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Thermochimica Acta 321 (1998) 197–206

thermochimica
acta

Non-invasive evaluation of moisture sorption and desorption processes in canvases

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Received 11 April 1997; accepted 8 June 1998

Abstract

Dielectric analysis using the open-ended coaxial probe technique was applied to the non-invasive monitoring of moisture sorption and desorption processes in three different samples. Results are reported for the humidification and dehumidification studies in naturally aged unprimed canvas containing remnants of aged lining adhesive, the response of artificially aged primed canvas sample to atmospheres of relative humidities corresponding to 60, 80 and 95%, and the effect of temperature variation on moisture sorption processes in a sample of naturally aged primed canvas from Landseer's *Study of a Lion*. © 1998 Elsevier Science B.V.

Keywords: Canvas; Non-invasive dielectric analysis; Open-ended coaxial probe; Moisture sorption and desorption

1. Introduction

This paper describes the application of dielectric analysis using the open-ended coaxial probe technique [1] to obtain a non-invasive evaluation of the moisture sorption and desorption processes. These occur, for example, during humidification procedures using suction-table techniques on canvas paintings. The conservation of canvas paintings by means of suction-table (low-pressure) techniques was developed in the 1960s in Denmark [2], while other suction-table techniques were developed in the 1970s in the Netherlands [3]. Since that time, these techniques have enjoyed wide recognition and their use is rapidly spreading [4]. In general, it has been recognised that a combination of heat, moisture, aqueous glues and minimal pressure has, for a long time, proved useful in the relaxation, regeneration and consolidation of paintings on canvas [5,6]. A major advantage of suction-table techniques is the possibility of controlled use of humidity as part of conservation procedures, as in the regeneration of aged and partially deteriorated animal glue in canvas paintings, and in flattening of deformed painted structures and cupped paint layers. An additional advantage is that part of the treatment can be carried out without covering the painting under treatment with a facing or membranes; this makes it possible to gain access to the paint surface during treatment for local intervention. This would allow a small dielectric probe, such as the one used in this experiment, to be placed onto the surface being treated to monitor moisture uptake through the material.

In this paper, preliminary measurements are described where a small coaxial probe is placed on the surface of a sample contained in a glass cell. The

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PII: S0040-6031(98)00460-2

glass cell is attached to a humidification system, so that air at a controlled humidity passes from the bottom of the cell and flows through the sample for defined periods of time. The first example to be discussed in this paper is the effect of humidification treatment at room temperature on aged lining adhesive on a sample of 19th century canvas from an unknown painting. The second example considers the effect of humidification on an artificially aged sample of primed glue-sized canvas, where the priming consists of a layer of cremnitz white basic head carbonate in oil. The third example demonstrates the effect of temperature on moisture uptake in the case of a naturally aged sample (19th century Landseer's *Study of a Lion*). This sample was chosen, since a large amount of information already exists on its behaviour with respect to relative humidity. Originally, only its mechanical behaviour during relative humidity cycling [7] was studied. The sample is on closely woven linen and is primed with a lean mixture of lead white and calcium carbonate. Its response to variations in relative humidity and temperature has also been studied by thermomechanical and dielectric techniques [8,9]. Information, therefore, exists on the value of its softening temperature (in the region of 50°C at relative humidity of 50%), and how this varies with exposure to different values of relative humidity (nearly room temperature at relative humidity above 90%) [10].

The technique of dielectric analysis involves the application of an alternating electric field to a sample. If the sample is polar, the dipoles within that material will orientate themselves in order to reduce their free energy to a minimum. The rate at which these relaxation processes occur provides information on the structure and behaviour of a given sample. In previous studies, low frequency dielectric analysis has been used to measure the degree to which water is bound within the system [6]. This is of considerable interest both to conservation treatment involving humidification and the effect of environmental variations on the painting. In this paper, the dielectric analysis measurements have been made in the microwave region. In the frequency region between 2.45 and 20 GHz the dielectric constant (ϵ') and the dielectric loss factor (ϵ'') are highly correlated with moisture content, since the permittivity of water greatly exceeds that of the dry sample. The relaxation processes of the dipoles associated with the sample are not observed. What is observed, however, are the relaxation processes of water molecules and other small molecules, such as methanol.

Since the behaviour of the dielectric constant is more regular than that of the loss factor with respect to changes in moisture content and the frequency of the applied fields [11], it is this parameter that has been monitored in this experiment.

