ELSEVIER

Thermochimica Acta 263 (1995) 7–21

thermochimica acta

# Evaluation of relative humidity effects on fabric-supported paintings by dynamic mechanical and dielectric analysis

M. Odlyha*, T.Y.A. Chan, O. Pages

*Chemistry Department, Birkbeck College, University of London. Gordon House, 29 Gordon Square, London WC1H OPP, UK*

Received 9 January 1995; accepted 24 March 1995

**Abstract**

Measurements have been made of the glass transition temperature and the viscoelastic parameters of prepared paint samples and complex samples from paintings at increasing values of relative humidity in the range 54–94%. The complex modulus data obtained from dynamic mechanical measurements were fitted to the Williams Landel Ferry equation. The real part of the complex modulus was found to fit the equation, and time temperature superposition was used to make predictions on the long term effects on the storage modulus of samples exposed to these conditions. The lack of fit of the loss data, however, made it necessary to consider an alternative model which takes into account several relaxation processes. Dielectric measurements on these samples showed that the resulting complex permittivity data could be fitted using a cooperative model given by the Dissado-Hill function. Values of the parameters calculated by this function are given for the corresponding values of relative humidity.

*Keywords:* Painting; Relative humidity; Viscoelastic parameter; Thermomechanical; Dielectric technique

## 1. Introduction

It has become recognised in recent times that changes in the relative humidity (RH) and temperature of the environment surrounding paintings are factors which contribute to their damage [1]. An example can be found in paintings which hang on external walls of art galleries, museums or historic houses [2]. Alterations which occur to paintings, par-

* Corresponding author.



*SSDI* 0040-6031 (94) 02387-9

ticularly those on the surface, detract from the aesthetic appearance of the art work. Recent evidence of these effects have been observed in the Stanley Spencer paintings at Sandham Memorial Chapel during their conservation treatment [3]. In this case some of the paintings had a patchy blanched appearance particularly in the darker areas of the paintings which may have been provoked by environmental fluctuations. Although the chapel currently provides relatively stable environmental conditions there have been problems in the past of excessive moisture transfer from the walls and condensation forming inside the chapel. In this particular case the fluctuations in environmental conditions induced formation of whitish surface deposits. There are also other cases where the generation of internal forces in the various layers of the paintings have caused stress-related cracking and eventual paint loss. This may be particularly exacerbated through the differential response of the layers, the paint, ground and size, to moisture [4].

An approach which can be used to measure the effect of moisture on the structure is to consider that the layers are amorphous or semi-amorphous polymers and to apply thermomechanical techniques. Measurement of the glass transition temperature will provide an indication of the effects of environmental fluctuations, degree of pigmentation, and ageing. The paint layer itself consists of a polymerised oil network with varying levels of pigmentation. Its glass transition temperature and that of the overall composite layer structure can be measured. The importance of the glass transition temperature has been well recognised in polymer chemistry and the fact that many properties are modified around that temperature such as modulus and the thermal expansion coefficient. It has also been recognised that it is important to know if the $T_g$ is modified by the incorporation of pigment and, if so, how it is affected. In the studies of paint layers in paintings no measurements have as yet been made of the $T_g$. In this paper measurements of the $T_g$ are presented on prepared and naturally aged paint films and on samples of 19th century primed canvas. The variation in the $T_g$ and modulus values with relative humidity is then used as a basis for predicting long term effects on the composite structure.

This paper is part of a series which explores the role of thermomechanical and dielectric techniques in measuring the effect of fluctuations in relative humidity and temperature on the mechanical and electrical properties of paintings. Previous work has shown that the softening temperature of complex composite samples from paintings is lowered by increasing the relative humidity of the environment [4].

## 2. Experimental

### 2.1. Samples

Samples of naturally aged paint prepared in 1978 from commercial linseed oil and safflower oil supplied by Grumbacher were used for the measurements [1]. Two types of pigmented samples were chosen: brown samples containing the burnt sienna pigment and which have a high medium content (ochre pigments containing iron oxide are known to absorb relatively high proportions of oil in the region of 80%), white samples containing the pigment basic lead carbonate and which have a low medium content (basic lead carbonate is known to absorb relatively low proportion of oil in the region of 30%).

Samples originally from the rear primed support of Landseer's painting 'Study of a Lion' (ca. 1862) were tested. They consist of a white pigmented layer containing oil, the priming, a layer of natural glue and canvas. The composition of the pigments, the basic lead carbonate and the calcium carbonate in the layer of priming, has been described elsewhere [5].

### 2.2. Thermomechanical analysis

The aim of the TMA measurements was to measure the glass transition temperature ($T_g$) of small paint samples (ca. 2 mm × 3 mm) which had been naturally aged for periods of up to 15 years at the time of these measurements. These samples are particularly difficult to measure since they contain a high proportion of pigment and a small amount of medium and are relatively thick (0.25 mm). The paint was cast using originally two and three layers. The softer brown samples were measured in compression mode and the harder white samples were measured using the three point bending mode with static (60 mN) and dynamic load (30 ± 20 mN). Samples of 19th century canvas were also measured in three point bending mode. In the three point bending measurements the dimensions of the support were 4 mm × 4 mm and the distance between the supporting ends was 3.0 mm and the load was 210 mN. The instruments used were the Mettler TMA 4000 and the Stanton Redcroft Thermomechanical Analyser 691.

Samples of similar dimensions but thinner (0.1 mm) and which had been more recently prepared [6] from tube paint containing lead white pigment in safflower oil were also evaluated in compression mode (static load 100 mN). The effect on the $T_g$ of the presence of additives (resin mastic) as used in 19th century paint media and thermal ageing (34 days at 70°C and 50% RH) were also evaluated.

