

## Chapter 4

### THERMOMECHANICAL, DYNAMIC MECHANICAL AND DIELECTRIC METHODS

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#### INTRODUCTION AND PRINCIPLES

The dimensional and mechanical stability of materials is of paramount importance to their use in the everyday world where they may encounter a wide variation in temperature through design or by accident. Many polymers are processed at elevated temperatures so as to enable them to flow and be more amenable to fabrication. Food items are cooked, pasteurised or otherwise heated or frozen. Ceramics are fired so as to consolidate their final structure. The relationship between a material's dimensional and mechanical properties and its temperature is studied by the techniques described within this chapter and, due to common concepts, the effect of heat on the electrical properties of materials is also considered.

#### Thermomechanical Analysis and Thermodilatometry

Thermomechanical Analysis (TMA) can be defined as the measurement of a specimen's dimensions (length or volume) as a function of temperature whilst it is subjected to a constant mechanical stress. In this way thermal expansion coefficients can be determined and changes in this property with temperature (and/or time) monitored. Many materials will deform under the applied stress at a particular temperature which is often connected with the material melting or undergoing a glass-rubber transition. Alternatively, the specimen may possess residual stresses which have been "frozen-in" during preparation. On heating, dimensional changes will occur as a consequence of the relaxation of these stresses.

Stress ( $\sigma$ ) is defined as the ratio of the mechanical force applied ( $F$ ) divided by the area over which it acts ( $A$ ):

$$\sigma = F/A \quad (1)$$

The stress is usually applied in compression or tension, but may also be applied in shear, torsion, or some other bending mode as shown in Figure 1. The units of stress are  $\text{N m}^{-2}$  or Pa.

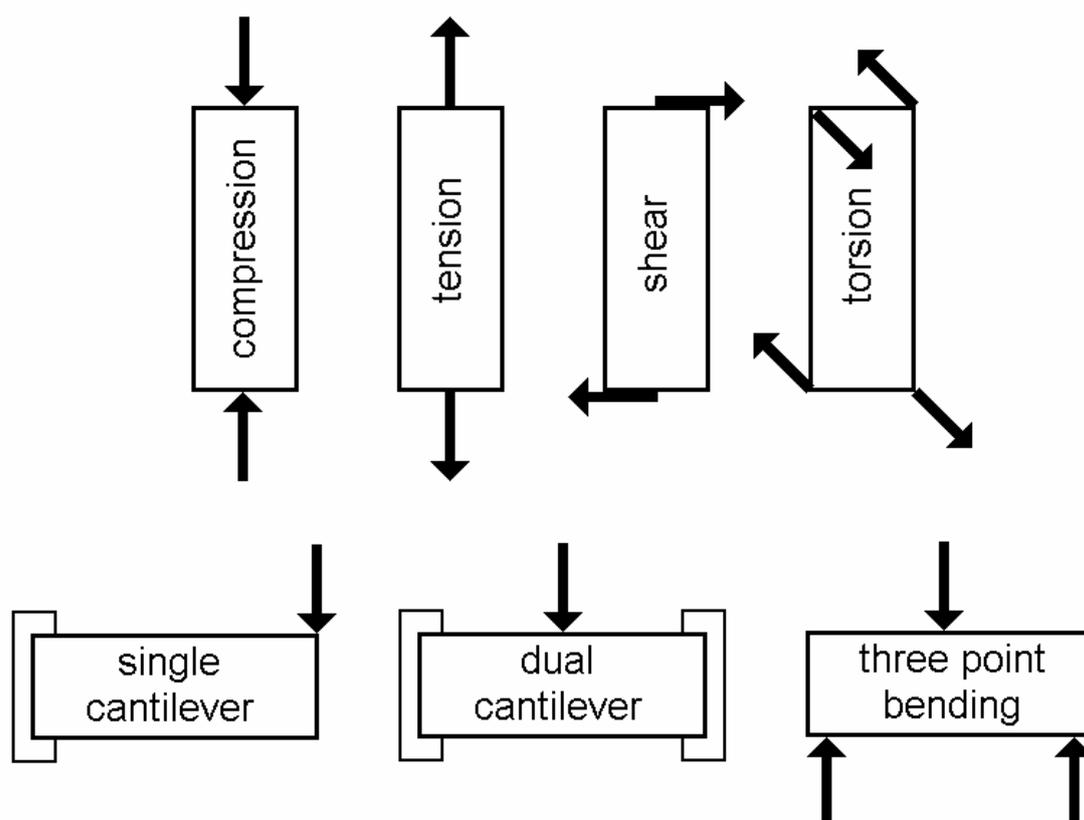


Figure 1. Common mechanical deformation modes: compression, tension, shear, torsion, bending (single cantilever, dual cantilever, three point bending).

If the applied stress is negligible then the technique becomes that of thermodilatometry. This technique is used to determine the coefficient of thermal expansion of the specimen from the relationship:

$$\alpha \cdot l_0 = d l / d T \quad (2)$$

where  $\alpha$  is the coefficient of thermal expansion ( $\text{ppm } ^\circ\text{C}^{-1}$  or  $\mu\text{m m}^{-1} ^\circ\text{C}^{-1}$ ),  $l_0$  is the original sample length (m) and  $d l / d T$  is the rate of change of sample length with temperature ( $\mu\text{m } ^\circ\text{C}^{-1}$ ).

### Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is concerned with the measurement of the mechanical properties (mechanical modulus or stiffness and damping) of a specimen as a function of temperature. DMA is a sensitive probe of molecular mobility within materials and is most commonly used to measure the glass transition temperature and other transitions in macromolecules, or to follow changes in mechanical properties brought about by chemical reactions.

For this type of measurement the specimen is subjected to an oscillating stress, usually following a sinusoidal waveform:

$$\sigma(t) = \sigma_{\max} \sin \omega t \quad (3)$$

where  $\sigma(t)$  is the stress at time  $t$ ,  $\sigma_{\max}$  is the maximum stress and  $\omega$  is the angular frequency of oscillation. Note that  $\omega = 2\pi f$  where  $f$  is the frequency in Hertz.

The applied stress produces a corresponding deformation or strain ( $\varepsilon$ ) defined by:

$$\varepsilon = (\text{change in dimension})/(\text{original dimension}) = \Delta l / l_0 \quad (4)$$

The strain is measured according to how the stress is applied (e.g. compression, tension, bending, shear etc.). Strain is dimensionless, but often expressed in %.

