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THE USE OF THERMAL AND SPECTROSCOPIC METHODS TO STUDY CHEMICALLY MODIFIED MATERIALS

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The application of thermal and spectroscopic techniques in the characterisation of chemically modified materials is illustrated with several examples: ethylene vinyl acetate (EVA) copolymers which had been hydrolysed under alkaline conditions, amosite asbestos fibres which had been reacted with alkyldimethylchlorosilanes, and a polymeric composite material which had been affected by moisture.

Keywords: chemically modified materials, EVA

Introduction

The chemical modification of materials, whether by chemical reaction or by changes which occur through the effect of moisture acting on the surface, requires detailed evaluation where materials are being developed for new applications. In this paper three important areas will be considered and these have direct relevance to biomedical application, reduction of toxicity of materials, and the field of conservation of cultural objects.

The first topic of study was the characterisation of modified EVA copolymer for biomedical application as a bile duct prosthesis (stent). Devices in current use are made from hydrophobic materials such as polyethylene. These are prone to protein adhesion and the formation of a bacterial biofilm which results in the precipitation of calcium bilirubinate and calcium salts of fatty acids. Such deposits cause blockage and necessitate the replacement of the stent which is traumatic to the patient. It is therefore essential to develop a material where the surface is resistant to such processes and blockage is avoided. To achieve this purpose it is necessary to create a hydrophilic surface which will discourage protein adhesion and the concomitant formation of deposits.

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At the same time the polymeric material must retain its mechanical properties and stability. Ethylene vinyl acetate (containing 28% vinyl acetate) was chosen since it retains the basic structure of the polyethylene skeleton and presumably the same mechanical strength. Furthermore it is likely that the acetate groups can be readily hydrolysed to give hydroxyl groups on the EVA copolymer surface and thus create the required hydrophilic surface.

The second topic of study deals with the characterization of modified asbestos fibres where effectively C8 and C18 hydrocarbon chains have been added to terminate the fibres.

The structure of asbestos can be described as consisting of a double chain of silica tetrahedra cross-linked with bridging cations that are predominantly Fe^{2+} with some Mg^{2+} and some smaller variable amounts of Fe^{3+} and other cations. The silica chains terminate in silanol groups. The presence of these groups confers a hydrophilic nature to the fibre and is considered to be the reason for their interaction with lung tissue. A way to prevent such an interaction would be to replace the silanols with a hydrophobic moiety. Reaction with alkyldimethylchlorosilanes would form such a fibre where the silanol groups would be replaced by the corresponding trialkylsilyl groups bonded through siloxane linkages to the fibre. Recent investigations have shown that the altered fibres interact less readily with cells *in vivo* and are less cytotoxic [1]. The C8 modified fibres behaved in a manner similar to the parent fibres with regard to the number of mesotheliomas produced in whole animals. However the rate of formation of the tumours occurred earlier with the unmodified material. The C18 derivatized fibre, however, was markedly less active, if at all, in the production of tumours. This is the first time that similar size fibres with differing terminal groups have been observed to give different pathogenic properties. Moreover the reduction in short-term cytotoxicity and carcinogenicity suggests that the nature of the surface of a fibrous material is an important factor in determining biological activity.

In this paper preliminary measurements are reported on the characterization of the surface of asbestos fibres which had been treated with a wider range of long chain hydrocarbons (C12, C18, C30). The work is being carried out in collaboration with the MRC Toxicology unit where the altered fibres are being presently tested with live tissue.

The final topic of the study describes the work which is being carried out in collaboration with the Courtauld Institute of Art and which is highly relevant both to the development of improved conservation treatment of easel paintings and to their cleaning using new aqueous based preparation.

The Tate Gallery provided samples for this work. The samples were of primed canvas from the back of a Landseer painting 'Study of a Lion' (c. 1862). The primed canvas samples were on closely woven linen and contained lean mixtures of lead white and calcium carbonate.

The aim of the project is to quantify the effects of moisture, temperature and pressure on a sample of primed canvas with a view to optimize procedures where these variables are used to correct deformations which occur in the paint layers of easel paintings, particularly if they have been water-damaged at any time. The response of the individual layers (e.g. the paint layer or priming, the layer of natural glue which serves to adhere the top layer to the support and the canvas) to the variables mentioned above (RH, temperature and pressure) have previously been reported. In this paper the preliminary results of work which has been carried out on testing the composite sample will be reported. This is the first time that samples on a canvas support from an actual painting have been measured using Thermomechanical Analysis, Dynamic Mechanical Thermal Analysis, and Dielectric Thermal Analysis.

Experimental technique

Samples of the various materials were examined using the full range of thermoanalytical techniques {DSC (P-E DSC-7), TGA (P-E TGA-7) TMA (Stanton Redcroft 691) DMA and DETA (PL Thermal Sciences)}, and the spectroscopic techniques Diffuse Reflectance FTIR (DRIFTS)(P-E 1710), and FTIR microscopy (P-E 1725X Research IR PLAN Microscope). Elemental analysis was carried out by means of EDX (Energy dispersive X-ray analysis) and micro analysis.

Results and discussion

Modified polymers

An EVA copolymer containing VA (28%) was hydrolysed using methanolic KOH [2]. When the EVA copolymers were examined using FTIR microscopy (Fig. 1*a*), the effect of the hydrolysis treatment could be clearly seen. The most significant change is the appearance of an additional broad peak in the region of 3400 cm^{-1} (Fig. 1*b*). This corresponds to the formation of hydroxyl groups in the modified EVA. There is also some evidence of peaks which correspond to C–O stretching and OH deformation absorptions in the region of 1100 cm^{-1} and 1260 cm^{-1}.