### 2.3. Dynamic mechanical analysis

The instrument used was a Rheometric Scientific dynamic mechanical thermal analyser (DMTA). The particular instrument head applies a strain-controlled sinusoidal load in bending mode with single cantilever geometry. Strain frequency is variable between 0.01 and 200 Hz in 16 steps and peak to peak strain amplitude can be varied between 11 and 256 mm in 10 steps. Temperature is controllable between −150°C and +300°C. Entrance and exit ports allow gases or humid air to be introduced into the sample environment.

The moisture content of the samples treated in this study was controlled by first conditioning them at a particular RH in a glass jar containing saturated salt solution (e.g. magnesium nitrate for 54%) and then lightly coating the samples before measurement with silicon oil. Instrument control, data logging and analysis were carried out by a computer. Data logging was performed at time intervals commensurate with the frequency used and signal to noise limitations. The bending mode was chosen since it has been shown [7] that mechano-sorptive effects are more pronounced in bending mode than in compression and tension. The outer layers have a proportionally greater influence on bending stiffness, and this is where adsorption or desorption of moisture first occur. The strain level (×2) was set to that generally used for non-linear elastic materials such as highly filled or semi-crystalline materials.

The equilibrium moisture content of the primed canvas samples at different relative humidities and the rate of sorption of moisture were measured by daily weighing the samples on a Sartorius electronic microbalance over a period of 5 days at the various RH values.

Measurements were also made of the primed canvas samples at a given temperature for a fixed period of time and the frequency was varied over the range 0.3 Hz to 30 Hz. Samples used were 4 mm wide × 8 mm long × 0.5 mm thick and measurements were made in bending mode. This procedure was repeated at 5°C intervals over the range −50°C to 120°C to determine how the viscoelastic properties vary with frequency for a given temperature.

## 3. Results and discussion

### 3.1. Thermomechanical analysis

In the medium rich burnt sienna paint film there are two distinct regions of softening: the first occurs in the region of −15°C and the other in the region of 50–70°C. Fig. 1(a) shows the TMA curve and Fig. 1(b) shows the DLTMA curve and its first derivative. The first stage corresponds to the transition from the elastic or glassy state to the viscoelastic region, the $T_g$ of the paint film. The value lies in the region quoted for unpigmented oil films of about 12 months which is at about −20°C [8]. The origin of the second transition was not immediately clear. Multiple transitions have been reported for other systems such as zinc oxide and alkyd films [9]. It was found that immersion or surface treatment with propanone removed this transition [10]. GC/MS studies on extracts of leaching of the paint films showed the presence of palmitic and stearic acids [11]. The temperature of the second transition lies in the region of the melting range of these acids.

Fig. 2(a) shows the $T_g$ of unsupported lead white paint films using relatively small sample size (2 mm × 3 mm). Fig. 2(b) shows the change in $T_g$ with different values of RH. The $T_g$ value at 54% RH is similar to the value obtained for that of the burnt sienna sample also measured at the same value of RH and it corresponds to that of the oil alone. The effect of pigment type on the $T_g$ can be classified into two groups: (a) $T_g$ does not change with pigment type and (b) $T_g$ increases with pigment type. In the case of thermosetting acrylic paints it has been observed that $T_g$ did not change in the presence of untreated $TiO_2$; it dropped however, when surface treated $TiO_2$ was used [12]. Thus the effect on the $T_g$ value can give information on polymer/pigment interactions.

Fig. 3 shows the variation of $T_g$ with moisture content for a naturally aged lead white linseed oil sample [13]. Fig. 4 shows the effect on the $T_g$ of lead white paint films of additives and ageing. In (a) the $T_g$ again appears at about −15°C and onset of overall softening occurs in the region of 40°C. The presence of resin mastic in equal proportions produces an overall softening of the film and the $T_g$ and the temperature of the softening of the film moves to lower values. The effect of light and heat ageing is to move the $T_g$ and the softening temperature to higher values. These are preliminary results of a project in collaboration with the Tate Gallery on the characterisation of 19th century paint media. The $T_g$ values for the composite paint samples obtained from three point bending