For an elastic material, Hooke's law applies and the strain is proportional to the applied stress according to the relationship:

$$E = d\sigma/d\varepsilon \quad (5)$$

Where  $E$  is the elastic, or Young's modulus with units of  $\text{N m}^{-2}$  or Pa. Such measurements are normally carried out in tension or bending, when the sample is a soft material or a liquid then measurements are normally carried out in shear mode, thus a shear modulus ( $G$ ) is measured. The two moduli are related to one another by:

$$G = E/(2 + 2\nu) \quad (6)$$

where  $\nu$  is known as the Poisson's ratio of the material. This normally lies between 0 and 0.5 for most materials and represents a measure of the distortion which occurs (i.e. the reduction in breadth accompanying an increase in length) during testing.

If the material is viscous, Newton's law holds. The specimen possesses a resistance to deformation or viscosity,  $\eta$ , proportional to the rate of application of strain, i.e.:

$$\eta = d\sigma/(d\varepsilon/dt) \quad (7)$$

The units of viscosity are Pa s.

A coil spring is an example of a perfectly elastic material in which all of the energy of deformation is stored and can be recovered by releasing the stress. Conversely, a perfectly viscous material is exemplified by a dashpot, which resists extension with a force proportional to the strain rate but affords no restoring force once extended, all of the deformation energy being dissipated as heat during the loading process. In reality, most materials exhibit behaviour intermediate between springs and dashpots – viscoelasticity.

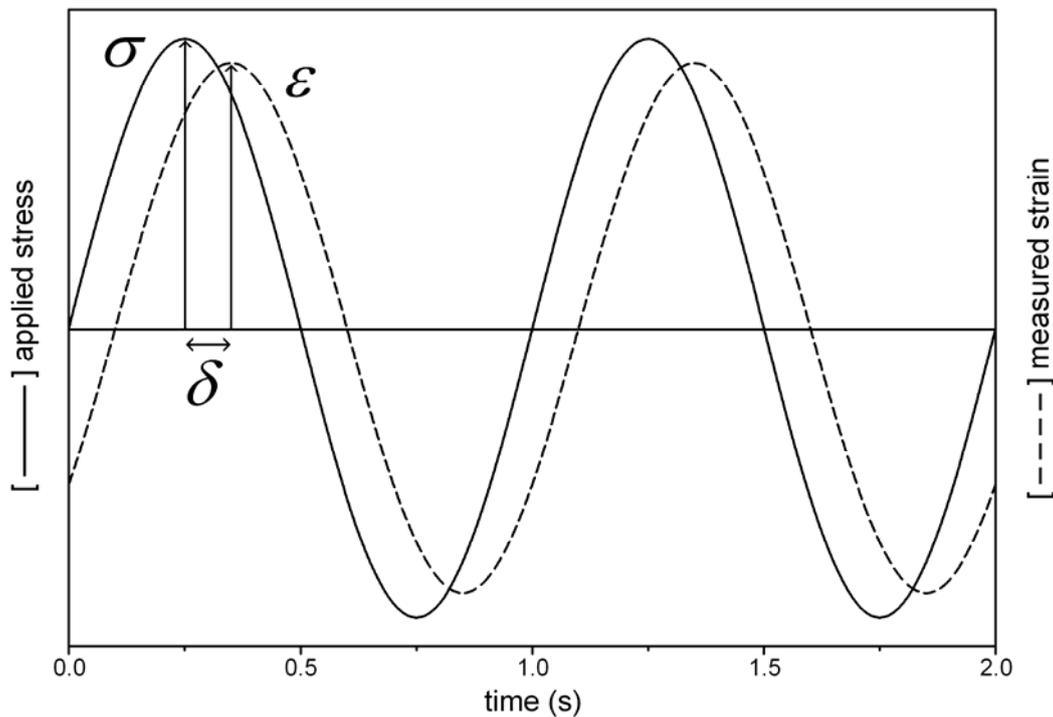


Figure 2. Relationship between stress ( $\sigma$ ) and strain ( $\epsilon$ ) during a dynamic mechanical test.

If, as in the case of DMA, a sinusoidal oscillating stress is applied to a specimen, a corresponding oscillating strain will be produced. Unless the material is perfectly elastic, the measured strain will lag behind the applied stress by a phase difference ( $\delta$ ) shown in Figure 2. The ratio of peak stress to peak strain gives the complex modulus ( $E^*$ ) which comprises an in-phase component or storage modulus ( $E'$ ) and a  $90^\circ$  out-of-phase (quadrature) component or loss modulus ( $E''$ ).

The storage modulus, being in-phase with the applied stress, represents the elastic component of the material's behaviour, whereas the loss modulus, deriving from the condition at which  $d\epsilon/dt$  is a maximum, corresponds to the viscous nature of the material. The ratio between the loss and storage moduli ( $E''/E'$ ) gives the useful quantity known as the mechanical damping factor ( $\tan \delta$ ) which is a measure of the amount of deformational energy that is dissipated as heat during each cycle. The relationship between these quantities can be illustrated by means of an Argand diagram, commonly used to visualise complex numbers, which shows that the complex modulus

