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CONTROLLED TEMPERATURE AND RELATIVE HUMIDITY DYNAMIC MECHANICAL ANALYSIS OF PAINT FILMS

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Abstract

A description is given of modifications to a dynamic mechanical analyser (DMA) to allow controlled relative humidity (*RH*) experiments to be performed under isothermal or thermal scanning conditions. Free film samples of polyester melamine paints (under-cured, normal-cured and over-cured) were supplied and the viscoelastic properties measured in the tensile mode of the DMA. A reduction in the glass transition temperature (T_g) of up to 10°C was found as the controlled *RH* was increased.

Keywords: dynamic mechanical analyser, films, paint, relative humidity

Introduction

Work has been carried out to monitor the effect of humidity, especially in the area of historic materials conservation [1–3] and automotive paint systems [5],fibres [6, 7], thermosets [8, 9] and wood [10, 11]. The work demonstrated that changes in humidity had an effect on the mechanical properties. Some DMA testing has been carried out on artists' paint [12–15], but the control of humidity proved difficult to achieve.

DMA provides a measurement of the viscoelastic properties of a material [16]. Normally, DMA experiments are carried out with limited or no *RH* control but in the work alluded to above, the tests were either performed at room temperature or the samples were preconditioned in a humid atmosphere prior to the testing. The focus of this work is to produce a DMA, which is capable of controlled *RH* at elevated temperatures.

This work demonstrates how a DMA can be modified to take a custom-built *RH*/temperature control system and investigates this apparatus for use on paint films.

Modifications to DMA

In order to accommodate the *RH*/temperature control system, modifications were made to a Rheometric Scientific DMA Mk3. In normal use, this machine would operate with

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the drive shaft either operating vertically below the specimen clamps or in a horizontal orientation. In order to protect the internal electronics from the high *RH*, which would be generated during the testing, the DMA measuring head had to be placed in an inverted orientation. The drive shaft then operated vertically downwards and a specialised stand was constructed to achieve this. In order to provide a safe working distance from the electronics, the drive shaft and supporting pillars were extended by 150 mm. To accommodate these extended shafts, the furnace lid was removed and its normal automatic operation overridden. These modifications allowed the *RH* system to be fitted.

Humidity system: design

Due to safety constraints and limited space, it was not possible to use the existing oven unit on the DMA. Therefore, in addition to providing the *RH* control, the system was also required to control temperature. Glassware was designed and manufactured to fit around the extended drive shafts. A silicon washer was manufactured to provide an adequate seal between the glassware and the DMA measuring head. A complete seal was difficult to achieve because of the clearance required for the drive shaft, where it entered the DMA head. In order to provide thermal control, the glassware incorporated a water jacket with an inlet and outlet port. The ports allowed water to be pumped around the inner cell, which was supplied by a temperature controllable water bath. In order to monitor temperature, the DMA's existing platinum resistor was used, although it had to be repositioned closer to the sample. The basic set-up of the *RH* system is shown in Fig. 1. It consisted of separate dry air and 100% *RH* supplies regulated independently by 2 valves. The air streams from the two supplies were mixed just before entering the *RH* cell through an inlet port, which passed through the outer water jacket directly into the inner cell. By altering the flow through the lines, any value of humidity could be generated inside the cell. The volumetric flow rate was kept constant, in order to maintain the temperature of the humid air that entered the cell, the same as the air already inside. The pipe work and bubbler were placed in-

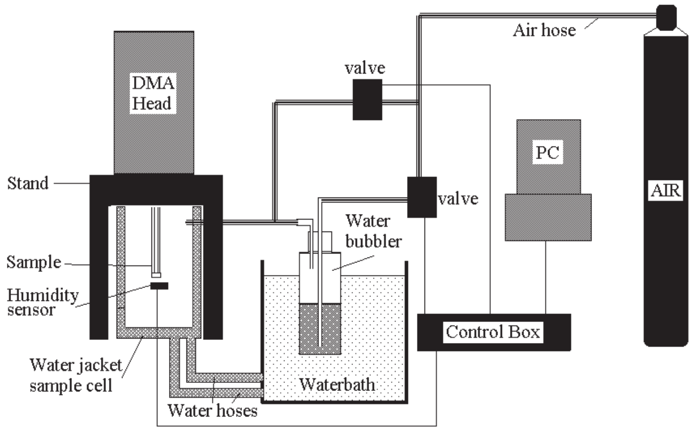

Fig. 1 Schematic representation of controlled relative humidity DMA system

side the same water bath, which supplied water for the thermal jacket. To measure and control the humidity, a *RH* sensor was fitted inside the environmental cell. The sensor was interfaced to a PC that logged the data and controlled the valves.