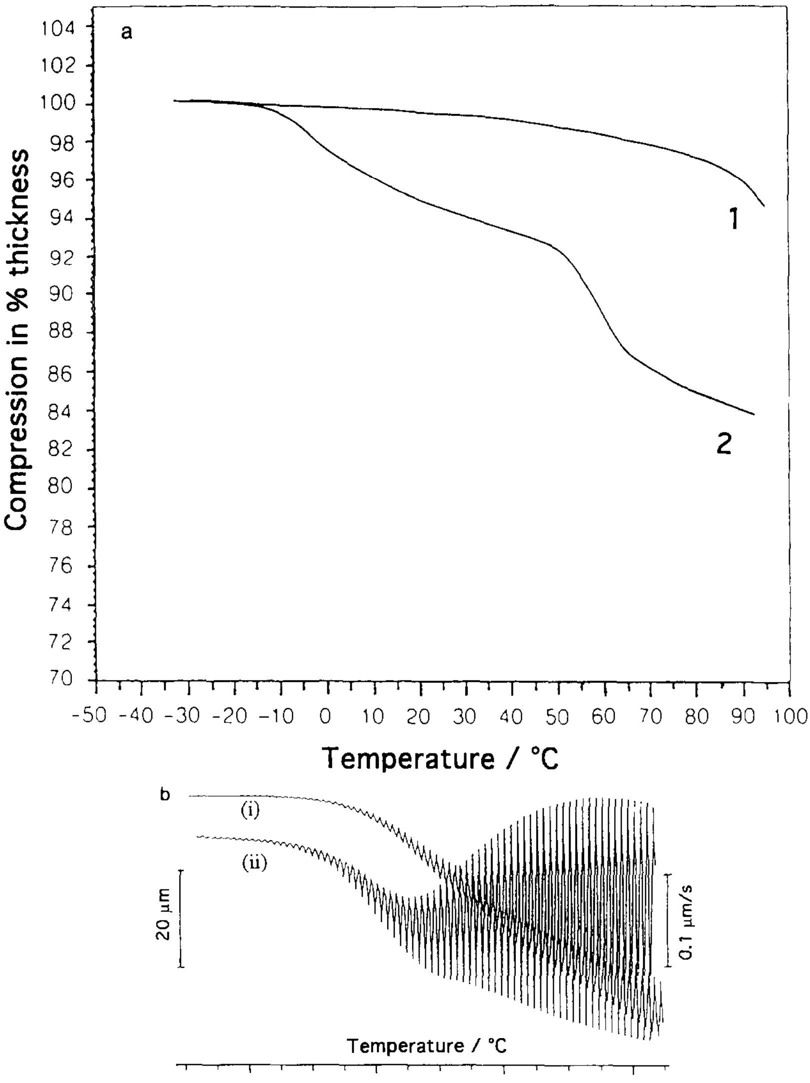


Fig. 1. (a) TMA compression curves for the control samples; (1) lead white and (2) burnt sienna. (b) DLTMA compression curves (i) and its first derivative (ii) for control burnt sienna oil sample in the $T_g$ region of linseed oil.

measurements are shown in Fig. 5(a). Fig. 5(b) shows the structure of the composite sample which contains a paint layer (the ground or preparation layer) over a glue layer and then the canvas support. The measured $T_g$ values differ from those of the free paint films; the paint film is of a different age to that of the paint composite and it also contains several layers which show a differential response to moisture. Moreover, in thermomechanical studies of organic coatings, it has been reported that a composite does behave differently from a free film [14].

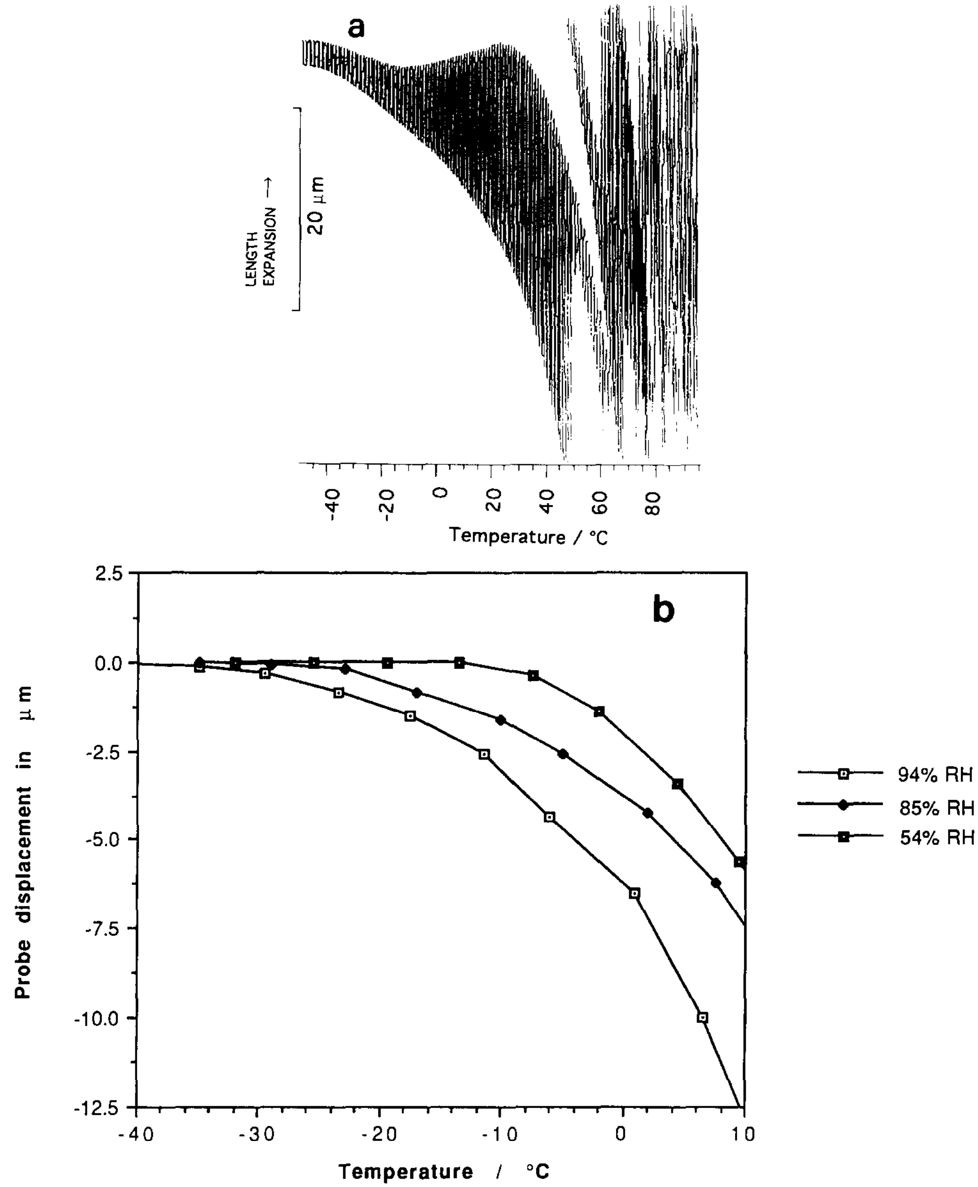


Fig. 2. (a) DLTMA three point bending curves for the control lead white linseed oil samples in the $T_g$ region of linseed oil. (b) TMA three point bending curves for the control lead white linseed oil samples conditioned at different RH.

