3.14	72.6
Alum W	–2.93	–4.55	160.7
Alum W 400	–2.28	–3.70	51.5
GRW2	–3.10	–3.97	56.1
GRW2 400	–2.92	–3.76	55.3
RW1_wl	–4.21	–4.69	55.8
RW1_wl 400	–2.91	–3.49	61.1
RW1	–3.88	–5.25	114.3
RW1 400	–2.87	–3.39	69.4
RW2	–7.13	–9.62	69.4
RW2 400	–4.28	–6.16	66.5
RW2_wl	–4.68	–6.41	70.9
RW2_wl 400	–4.46	–6.43	56.7
RW3	–5.51	–5.51	64.8
RW3 400	–4.60	–4.60	60.7
RW3_wl	–3.87	–3.87	67.4
RW3_wl 400	–1.32	–1.32	45.5
RW4	–5.21	–5.21	86.0
RW4 400	–5.74	–5.74	106.4
RW5	–7.16	–7.16	134.0
RW5 400	–7.70	–7.70	69.8
BLKW1	–4.44	–6.51	84.5
BLKW1 400	–3.85	–6.01	56.4
Oak Gall W	–0.45	–0.90	56.1
Oak Gall W 400	–1.50	–2.92	76.0
BLKW2	–1.53	–2.65	47.0
BLKW3	–3.03	–3.98	85.4
BLKW4	–3.81	–4.74	83.4

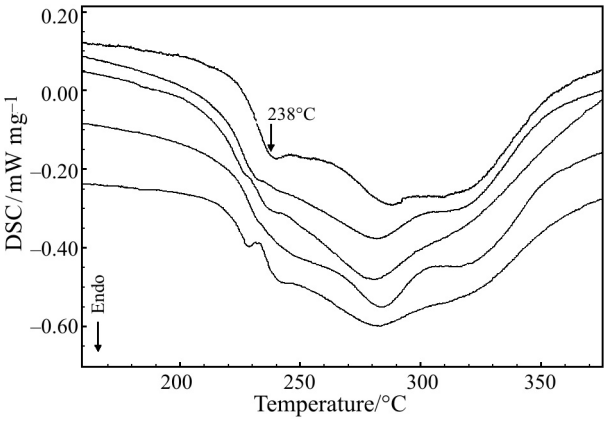

Fig. 4 DSC curves of black model wool tapestries, showing difference in peak at 238°C. From top to bottom: Control, BLKW1, BLKW2, BLKW3 and BLKW4

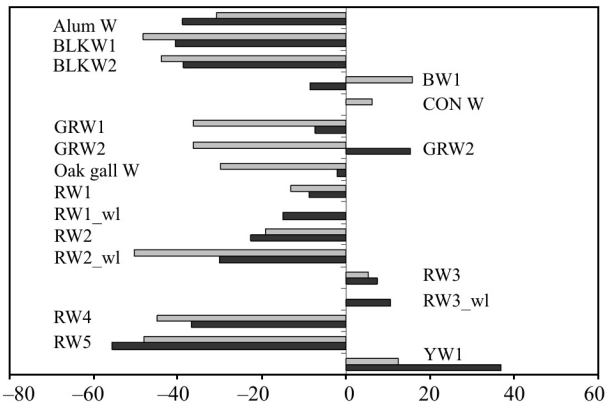

Fig. 5 Rate of moisture uptake (RH) relative to the control (%tage) for woollen samples (positive indicates a faster and negative side a slower rate)

(blue/W1) and weld (yellow/W1) dyed samples, all unaged, have been studied. Of these the most responsive to moisture relative to the control were weld and then woad. This can be explained on the basis of the chemical structures:weld and woad are classified as flavone and indigoid dyes respectively. The behaviour of cochineal dyed was similar to the control. Further work is in progress to characterise the remaining dyed silk samples.