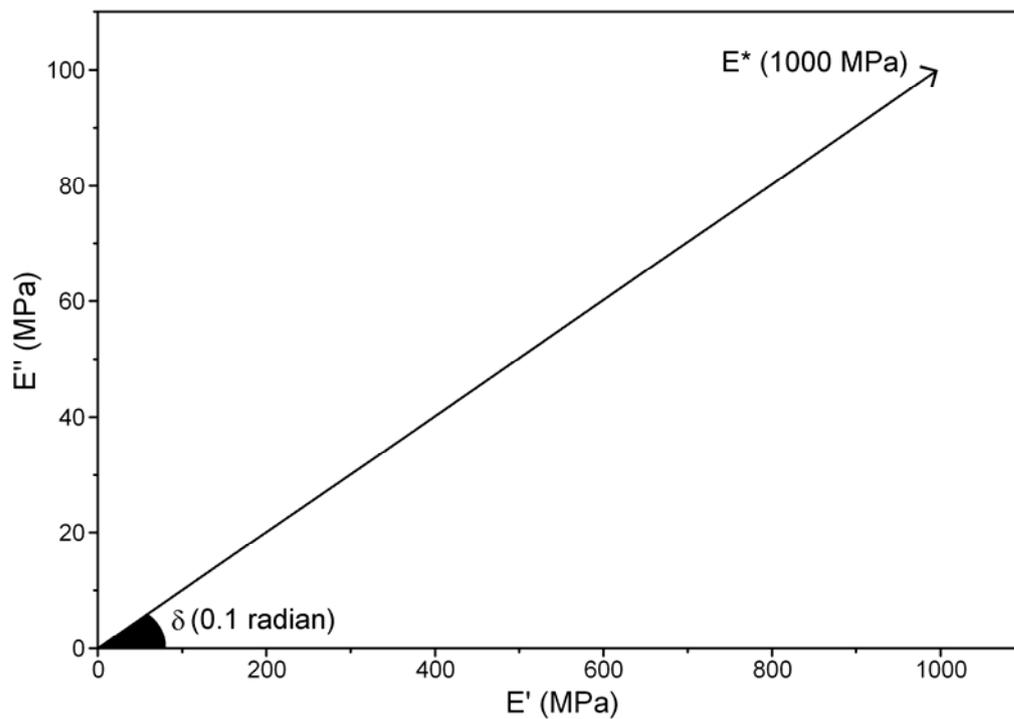


Figure 3. Argand diagram to illustrate the relationship between complex modulus ( $E^*$ ) and its components.

is a vector quantity characterised by magnitude ( $E^*$ ) and angle ( $\delta$ ) as shown in Figure 3.  $E'$  and  $E''$  represent the real and imaginary components of this vector thus:

$$E^* = E' + iE'' = \sqrt{(E')^2 + (E'')^2} \quad (8)$$

So that:

$$E' = E^* \cos \delta \quad (9)$$

and

$$E'' = E^* \sin \delta \quad (10)$$

### Dielectric Techniques

In a manner analogous to TMA and DMA, a specimen can be subjected to a constant or oscillating electric field rather than a mechanical stress during measurements. Dipoles in the material will attempt to orient with the electric field, while ions, often present as impurities, will move toward the electrode of opposite polarity. The resulting current flow is similar in nature to the deformation brought about by mechanical tests and represents a measure of the freedom of charge carriers to respond to the applied field. The specimen is usually presented as a thin film between two metal electrodes so as to form a parallel plate capacitor. Two types of test can be performed:

*Thermally Stimulated Current Analysis (TSCA).*

In this technique the sample is subjected to a constant electric field and the current which flows through the sample is measured as a function of temperature. Often, the sample is heated to a high temperature under the applied field and then quenched to a low temperature. This process aligns dipoles within the specimen in much the same way that drawing a material under a mechanical stress would bring about orientation of molecules in the sample. The polarisation field is then switched off, and the sample is re-heated whilst the current flow resulting from the relaxation of the induced dipoles to the unordered state is monitored.

*Dielectric Thermal Analysis (DETA).*

In this technique the sample is subjected to an oscillating sinusoidal electric field. The applied voltage produces a polarisation within the sample and causes a small current to flow which leads the electric field by a phase difference ( $\delta$ ) (Figure 4). Two fundamental electrical characteristics, conductance and capacitance, are determined from measurements of the amplitude of the voltage ( $V$ ), current ( $I$ ) and  $\delta$ . These are used to determine the admittance of the sample ( $Y$ ) given by:

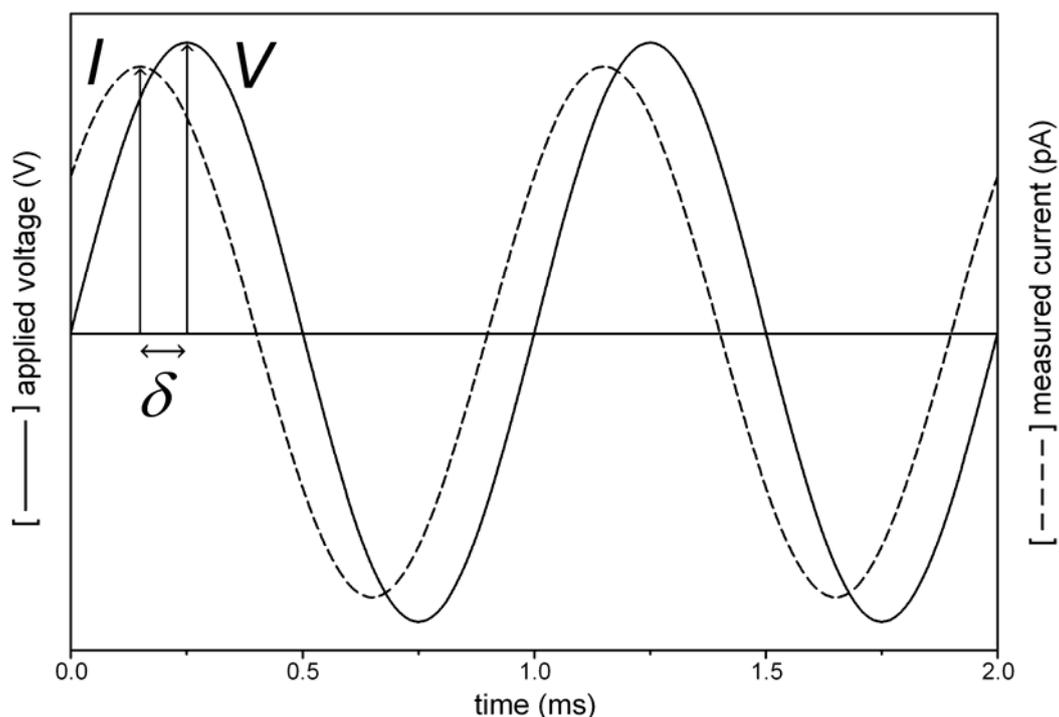


Figure 4. Relationship between voltage and current in a capacitor (c.f. figure 2).

$$Y = I/V \quad (11)$$

$Y$  is a vector quantity, like  $E^*$  discussed earlier, and is characterised by its magnitude  $|Y|$  and direction  $\delta$ .