The objectives of this experimental study were:

(a) to set-up a system for the humidification of canvas samples;
(b) to use the small coaxial probe (0.86 mm o.d) to monitor changes in the sample during humidification and dehumidification processes and in atmospheres of defined relative humidities;
(c) to evaluate the effect of temperature variation (in the 20–60°C range) on moisture sorption; and
(d) to provide information on the actual moisture content of the samples during these processes.

Evaluation of these effects (b–d) is of importance, since the equilibrium moisture content of the sample as well as the rate at which the sample absorbs moisture are controlled by the relative humidity of the environment and temperature of the sample. In studies of composite materials [12], several routes by which water is absorbed into a composite have been identified: absorption by the matrix, penetration through surface crazes and cracks, absorption along fibres through capillary action and moisture absorption by the reinforcement. These processes can also be considered as occurring in the primed canvas samples. Such intrusion by moisture, which may also be caused by environmental exposure for extended periods, is known to have adverse effects on the structural integrity of polymer matrix composite materials [13]. Diffusion through the organic matrix may lead to degradation of the polymer structure and moisture migration along the fibre–matrix interface which weakens the interfacial bond.

2. Experimental procedure

2.1. Measuring system

The equipment used in this study consisted of an 8720C Hewlett–Packard network analyser system.

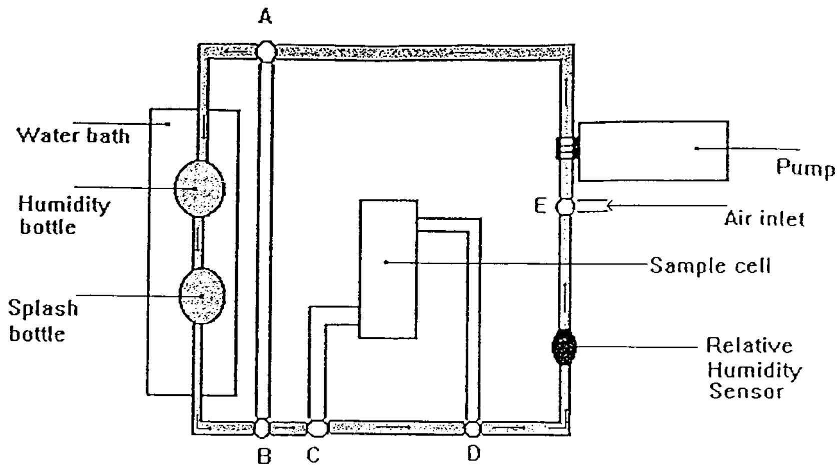

Fig. 1. Experimental humidification system used for aged lining adhesive. This shows initial circulation of humid air in a closed system which excludes the sample cell.

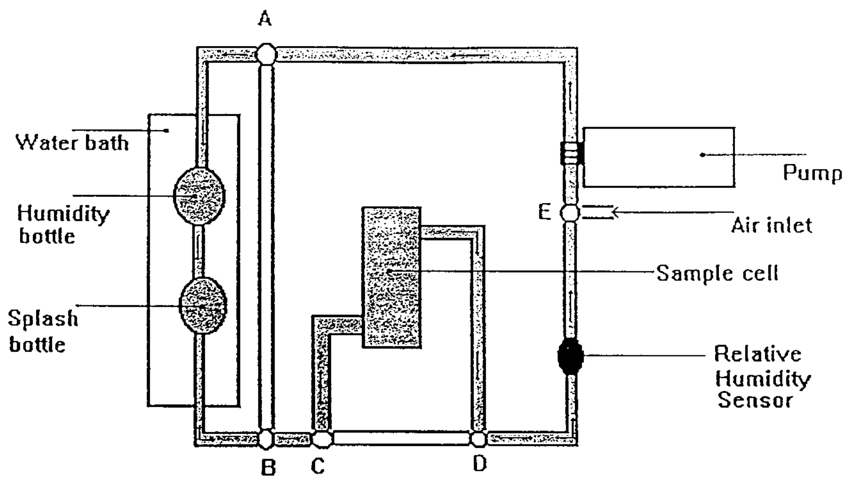

Fig. 2. Experimental humidifcation system used for aged lining adhesive. This shows circulation of humid air in a closed system which includes the sample cell.

with a semi-rigid coaxial probe. The open end of a coaxial probe (0.86 mm o.d.) was placed in contact with the sample and the reflection characteristics at the interface were measured using the network analyser. The methodology and measurement technique have been reported elsewhere [1]. In this paper, further developments in the software have made it possible to record permittivity[1] values of the samples as a function of time in a continuous manner and, hence, to directly monitor changes in the samples during their exposure to different environments.

