

Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

CHARACTERISATION OF LEATHER SAMPLES BY NON-INVASIVE DIELECTRIC AND THERMOMECHANICAL TECHNIQUES

M. Odlyha^{1}, G. M. Foster¹, N. S. Cohen¹ and R. Larsen²*

¹Chemistry Department, Birkbeck College, University of London, 20 Gordon St., London WC1H 0AJ United Kingdom

²Det Kongelige Danske Kunstakademi – Konservatorskolen Esplanaden 34, 1263 København Denmark

Abstract

A description is given how the dielectric coaxial technique measuring in the microwave region has been used for monitoring drying processes in leather samples. It is also shown how the coupling of this technique together with dynamic mechanical analysis enables the simultaneous recording of changes in the dielectric properties, related to the moisture content of the material, together with the mechanical properties as a function of time or temperature. The samples studied include unaged and artificially aged goat and calf leathers. Measurements using the dynamic mechanical analyser are presented over a range of temperature which includes the shrinkage temperature. During the drying process, values of mechanical modulus or displacement and dielectric permittivity are recorded as a function of time or temperature which includes the temperature range of leather shrinkage, and from previous research report of Larsen [1] this has been associated with the chemical state of the leather samples.

Keywords: dielectric coaxial probe, drying profiles, dynamic mechanical analysis, leather, microwave, moisture content, permittivity

Introduction

In a previous paper it was demonstrated that the rate of humidification of artificially and naturally aged canvas samples could be monitored and that the values for the corresponding moisture content of the samples could be calculated using the coaxial dielectric probe technique in the microwave region [1]. In this paper further work, in collaboration with the School of Conservation of the Royal Danish Academy of Art, is described using the coaxial probe technique and measurements are presented which have been made on leather samples. Additional measurements are included where the coaxial probe and network analyser is coupled to the dynamic mechanical analyser. In the case of the latter the sample was heated through the temperature range which includes the shrinkage temperature of the leather. Hence the change in

* Author for correspondence: e-mail: m.odlyha@chem.bbk.ac.uk

the viscoelastic properties of leather through the shrinkage temperature can be measured. This is an important parameter since it has been demonstrated that its value directly relates to the age of the leather sample and its state of preservation, and hence to changes in the collagen structure [2]. Other measurements made on the same samples are reported elsewhere [3].

The open-ended coaxial dielectric technique

The present work uses the dielectric analysis technique in the microwave frequency range, in particular 2.45 to 20 GHz. In this frequency range only the response of small polar molecules can be observed and so it can respond directly to the presence or absence of water in the material. The measuring system also differs from the one used at lower frequencies where the sample is placed between two parallel plates. A coaxial line is used to convey the signal (originating from a network analyser—a microwave source) to the sample and the reflection characteristics of the signal are analysed. The resulting complex permittivity of the sample undergoing measurement is related to the reflection coefficient by matching the fields at the boundary of the probe and the sample [4].

The value of relative permittivity of water at the lower end of this frequency range 2–3 GHz is constant and is called the static permittivity (or dielectric constant). Water has a high static permittivity (80.1 at 20°C) so its presence (or absence) can easily be detected. This particular property of water has made it possible to measure the moisture content of a number of materials such as grains [5], foods [6], wood [7], and textiles [8]. Thus the value for the permittivity (or relative permittivity ϵ') of materials in this frequency range is highly correlated with the moisture content of the material. Recent work has indicated the potential of using a micro probe (0.86 mm OD) [9] to measure non-invasively the moisture content of a range of materials.

The coaxial probe in this frequency region measures the free water which is present in the sample. The amount of free water in the sample can be estimated by measuring the permittivity value for the humidified sample (at 2.45 GHz) and dividing it by the value for water at 2.45 GHz at room temperature. To confirm this approach, independent measurements were initially made by thermogravimetry (TGA).