Capacitance ( $C$ ) is the ability to store electrical charge and is given by:

$$C = |Y| \sin \delta / \omega \quad (12)$$

Conductance ( $G_c$ ) is the ability to transfer electric charge and is given by:

$$G_c = |Y| \cos \delta \quad (13)$$

More usually data is presented in terms of the relative permittivity ( $\epsilon'$ ) and dielectric loss factor ( $\epsilon''$ ) – these are related to capacitance and conductance by:

$$\epsilon' = C / (\epsilon_0 A / D) \quad (14)$$

and

$$\epsilon'' = G_c / (\omega \epsilon_0 A / D) \quad (15)$$

where  $\epsilon_0$  is the permittivity of free space ( $8.86 \times 10^{-12} \text{ F m}^{-1}$ ) and  $A/D$  in  $\text{m}$ , is the ratio of electrode area ( $A$ ) to plate separation or sample thickness,  $D$  for a parallel plate capacitor. More generally,  $A/D$  is a geometric factor which is found by determining the properties of the measuring cell in the absence of a sample.  $\epsilon'$  and  $\epsilon''$  are dimensionless quantities.

The ratio  $\epsilon'' / \epsilon'$  is the amount of energy dissipated per cycle divided by the amount of energy stored per cycle and known as the dielectric loss tangent or dissipation factor ( $\tan \delta$ ).

## INSTRUMENTATION

### Thermomechanical Analysis

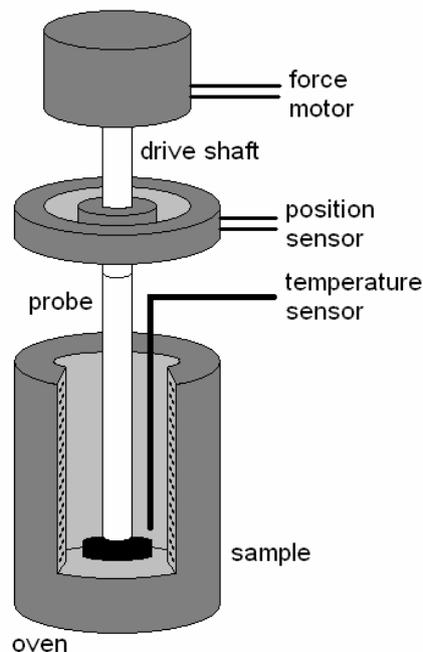


Figure 5. Schematic diagram of a thermomechanical analyser.

A schematic diagram of a typical instrument is shown in Figure 5. The sample is placed in a temperature controlled environment with a thermocouple or other temperature sensing device, such as a platinum resistance thermometer, placed in close proximity. The facility to circulate a cryogenic coolant such as cold nitrogen gas from a Dewar vessel of liquid nitrogen is useful for subambient measurements. The atmosphere around the sample is usually controlled by purging the oven with air or nitrogen from a cylinder. Because of the much larger thermal mass of the sample and oven compared to a differential scanning calorimeter or a thermobalance, the heating and cooling rates employed are usually much slower for TMA. A rate of  $5^{\circ}\text{C min}^{-1}$  is usually the maximum recommended value for good temperature equilibration across the specimen. Even this rate can be a problem for some specimens where appreciable temperature gradients can exist between the middle and ends of the sample particularly around the test fixtures - which can represent a significant heat sink.

For compression measurements (as illustrated) a flat-ended probe is rested on the top surface of the sample and a static force is applied by means of a weight or (more commonly in the case of modern instrumentation) an electromagnetic motor similar in principle to the coil of a loudspeaker. Some form of proximity sensor measures the movement of the probe. This is usually achieved by using a linear variable differential transformer (LVDT) which consists of two coils of wire which form an electrical transformer when fed by an AC current. The core of the transformer is attached to the probe assembly and the coupling between the windings of the transformer is dependent upon the displacement of the probe. Other transducers such as capacitance sensors (which depend on the proximity of two plates – one fixed the other moving) or optical encoders are used in certain instruments.

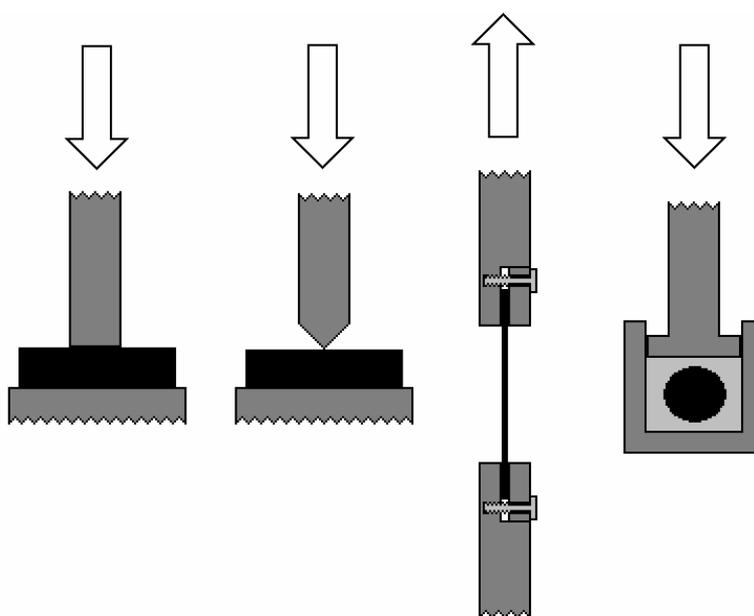


Figure 6. TMA probe types (left-right): compression, penetration, tension, volumetric.

Most commercial instruments are supplied with a variety of probes for different applications (Figure 6). A probe with a flat contact area is commonly used for thermal expansion measurements where it is important to distribute the applied load over a wide area. Probes with sharp points or round-ended probes are employed for penetration measurements so as to determine the sample's softening temperature. Films and fibres, which are not self-supporting, can be measured in extension by clamping their free ends between two grips and applying sufficient tension to the specimen to prevent the sample buckling. Volumetric expansion can be determined using a piston and cylinder arrangement with the sample surrounded by an inert packing material such as alumina powder or silicone oil.

The equipment must be calibrated before use. The manufacturers, as well as various standardisation agencies, usually provide recommended procedures. A full list of standard methods and calibration protocols for all thermal methods is given in the Appendix. Temperature calibration is usually carried out by preparing a sample comprising a number of metal melting point standards, such as those used for differential scanning calorimetry, sandwiched between steel or ceramic discs. The melting of each standard causes a change in height of the stack as each metal melts and flows (Figure 7). Force calibration is often performed by balancing the force generated by the electromagnetic motor against a certified weight added to the drive train. Length calibration can be more difficult to carry out. A common check on the performance of the instrument is to measure the thermal expansion of a material whose values are accurately known (such as aluminium or copper).