[1]Note: The term permittivity (ϵ) used in this paper is actually the complex relative permittivity (ϵ_r), and is defined as the permittivity relative to the permittivity of free space (ϵ_0=8.854$\times$10^{-12} F/m) and so it will have no units.

2.2. Humidification of naturally aged canvas containing remnants of aged lining adhesive

A glass sample cell was connected to a system which included a peristaltic pump and two Dreschel bottles placed in a water bath at 25°C (Fig. 1). A humidity sensor was placed in line to measure the

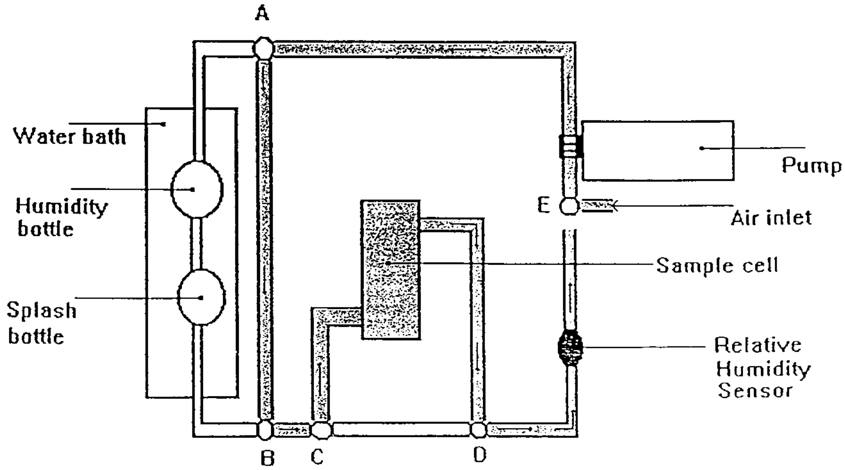

Fig. 3. Experimental system used for aged lining adhesive. This shows circulation of air in a closed system excluding the humidification system in the water bath.

