Dynamic Mechanical Analysis – a Versatile Technique for the Viscoelastic Characterisation of Materials

I.F. Groves, T.J. Lever and N.A. Hawkins*

Summary

In today's increasingly competitive environment the development of high performance advanced materials is very important. Many material manufacturers no longer specialise in a single product area but have diversified. As a result research and development laboratories often work on a range of materials that can have significantly different physical and chemical properties. For this reason analytical instrumentation must be extremely flexible in that it must be able to accommodate samples existing in a variety of physical states without compromising sensitivity and reproducibility. Dynamic mechanical analysis (DMA) is no exception and this review will discuss the use of DMA for the viscoelastic characterisation of a wide range of samples including liquids, polyester film, latex rubber, prepreg and composites.

Introduction

When using a fixed frequency of oscillation an applied stress forces the sample to undergo sinusoidal oscillation at a frequency and amplitude (strain) selected by the operator. For purely elastic materials (spring steel) the strain will be exactly in phase with the applied stress whereas for purely viscous materials (Newtonian fluids) the strain will be 90 degrees out of phase with the applied stress. In most samples energy dissipation causes the strain to be out of phase with the applied stress by an angle between zero and 90 degrees. In other words the sample is viscoelastic. This phase shift or lag between stress and strain, defined as the phase angle (δ), is measured and used along with the sample geometry and driver energy (required to produce the strain within the material) to calculate the viscoelastic properties of the sample.

DMA is probably the most sensitive single technique available for characterising and interpreting the mechanical behaviour of materials. The TA Instruments 983 DMA uses a flexural bending mode of deformation to produce the strain within the sample (shear deformation is also available).

The technique separates the viscoelasticity of a material into the two components of modulus (E*); a real part which is the elastic modulus (E′) and an imaginary part which is the damping or viscous component (E″). The standard complex variable notation is: $E^* = E' + iE''$

This separation of the two components describing two independent processes within the materials – elasticity (energy storage) and viscosity (energy dissipation) – is the fundamental feature of dynamic mechanical analysis which distinguishes it from other mechanical testing techniques.

In the work discussed here materials have been characterised in terms of their elastic (storage) and damping (loss) properties. The ratio of the samples loss to storage properties is tan delta which is another parameter used to characterise materials.

Experimental

All analyses were undertaken using the Model 983 Dynamic Mechanical Analyser, in fixed frequency mode, manufactured by TA Instruments. Experimental set-up, control, data collection and manipulation were facilitated using the Thermal Analyst 2000 Controller with operating and standard data analysis software. For sub-ambient operation a microprocessor controlled Liquid Nitrogen Cooling Accessory was used. In all cases samples were analysed under flexural deformation at a fixed frequency

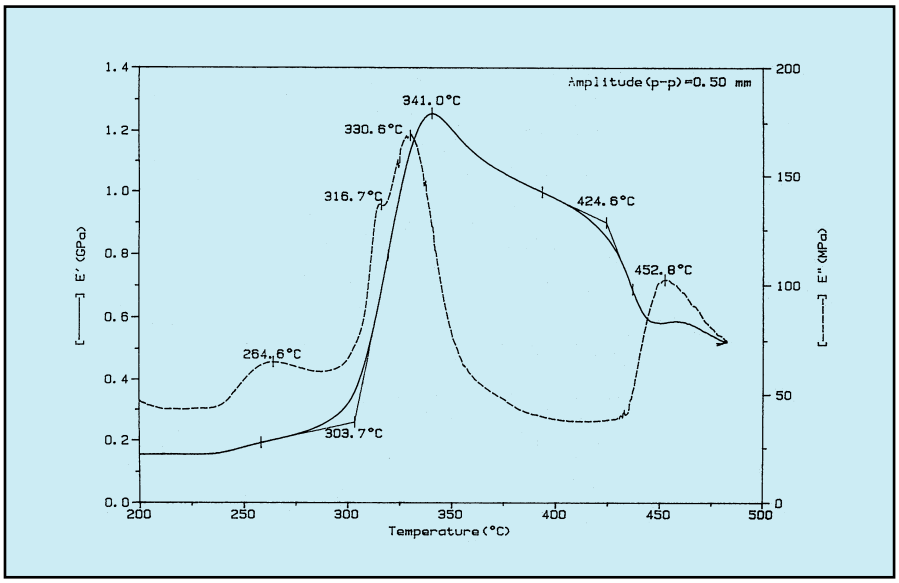

Fig. 1 Storage and loss modulus profiles from the dynamic cure of a graphite based liquid.