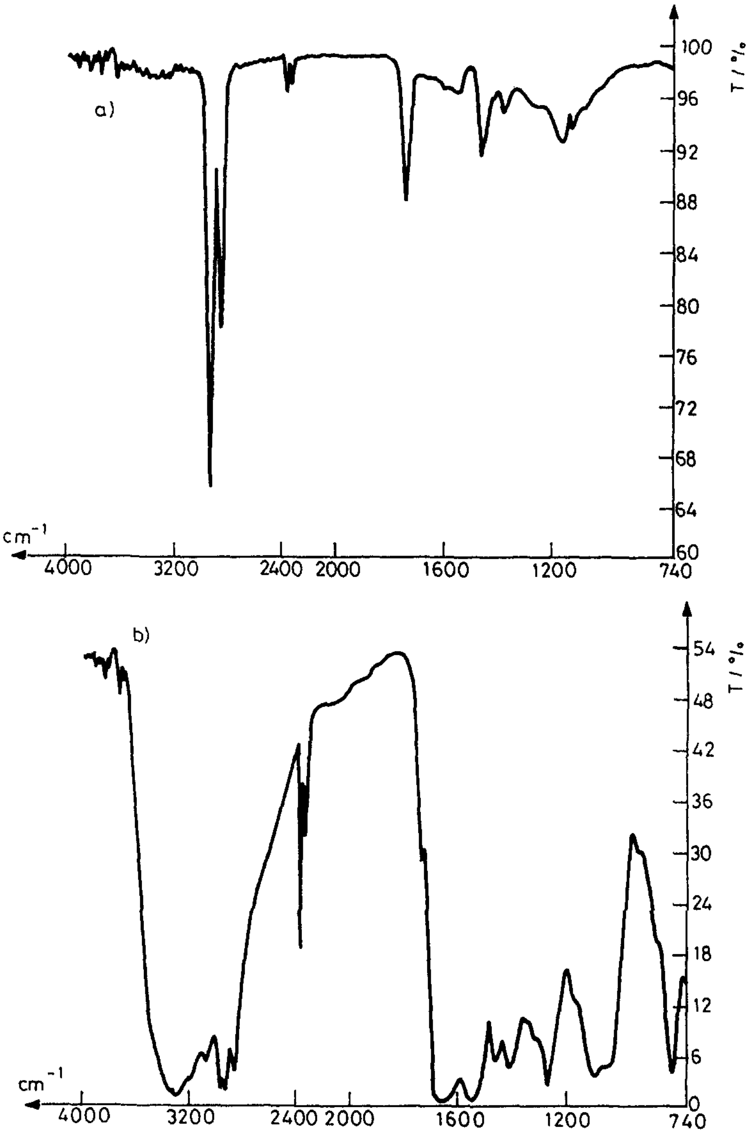

Fig. 1 FTIR spectra of EVA copolymer; (*a*) EVA copolymer before hydrolysis, (*b*) EVA copolymer after hydrolysis

Then to conclusively demonstrate that hydroxyl groups had been formed, the treated polymer was reacted with trifluoroacetic anhydride in diethyl ether to give the intense C–F stretching absorptions in the region 1200–1000 cm^{-1} (Fig. 1*c*) and absence of the hydroxyl bands.

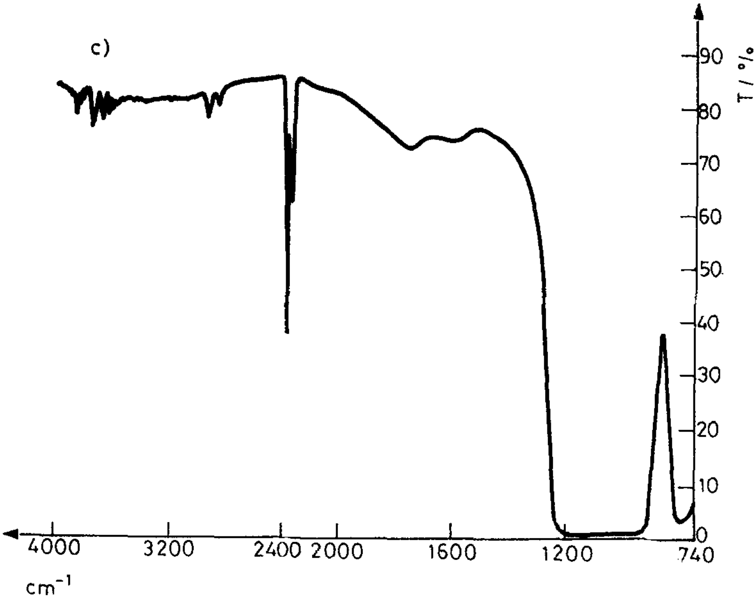

Fig. 1 FTIR spectra of EVA copolymer; (c) EVA copolymer after hydrolysis and treatment with trifluoroacetic anhydride in diethyl ether.

In order to assess whether the hydroxyl groups have an effect on the mechanical properties of the treated polymer TMA measurements were made in the penetration mode (Fig. 2). It is clear that, though two stages of softening are maintained in the region of 30° and 50°C respectively, the degree of penetration in the case of the treated polymer has been significantly decreased, which demonstrates that a hardening of the surface has occurred. This is to be anticipated. The acetate groups are being replaced by the more polar hydroxyl groups and this should cause an increase in the glass transition temperature of the polymer and a hardening of the material. If it is only the surface which is undergoing change, then the overall mechanical properties of the treated material should not be affected to any extent.

DMA of both treated (Fig. 3*b*) and untreated samples (28% VA) (Fig. 3*a*) in the bending mode showed that at low strain there are no significant changes and so the mechanical properties have been virtually retained. However, in the treated sample, the second stage of softening (at 50°C) had disappeared which agrees with the TMA data where hardening of the surface was apparant. The glass transition temperature (tan δ peak) for the untreated material (28% VA) occurs at –10.7°C. (Literature values [3] for the T_g poly(ethylene vinyl acetate) copolymer extend over the range –20° to 20°C depending mainly on variables such as plasticizer and ethylene content.) In the treated material the tan δ peak has moved to slightly lower temperatures (–11.9°C) and a smaller additional peak appears at 40.3°C (Fig. 3*b*). This is indicative of the presence of the more polar hydroxyl group at the higher T_g value.