Dynamic mechanical thermal analysis

DMTA measures the viscoelastic properties of materials. A variable amplitude sinusoidal mechanical stress is applied to the sample to produce a sinusoidal strain of pre-selected amplitude. The parameters measured are the complex modulus E^* which is resolved into real and imaginary components, E' (Pa) and E'' (Pa), and these are known as the storage and loss modulus respectively. The ratio of the loss modulus to the storage modulus (E''/E') is referred to as $\tan\delta$. E' is related to the stiffness of the material and $\tan\delta$ gives a measure of the degree of elasticity of the material. Also changes in the displacement (in terms of micrometers) either under a given load (at a particular frequency) or static load (i.e. DMTA in TMA mode) can be measured.

Samples

The following sumac leather samples were chosen for this study: (a) unaged goat leather (b) artificially aged (10 years) goat leather (c) unaged calf leather (d) artificially aged calf leather. These are reference materials which were used to test the methodology and new instrumentation to demonstrate the potential of the measuring system [3].

Objectives

The first objective was to show that leather samples after immersion in water can be measured using a non-invasive non-destructive dielectric technique. The difference in behaviour after water immersion for a selected time (e.g. 24 h) can then be considered as a marker to distinguish between unaged and aged leather samples of a given type. The drying profiles of these samples were also recorded as a function of time. This again could provide valuable information on differences in the behaviour of aged leather samples. In addition some historic samples from bookbinding leathers were examined [1]. Where immersion in water was not performed and where perhaps it was inappropriate, the moisture content of the samples was determined by thermogravimetry (TGA). In addition to estimation of moisture content, the objective was to determine the shrinkage temperature (T_s) and accompanying changes in the modulus or stiffness of the samples by dynamic mechanical analysis (DMTA).

Experimental procedure

Dielectric coaxial probe

The equipment used in this study consisted of an 8720C Hewlett-Packard Network Analyser system with a semi-rigid coaxial probe. The methodology and measurement technique have been described elsewhere [2, 9]. The open end of a coaxial probe (0.86 mm O.D.) was placed in contact with the sample and the reflection characteristics of the signal at the interface were measured using the network analyser. Further developments in the software have made it possible to record complex relative permittivity values of the samples in a continuous manner as a function of time and at a selected frequency, and hence to directly monitor changes in the samples during their exposure to different environments. The frequency selected for the measurements as a function of time in this chapter is 2.45 GHz and the frequency scans were made over the range 2.45 to 20 GHz.

The system as shown in Fig. 1(a) was used to monitor the drying of leather samples. Samples were placed on the wire gauze in the sample cell (Fig. 1(b)) and the coaxial probe was positioned on the sample with optimum contact (determined by the level of noise obtained in the frequency scan). The starting values for sample complex permittivity were recorded. The measuring system was activated to read complex permittivity values of the sample continuously as a function of time.

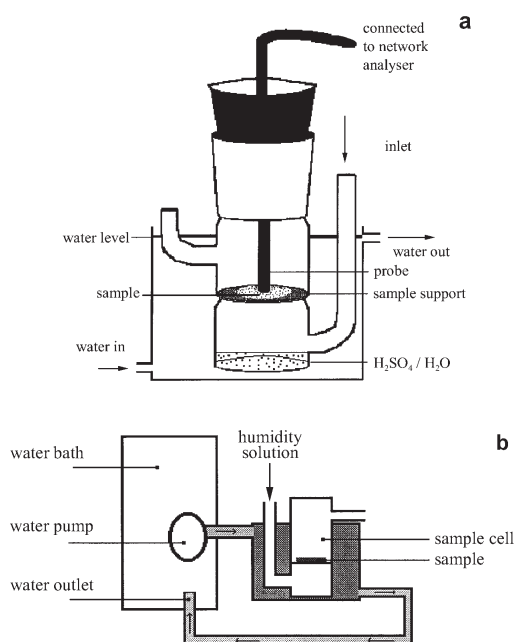


Fig. 1 Modified glass sample cell for the drying of leather samples (a); Experimental system used for humidification and drying studies (b) (Odlyha, 1996)

For the drying of samples solutions of H_2SO_4/H_2O (w/w) were used to generate the required environment (RH 33%). They were introduced in turn through the side arm with a teat pipette. Air was bubbled through these solutions using a peristaltic pump to assist in the circulation of air at the required relative humidity and temperature.