* *I.F. Groves, T.J. Lever and N.A. Hawkins, Marlin Scientific Ltd., Watford, UK.*

of 1Hz.

It should be noted that along with the Fixed Frequency mode of operation discussed here, the 983 DMA can also operate in Resonant Frequency mode (more sensitive to damping), and the two time dependent modes of Stress Relaxation and Creep which monitor a material's ability to withstand loading and deformation influences. Thus complete viscoelastic characterisation is possible within the single instrument.

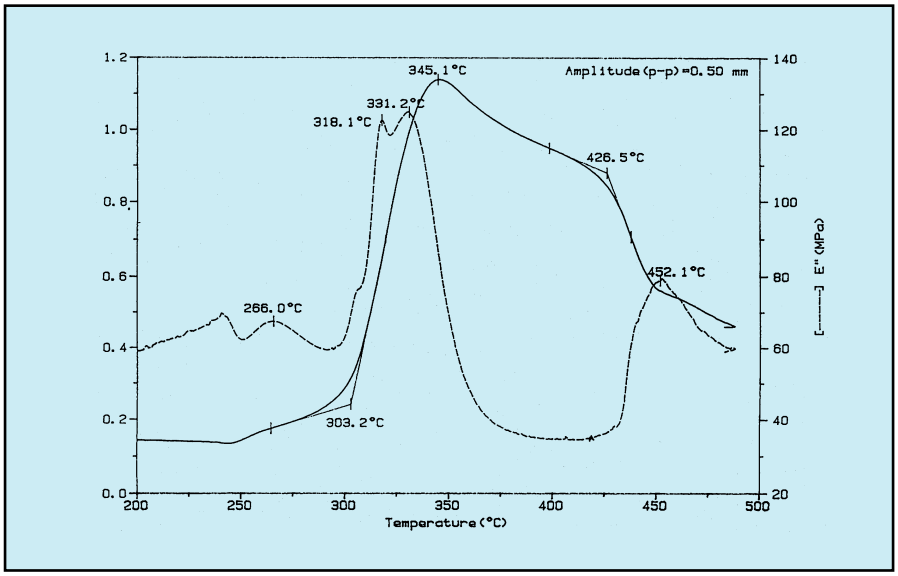

Fig. 2 Results from the duplicate analysis of a graphite based liquid.