### *3.2. Dynamic mechanical analysis*

Dynamic mechanical measurements on 19th century samples of primed canvas have confirmed previously reported observations [15]. Changes are observed in the viscoelastic properties as the level of relative humidity increases; there is both a reduction in the

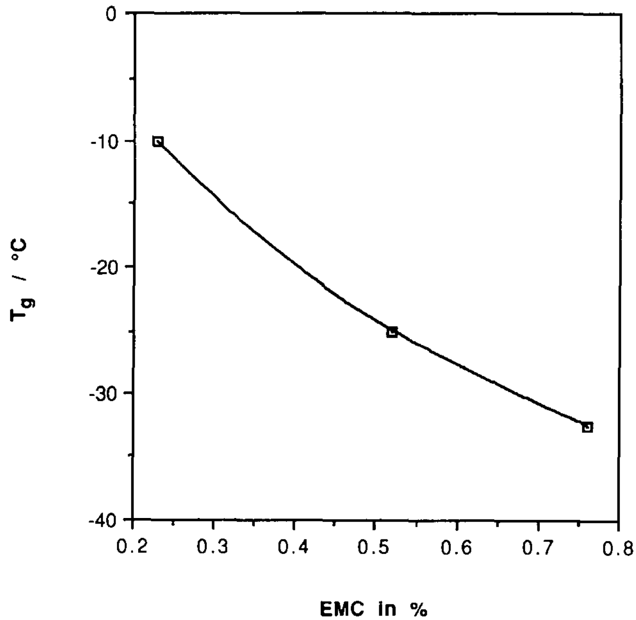


Fig. 3. Plot of $T_g$ against equilibrium moisture content (EMC) for a naturally aged lead white linseed oil sample.

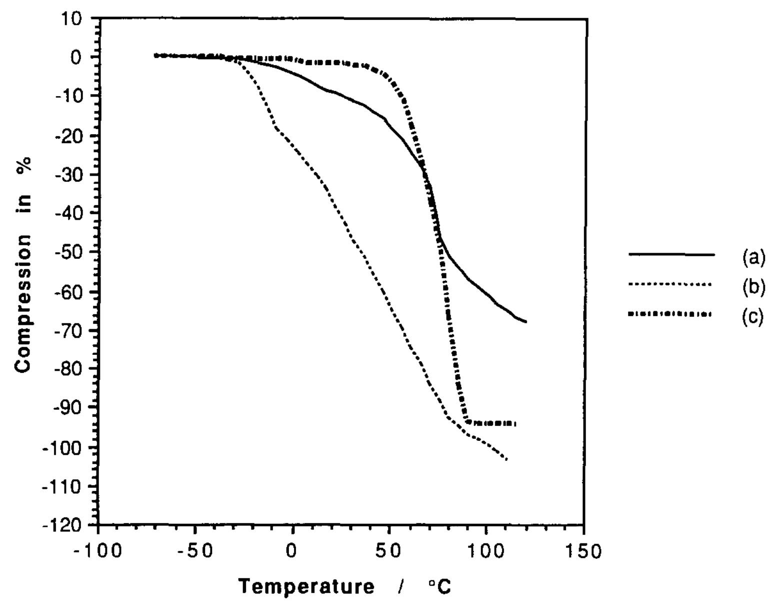


Fig. 4. TMA compression curves for the lead white paint film sample (a), sample with equal proportion of resin mastic (b), and sample after heat ageing (c).

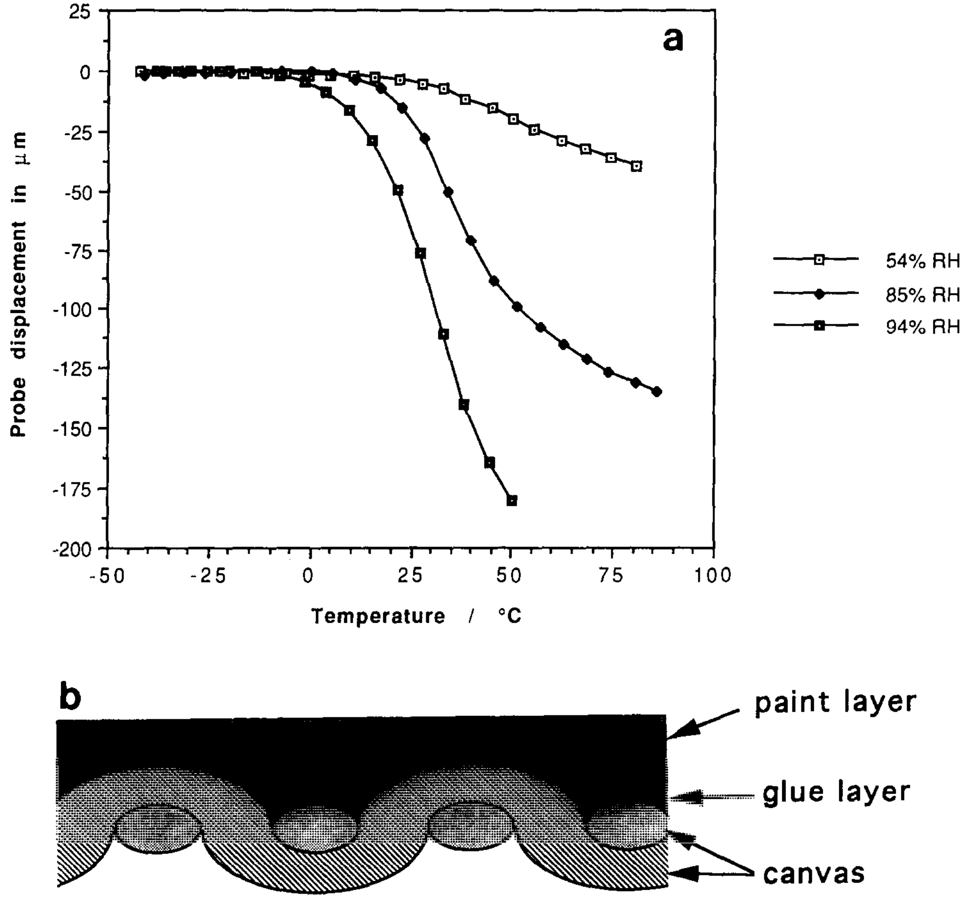


Fig. 5. (a) TMA three point bending curves for control composite paint sample conditioned at different RH. (b) The structure of the composite paint sample.