Thermal scans

The thermal scans provide the variation in storage modulus (elastic component) and tan delta (ratio of inelastic to elastic contributions from the amorphous state of the sample) with temperature. The maximum in the tan delta peak was taken as the (T_g) which for both wool and silk in the 'as-received' state was found to occur at high temperatures (above 200°C) and just before the onset of degradation (c. 250°C). Light ageing of the undyed threads caused a shift to higher temperatures. The effect of dyeing as measured for weld and woad dyed samples caused a shift of about 5°C to lower temperatures. In wool the transition in this temperature range has been correlated with loss of α-helical content of keratin and shrinkage [9]. The transition in silk threads is not so clearly documented. A recent paper suggests that a conformation change of silk fibroin occurs from a random coil to a beta-sheet structure at 230°C [10].

TG

TG results on samples (woven wool pieces) showed differences between control and dyed (unaged and aged) samples, particularly in the temperature region 420–600°C. The effect of dyes and mordants can be separated into two groups: in the first the temperature at which degradation of the dyed samples occurs is lower (hence lower thermal stability) than that of the undyed sample and this group contains alder bark, alum mordants, and black dyed samples (containing $FeSO_4$), in the second the temperature at which degradation of the dyed samples occurred is almost equal to or higher than that of the control contains all the red, green, blue, and yellow dyes, and oak gall mordant.

Of the black dyes in the first group, BLKW4 showed the significantly reduced thermal stability as it was completely degraded at much lower temperatures (about 500°C), while the other black dyes (BLKW1, BLKW2 and BLKW3) were completely degraded at temperatures near 600°C (Fig. 6). This is probably due to the additional effect of the copper sulphate which is used together with iron sulphate in BLKW4 but is not present in the others.

In the second group the effect of the dye (from lowest to highest) can be summarised as follows: red/W1 without lye (almost no visible difference from the control)<red/W2 without lye<red/W3 with lye and without lye, red/W4<red/W1 with lye<red/W2 with lye, red/W5 (Table 1). This indicates that lye has had an ef-

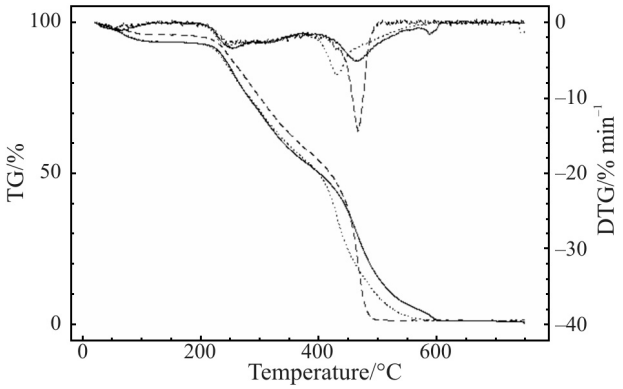

Fig. 6 TG and DTG curves for control (full line), BLKW2 (dash) and BLKW4 (dot)

Table 5 Enthalpy of historical silk threads relative to the control sample

Sample	Colour	$\Delta H/\Delta H_c$
Model silk tapestry		
CON S		1.00
CON S 400		0.93
RS3	Red	0.94
RS3 400		0.89
YS1b	Yellow	0.91
YS1b 400		0.93
BS1	Blue	0.90
BS1 400		0.91
RS2a	Red	0.99
RS2a 400		0.89
RS1a	Red	0.91
RS1a 400		0.88
RS1b	Red	0.90
RS1b 400		0.90
RS2b	Red	0.91
RS2b 400		0.84
RS2c	Red	0.91
RS2c 400		0.84
GS1b	Green	0.90
GS1b 400		0.93
Historical		
HRP1/5	Green	0.62
HRP1/9	Beige	0.60
HRP2/51	Green	0.85
HRP2/59	Green	0.81
HRP2/29	Blue	0.80
HRP2/42	Yellow/Green	0.77
HRP2/28	Beige	0.71
HRP2/18	Pink/Purple	0.71
HRP2/32	Green	0.71
HRP2/22	Yellow	0.71
HRP2/47	Blue	0.70
HRP2/49	Green	0.63
HRP2/48	Pink	0.61
HRP2/45	Yellow	0.59
HRP2/50	Blue	0.59
HRP2/16	Red	0.58
PNM1/14	Green	0.67
PNM 1/48	Green	0.63
PNM1/51	Yellow	0.54
PNM1/13	Green	0.51
PNM2/11	Yellow	0.60
PNM2/9	Yellow	0.56
PNM2/10	Green	0.49
PNM2/29	Green	0.42
PNM2/21	Green	0.42
PNM2/23	Yellow	0.41
PNM5/19	Yellow	0.62
PNM7/17	Yellow	0.72
PNM7/18	Yellow	0.53
PNM8/3	Yellow	0.80
PNM8/16	Yellow	0.80
PNM8/9	Yellow	0.66
PNM8/17	Yellow	0.57
BXL1/12	Yellow	0.33
BRU1/13	Beige	0.88
BRU2/13	Red	0.47
BRU3/12	Yellow	0.62