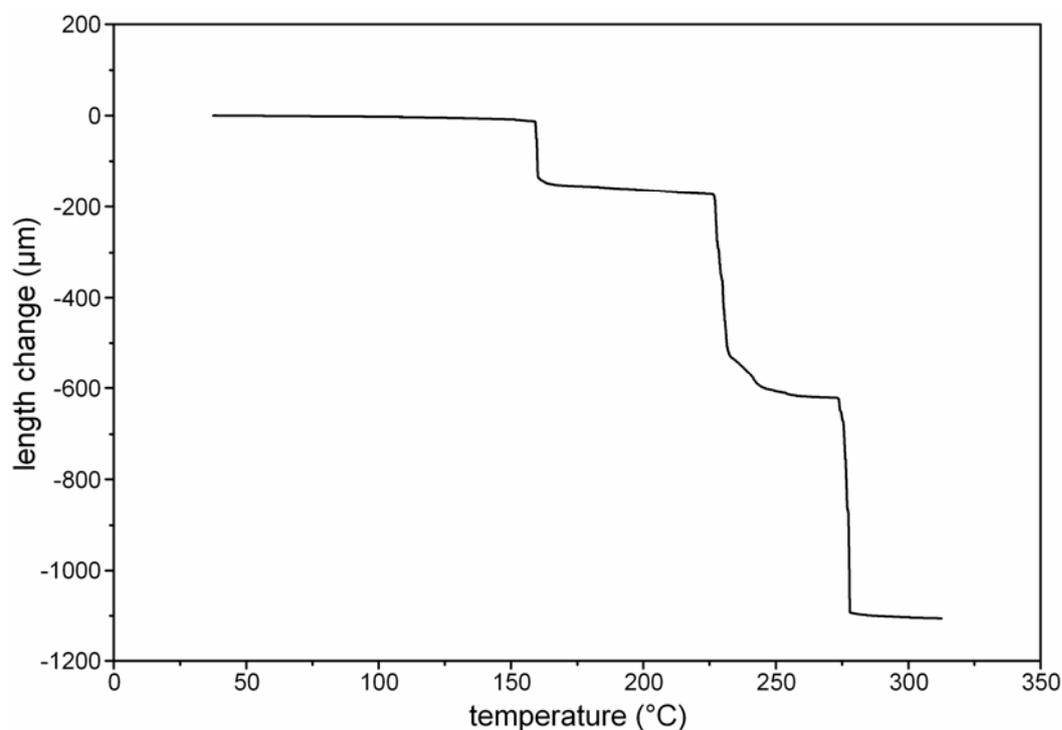


Figure 7. TMA temperature calibration using indium (156.6°C), tin (232.0°C) and bismuth (271.4°C). Heating rate: 5°C min<sup>-1</sup>, force 1 N, static air atmosphere.

### Dynamic Mechanical Analysis

The distinction between a thermomechanical analyser and a dynamic mechanical analyser is blurred nowadays since many instruments can perform TMA-type experiments. The configuration of a DMA is essentially the same as the TMA shown in Figure 5 with the addition of extra electronics to apply an oscillating load and the ability to resolve the resulting specimen deformation into in-phase and out-of-phase components so as to determine  $E'$ ,  $E''$  and  $\tan \delta$ . The facility for sub-ambient operation is more common on a DMA than a TMA. The same recommendations about modest rates of temperature change are even more important for the larger samples used in DMA. Stepwise-isothermal measurements are often carried out for multiple frequency operation. In this experiment the oven temperature is changed in small increments and the sample allowed to come to thermal equilibrium before the measurements are made. The frequency range over which the mechanical stress can be applied commonly covers 0.01 to 100 Hz. The lower limit is determined by the amount of time that it takes to cover enough cycles to attain reasonable resolution of  $\tan \delta$  (10 s for one measurement at 0.01 Hz – though normally some form of data averaging is applied meaning that a measurement at this frequency can take a minute or more). The upper limit is usually determined by the mechanical properties of the drive system and clamps.

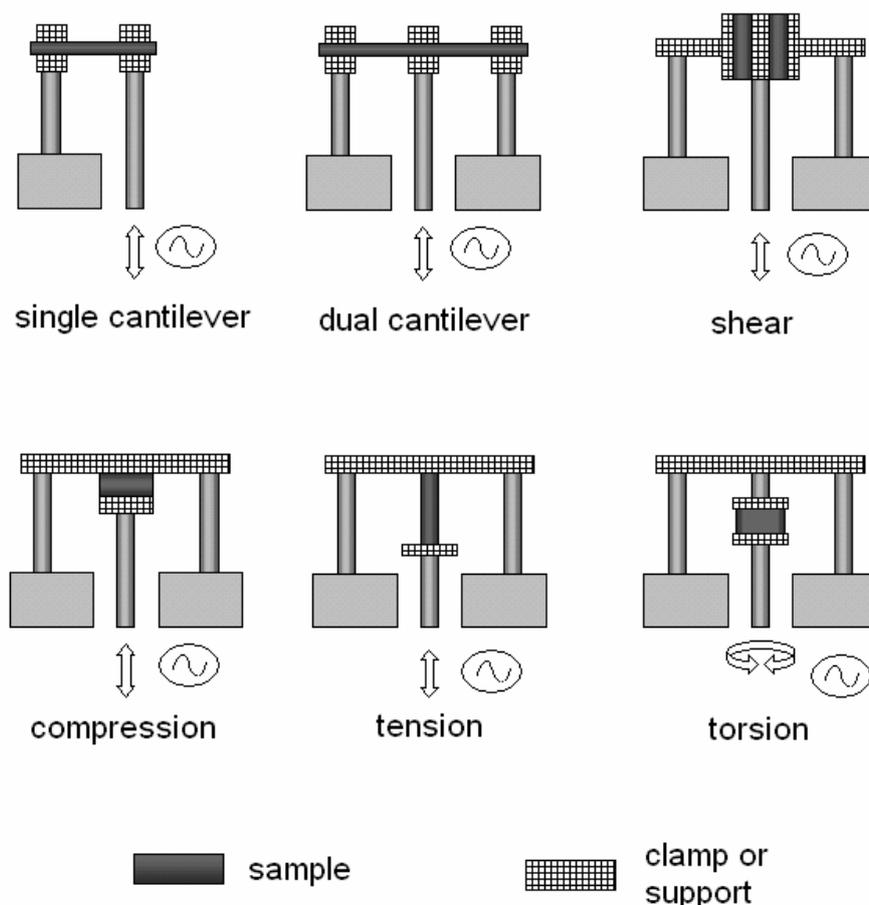


Figure 8. Common clamping geometries for dynamic mechanical analysis (c.f. figure 1).