temperature at which softening occurs of the storage modulus and there is a shift in the tan $\delta$ peak to lower values of temperature (Fig. 6). The paint composite sample behaves in a manner commonly observed in polymeric materials where plasticisation occurs with increasing humidification of the samples. This can also be seen in the increase in the values of the tan $\delta$ peak and hence an increase in the proportion of the viscous component present. The shape of the tan $\delta$ peaks are complex and appear to change with the degree of humidification: at 54% RH the peak is broad and may contain a number of different contributions to the overall relaxation process of the composite. At 85% RH the peak becomes slightly narrower and better defined. This may indicate that one of relaxation processes has become more dominant. Work is in progress to also measure the behaviour of the individual components of the system. As mentioned previously it is already known that the canvas and glue respond more readily to moisture than the paint layer.

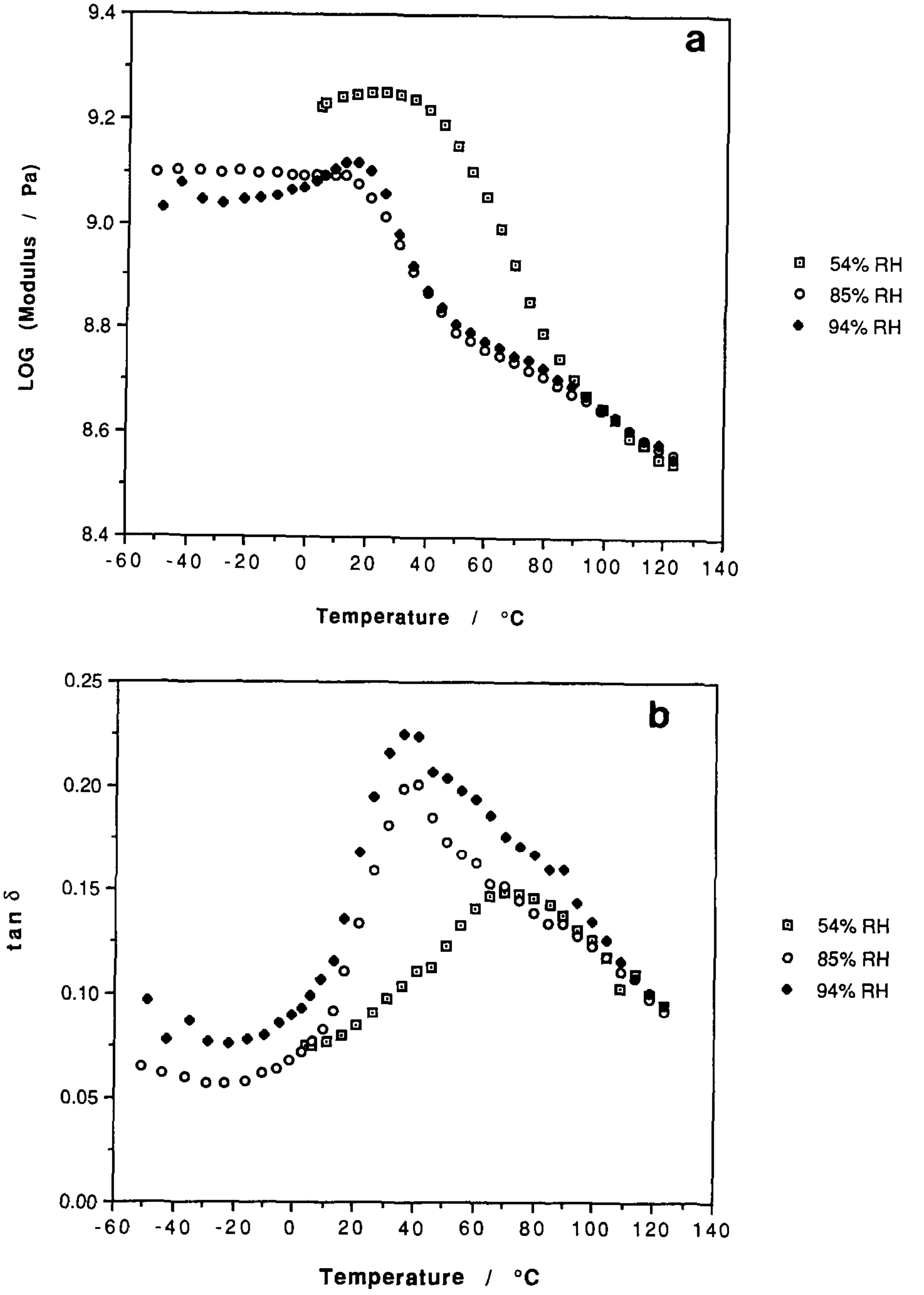


Fig. 6. DMTA curves for control composite paint sample conditioned at different RH and at a frequency of 1 Hz; (a) modulus and (b) tan $\delta$.