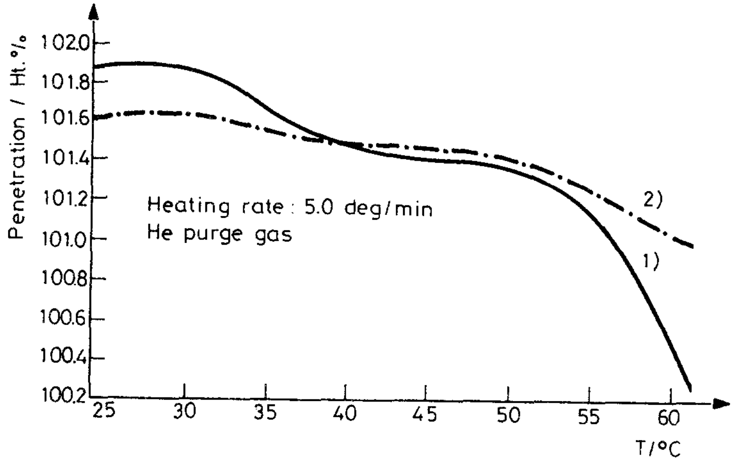

Fig. 2 Thermomechanical data for (1) EVA copolymer and (2) hydrolysed EVA copolymer

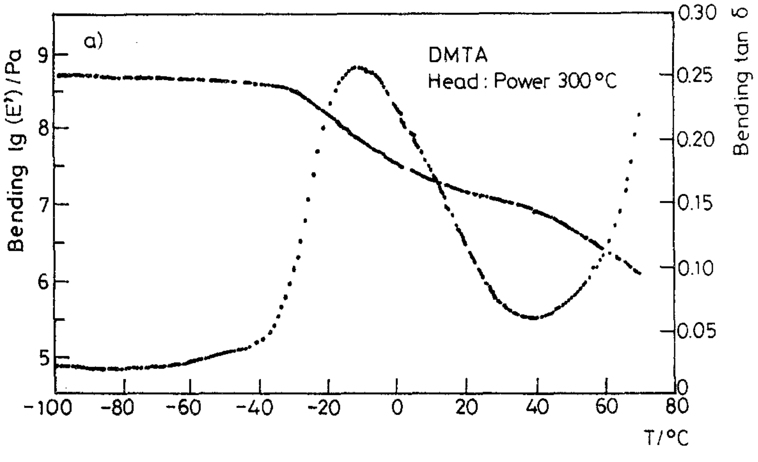

Fig. 3 Dynamic Mechanical data for (*a*) EVA copolymer

The actual value of tan δ has noticeably decreased indicating a reduction in the viscous component, which is in accord with the previously observed hardening of the surface. In addition the shape of the tan δ peak has significantly broadened to encompass body temperature (37°C). The peaks overlap and this creates a broad glass transition temperature region where there is molecular mobility and the material is more susceptible to moisture uptake and diffusion processes. A negative aspect in terms of the mechanical properties of the treated material is that the broad T_g includes the body temperature. The aim therefore would be to produce a material where the modified T_g does not lie in the region of body temperature to ensure the stability of the material during prolonged use within the body.

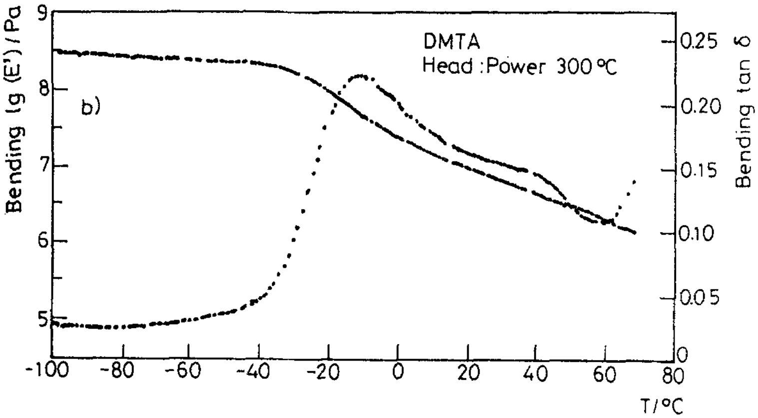

Fig. 3 Dynamic Mechanical data for (*b*) hydrolysed EVA copolymer.

The original polar nature of the copolymer and then the introduction of the hydroxyl groups makes it possible to follow the changes produced by the treatment with DETA. Changes were observed both in the dielectric loss permittivity data and the tan δ values. Figure 4*a* shows the dielectric loss peaks for the untreated material, and Fig. 4*b* shows that an additional loss peak has appeared in the region of 55°C. The tan δ (Fig. 4*c*) appears in the untreated material at about 10°C; in the treated sample (Fig. 4*d*) its value is reduced and the peak maximum moves to slightly lower temperatures. Furthermore the peak is noticeably broadened and overlaps with a smaller peak in the region of 60°C. This is analogous to the effects observed on the mechanical tan δ after the treatment. The temperatures at which then tan δ peaks appear to differ from those obtained from the mechanical measurements because the DETA measurements were made at a higher frequency

(100 KHz). In the case of the mechanical measurements a frequency of 10 Hz was used.

It is pertinent to note that this surface modification did in fact prevent protein adsorption but clearly more work is necessary on this topic [2].