Combined technique (microwave coaxial dielectric & dynamic mechanical analyser)

One of the problems in making measurements on solid surfaces is to provide good contact between the end of the probe and the sample and to use reproducible pressure during the measurement. The addition of a Rheometric Scientific DMTA Mk3 instrument has provided a means of controlling the pressure [10]. Figure 2 shows how the sample is held in the clamp of the DMTA under tension and the position of the coaxial probe as it is held in the clamp. This has allowed the measurement of changes in displacement under a tensile force with changes in moisture content of the sample at a particular temperature.

Modifications were made to the DMTA measuring head which involved the removal of the optical window assembly and its replacement by two 3 mm aluminium plates (3 mm thickness) in which 10 mm holes had been drilled to accommodate the coaxial probe. This is described in detail elsewhere [10]. In order to maintain the

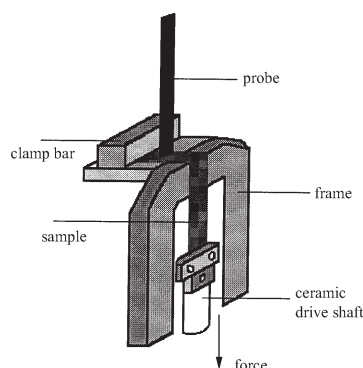


Fig. 2 Modified tensile clamp to allow drying under load (DMTA), with dielectric probe attachment for moisture content determination

probe in a vertical position over the DMTA head a clamping system with vertical and horizontal adjustment was constructed to hold the probe.

Dynamic mechanical analysis

A Rheometric Scientific DMTA Mk3 instrument was used to provide a measure of the viscoelastic properties and changes in displacement under a tensile force. Measurement of these parameters was made over a temperature range that included the shrinkage temperature. Leather samples (goat and calf) were also measured by DMTA in the TMA mode (i.e. under a static compressive force of 0.2 N) in order to investigate their drying behaviour. Samples were soaked in water for 24 h and then placed in aluminium DSC crucibles to provide support. Two experiments were performed. One set of samples was held at a constant 30°C, and the displacement change was plotted as a function of time as the leathers dried. Similar samples were then heated at 2°C min⁻¹ through the shrinkage temperature and the displacement change plotted against temperature.

Results

Dielectric coaxial probe: drying profiles and moisture content determination

The drying of wet leather samples (previously immersed in water) was performed in a modified glass cell containing (H₂SO₄/H₂O) corresponding to 33% RH. The results are shown for two different leathers: aged goat leather and aged calf leather [Figs 3(a)–(f)]:

Figure 3(a) provides the variation in relative permittivity (ϵ') vs. time (min) during the drying of aged wet goat leather which had been immersed for 24 h in water prior to the measurement. The lower curve in Fig. 3(a) shows the loss component (ϵ'') as a function of time. The initial moisture content was estimated from the value of