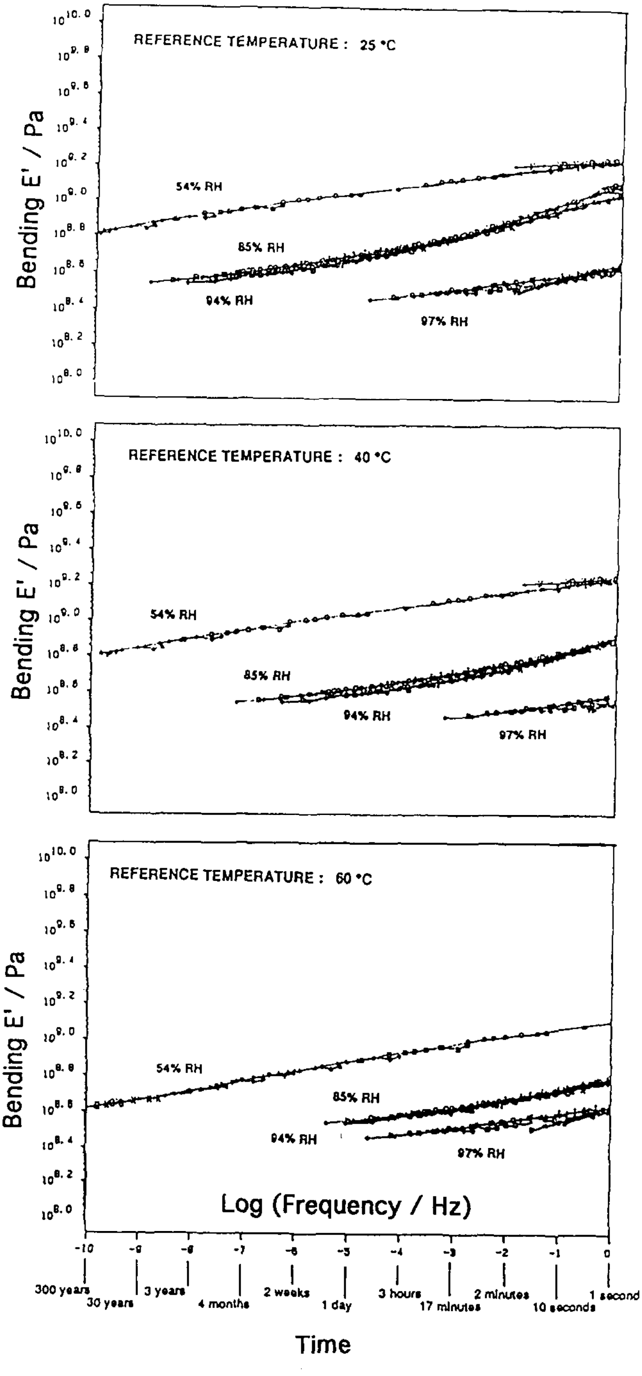


Fig. 7. The 'master curves' of the resulting dynamic mechanical data at four different values of relative humidity and at three selected temperatures.

### 3.3. Use of WLF equation

The Williams Landel Ferry time temperature superposition principle was then used to fit the resulting dynamic mechanical data. Fig. 7 shows the variation of the storage modulus ($E'$) with log frequency (and time) at four different values of relative humidity (from 54% to 97%) and at three selected temperatures, namely 25°C, 40°C and 60°C. The 'master curves' have been generated by shifting the curves describing frequency scans to a particular reference temperature. The resulting curve then covers a larger effective frequency range than the original measurements and is used to predict the period of time in which the storage modulus will remain in the glassy or the rubbery state.

The curves show that the real part of the complex modulus, the storage modulus, was found to fit the equation, and time temperature superposition could be used to make predictions on the long term effects on the modulus of samples exposed to these conditions. The lack of fit of the loss data, however, makes it necessary to consider an alternative model which takes into account the existence of several relaxation processes.

### 3.4. Use of the Dissado-Hill function

The Dissado-Hill function has already been used to fit data from the dielectric analysis of these paint composite samples [16]. Measurements were made in the low frequency range ($10^{-3}$ to $10^5$ Hz). The procedure and the measuring system have been described elsewhere [16]. The parameters measured are the in-phase and out-of-phase components of the complex capacitance of the sample as a function of the AC frequency. The former is related to the real part of permittivity, $\varepsilon'$, by the geometric cell factor. The latter is related to the imaginary part of permittivity, $\varepsilon''$, and the conductance of the system. The dielectric response can be interpreted in terms of a mathematical function developed by Dissado and Hill [17] to describe the frequency dependence of the complex capacitance.

Previous measurements on the complex paint samples have shown that the measured data at two values of relative humidity can be fitted to this function. It uses five parameters to describe each relaxation process: the first one is the amplitude of the complex capacitance, the second parameter is the critical frequency, $\omega_c$, which may be approximated to the frequency at which the real and imaginary components of the response are numerically equal, the third parameter, $p$, is a measure of charge exchange between clusters, with a high value of $p$ indicating a high degree of exchange, the fourth parameter, $n$, represents the homogeneity within the individual clusters, which will be low for substances which are highly bound to a solid substrate and the fifth parameter is the real capacitance at very high frequencies. Measurement of these exponents indicates the number and rate of charges (such as hydroxyl, hydronium ions or dissolved ionic material) which move through the system.

The results of the dielectric analysis show that two relaxation processes are occurring which can be described at the low frequency end in terms of charge hopping and at the higher frequency in terms of dipolar relaxation (Fig. 8). A description of the actual mechanism is discussed in another publication [18]. The parameters calculated at 54% and 85% RH for the relaxation processes which are occurring in the paint composite samples are given in Table 1. The most significant changes with relative humidity occur