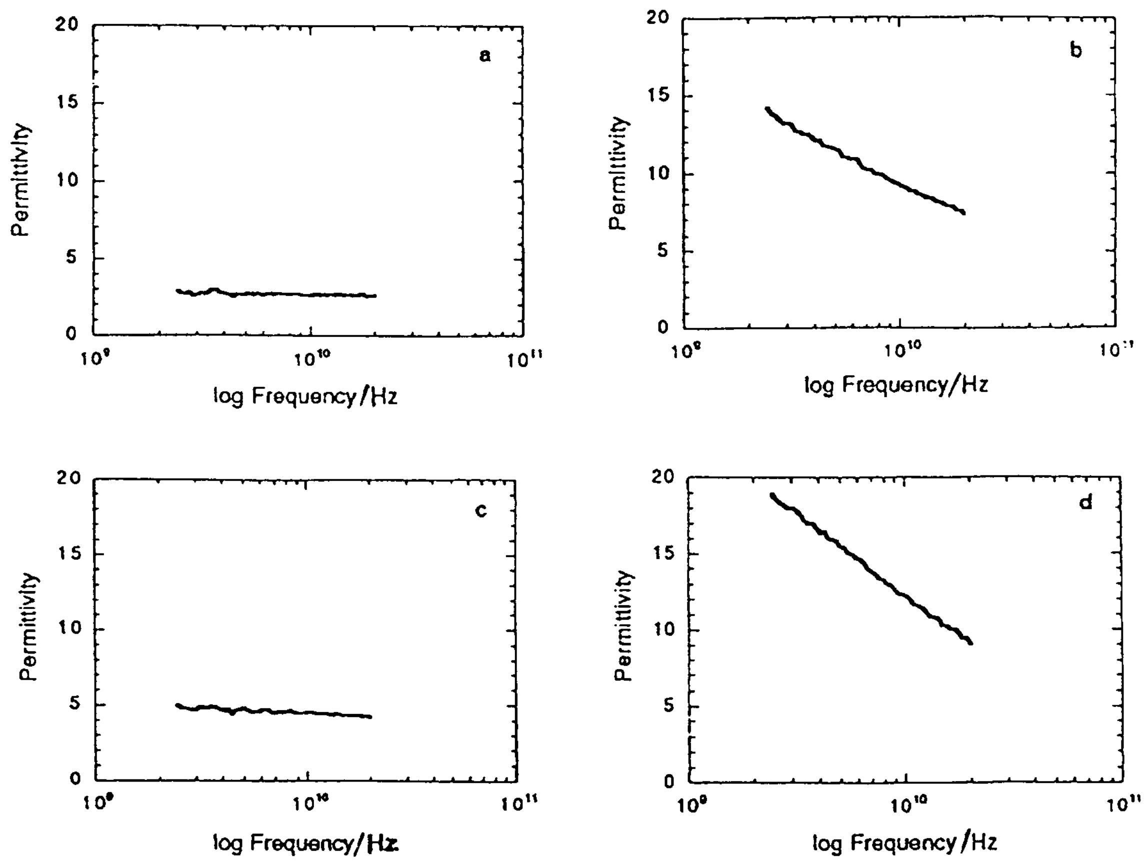

Fig. 4. Plot of relative permittivity against frequency (a) before humidification, (b) after humidification, (c) after dehumidification, and (d) after rehumidification.

relative humidity and temperature of the system. Humidified air was initially circulated in the closed system to establish equilibrium conditions (Fig. 1). After ca. 30 min, taps A,C and D were opened to include the sample cell (Fig. 2). Taps A and B were then turned to a position so as to close the circulation of humid air and allow the system to dry out and dehumidify (Fig. 3).

Readings of permittivity were made against frequency (2.45–20 GHz) before introducing the humid air (Fig. 4(a)), and then after the introduction of air saturated with water vapour (corresponding to 100% RH) at room temperature (Fig. 4(b)). The sample was then dehumidified and readings were taken after about an hour of drying the sample and when there were no further changes to the values recorded (Fig. 4(c)), the sample was then rehumidified (Fig. 4(d)).

Permittivity data were also recorded continuously as a function of time at a select frequency (2.45 GHz) for a period of 200 min. The results are shown in Fig. 5 (Fig. 5(a–e) humidification, and Fig. 5(b–f) dehumidification processes).