Different clamping geometries are used to accommodate particular specimens (Figure 8). Single or dual cantilever bending modes are the most common for materials which can be formed into bars. Shear measurements are used for soft, thick samples. Films and fibres are usually mounted in tension with loading arranged so that the sample is always in tension. Torsion measurements are normally done with a special design of instrument since most DMA's can only exert a linear rather than a rotational force.

The effect of temperature on the mechanical properties of a liquid can be investigated using a special type of dynamic mechanical analyser called an oscillatory rheometer. In this instrument the sample is contained as a thin film between two parallel plates. One of the plates is fixed while the other rotates back and forth so as to subject the liquid to a shearing motion. It is possible to calculate the shear modulus from the amplitude of the rotation and the resistance of the sample to deformation. Because the test is performed in oscillation, it is possible to separate the shear modulus ( $G$ ) into storage ( $G'$ ) and loss modulus ( $G''$ ) by measuring the phase lag between the applied strain and measured stress. Other geometries such as concentric cylinders or cone and plate are often used depending on the viscosity of the sample.

An alternative method for examining the dynamic mechanical properties of liquids is to coat them onto an inert support (typically a glass fibre braid). This measurement is termed Torsional Braid Analysis and does not provide quantitative modulus measurements since it is difficult to decouple the response of the substrate from that of the sample.

The method of calibration of DMA's varies from instrument to instrument and it is essential to follow manufacturer's recommendations. Temperature calibration can sometimes be done as for TMA's since many instruments can operate in this mode. Load or force calibration is often carried out using weights. It is difficult to achieve the same degree of accuracy and precision in modulus measurements from a DMA as might be obtained by using an extensometer without taking great care to eliminate clamping effects and the influence of instrument compliance (which can be estimated by measuring the stiffness of a steel beam). Extensometers are much bigger instruments and the size of test specimens is correspondingly larger. Additionally, they often only operate at room temperature. For many applications the user is, however, mainly interested in the temperatures at which changes in mechanical properties occur and the relative value of a material's properties over a broad range of temperatures.

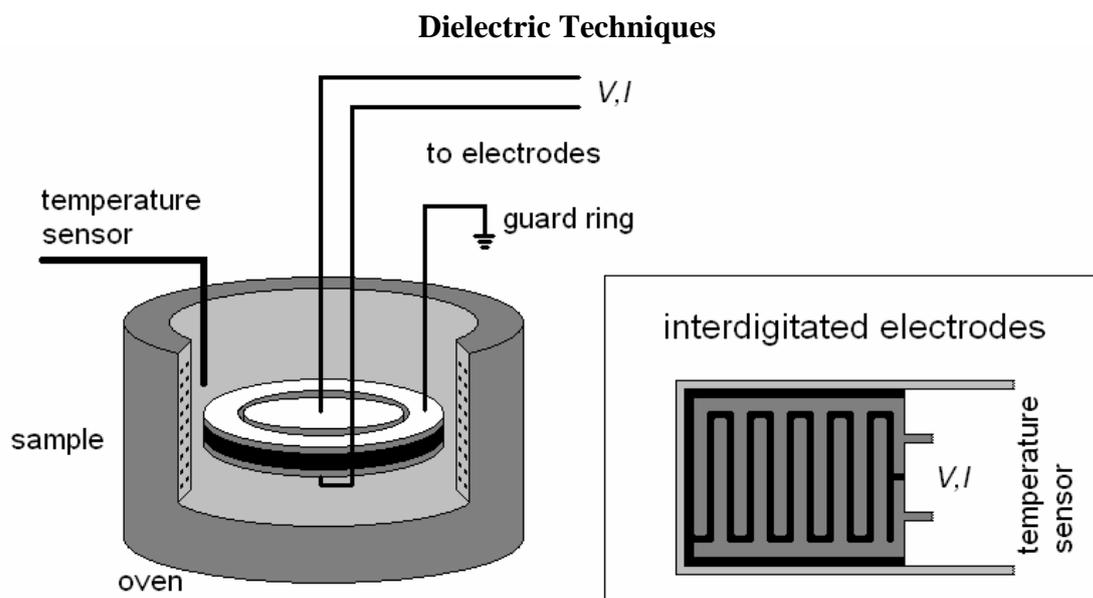


Figure 9. Schematic diagram of a dielectric thermal analysis instrument. Inset shows single-surface interdigitated electrode.

A schematic diagram of a typical instrument is shown in Figure 9. The sample is presented as a thin film, typically no more than 1 or 2 mm thick, between two parallel plates so as to form a simple electrical capacitor. A grounded electrode surrounding one plate, known as a guard ring, is sometimes incorporated so as to improve performance by minimising stray electric fields. A thermocouple or platinum resistance thermometer is placed in contact with one of the plates (sometimes one on each plate) so as to measure the specimen's temperature. For specialised applications, such as remote sensing of large components, an interdigitated electrode is used, shown inset into Figure 9. These employ a pair of interlocking comb-like electrodes and often incorporate a temperature sensor (resistance thermometer). These can be embedded in structures such as a thermosetting polymer composite and the dielectric properties of the material monitored while it is cured in an autoclave.

A usual part of the calibration protocol for DETA is to measure the dielectric properties of the empty dielectric cell so as to take into account stray capacitances arising from the leads which must be of coaxial construction. Temperature calibration can be done by measuring the melting transition of a crystalline low molecular weight organic crystal such as benzoic acid placed between the electrodes.

## TYPICAL EXPERIMENTS

This section discusses the most common types of experiments performed using TMA, DMA, TSCA and DETA by way of introduction to some of the more advanced applications described later.

### Thermomechanical Analysis

Thermomechanical measurements can be carried out on a wide range of solid samples. The most usual mode of measurement is either in compression (for self-supporting samples) or tension (for thin films and fibres). Some materials exhibit anisotropic behaviour (particularly films or crystals) in that changes in dimensions will differ depending upon which axis the measurements are performed.