fect on the thermal stability of red/W1 and red/W2 but not so much in the case of red/W3. Yellow/W1 and W2, green/W1 and W2 are among those with greater difference from the control. The effect of oak gall mordant is similar to that of red/W3 in terms of its thermal stability and differs from that of the other mordants.

TG results on the light aged samples showed that most aged dyed samples had a decreased thermal stability compared to the corresponding unaged ones. Among those, green/W1 and red/W2 with lye were significantly changed. Some showed the reverse effect and this was most pronounced for Red/W2 without lye, and alum mordant samples. There are no apparent differences for yellow dyed, oak gall mordant, and alder bark mordant samples in terms of the TG results.

DSC

DSC thermooxidative degradation studies on silk samples showed a major exothermic peak between 210–420°C. Measurements of peak area showed a decrease for accelerated light aged and historical samples. A ratio of the measured peak area relative to that of the control sample was calculated and values are shown in Table 5. All model tapestry samples gave values between 1–0.84. Historical samples (PNM 1–2) were in the range 0.72 to 0.41. Red silk thread (BRU2/13) from the Bruges tapestry (1639) also gave a value close to the lower range of the PNM tapestries (0.44). The lowest value obtained so far (0.30) was for yellow silk thread (BXL1/12) [Brussels tapestry

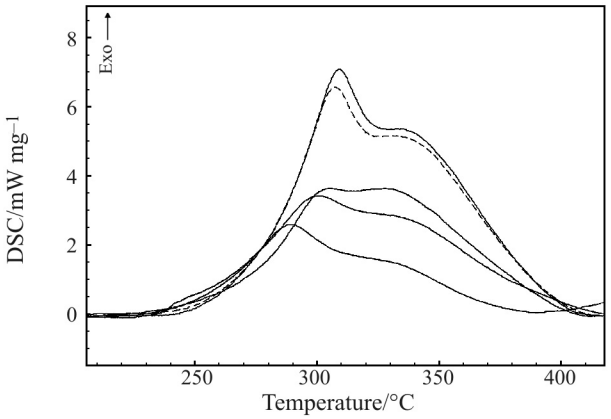

Fig. 7 DSC curves of model and historical tapestries, showing difference in peak between 210 and 420°C. From top to bottom: undyed unaged, light aged undyed for 400 h, BRU3/12, PNM2/11 and BXL1/12

(1519–1524)]. Samples from Hampton Court Palace (HRP 1) gave values of 0.60 and 0.62, and (HRP 2) values between 0.85 and 0.58 (Table 5). Low values indicate that the sample is more altered in its chemical composition and more damaged.

Figure 7 shows the DSC curves for the control and light aged sample together with selected historical threads (yellow). Sample BXL1/12 [from Brussels tapestry BXL1 (1519–1524)] has the lowest enthalpy value and appears to be the most damaged.

Woollen threads also show an exothermic peak in a similar temperature region as the silk samples but with a reduced intensity. Historical samples tested so far do not show values as low as those for silk. This approach may prove to be a useful rapid test for damage assessment of threads.