Chemistry and material background

The paints used were coil coatings based on polyester/melamine technology. Coil coatings are paints that are applied to continuous strips of metal, chiefly hot dip galvanised steel, cold rolled steel or aluminium, by a roller coater [17]. Shortly after application the strip passes into a series of ovens (between 30 and 50 m long) that heat it from ambient conditions to temperatures in excess of 200°C with dwell times of less than forty seconds. Twenty second dwell times are becoming more common as line speeds increase from 80–90 to 120–150 m min^{-1}. The heat supplied causes solvent evaporation and induces a reaction between the polyester resin and melamine cross-linker, a process known as curing. Once curing is complete, the strip is rapidly cooled with water at the exit to the ovens and rewound into a coil. The coated metal is then formed, on a roll-forming line, with many tight bends introduced. Seventy percent [18] of the production is used by the construction industry for roofing or façades of buildings such as warehouses and factories. Thus the paint must have the following properties; abrasion resistance, capability of being formed without loss of adhesion or cracking and a capacity to withstand the ravages of the weather over extended periods of time.

The cure reaction involves an acid-catalysed trans-etherification between the hydroxyl groups of the polyester and the methoxy groups on a hexa-methoxymethyl melamine [19]. There are normally at least two hydroxy groups per polyester molecule and in theory the melamine resin can bond six times. The melamine resin is typically in excess and it is known [20] that not all the CH_2OH or NH groups of the parent molecule are blocked with methanol, hence some self-condensation can occur. (Typically only 5 of the 6 arms are methoxy-blocked in a HMMM resin.) The greater the number of times a melamine molecule reacts, the higher the cross-link density and the more brittle the material. Cross-link density is directly proportional to the rubbery storage modulus (E', Pa) [21] of a thermoset system. Hence an indication of the extent of reaction can be obtained from a DMA trace. Along with the increase in storage modulus (E', Pa) there is an increase in the glass transition (T_g) [22] of a thermoset system and a decrease in the free volume (a quantity which relates to the area under the tan delta peak of the DMA trace).

Experimental

Free films of a polyester melamine based paint with different cure levels were evaluated. The three cure levels will be referred to as under-cured, normal-cured and over-cured.

DMA measurements were made under tension mode using a sample 10 mm wide and with a free length of 5 mm. Each specimen was approximately 0.03 mm thick. It is acknowledged that this ratio of dimensions will not yield absolute modulus data, but it proved impossible to run the samples with a more correct ratio, as they were so thin and hence fragile. A static load of 1N was applied to each sample at the start of the test. The

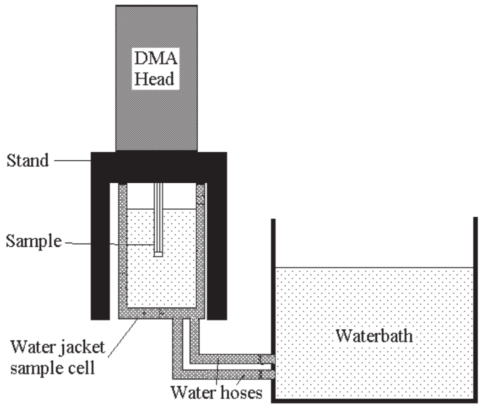

Fig. 2 Schematic representation of immersion DMA system

machine was then set to reducing force mode, which causes the static load to reduce throughout the test in proportion to its stiffness. A frequency of 1 Hz and a strain level of 15 μm (peak to peak displacement) were applied to the sample.

One of two tests was then performed:

A) Controlled relative humidity thermal scan (at 20 or 80% *RH*)
B) Immersion thermal scan (sample tested underwater)

The set-up for test *A*) is shown in Fig. 1 and for test *B*) in Fig. 2.