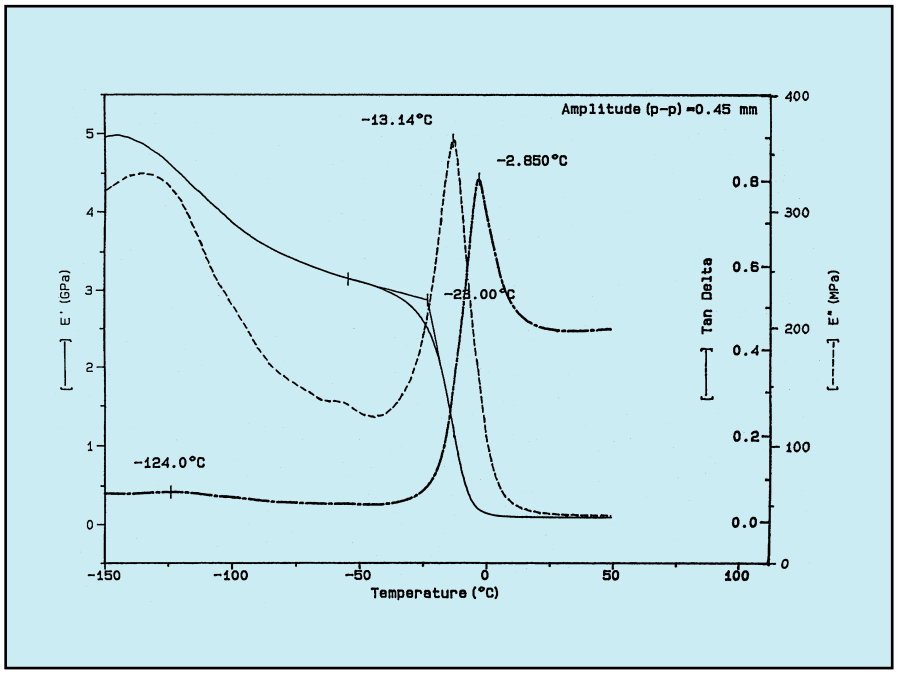

Fig. 3 Storage modulus, loss modulus and tan delta profiles from the dynamic analysis of a thin latex film.

Results

1. Liquid Curing Systems

Figure 1 shows the results from the analysis of a graphite based liquid used in the coating of metals. The liquid was applied to a glass braid and clamped in the vertical plane using low mass clamps specifically designed for the analysis of low modulus and thin film materials. This flexural mode of deformation is less severe than shear and eliminates any buckling of the sample. Using quarter size magnets in the electromagnetic motor gives improved signal to noise response from the mechanical drive assembly. A dynamic temperature ramp of 5°C/min was used.

Below 200°C the sample was a very low viscosity liquid and the only mechanical contribution to the system was from the glass braid support cloth. At around 235°C the sample began to cure as shown by the gentle increase in storage modulus. Above 304°C there was a significant increase in storage modulus corresponding to the rapid increase in cross link density as cure proceeded. The storage modulus for the sample reached a maximum at 341°C and slowly declined to 425°C beyond which it displayed a precipitous drop corresponding to decomposition within the sample.

The loss modulus displayed a peak at 265°C as the sample began to cure (this could be attributable to the gel point). A subtle peak in loss modulus was seen at 317°C corresponding to the point of greatest rate of change in storage modulus. The loss modulus peaked at 331°C, declined rapidly to 360°C, levelled off to 430°C and then peaked at 453°C which corresponded to the decomposition.

The reproducibility of the technique is represented in *Figure 2.* The analysis of a second sample of the same material produced results with a very similar profile to those discussed above and with temperatures of the various thermal events within a few degrees of each other. It is important to note that in both of the above analyses the viscoelastic properties cannot be considered quantitative due to the contribution of the glass braid and the fact that the liquid sample cannot be applied evenly. The examples do show however the value of the technique to monitor the cure profile of liquid samples.

2. Latex rubber

The low mass clamp configuration was employed for the analysis of a thin film of natural latex rubber used in the manufacture of surgical gloves and condoms. The sample was subjected to a dynamic heating profile of 4°C/min and the results are shown in *Figure 3.*

The storage modulus of the material produced a gradual decline from –150°C and the loss modulus was relatively high between –150°C and –110°C above which it declined through to –50°C. This would suggest that the sample was part way through a low temperature beta transition at the start temperature of –150°C. This was most likely due to a low energy molecular relaxation. A very subtle broad peak in tan delta corresponding to this low energy transition was seen at –124°C.

Between –85°C and –40°C the storage modulus displayed a plateau before declining rapidly as shown by the onset at –23°C. This very sharp drop in modulus, due to the glass transition of the rubber, produced corresponding peaks in loss modulus and tan delta at –13°C and –3°C respectively.

3. Polyester Thin Film

The same Low Mass Clamp and quarter magnets configuration was used to analyse a thin film of Melinex – a biaxially oriented, highly crystalline, stretched polyethylene terephthalate (PET) – of the type used in general packaging. The sample was subjected to a dynamic heating rate of 4°C per minute and the results are displayed in Figure 4.

The storage modulus displayed a slow decline between –115°C and –30°C due to a low energy molecular relaxation in the polyester. Corresponding peaks in loss modulus and tan delta were produced at –125°C and –123°C respectively. Below the main glass transition of the polyester a plateau was produced in the storage modulus between –25°C and 80°C. The main decline in storage modulus, due to the glass transition, showed an onset of 87°C. In addition to this decline in storage modulus a doublet peak in loss modulus at 106°C and 124°C can be seen along with a peak in tan delta at 125°C with a shoulder on the leading edge.