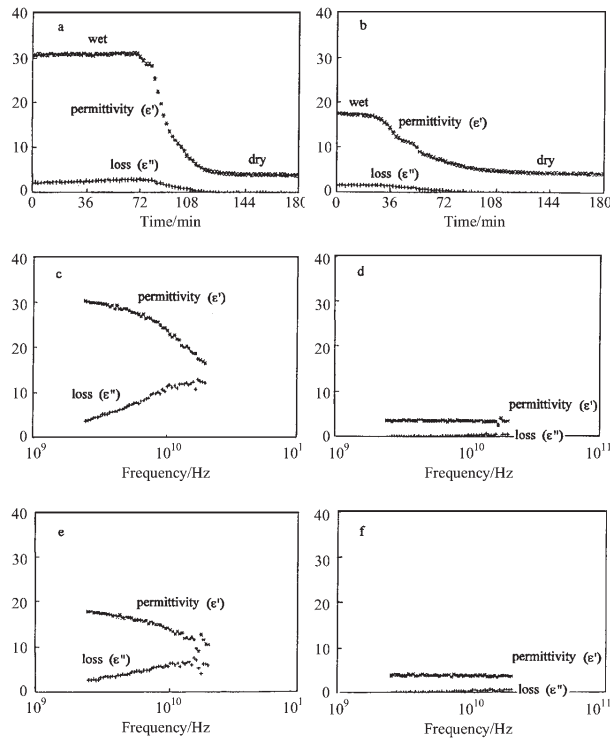


Fig. 3 Drying curves of aged goat leather (a) and of aged calf leather (b) (samples previously immersed in water for 24 h [ϵ' vs. time and ϵ'' vs. time]), aged goat leather sample before (c) and after drying (d) [ϵ' vs. $f(\text{Hz})$ and ϵ'' vs. $f(\text{Hz})$], aged calf leather sample before (e) and after drying (f) [ϵ' vs. $f(\text{Hz})$ and ϵ'' vs. $f(\text{Hz})$]

permittivity ϵ' of wet leather in comparison to that of water at the same temperature and frequency. In this frequency range only the response of the water in the sample is measured. Previous calibration of the probe has been reported elsewhere [9]. After about 70 min there is a decrease in the permittivity as moisture is lost from the sample. (For comparison, the wet unaged goat leather took 104 min to dry.)

Figure 3(b) describes the variation of permittivity vs. time during the drying of aged calf leather, previously soaked in water as in (a) above. Comparison of the permittivity curves in (a) and (b) show that the wet calf leather absorbs a significantly lower quantity of water than the goat leather, and also dries more rapidly (35 min compared with 70 min). Additionally, in both (a) and (b) the values of the loss components are much lower than those of permittivity and thus the advantages of measuring changes in the permittivity values at this frequency (2.45 GHz) for moisture loss can be seen.

Figure 3(c) shows the variation in permittivity and loss with frequency (2.45 to 20 GHz) on wet aged goat leather measured prior to the drying of the sample.

Permittivity and loss components show the characteristic response for water. Good contact with the probe has been achieved with this sample, as the observed level of noise is low.

Figure 3(d) shows the variation in permittivity vs. frequency on the same sample after drying. The permittivity value has been drastically lowered and the curve has lost the shape observed at higher moisture content (i.e. before drying). The final moisture content, as seen from the permittivity value, is low.

Figures 3(e) and 3(f) show the equivalent set of wet/dry results for calf leather. The initial lower moisture content of the wet sample compared with the goat leather affects the shape of the permittivity vs. frequency curve and the amount of curvature is smaller (i.e. the curve is flatter) than in Fig. 3(c). The measurement shows some noise at the higher frequency end indicating that the contact between probe and sample has worsened. However, the permittivity of the dried calf leather shows the same flat response as was seen with the dried goat leather, and the final moisture content, calculated from the permittivity value, is also low. The value of the moisture content in the dry state has been confirmed by thermogravimetry (TGA).

Drying of leather using the combined technique (dielectric & DMTA)

Figure 4 shows drying profiles and accompanying changes in the displacement (%) of the samples and in the relative permittivity (ϵ') of the sample as a function of temperature. In this case the DMTA was used in the TMA mode and the sample was placed between the two plates as shown in Figure 4. Measurements were also made in the tensile mode (Fig. 2). The change in displacement occurs in the region of the shrinkage temperature of leather [11] which also corresponds to one of the glass transition temperatures observed in collagen [12]. The T_g is associated with the relaxation of the main backbone chain of the particular polypeptide sequence (e.g. polypeptide based on sequence glycine-valine-glycine-glycine-leucine has the glass transition of 66°C [13]). In the two measured samples the change in displacement occurred at slightly differing temperatures. The sam-