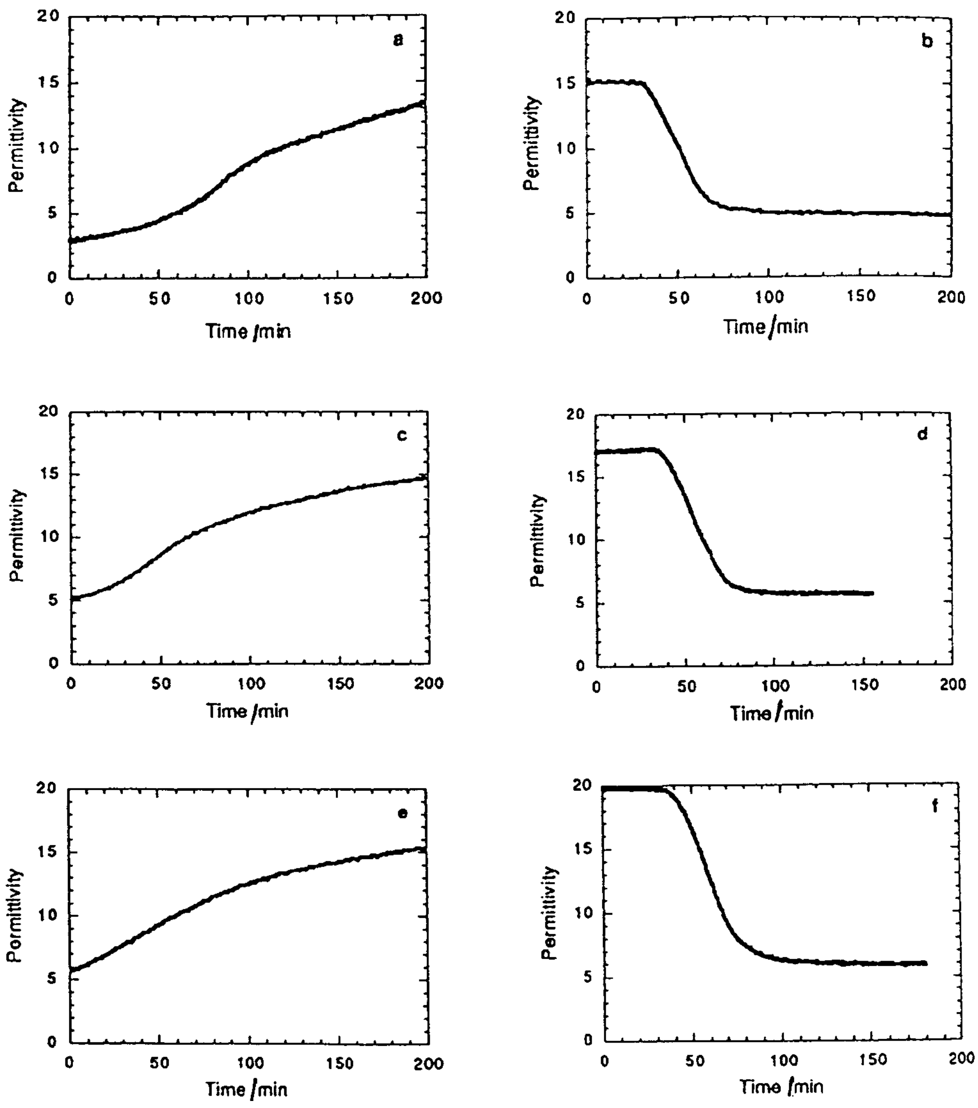

Fig. 5. Plot of relative permittivity against time ((a–e) humidification and (b–f) dehumidification) at 2.45 GHz.

2.3. Humidification of the artificially aged primed canvas sample

The system was modified as shown in Fig. 6 to provide temperature control in the sample chamber. Water was pumped from the water bath. and circulated around the chamber. The shape of the cell was also modified to provide a small lower compartment to hold H_2SO_4/H_2O mixtures for generating environments of specified RH.

Prior to exposure of the samples to humid air, values of the glass-transition temperature (T_g) and initial moisture content of the samples were determined by dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA), respectively. The moisture content was measured from the thermogravimetric curve by measuring the weight loss between 30° and 150°C. After this evaluation, samples were placed on the wire gauze in the sample cell, the dielectric probe positioned on the sample with optimum contact (determined by the level of noise obtained in the response); the whole system was thoroughly dried, the starting sample permittivity values recorded and the measuring system activated to read continuously as a function of time. Solutions containing known amounts of H_2SO_4/H_2O were introduced through the side arm with a teat pipette. Air was bubbled through these solutions via a peristaltic pump to assist in the circulation of the required humidity.

After humidification, samples were rapidly removed and sealed into aluminium crucibles. A small hole was pierced in the crucible and the sample was promptly heated in a thermogravimetry system (Shimadzu TG-50 thermogravmetric analyser) to 200°C, to determine the weight loss due to moisture uptake and to provide a means of correlating measured weight to permittivity values.

2.4. Humidification of Landseer's Study of a Lion at varying temperatures

A similar experimental procedure was followed, as already described, for the previous primed sample. Differences can be summarized as follows: the lower compartment of the sample chamber was replaced by water (temperature variation provides variation in RH and so it was decided to work at saturated water-vapour conditions), and there was no bubbling of air through the lower compartment, as with increase in temperature this led to problems of wetting of the sample (Fig. 6).

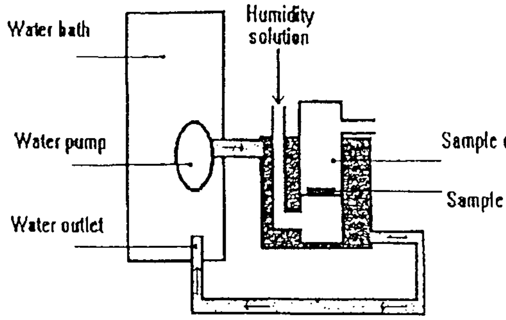

Fig. 6. Modification of experimental system for humidification studies of primed canvas samples.

3. Results and discussion

3.1. Humidification of naturally aged canvas containing remnants of aged lining adhesive

Fig. 5(a) shows the increase in permittivity with time, during humidification with air saturated with water vapour at 25°C. The first 50 min shows a slow increase in permittivity. This is then followed by a more pronounced increase over the next 40 min. which again changes to a slower rate after 100 min. The changes in slope at different times indicate different rates of sorption and are indicative of different mechanisms which may be occurring in the composite sample. The passage of humid air passes through the side of the canvas and then migrates through the composite. Fig. 5(b) shows the dehumidification of the sample. Moisture is lost after 30 min, and the moisture loss extends over a period of 40 min. Dehumidification or drying of the material was continued for a period of 200 min and to a stage where the permittivity value had reached a definite plateau.