The doublet in the damping peak is interesting and may be explained by shrinkage in the film on the high temperature side of the glass transition. The high temperature peak in loss modulus at 122°C was produced at the same point as the subtle inflection in the storage modulus profile between 110°C and 140°C. This inflection can be explained by the apparent increase in modulus as the film shrinks in competition with the continuing softening process with increasing temperature.

4. Cure of a Prepreg Material

The cure of a single ply of prepreg can be readily followed using the 983 DMA. *Figure 5* shows the results from the analysis of a single ply carbon fibre epoxy prepreg. The low mass clamps were used

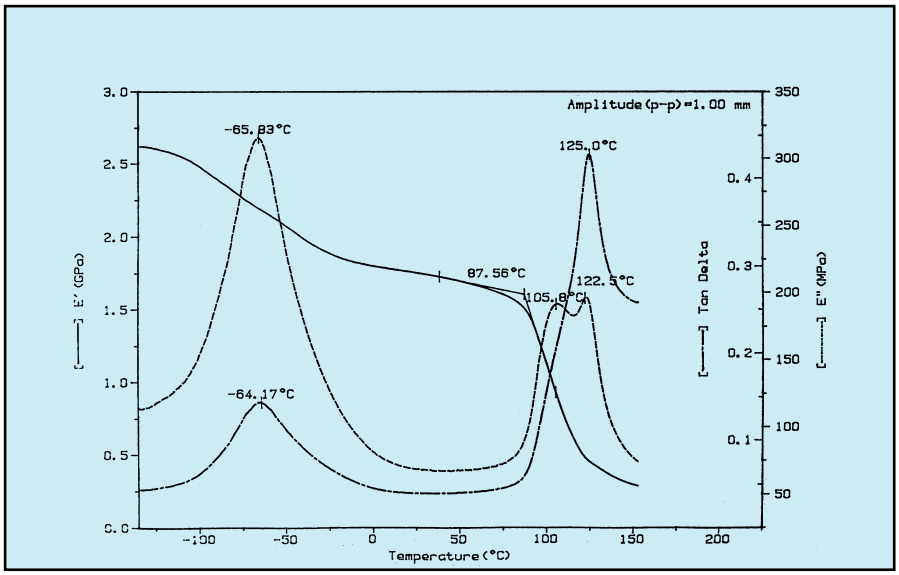

Fig. 4 Profiles of storage modulus, loss modulus and tan delta from the analysis of a thin polyester film.

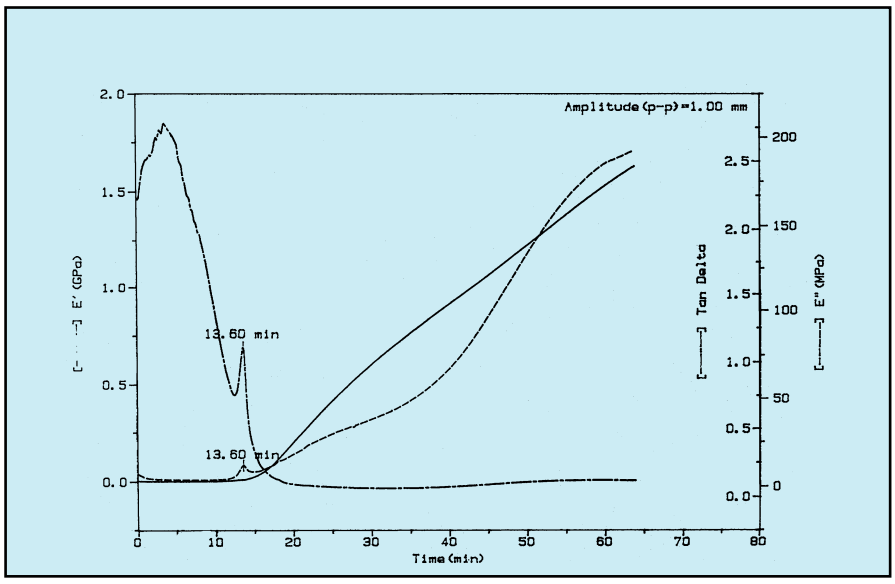

Fig. 5 Results from the isothermal cure at 150°C of a single ply of prepreg.

to mount the sample. The prepreg was cured isothermally at 150°C by ramping the temperature at 50°C/min to 150°C where it was then held isothermally for sixty minutes.