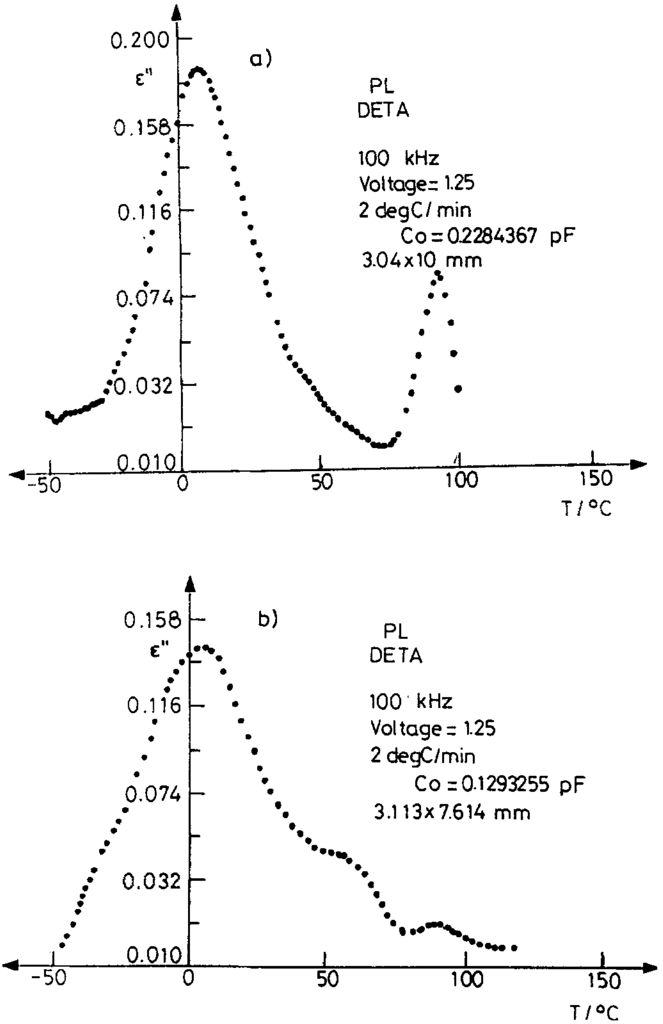

Fig. 4 Dielectric data for EVA copolymer: dielectric loss permittivity *vs*. temperature for (*a*) untreated EVA (*b*) hydrolysed EVA

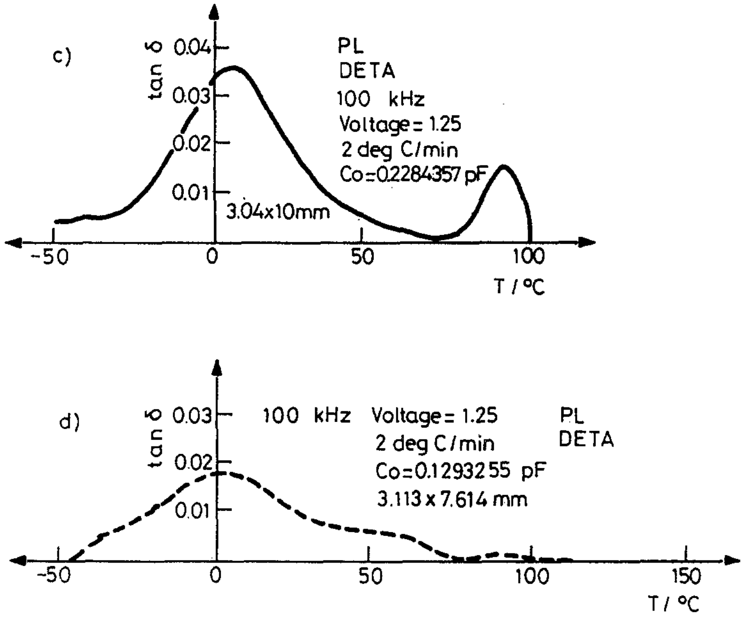

Fig. 4 Dielectric data for EVA copolymer: tan δ *vs.* temperature for (*c*) untreated EVA (*d*) hydrolysed EVA

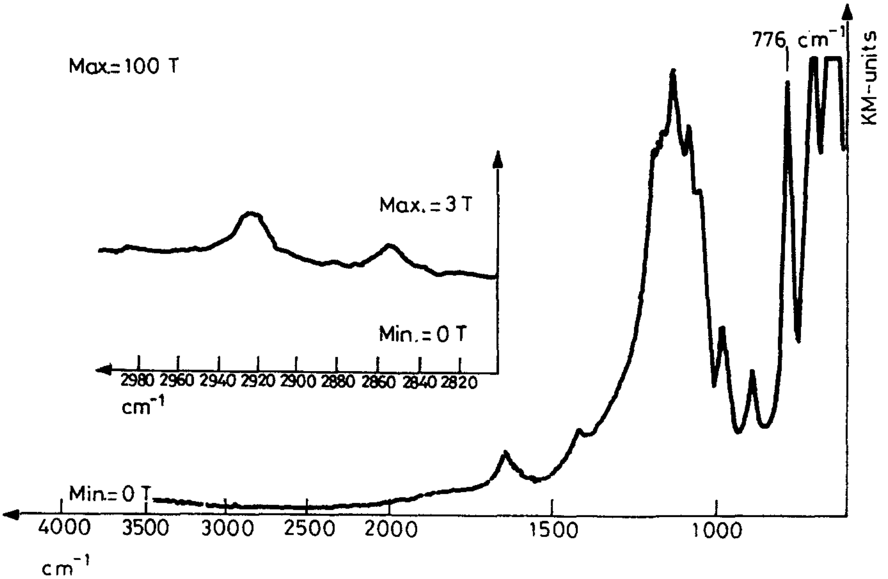

Fig. 5 DRIFT spectra of modified asbestos fibres (C30). Enlarged section shows the presence of the CH2 str. frequency