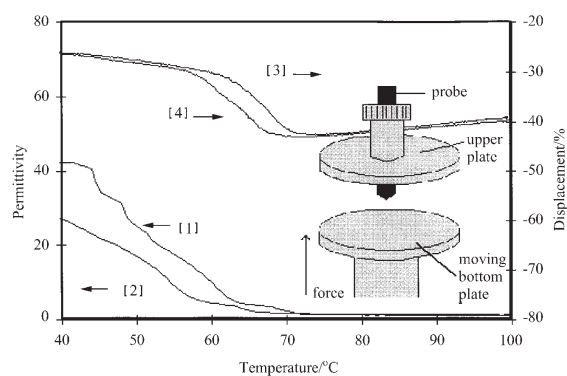


Fig. 4 Drying profiles of goat leather samples: [1] and [2] changes in permittivity (unaged and aged leather respectively), [3] and [4] changes in percentage displacement (unaged and aged respectively) [10]

ple with the lower temperature of onset of shrinkage (aged sample) corresponds to the sample of lower initial moisture content, as measured from the relative permittivity values (ϵ'). It can also be seen (Fig. 4) that the change in the moisture content occurs before the change in mechanical response (shrinkage).

Dynamic mechanical analysis

Tensile mode

Parameters measured by DMTA in tensile mode include $\tan\delta$. The value for $\tan\delta$ is taken as the glass transition temperature (T_g) of polymers and in this case as the shrinkage temperature. In Fig. 5a $\tan\delta$ curves are given: the unaged calf leather sample has its $\tan\delta$ peak at higher temperature (70°C) than the aged calf leather sample (52°C). The intensity of the $\tan\delta$ peak for the aged leather sample is also less than for the unaged i.e. it is less viscoelastic in nature. Figure 5(b) provides information on the behaviour of the modulus of the same samples with temperature. At room temperature the modulus is higher for the aged than the unaged i.e. at the starting temperature the aged leather is stiffer than the unaged. As both samples are heated through the shrinkage temperature the modulus of the aged leather shows a smaller increase than the unaged sample which becomes significantly stiffer. The additional stiffness is introduced probably through the loss of moisture, which occurs during heating and which is larger for the unaged sample as it has a higher initial moisture content as measured by the dielectric coaxial probe.

Table 1

Sample	Shrinkage temperature/°C	Shrinkage/%
Unaged goat leather	62(±1)	16.2(±1.0)
Aged goat leather	58	16.5
Unaged calf leather	57	7.0
Aged calf leather	43	16.8

TMA mode

In Fig. 6(a) there are clear differences in behaviour between the goat and calf leather, and between the aged and unaged samples. Unaged calf leather shrinks or contracts after about 20 min whereas the aged sample shrinks after only 10 min. Previous DSC measurements have also shown a reduction in hydrothermal stability with ageing [14]. The unaged sample shows a longer drying time than the aged sample and a smaller initial displacement. Similar but less distinct changes are seen in the unaged and aged goat leather samples, but more significantly these samples take longer to dry than the calf leather. The initial displacement in both goat leather samples is also larger than that in the calf leather, indicating a softer material. From values of displacement recorded as a function of temperature (Fig. 6(b)), it is possible to calculate values for the shrinkage temperature and the amount of shrinkage

Table 2 Values of observed and predicted T_s , B/A value, sulphate content, tannin monomers, pH and hydrogen ion concentration of the British bookbinding leathers

Sample no.	$T_{s_{obs}}$ /°C	$T_{s_{pre}}$ /°C	B/A value	Sulphate of dry mass/%	Tannin monomers/%	pH water extract	$[H^+] \cdot 10^4$
166	35.7	35.65	0.58	6.8	2.4	2.52	30.20
166P	60.8	60.75	0.55	6.6	2.4	2.79	16.22
103	65.7	66.57	0.63	2.6	0.3	2.76	17.38
140	68.5	67.89	0.63	1.9	0.2	2.78	16.60
141	68.4	68.55	0.60	2.3	0.2	2.73	18.62
95T	64.8	64.58	0.60	3.5	0.3	2.95	11.22
109X	62.5	62.30	0.64	3.9	0.7	2.53	29.52

Sulphate content, tannin monomers and pH are from [15]