Finally a temperature ramp program of 1°C min^{-1} was activated and data logged.

Results and discussion

Figures 3 and 4 show the DMA results for the controlled humidity scans of the over-cured and under-cured materials. These tests were performed under 20 and 80% *RH* conditions. A clear shift in tan delta peak position is observed. This data has been summarized in Table 1. The expected change in tan delta peak position is seen between the over-cured and under-cured materials, but a shift can also be seen due to the variation in humidity.

Table 1 Temperature of tanδ peak maximum position, for controlled *RH* thermal scans

Paint sample	Tanδ peak maximum temperature/°C
Under-cured 80% *RH*	33.4
Under-cured 20% *RH*	42.7
Over-cured 80% *RH*	49.7
Over-cured 20% *RH*	58.5

Figures 5 and 6 show the DMA results for the immersion tests on all the samples. Once again, the expected shift in tanδ peak position is observed and this is summarized in Table 2.

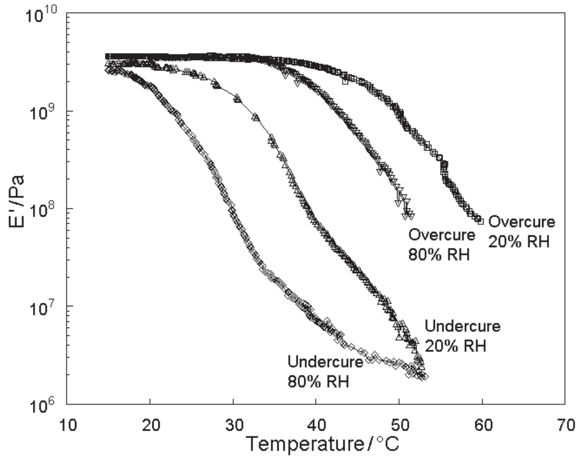

Fig. 3 DMA controlled *RH* thermal scan of polyester paint film. Graph of storage modulus (*E*', Pa) *vs*. temperature

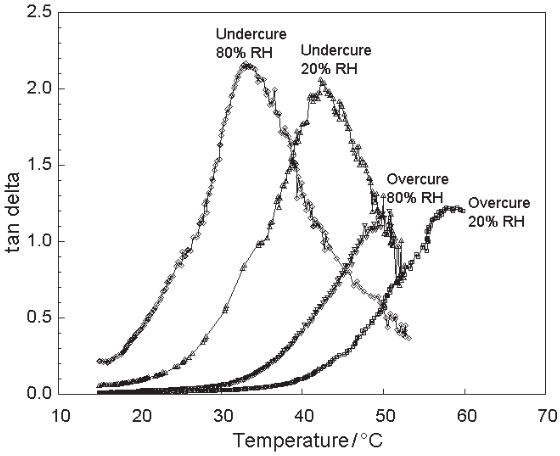

Fig. 4 DMA controlled *RH* thermal scan of polyester paint film. Graph of tanδ *vs*. temperature

Table 2 Temperature of tanδ peak maximum position, for immersion thermal scans

Paint sample	Tanδ peak maximum temperature/°C
Under-cured	28.9
Normal-cured	41.6
Over-cured	44.1

The increase in T_g with increasing degree of cure can be seen in Fig. 3, with the onset moving from about 20 to 45°C for the samples under 20% *RH* conditions. Similarly

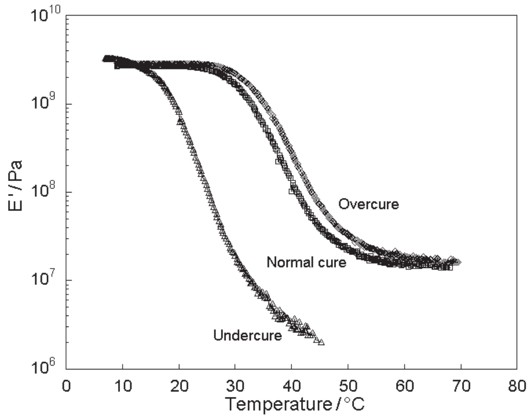

Fig. 5 DMA immersion thermal scan of polyester paint film. Graph of storage modulus (E', Pa) *vs*. temperature