Fig. 5(c) shows re-humidification of the same sample. The starting value of the permittivity is higher than the original value. This indicates that the material has retained some of the absorbed moisture. The response to initial uptake is also faster than in the original case and the overall increase in permittivity is higher. The dehumidification starts at a higher value of permittivity (Fig. 5(d)), but the overall shape of the curve is similar to that of the curve in Fig. 5(b).

Fig. 5(e) shows the second re-humidification of the sample. These processes were recorded without removing the probe from the sample. The curve shows no initial delay as in curves Fig. 5(a and c). and the starting value of permittivity is once again higher than in the previous two cases. Fig. 5(f) shows the third de-humidification process. The starting value is higher than in the previous two cases. The loss occurs after the initial 30 min and continues, until 90 min.

3.2. Humidification of the artificially aged primed canvas sample

The sample exposed to 60% RH showed a small increase in permittivity over the period of 150 min. The increase in permittivity is shown as a function of time in Fig. 7.

The sample, exposed to 85% RH (Fig. 7), showed a slightly faster rate in moisture uptake than 60% RH. At the end of the first 40 min, there is an increase in the rate of uptake for the next 30 min and this is followed by a levelling-off to a higher value than that obtained for the 60% RH.

The sample exposed to 90% RH (Fig. 7) immediately shows a more rapid rate of uptake, and the final value is considerably higher than in the other two cases.

The corresponding weight uptakes for the three samples (measured as a mass loss by thermogravimetry between 30° and 150°C) were 2.7, 3.7 and 5.3% (Fig. 8). The weight loss for an untreated sample under normal laboratory conditions was 2.2%. The difference corresponds to the amount of moisture present in the sample after humidification for 150 min and shows a definite increase in weight with increasing RH. An increase in relative humidity is known to increase the moisture content of samples and it can be measured in this experiment in terms of increasing values of permittivity. Thus, values of permittivity can be directly related to increasing values obtained for the weight losses.

An explanation of the enhanced moisture uptake at higher values of relative humidity can be made in

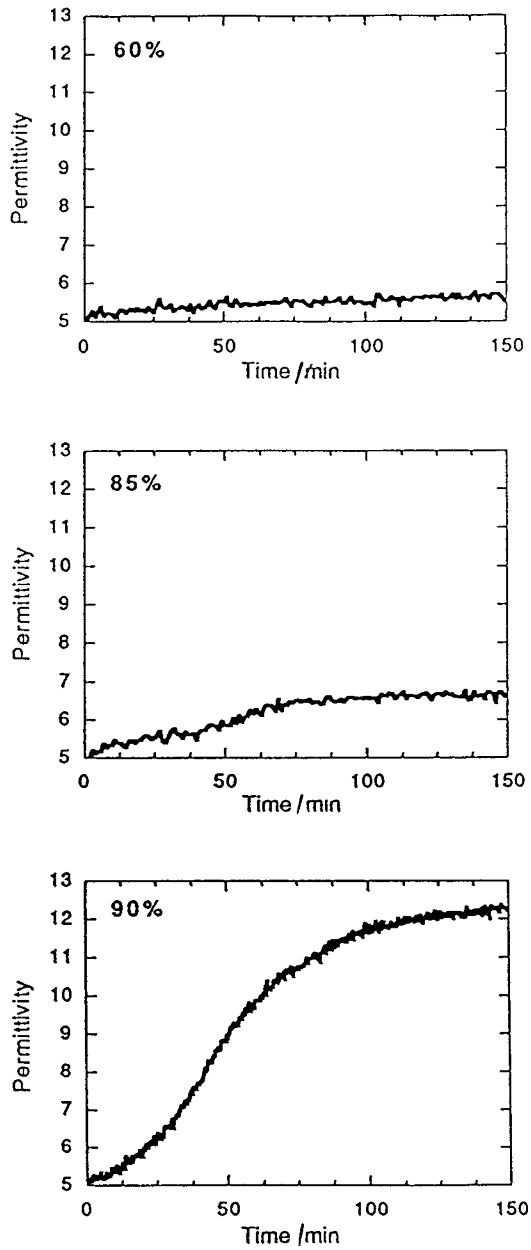

Fig. 7. Plot of relative permittivity against time for response of artificially aged modern, commercially primed canvas to 60, 85 and 90% RH.

terms of the glass-transition temperature. It is a well-established fact in polymer science that water sorption below the T_g of materials is lower than at temperatures above T_g. T_g of the sample studied was found to be ca.