The storage modulus curve was flat for the first 15 minutes after which it rose steeply to 30 minutes and then continued to rise through to the end of the analysis. The loss modulus exhibited a peak at 13.6 minutes, increased slowly to 40 minutes after which it increased steeply before levelling out at the end of the analysis. Tan delta also displayed a peak at 13.6 minutes above which it declined steeply to 20 minutes before showing an increase above 40 minutes – corresponding to the sharp increase in loss modulus in this region.

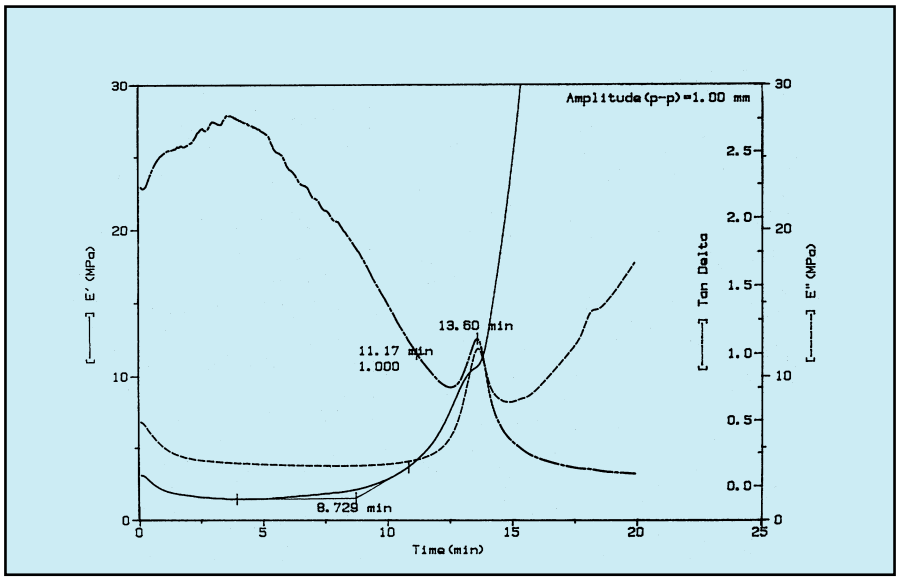

Fig. 6 Expanded plot of the early stages of the cure of a single ply of prepreg.