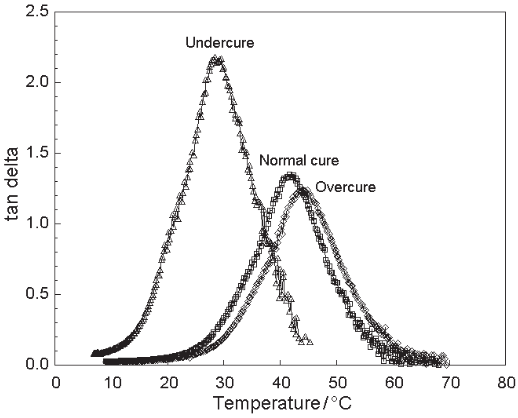

Fig. 6 DMA immersion thermal scan of polyester paint film. Graph of tanδ *vs*. temperature

the tan delta curves, shown in Fig. 4, show dramatic drops in peak height with increases in the degree of cure and an increase of the peak temperature from 43 to 59°C.

The shift, to lower temperature, of the tan delta peak with increasing relative humidity is important, as this could have important consequences during the forming process. If the product is formed at a temperature near its glass transition, it is more likely to stretch and yield as opposed to break; the latter scenario would be the case if forming takes place in the glassy region. Hence control of relative humidity could avoid cracking during forming. However, exposure of the painted substrate to high humidity, once in service, may lead to less desirable reductions in T_g. If the T_g falls below the ambient condition it could lead to moisture ingress, increasing the possibilities for corrosion and UV initiated degradation.

Figures 7 and 8 (under-cured samples only) show the combined data for the controlled relative humidity and the immersion testing. The effect of moisture on the glass

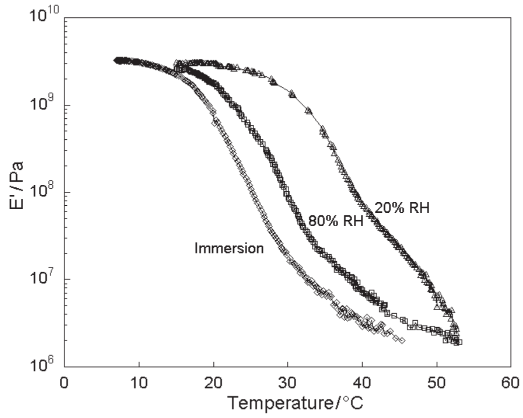

Fig. 7 DMA thermal scan of polyester paint film. Under-cured sample. Graph of storage modulus (*E*', Pa) *vs*. temperature

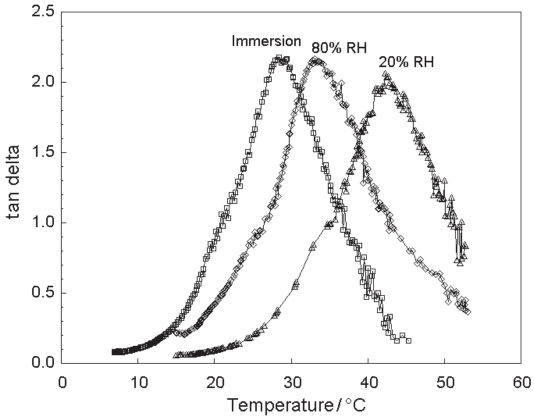

Fig. 8 DMA thermal scan of polyester paint film. Under-cured sample. Graph of tanδ *vs*. temperature

transition temperature can be clearly seen. As the moisture around the sample increases there is a corresponding drop in glass transition temperature. The changes in magnitude of storage modulus, and the position and height of the tan delta peak, when the degree of cure is increased, are obvious from Figs 7 and 8. Moreover the magnitude of the change between under-cured and normal-cured is much greater than that between normal-cured and over-cured. This indicates the ease with which over-cure can occur.

Conclusions

These examples show the potential of controlled relative humidity thermal scans on paints. A clear shift in glass transition temperature is observed. In this paper, emphasis has been given to the instrumentation. A detailed account of related paint measurement will be reported later. The application of this approach to dynamic mechanical analysis presents interesting possibilities in a number of areas. Furthermore, it is planned to correlate DMA data with tensile test data for the same paints.

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