*Thermal expansion measurements and softening temperatures.*

Plots of the change in length of a sample of a silicone gum rubber are shown in Figure 10. Three experiments were carried out on the material with different applied forces [1].

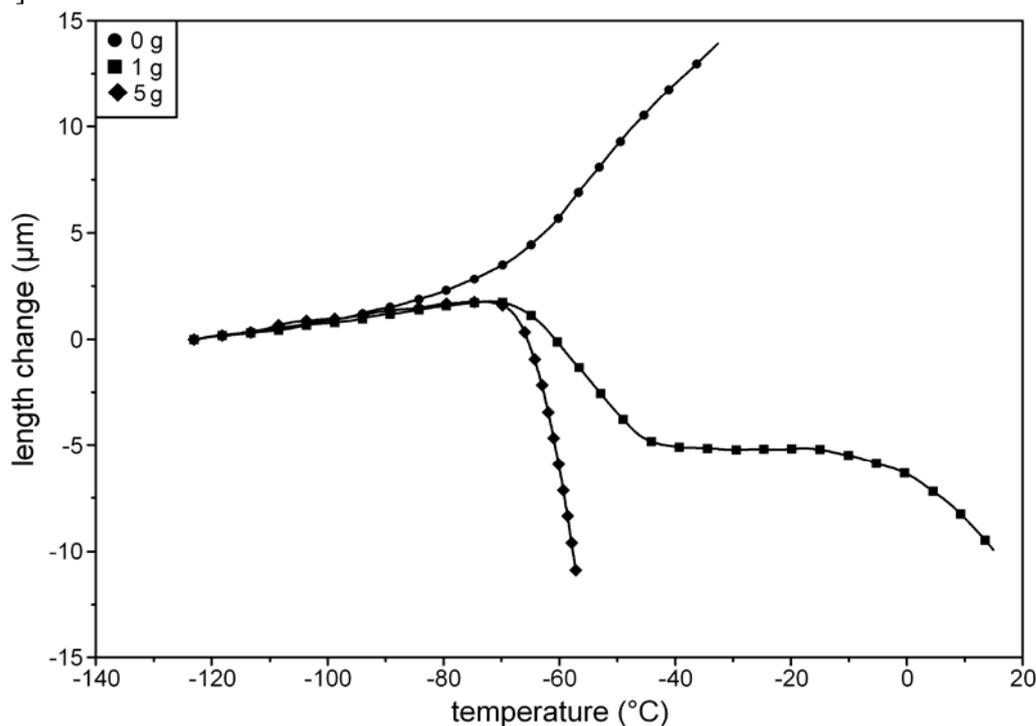


Figure 10. Plots of change in length for a sample of silicone rubber under different applied loads on a flat-ended probe of 0.92 mm diameter. Heating rate  $10^{\circ}\text{C min}^{-1}$  under nitrogen, initial sample thickness 2.5 mm in all experiments.

At zero force a change in slope of the curve can be seen around  $-60^{\circ}\text{C}$  due to the sample undergoing a change from glassy to rubbery behaviour. At this temperature the polymer chains acquire additional degrees of mobility which is seen as an increase in thermal expansion coefficient. The glass transition temperature ( $T_g$ ) can be defined by finding

the intercept of tangents to the linear portions of the length versus temperature plot above and below this region. When a force is applied to the specimen the probe deforms the material in inverse proportion to its stiffness. Below  $T_g$  the polymer is rigid and is able to resist the applied force therefore its deformation is negligible. Above  $T_g$  the polymer becomes soft and the probe penetrates into the specimen. The temperature at which this occurs is called the materials' softening temperature and is highly dependent on the force applied to the sample.

Measurements of thermal expansion coefficients are useful in assessing the compatibility of different materials for fabrication into components. Mismatches in behaviour can cause stresses to build up when temperature changes occur resulting in eventual weakening and failure of the structure. Many crystalline materials can exist in a number of polymorphic forms which are stable at different temperatures. The transition between crystal structures is usually accompanied by a change in density and thermal expansion coefficient which can be detected by TMA.

Supporting information from differential scanning calorimetry is often useful in interpreting information from TMA – particularly when softening point determinations are made – since loss of mechanical integrity can occur due to melting, which gives an endothermic peak in DSC or a glass-rubber transition, which causes a step change in heat capacity.

#### *Dynamic force thermomechanical analysis.*

Half way between conventional thermomechanical analysis and dynamic mechanical analysis is the technique of dynamic force (or load) TMA. This method uses a standard TMA instrument but the force is changed between two values in a stepwise (or sometimes sinusoidal) fashion. The dimensional changes of the specimen are monitored as a function of time (and temperature) but no attempt is made to determine the modulus and damping properties of the material.

An example of this is shown in Figure 11 for a carbon fibre reinforced epoxy resin composite beam measured in three point bending mode. The force on the probe was changed between 0.5 and 1.5 N and back every 12 s during the measurements. The average position of the sample deflection corresponds to a conventional TMA experiment under a force of 1 N. Above 90°C the epoxy resin undergoes a glass-rubber transition and the specimen begins to deform under the applied load. The peak to peak amplitude of the probe movement is proportional to the compliance (=1/stiffness) of the sample. This confirms that the sample is softer (more compliant) above  $T_g$ . It is possible to calculate the complex modulus of the material from the geometry of the sample, configuration of the test, applied forces and change in dimensions [2], although such measurements are best carried out using a dynamic mechanical analyser where this is done automatically.