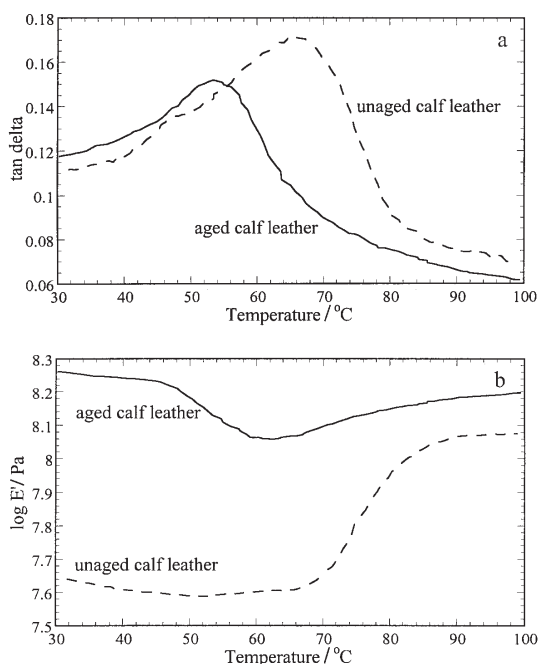


Fig 5 $\tan\delta$ curves for unaged and aged calf leather (a), $\text{Log}(E'/\text{Pa})$ curves for unaged and aged calf leather (b)

(in terms of percentage displacement change) in this temperature range. The measurement of this change for the unaged goat leather is shown in Fig. 6(b), in the range 60–70°C. At higher temperatures a second process (due to water loss) can be seen to reduce the displacement. Values for the samples are given in Table 1 below.

The work described above was performed on reference samples used for developing methodology. In addition some data are reported for measurements on historic samples (Bookbinding leathers from 1932) [11, 15]. The shrinkage temperatures are reported in Table 2, which shows the observed T_s ($T_{s\text{Obs}}$) together with the predicted T_s ($T_{s\text{Pre}}$) and the parameters which affect the values. The amino acid profiles of these samples are given elsewhere [11]. TGA measurements were made on these samples to determine the moisture content. Data are given in Table 3.

Discussion

The shrinkage temperature T_s is a measure of the breakdown of the leather. It has been shown that the chemical breakdown of vegetable tanned leathers is caused by two main mechanisms in the form of an acid hydrolytic and an oxidative breakdown of the collagen and tannin structures. Moreover, the two mechanisms are interactive and their rate depends on the storage conditions. Among other things, the breakdown of the vegetable tannins is characterised by a decrease in tannins extractable in ace-

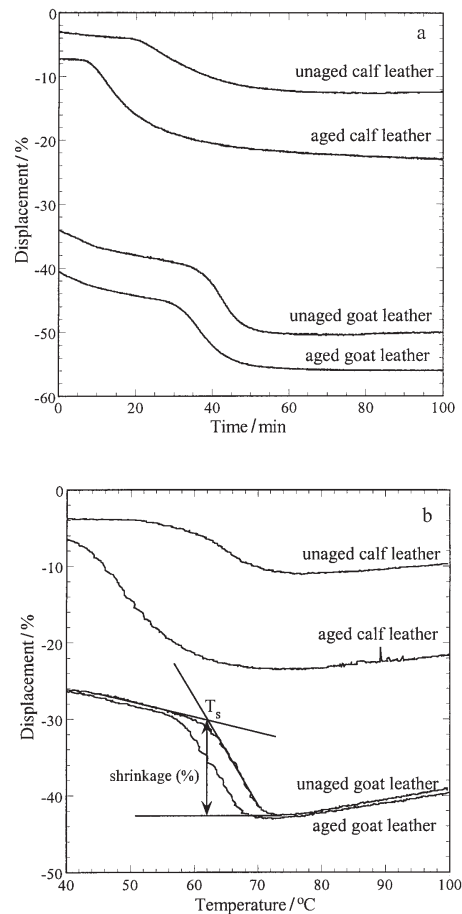


Fig. 6 Displacement (%) vs. time for unaged and aged goat and calf leathers (a). Displacement (%) vs. temperature for unaged and aged goat and calf leathers (b)