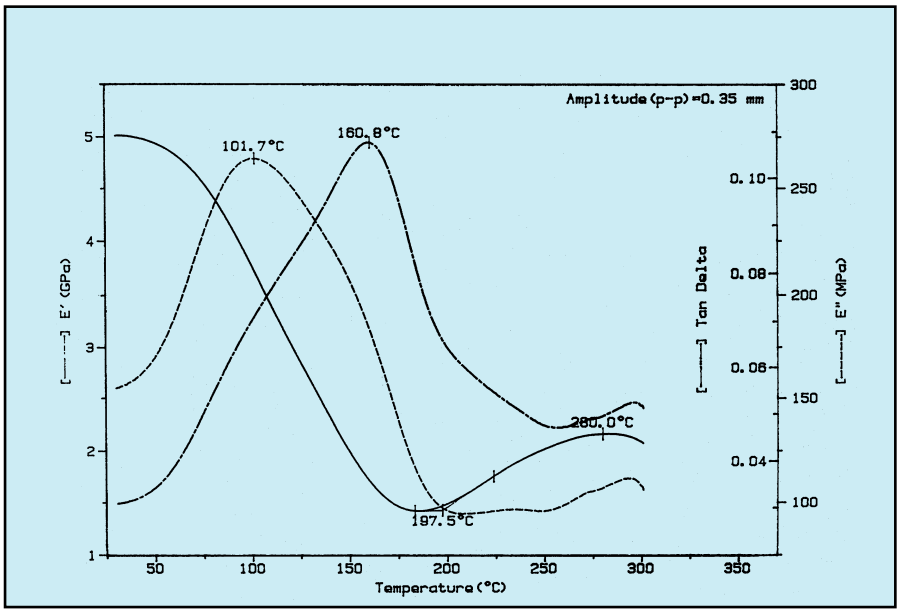

Fig. 7 Storage modulus, loss modulus and tan delta profiles from the dynamic analysis of a cured single ply of prepreg.

The increase in storage modulus after 15 minutes was clearly due to the cure of the prepreg imparting mechanical strength to the sample as it was held at the isothermal temperature. As the storage modulus continued to increase through the end of the experiment it would suggest that the sample had not achieved full cure – this can be verified by cooling the sample to room temperature and re-running it.

Figure 6 shows the detail from the first twenty minutes of the experiment. The storage modulus at the start of the experiment showed a small decline as the temperature was ramped up to the isotherm. This corresponded to a drop in the viscosity of the resin as a function of increasing temperature. The first real increase in storage modulus appeared with onset at 8.7 minutes as the sample began to cross link. At 11.2 minutes the storage and loss moduli were equivalent and the curves crossed. At this point tan delta equalled 1.0 and many processors consider this to be the gel time for the prepreg. The gel time is critical as it represents the end of the processing window, beyond this point air pockets may be trapped in the composite as it is pressed since the resin is too viscous to flow correctly. Conversely pressing the composite too far in advance of the gel time will force the resin out of the mould as its viscosity will be too low. In either case the mechanical properties of the finished material will be compromised. Beyond the gel time the storage modulus increased corresponding to the onset of matrix formation and just below the peaks in loss modulus and tan delta it showed an inflection before increasing sharply as the cure process continued. This inflection in storage modulus and peaks in loss modulus and tan delta represents the softening of the partially cured matrix.

Figure 7 represents the DMA profile from the re-run of the cured prepreg. The storage modulus showed a sharp decline at temperatures above 60°C through to 180°C. At 198°C the storage modulus began to rise again and peaked at 280°C. This is a clear indication that the sample was not fully cured during the sixty minute isotherm at 150°C and this dynamic heating profile imparted post cure to the sam-

ple. The very broad and unsymmetrical loss modulus and tan delta peaks at 102°C and 161°C respectively are also evidence that the prepreg did not achieve full cure during the isothermal hold.

5. Rigid Composite

The standard clamping configuration is designed for very rigid materials such as carbon fibre-epoxy composites. *Figure 8* shows the results from the analysis of a 2.0mm thick epoxy-carbon composite over the temperature range ambient to 270°C at a heating rate of 5°C/min.