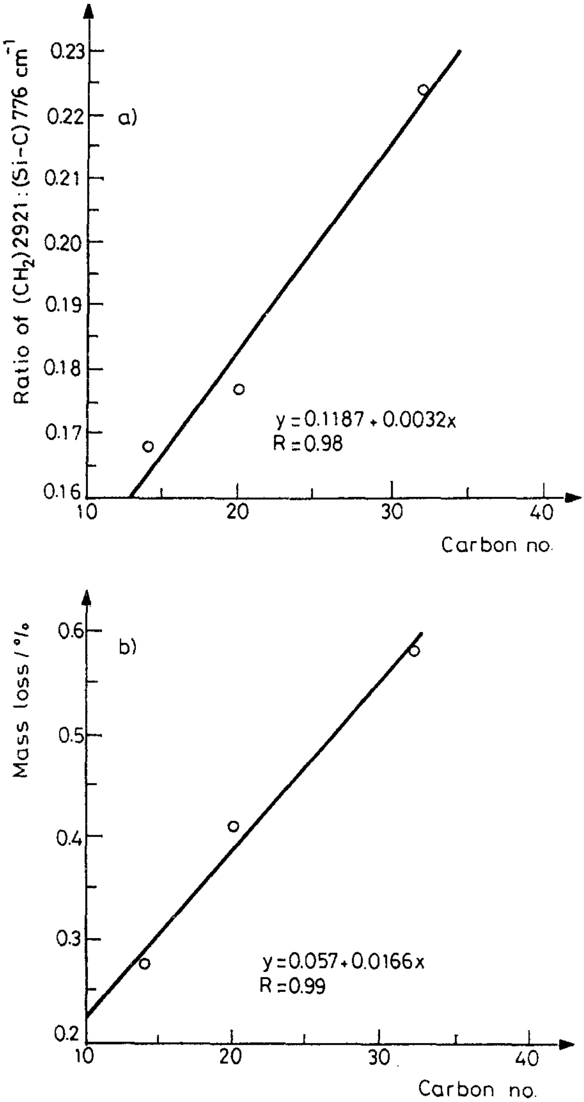

Fig. 6 (*a*) Ratios of peak heights of CH_2 str. (2921 cm^{-1}): Si-C str. (776 cm^{-1}) from DRIFT spectra *vs.* Carbon no. of derivatizing agent used for fibre modification (*b*) % mass loss (TG) measured between 230C&490C (C30 modified fibre also determined by microanalysis) *vs.* Carbon no. of derivatizing agent used for fibre modification

Asbestos fibres

DRIFT spectra were collected on bulk samples of fibres (C12, C18 and C30). There was a progressive increase in the intensity of the CH_2 absorption peak (2921 cm^{-1}) (Fig. 5). The ratio CH_2:Si-C (776 cm^{-1}) was plotted against total carbon number and showed a substantially linear relationship for the three samples examined (Fig. 6*a*).

TG analyses (30–850°C at 2 deg·min^{-1}) were also carried out on the same samples (Fig. 7) and again showed a linear relationship between weight loss of hydrocarbon *vs.* total carbon number (Fig. 6*b*). It is of interest to note that over the temperature range 550–850°C an equivalent percentage weight gain was obtained on all three samples. This was ascribed to oxidation of the iron content of the amosite fibres and demonstrated by dissolving the brown residue in HCl and testing with ammonium thiocyanate when a blood red colour was obtained.

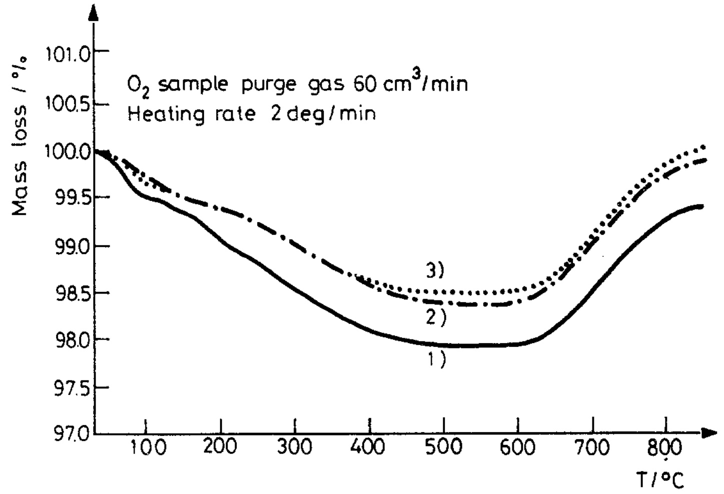

Fig. 7 Thermogravimetric analysis of modified asbestos (amosite) fibres (1) C30 (2) C18 and (3) C12

Examination of single fibres using FTIR microscopy was undertaken. The fibres were rolled flat on a BaF_2 1 mm window and the spectra recorded in transmission. The spectra of C8, C12, and C18 modified fibres showed a progressive increase in the intensity of the CH_2 peaks which corresponds to the presence of hydrocarbons on the fibre. Inconsistencies, however, were observed in the case of the C30 modified fibre where there was a sudden decrease in the carbon loading. Further detailed examination of several fibres showed an inhomogeneity of hydrocarbon distribution within the sample; there appeared to be CH rich waxy parts and fibres low in CH

(Fig. 8). This obviously demonstrates the value of detailed microscopic examination to understand the nature of the modified fibres.

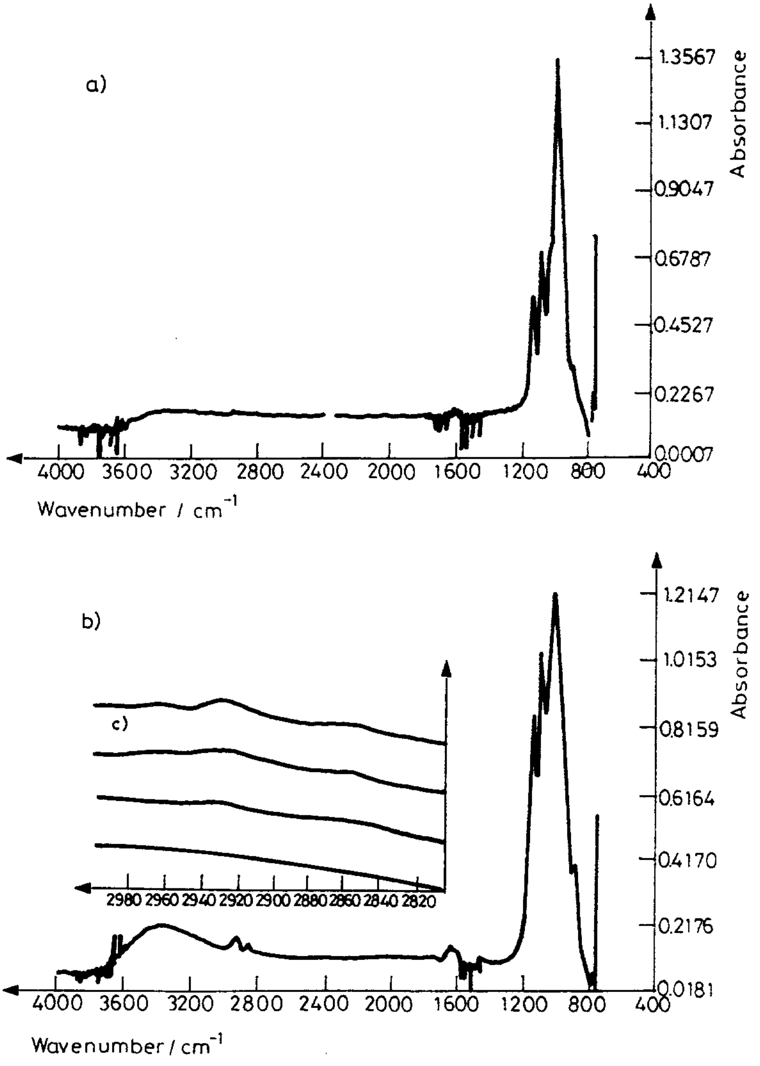

Fig. 8 IR Spectral analysis of several C30 modified asbestos fibres with the FTIR microscope (*a*) analysis of a fibre rich area (*b*) analysis of a waxy region (*c*) enlarged section showing single fibre analysis from top to bottom: amosite (C18, C12, C8 and blank)