Atomic Force Microscopy

Atomic force microscopy was performed on unaged (control) and light aged (400 h) silk fibres samples as shown in Figs 8a, b. As the fibres present a significant radius of curvature, it was more suitable to present the error-signal images as they would emphasis small height changes on the sample. Generally, the error signal image is taken as the derivative of the conventional height image. In Fig. 8a, one may notice the occurrence of long fibres along the length of the sample. It is known that the structure of silk is based on the six residue repeat Gly-Ser-Gly-Ala-Gly-Ala arranged in anti-parallel beta sheets which self assemble to form crystalline and non-crystalline regions [11]. The crystalline regions are sometimes referred to as (nano) fibrils and these are reported to have an average length of 1–2 μm with a width between 20 and 170 nm.

However, these structures seem to disappear on the aged sample (Fig. 8b). The long fibrils are now

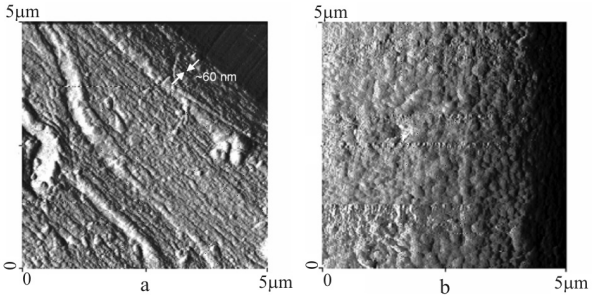

Fig. 8 AFM images: a – the control and b – the light aged silk sample

smaller segments, which suggests a loss in the fibrillar organization. This may be an indicator for ageing effect and/or damage fingerprint. This effect was also found to be the case on some of the historical samples. This leads to the conclusion that ageing does have a significant effect on the topology of the silk fibre. Further assessments are required to quantify this level of degradation using the AFM.

Conclusions

The testing of threads from model woollen tapestries has demonstrated that dyeing and mordanting procedures produce alterations in the physico-chemical properties of the threads which are then further affected by light ageing. The stiffness of the threads is reduced and some preliminary measurements using nanoscale X-ray diffraction techniques (to be reported elsewhere) show that the crystallinity of some light aged silk threads is reduced. DMTA (thermal scans) shows that dyeing reduces the glass transition temperature and so the structure of the amorphous part is also affected. DMTA (creep test) on wool demonstrates clearly the differential response of dyed (unaged and light aged) samples to wetting, shrinkage on heating to 90°C, and relative humidity increase from 10–80% RH. The increase in moisture uptake in the weld and woad dyed samples can be explained in terms of their lower T_g compared to the undyed sample. Differences can also be explained in terms of the surface effect of dyeing and mordanting which is further investigated by one of our partners in the MODHT project using X-ray surface analysis. Differences can also be explained in terms of changes in chemical composition (macro-scale) and this is demonstrated by changes in thermal stability of the samples from TG and DSC analyses. The testing of historical threads has shown that alterations in their physico-chemical properties are more significant than those for the model threads. As samples were removed from the back of the tapestries light cannot be considered as the main damaging factor. Other influences

such as fluctuations in temperature, relative humidity and exposure to pollutant gases need to be considered

The results have also demonstrated that damage is readily measured and varying degrees of damage can be identified and used to assess the state of samples from historical tapestries. Damage assessment as developed in these measurements can lead to early warning of alterations in the state of the threads and eventually in the fibres. Though measurements have focussed on threads recent progress in mounting of samples in the DMTA have shown that it is possible to measure the modulus of single fibres. On the basis of damage assessment at the macro level by DSC, samples were selected for assessment by atomic force microscopy. From DSC data sample BXL 1/12 (yellow silk, Brussels 1519–1524) showed a very low enthalpy ratio which means a high level of damage. In AFM for the control sample it was possible to image fibrils and measure their width. This structure was disrupted for the light aged sample and almost completely in the case of sample BXL1/12. This indicates in future it will be possible to relate changes at the macro level to alterations at the nanoscale by AFM.

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