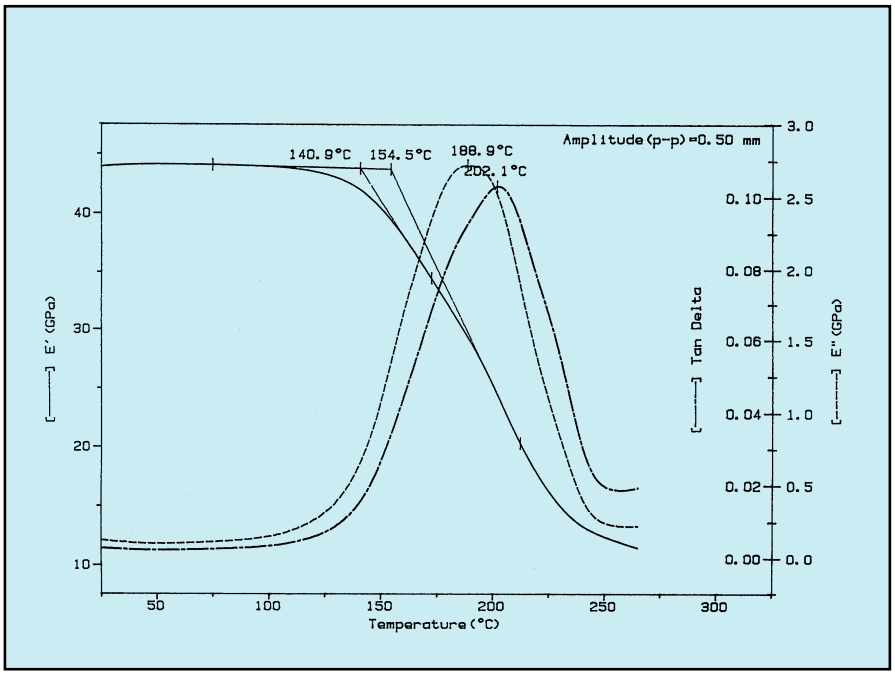

Fig. 8 Results from the analysis of a rigid carbon fibre-epoxy composite.

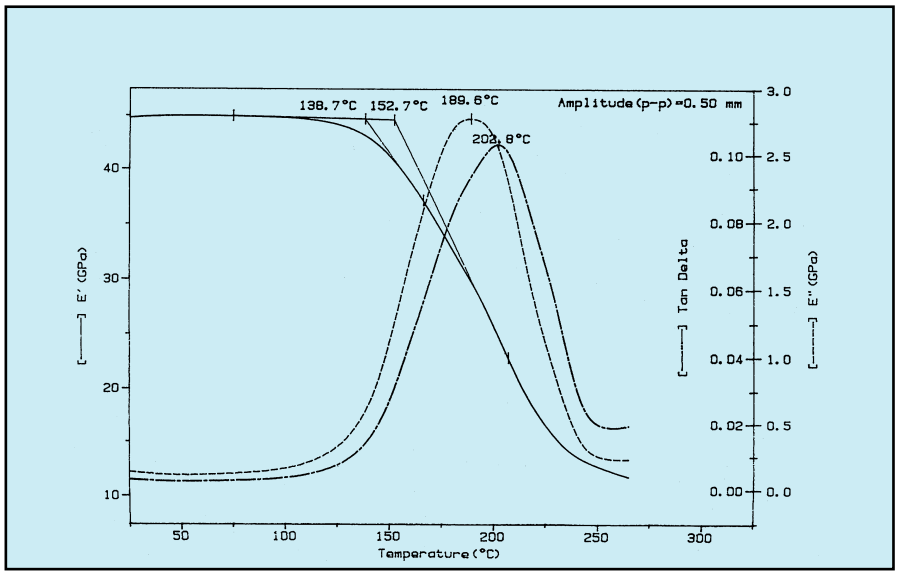

Fig. 9 Profiles of storage modulus, loss modulus and tan delta from the duplicate analysis of a rigid carbon fibre-epoxy composite.

The glass transition for the composite was shown by the two step drop in storage modulus with onset at 141°C and 155°C. This result is not typical, most composites exhibit a single step change in modulus at the glass transition, and may be explained by a small amount of residual cure within the sample that is brought about by the dynamic heating profile. The shape of the loss modulus and tan delta peaks in the region of the glass transition are also indicative of a small amount of residual cure as they were both unsymmetrical. The peaks for loss modulus and tan delta were produced at 189°C and 202°C respectively.

Figure 9 shows the results from the analysis of a second sample of the epoxy-carbon composite. The peak temperatures and quantitative viscoelastic values were in excellent agreement to those obtained from the first analysis.

Conclusion

DMA is a very powerful tool for the viscoelastic characterisation of materials. The above examples show the versatility of the instrument to analyse samples across the entire viscoelastic spectrum from liquids through to the most rigid composites. It should be noted that only a single mechanical driving system was required to accommodate the samples.

The very small enthalpy changes associated with the transitions discussed in this report would be impossible to detect using conventional calorimetric techniques. The corresponding change in mechanical properties are several orders of magnitude greater making DMA the most sensitive thermal technique.

Reproducibility has been proven for samples at the two extremes of viscoelasticity – a liquid and a rigid composite.

Acknowledgement

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A full reprint of this article is available from the authors.