Composite sample

The primed canvas samples were equilibrated at 4 different values of relative humidity, at 54%, 85%, 94.6% and 97.6% RH respectively. Samples were placed in open tubes in jars containing saturated solutions of the following: $Mg(NO_3)_2$, KCl, KNO_3 and K_2SO_4 for periods of at least one week. Measurements were then made using TMA in compression mode and DMA in the bending mode at a low value of strain. The information from the mechanical data shows the following:

(1) A broad tan δ peak which moves progressively to lower temperatures as the relative humidity increases-(Fig. 9*a*). There is a noticeable shift in the

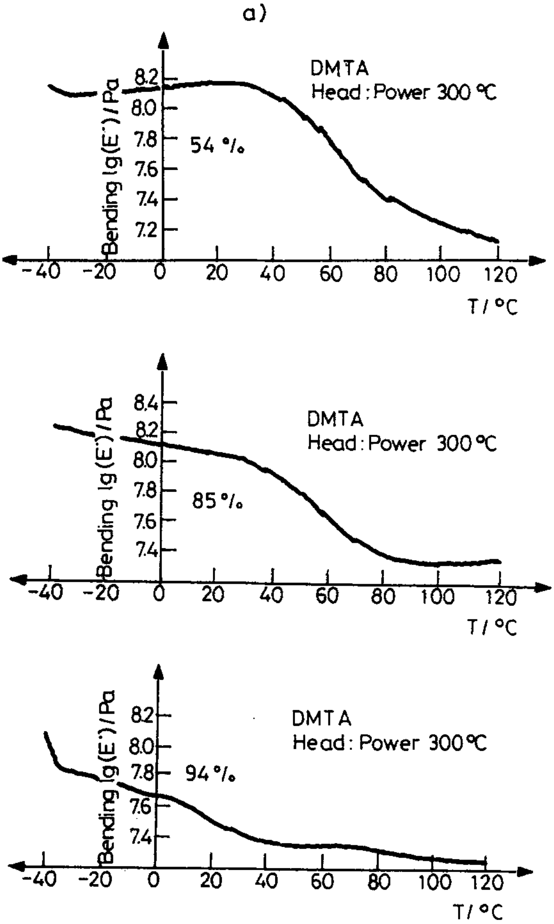

Fig. 9 Dynamic Mechanical and Thermomechanical data from Landseer primed canvas sample (labelled Tate 1): (*a*) Bending log(E') *vs.* temperature for 54%, 85% and 94% RH

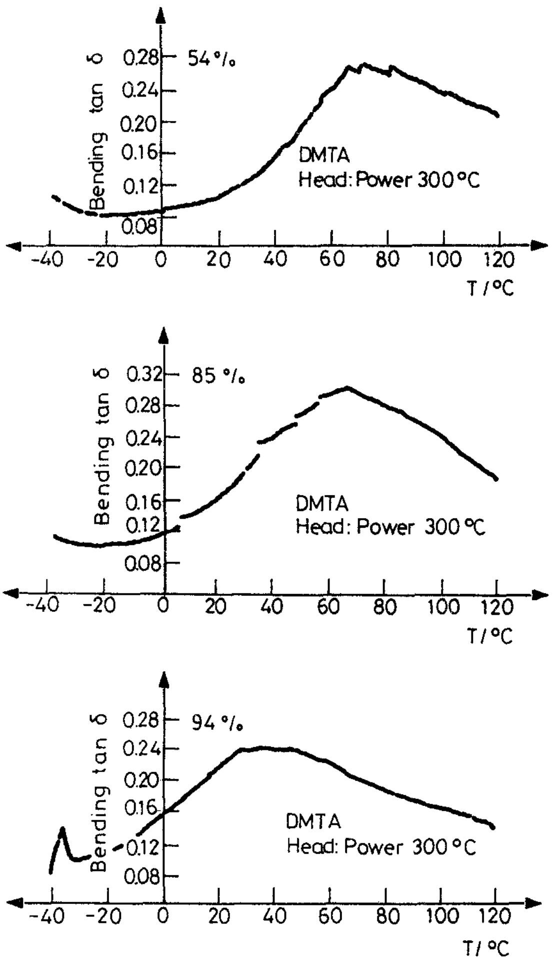

Fig. 9 Dynamic Mechanical and Thermomechanical data from Landseer primed canvas sample (labelled Tate 1): (*b*) tan δ *vs.* temperature for 54%, 85% and 94% RH

broad peak maximum from a value in the region of 80°C to 40°C as the relative humidity increases from 54% to 94%.

(2) A reduction in the value of the elastic modulus (*E*') with increasing relative humidity (Fig. 9*b*). Above 85% RH there is a significant loss in the mechanical strength of the sample; at 94% RH the mechanical strength of the sample has been reduced by a factor of five in the region of room temperature. This softening is also clearly seen in the TMA curves (Fig. 9*c*) where the temperature at which it occurs moves from the region of 40°C (at

54% RH) to about -20°C (at 94%). There is also an accompanying increase in the amount of compression which occurs.