tone/water and the formation of increasing amounts of minor breakdown products (tannin monomers) with increasing deterioration [15, 16]. The acid breakdown can be indirectly measured by the sulphate content in the vegetable tanned leathers [16]. The total effect of the two main type breakdown mechanisms is reflected in the hydrothermal stability of the leathers (e.g. the shrinkage temperature, T_s). Apart from direct chemical breakdown, the T_s may also be affected by changes in the acidity and salt content of the leathers. Thus, it has been shown that the T_s of vegetable tanned leathers can be predicted on basis of the B/A value (X_1), (the ratio between the sum of basic amino acids (B) and the sum of acid amino acids (A), the B/A value, [17], the sulphate content (X_2), % tannin monomers (X_3) and the hydrogen ion concentration calculated on basis of the measured pH in water extract (X_4). The prediction is made from the general model equation:

$$T_{s_{\text{Pre}}} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_1 X_2 X_3 X_4$$

The interactive nature of the breakdown is expressed in the equation by the interaction term ($X_1 X_2 X_3 X_4$) involving all four factors [17]. This expression has been developed on the basis of what has emerged from studies of the chemical processes in a large number of samples.

From evaluation of the standardised coefficients, the effect of the individual variables are as follows (greatest effect first least last):

Interaction term	-1.680
Monomers	1.062
Sulphate	-0.463
B/A	-0.138
[H ⁺]	0.137

This shows that the changes in T_s are explained first of all by the interaction effect from all the four factors affecting the breakdown and then secondly by the breakdown of the tannin monomers. In addition, the sulphate value shows a higher effect from acidic breakdown than oxidation (B/A). On basis of this, the equation can be simplified, and the shrinkage temperature predicted, based only on the interaction term and the tannin monomers (X_3):

$$T_{s_{\text{Pre}}} = \beta_0 + \beta_1 X_3 + \beta_2 X_1 X_2 X_3 X_4$$

This gives the following results for $T_{s_{\text{Pre}}}$:

	$T_{s_{\text{Pre}}}$	$T_{s_{\text{Obs}}} - T_{s_{\text{Pre}}}$
166	35.78	-0.08
166P	60.56	0.24
103	66.87	-1.17
140	66.86	1.64
141	66.66	1.74
95T	67.12	-2.32
109X	62.62	-0.12

The prediction is still significant with a correlation coefficient of 0.992. The degree of explanation of the model to the changes in the observed T_s is 98.42%. The coefficient conditions range from significant to highly significant. On basis of this and the previous similar results, it can be assumed that the pattern of the chemical breakdown in the same way may be reflected in the drying profiles and moisture content of the leathers. For example, the mass losses observed by TGA in Table 3 show that for the historic samples there are indications of some relationship between moisture content and % tannin monomers and % sulphate (Table 2). This needs to be investigated further.

Table 3 Moisture content of historic bookbinding leathers as measured by TGA

Sample no.	TGA mass loss (and moisture content of sample)/%
166	12.6
166P	12.6
103	11.0
140	11.8
141	11.1
95T	9.7
109X	12.2

Conclusions

a) The dielectric coaxial probe is sensitive to changes in the moisture content of the sample and provides the ability to monitor continuously and non-invasively as a function of time.

b) The combined methodology has shown that a change in moisture content occurs before the change in mechanical response (shrinkage). It also shows that the aged sample with a lower shrinkage temperature has a lower moisture content.

c) The DMTA in the normal tensile mode measures the viscoelastic parameter T_g , i.e. the shrinkage temperature. The DMTA in the TMA mode measures the shrinkage temperature and accompanying change in displacement.

d) In addition, the TGA measurements have shown a link between the moisture content of historical bookbinding leathers and their chemical state.

* * *

We acknowledge the research fellowship for Gary Foster from the EU funded project (ERA) Environment Programme for the Conservation of European Cultural Heritage, Grant number EV5V-CT94-0548.

- Scott Conrad of Hewlett Packard (U.S.A) for the loan of the network analyser.
- Dr. T. Y. A Chan for the use of the operating software for the coaxial line system controller.
- Christopher Calnan, Conservation Section, National Trust, England, for providing the leather samples.