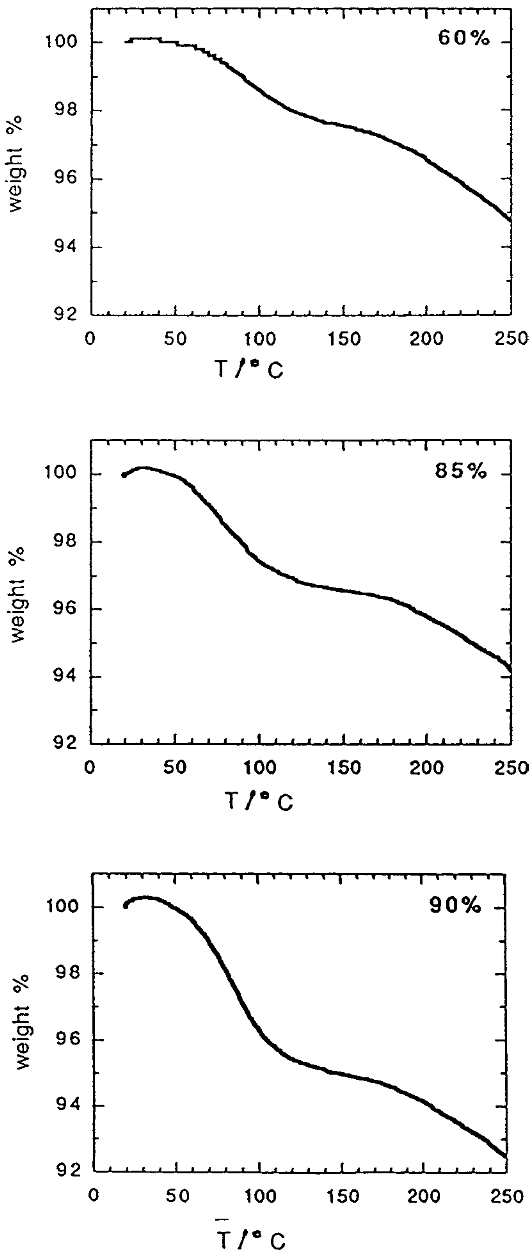

Fig. 8. TG curves for artificially aged modern, commercially primed canvas sample after exposure to 60, 85 and 90% RH.

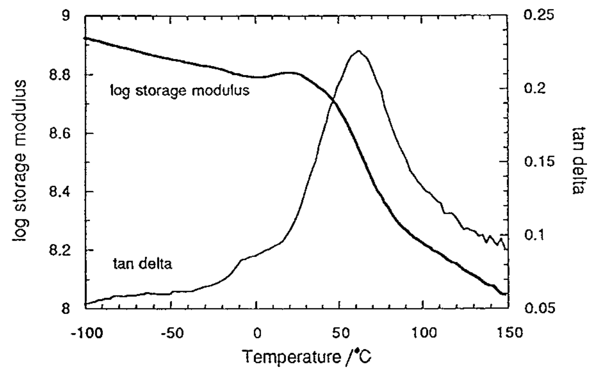

Fig. 9. Log storage modulus and tan δ for artificially aged modern, commercially primed canvas sample.

40°C. This is obtained from the dynamic mechanical thermal analysis (DMTA) curve (Fig. 9) at the temperature, where the storage modulus starts to fall in value or from the temperature of the tan δ peak. A discussion of the DMTA technique and the meanings of storage modulus and tan δ have been described elsewhere [8]. At higher values of relative humidity, the T_g of materials is lowered. Therefore, at 90% RH, the T_g value of the sample will be shifted to temperatures at which the measurements are being made (i.e. 25°C).

3.3. Humidification of Landseer's Study of a Lion at varying temperatures

Fig. 10 shows the results for the humidification (100% RH) of the 19th-century primed canvas sample at 25°C. There are three distinct regions of response: in the first 20 min a slow uptake followed by a sharp increase of over four units and a levelling-off in its value. At 40°C, there is an immediate linear increase in the first 10 min which then continues until it levels-off to a higher value of 14 at the end of 50 min. At 60°C, there is an increase of about eight units over a period of 5 min followed by a slower increase of four units over the next 20 min.