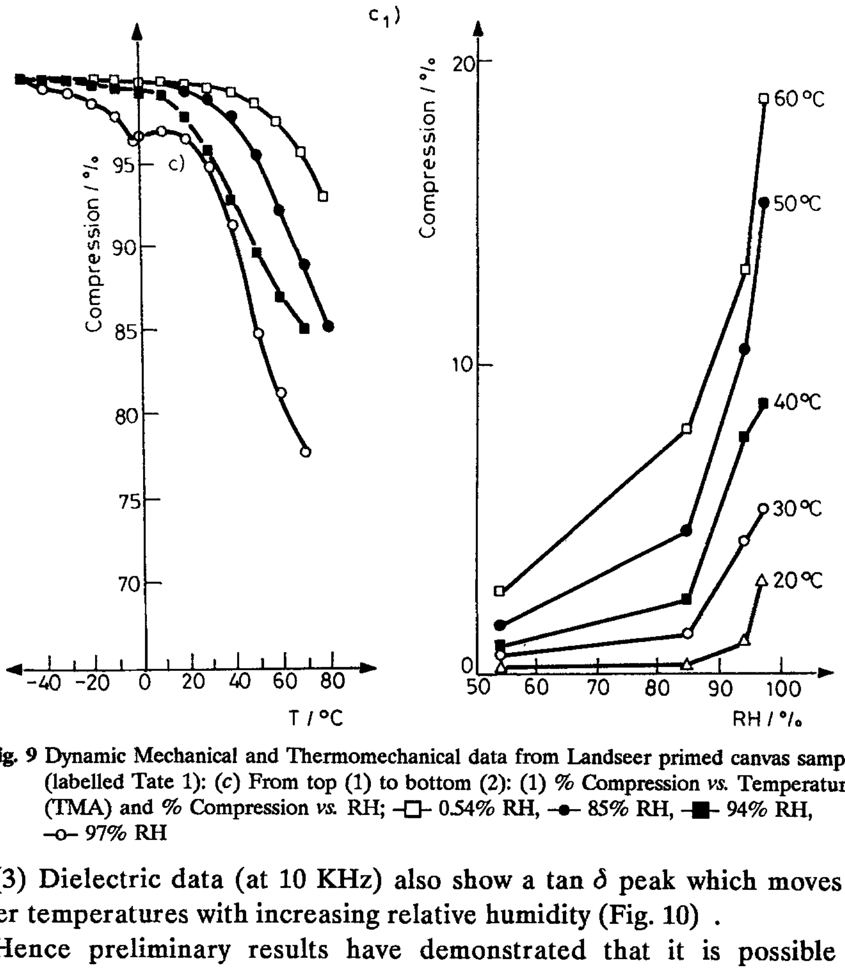

Fig. 9 Dynamic Mechanical and Thermomechanical data from Landseer primed canvas sample (labelled Tate 1): (*c*) From top (1) to bottom (2): (1) % Compression *vs.* Temperature (TMA) and % Compression *vs.* RH; -□- 0.54% RH, -●- 85% RH, -■- 94% RH, -o- 97% RH

(3) Dielectric data (at 10 KHz) also show a tan δ peak which moves to lower temperatures with increasing relative humidity (Fig. 10) .

Hence preliminary results have demonstrated that it is possible to measure the effects of increasing relative humidity on the composite sample. It is clear that the composite is being plasticized as the level of relative humidity increases, and that at 94% RH the sample shows a significant loss in mechanical strength. This is consistent with the effects generally seen of water transport through organic coatings [4]: a change in the mechanical and electrical properties of the coating. These are accompanied by an alteration of the coating composition (through leaching of additives, low molecular weight fractions) and a loss of adhesion from the substrate; the latter can be seen in water damaged paintings where delamination occurs

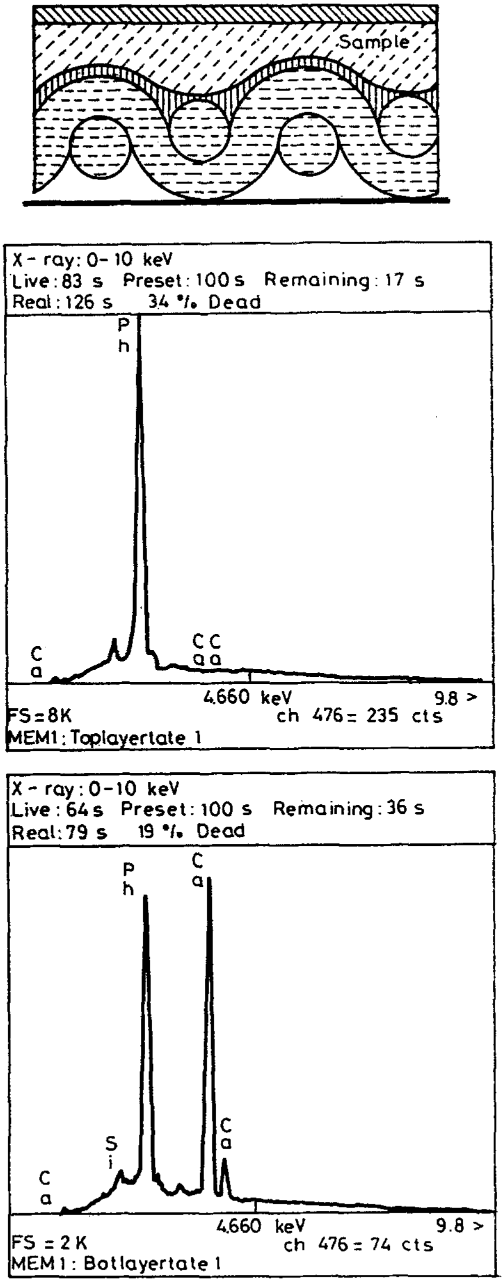

Fig. 9 Dynamic Mechanical and Thermomechanical data from Landseer primed canvas sample (labelled Tate 1): (c) From top (1) to bottom (2): (2) Cross section of sample showing from to to bottom: layer of lead white, calcium carbonate and lead white, layer of size and canvas with corresponding EDX data

and the paint layer comes away from the substrate. The paint layer is attached to a canvas support by means of a natural glue medium (rabbit skin glue).