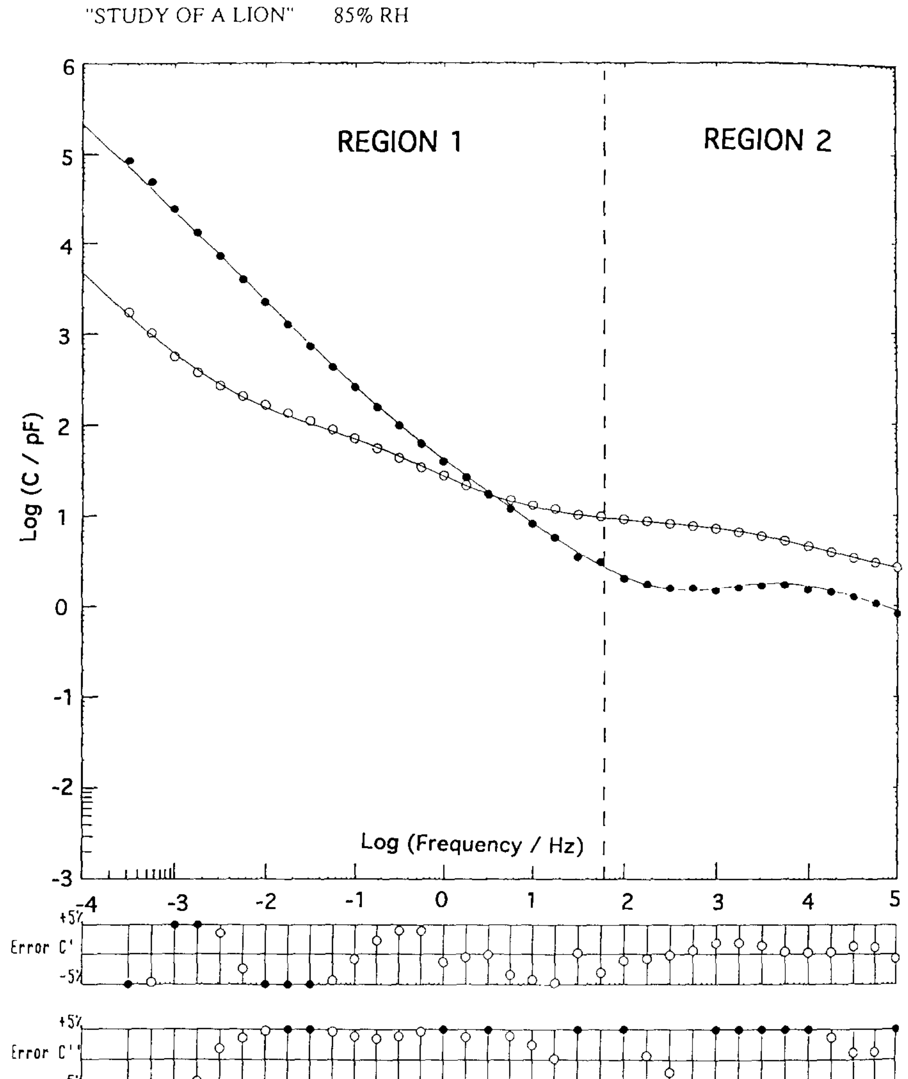


Fig. 8. The dielectric dispersions of a composite paint sample conditioned at 85% RH. Two relaxation processes are occurring which can be described at the low frequency end in terms of charge hopping (region 1) and at the higher frequency in terms of dipolar relaxation (region 2).

in the values of the amplitude of the complex capacitance and the critical frequency ($\omega_c$). This has already been reported for these samples and more recently for unsupported paint films [18]. The values of the parameters for the first relaxation process given by $p$ and $n$ are shown in a graphical plot (Fig. 9). The values of $p$ and $n$ indicate a high rate of charge exchange and that the binding between the adsorbed water and solid substrate is weak. The second relaxation process defined by parameters $m$ and $n$ and which describes a re-

Table 1

| Region | Parameter | Gelatin | Rabbit skin glue | Sturgeon glue | Paint composite | |
|---|---|---|---|---|---|---|
| | | | | | 54% RH | 85% RH |
| 1 Charge hopping dispersion | Amp/pF | 3029.5 | 747.7 | 5343.5 | 27.8 | 1516 |
| | $-p$ | 0.902 | 0.939 | 0.933 | 0.951 | 0.987 |
| | $n$ | 0.621 | 0.668 | 0.439 | 0.389 | 0.293 |
| | $\omega_c$/Hz | 2.219 | 7.414 | 0.105 | 0.01 | 0.344 |
| 2 Dipole dispersion | Amp/pF | | | 226.2 | 4.181 | 7.868 |
| | $m$ | | | 0.776 | 0.392 | 0.390 |
| | $n$ | | | 0.638 | 0.683 | 0.668 |
| | $\omega_c$/Hz | | | 15.11 | 33.67 | 4590 |

laxation of the dipoles present also shows small variation with differing values of relative humidity.

The results obtained from the thermomechanical and dielectric measurements show that the parameters which can be considered as indicators and which are most affected by changing conditions of RH are the values of $T_g$ and the critical frequency ($\omega_c$). The