References

- 1 R. Larsen, 'Summary, Discussion and Conclusion'. STEP leather Project. Research Report No.1. European Commission, Directorate – General for Science, Research and Development. The Royal Danish Academy of Fine Arts, School of Conservation, Denmark, 1994, ISBN 87-89730-01-1. pp. 165–180.
- 2 M. Odlyha, G. M. Foster and M. Scharff, 'Non-Invasive Evaluation of Moisture Sorption and Desorption Processes in Canvases', The International Council of Museums Committee for Conservation (ICOM), 11th Triennial Meeting, September 1996, Edinburgh, Preprints vol. 1 (1996) 297–303.

- 3 R. Larsen, C. Chahine, J. Wouters and C. Calnan, 'Vegetable Tanned Leather: Evaluation of the Protective Effect of Aluminum Alkoxide Treatment', The International Council of Museums Committee for Conservation (ICOM), 11th Triennial Meeting, 1–6 September 1996, Edinburgh, United Kingdom. Vol. II, 742–750, ISBN 1-873936-50-8.
- 4 T. Y. A. Chan, C. Gabriel and E. H. Grant, 'Modelling of the reflection of an open-ended coaxial line and its use for accurate complex permittivity measurement at frequencies up to 20 GHz', IEE DMMA, 363 (1992) 366–369.
- 5 R. J. King, IEEE Transactions of Instrumentation and Measurement, 41 (1992) 111.
- 6 M. Kent, 'Electrical and Dielectric Properties of Food Materials', Essex, England: Science and Technology Publishers, England, Essex 1987.
- 7 S. O. Nelson, Trans. ASAE, 16 (1973) 384.
- 8 W. R. Tinga and S. O. Nelson, Microwave Power, 8 (1973) 23.
- 9 T. Y. A. Chan, M. Odlyha and M. Scharff, Deutsche Gesellschaft für Zerstörungsfreie Prüfung, Berlin 1994, p. 510.
- 10 G. Foster, J. Thermal Anal., 49 (1997) 1069.
- 11 R. Larsen, 'General Discussion'. Deterioration and Conservation of Vegetable Tanned Leathers. ENVIRONMENT Leather Project (EV5V-CT-94-0514). European Commission. Protection and Conservation of the European Cultural Heritage. Research Report No. 6. The Royal Danish Academy of Fine Arts, School of Conservation, Denmark, September 1997. ISBN 87-89730-07-0. pp. 167–186.
- 12 A. N. Fraga and R. J. J. Williams, Polymer, 26 (1985) 113.
- 13 C. Megret, Thèse d'Université Toulouse, 1988.
- 14 C. Chahine and C. Rottier, 'DSC Measurement', in Deterioration and Conservation of Vegetable Tanned Leathers. ENVIRONMENT Leather Project (EV5V-CT-94-0514). European Commission. Protection and Conservation of the European Cultural Heritage. Research Report No. 6. The Royal Danish Academy of Fine Arts, School of Conservation, Denmark, September 1997. ISBN 87-89730-07-0. pp. 129–143.
- 15 J. Wouters and J. Claeys, 'Analysis of Tannins, Sulphate, Fat, Moisture and Ash: Evolution and Significance of Parameters to be Followed for Measuring the Degradation of Vegetable Tanned Leather'. Deterioration and Conservation of Vegetable Tanned Leathers. ENVIRONMENT Leather Project (EV5V-CT-94-0514). European Commission. Protection and Conservation of the European Cultural Heritage. Research Report No. 6. The Royal Danish Academy of Fine Arts, School of Conservation, Denmark, September 1997. ISBN 87-89730-07-0. pp. 87–94.
- 16 J. Wouters, 'Tannin and Ion Analysis of Naturally and Artificially Aged Leathers'. STEP leather Project. Research Report No 1. European Commission, Directorate - General for Science, Research and Development. The Royal Danish Academy of Fine Arts, School of Conservation, Denmark, 1994, ISBN 87-89730-01-1. pp. 91–105.
- 17 R. Larsen, 'Fundamental Aspects of the Deterioration of Vegetable Tanned Leathers', Ph.D. Thesis, The Royal Danish Academy of Fine Arts, School of Conservation, 1995.