The T_g of this sample is shown in Fig. 11 and the softening of the modulus value occurs in the region of 50°C. As the temperature of the water bath (Fig. 6) surrounding the sample increases (i.e. from 40° to 60°C) and approaches the T_g of the sample, an increase in moisture sorption occurs.

4. Conclusions

The dielectric probe is sensitive to changes in the moisture content of the sample. The ability to

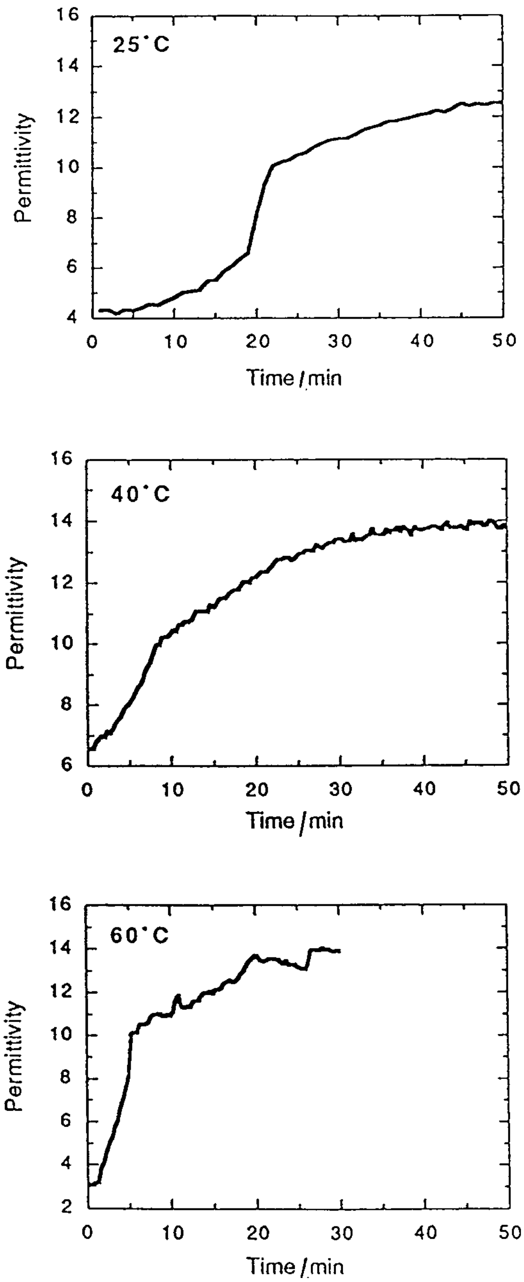

Fig. 10. Plot of relative permittivity vs. time for humidification of naturally aged Landseer's 19th-century primed canvas at 25°, 40°, and 60°C.

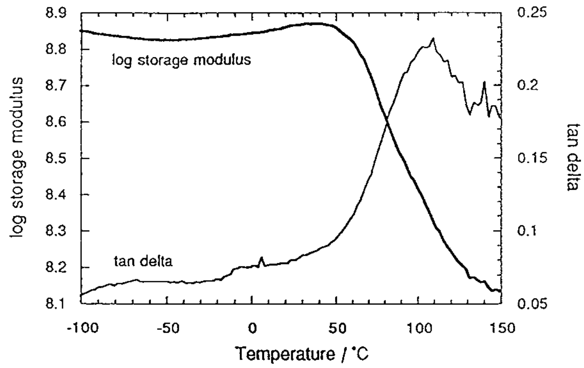

Fig. 11. Log storage modulus and tan δ for naturally aged Landseer's 19th-century primed canvas.

continuously monitor as a function of time provides the facility for understanding the response of the composite, whether moisture uptake occurs in a linear fashion or in a number of steps at differing rates.

Acknowledgements

The authors are most grateful to, and would like to sincerely thank Dr. Scott Conrad of Hewlett–Packard for providing the measuring system. Without his sympathetic attitude and practical assistance this paper would not have been possible. The authors would like to thank Dr. T.Y.A. Chan for the use of the software for operating the measuring system, Stephen Hackney and Dr. J. Townsend for providing the artificially aged sample and the Landseer primed sample, and Dr. Stella Casagrande in Felder for assistance in the preparation of the figures. Gary Foster acknowledges support from the EU funded project (ERA) Environment Programme for the Conservation of European Cultural Heritage.

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