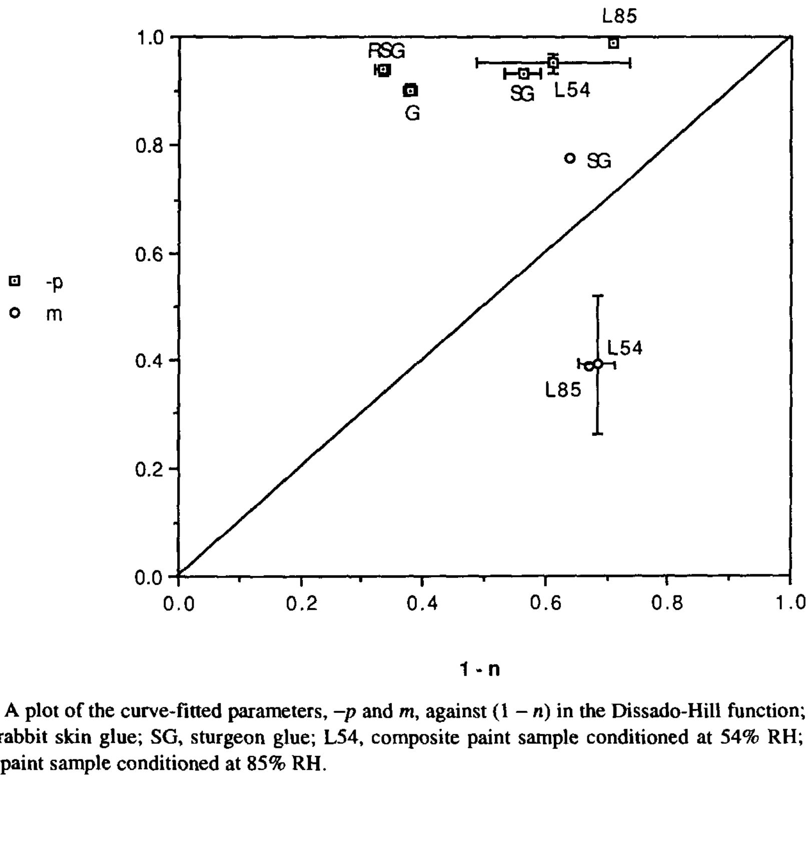


Fig. 9. A plot of the curve-fitted parameters, $-p$ and $m$, against $(1-n)$ in the Dissado-Hill function; G, gelatin; RSG, rabbit skin glue; SG, sturgeon glue; L54, composite paint sample conditioned at 54% RH; L85, composite paint sample conditioned at 85% RH.

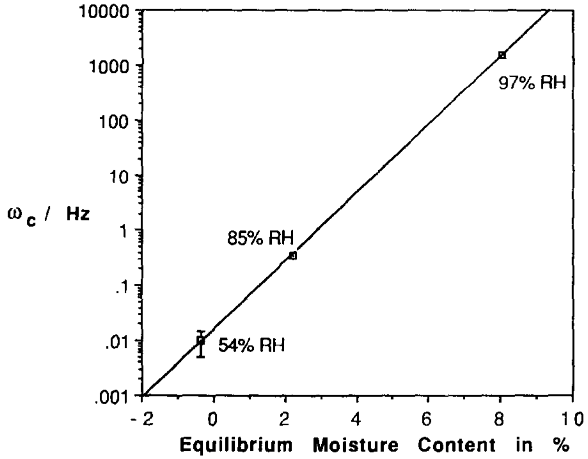


Fig. 10. A plot of critical frequency ($\omega_c$) against equilibrium moisture content of the composite paint samples.

variation in the value of critical frequency ($\omega_c$) with moisture content of the samples is given in (Fig. 10), and that of $T_g$ and moisture content is given in (Fig. 3).

Dielectric measurements on these samples have demonstrated that the complex permittivity data could be fitted using the cooperative model given by the Dissado-Hill function. Since this model has also been used to explain the mechanical relaxation behaviour of a wide range of solid materials [19], work is in progress to fit the mechanical data obtained from the complex paint samples to this function.

## Acknowledgements

(1) Commission of the European Communities, DG X11 Human Capital and Mobility Institutional Fellowships and Science and Engineering Research Council. (2) Science-Based Archaeology Committee, UK. (3) P. Larcey, J. Arthur and J. Duncan, Rheometric Scientific, UK. (4) R.M. Hill, L.A. Dissado and J.M. Alison, King's College London, UK. (5) G. Widmann, Mettler Toledo, Switzerland.

## References

[1] M.F. Mecklenburg and C.S. Tumosa, in M.F. Mecklenburg (Ed.), Art in Transit, National Gallery of Art, Washington, DC, 1991, p. 173.
[2] M. Ranacher, Report Kunsthistorisches Museum Gemäldegalerie 1992.
[3] A. Burnstock, M. Caldwell and M. Odlyha, ICOM, 10th Triennial Meeting Preprints, Washington, DC, 1993, p. 231.
[4] R. MacBeth, M. Odlyha, A. Burnstock, C. Villers and R.B. Gardner, ICOM, 10th Triennial Meeting Preprints, Washington, DC, 1993, p. 150.
[5] M. Odlyha, D.Q.M. Craig and R.M. Hill, J. Therm. Anal., 39 (1993) 1181.

[6] Collection of reference materials prepared by Katherine Ara, Conservation Department, Tate Gallery, London, 1992.
[7] E.L. Back, L. Salmen and G. Richardson, Svensl Papperstidning 86(6) (1983) R61.
[8] E. Krejcar and O. Kolar, Prog. Organic Coatings, 1 (1972/1973) 249.
[9] D.J. Mills and J.E.O. Mayne, J. Oil Col. Chem. Assoc., 66 (1983) 89.
[10] G. Hedley, M. Odlyha, A. Burstock, J. Tillinghast and C. Husband, J. Therm. Anal., 37 (1991) 2067.
[11] D. Erhardt and J.S. Tsang, Preprints of the International Institute for Conservation of Historic and Artistic Works (IIC) Brussels, 1990, p. 93.
[12] A. Toussaint, Prog. Organic Coatings, 2 (1973/1974) 237.
[13] R. MacBeth, Moisture sorption of eleven oil paint samples, Final year project, Technology Department, Courtauld Institute of Art, 1988, unpublished.
[14] D.J. Skrovanek and C.K. Schoff, Prog. Organic Coatings, 16 (1988) 135.
[15] M. Odlyha and C.F. Simpson, J. Therm. Anal., 38 (1992) 361.
[16] T.Y.A. Chan and M. Odlyha, Life Chem. Rep., 10 (1994) 269.
[17] L.A. Dissado and R.M. Hill, J. Chem. Soc., Faraday Trans., 2, 80 (1984) 291.
[18] T.Y.A. Chan and M. Odlyha, Evaluation of the effects of temperature, relative humidity and pigment type on paint films, presented as a poster at the 6th ESTAC, Grado, 1994.
[19] R.M. Hill and L.A. Dissado, J. Mater. Sci., 19 (1983) 1576.