Work is in progress to record the surface changes which occur, with both moisture absorption and desorption, on the upper paint layer of the composite, and the change in the composition of this paint layer. The passage of moisture through the composite is also being studied to determine precisely where the moisture goes within the structure and whether it is at any stage trapped within a layer. Preliminary results from the examination of samples in cross-section indicate that the moisture is attracted to the layer of glue which then probably softens to such an extent that it sinks into the canvas. This may explain the anomalous but reproducible effect observed in the TMA curves at high RH (97%) in the region of 0°C. This will be reported in a detailed paper on the composite sample in due course.

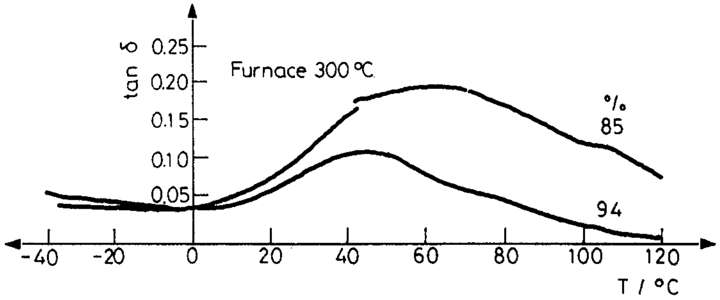

Fig. 10 Dielectric data from Landseer primed canvas sample: tan δ *vs.* temperature for samples equilibrated at 85% and 94% RH

The measurements obtained on the composite sample are already of some use to actual conservation treatment where it is necessary to expose selected regions of easel paintings to elevated RH value to correct deformations. TMA data gives the values for softening temperature and amount of compression which occurs. Then the DMA and DETA results describe what is happening to the overall composite. If this information is combined with what is known from previous work on the response of individual layers to increasing values of relative humidity, i.e. a sample of unsupported lead white linseed oil [5] will soften at room temperature only at 94% RH (Fig. 11*a*), a layer of glue or size will start to flow at this stage (Fig. 11*b*), and canvas will shrink [7] (Fig. 11*c*), then it becomes apparent that in order to plasticize the upper paint layer efficiently, it will be necessary to use a moisture gradient where the RH values decrease from the paint layer side to the canvas. In this

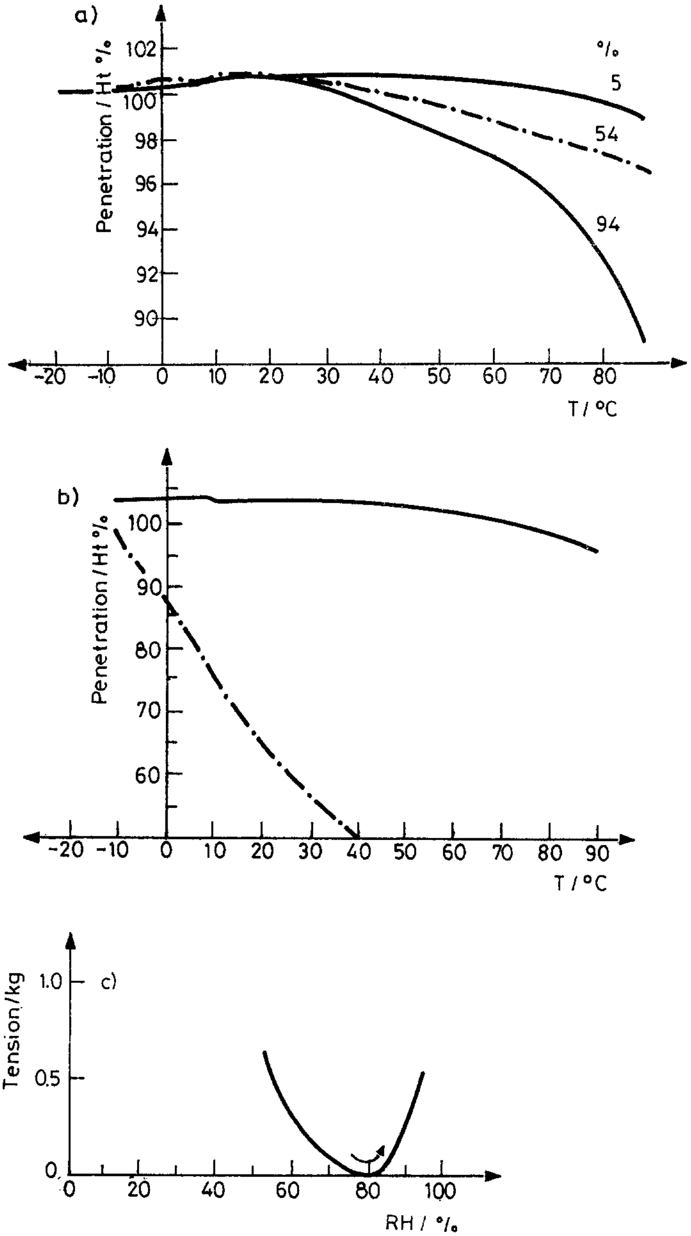

Fig. 11 Response of individual layers to variation in relative humidity: (*a*) lead white and linseed oil: TMA compression curves for 5%, 54% and 94% RH (*b*) compressibility of a fim of rabbit skin glue when desiccated over $CaCl_2$ and humidified over water (*c*) onset of canvas shrinkage

way the adverse effect of high RH on the canvas will be avoided. This approach has already been suggested in practice [6]. The fact that thermoanalytical results fully support previous observations and demonstrate for the first time that the effect of moisture on such a composite can be measured indicates that conservation treatment in the future will be more precisely controlled and that the mechanism of water transport understood.

* * *

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PL-Thermal Sciences (Epsom Laboratories) for the use of Dynamic Mechanical Thermal Analysis equipment.

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Zusammenfassung — Anhand verschiedener Beispiele wird die Anwendung thermischer und spektroskopischer Methoden zur Charakterisierung chemisch modifizierter Materialien gezeigt: Ethylenvinylacetatkopolymere (hydrolysiert unter alkalischen Bedingungen), Amosit Asbestfasern (nach zuvoriger Reaktion mit Alkyldimethylchlorsilanen) und polymere Verbundwerkstoffe (nach zuvoriger Einwirkung von Feuchte).