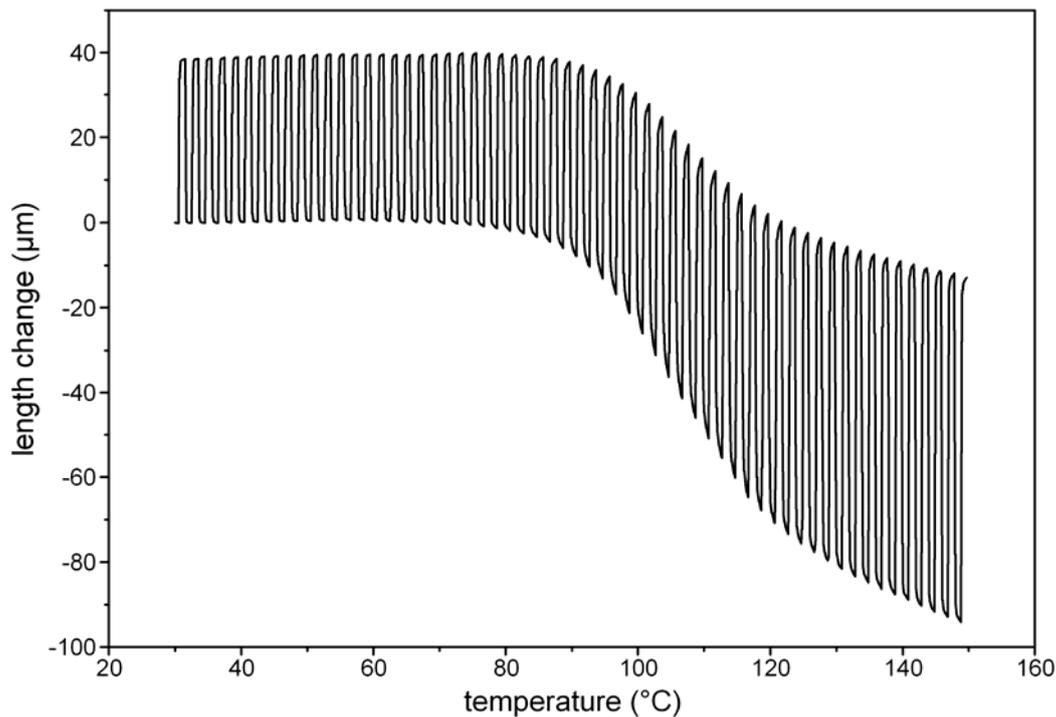


Figure 11. Dynamic load thermomechanical analysis of a carbon fibre/epoxy resin beam measured in three point bending. The force steps between 0.5 and 1.5 N and back every 12 s. Heating rate  $5^{\circ}\text{C min}^{-1}$  in air.

Some instruments are able to change the force on the sample during measurement so as generate force-displacement curves in a manner similar to a conventional extensometer with the additional advantage of good control of specimen temperature. As the stress on the specimen is increased the material may creep under the applied load. When the force is removed the sample may attempt to recover its original dimensions (stress relaxation). Such tests are useful in assessing the resilience of materials such as rubber gaskets, O-rings and the like. This behaviour is related to the time and temperature dependent viscoelastic properties of the material discussed in the next section.

### Dynamic Mechanical Analysis

Dynamic mechanical analysis is routinely used to investigate the morphology of polymers, composites and other materials. The technique can be particularly sensitive to low energy transitions which are not readily observed by differential scanning calorimetry. Many of these processes are time-dependent and by using a range of mechanical deformation frequencies the kinetic nature of these processes can be investigated.

*Single frequency temperature scans.*

The most common DMA experiment is simply to measure the storage modulus ( $E'$ ) and mechanical damping factor ( $\tan \delta$ ) against temperature at a single oscillation frequency. An example of this type of measurement is shown in Figure 12 for a specimen of the aliphatic polyester, polycaprolactone. This polymer is typically highly crystalline and melts around 50-60°C. However, the sample is not completely crystalline and contains

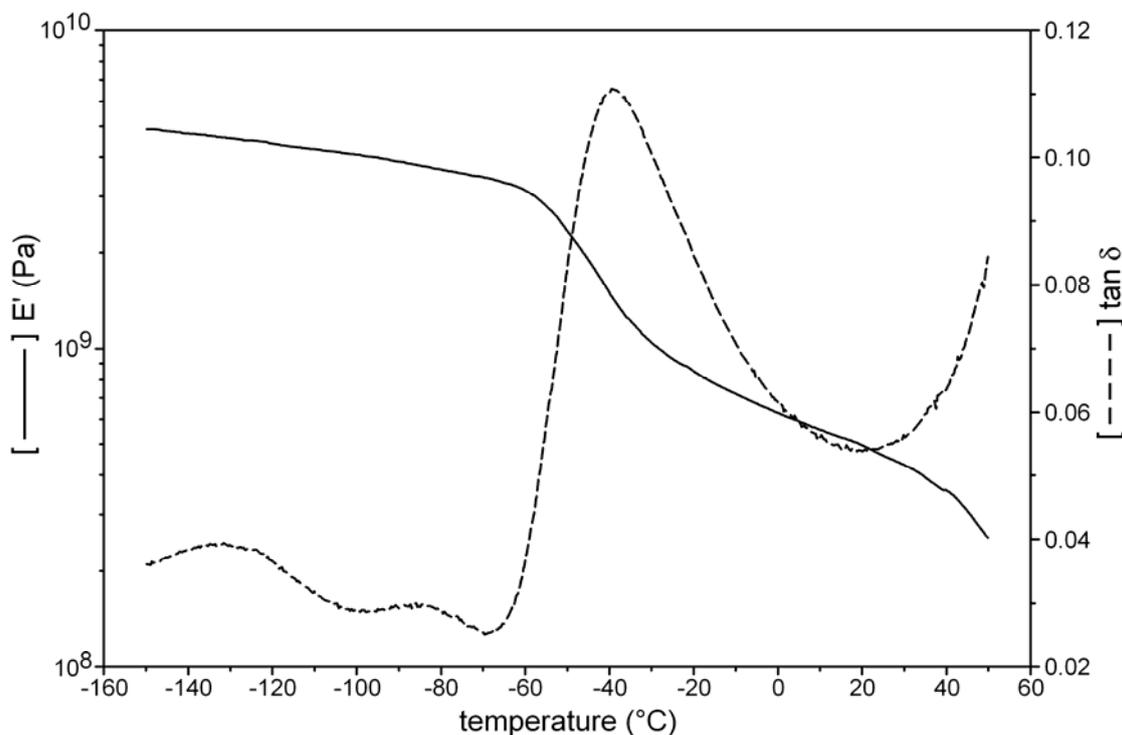


Figure 12. [DMA curve of poly(caprolactone) obtained in single cantilever bending at 1 Hz. Heating rate 2°C min<sup>-1</sup> in air.]

a small amount of amorphous material which undergoes a glass-rubber transition at -40°C. For DMA and DETA work the glass transition is often called the alpha ( $\alpha$ ) transition and all lower temperature transitions are given corresponding Greek symbols beta ( $\beta$ ), gamma ( $\gamma$ ) etc. The peaks in  $\tan \delta$  at -85°C and -130°C correspond to the  $\beta$  and  $\gamma$  transitions in the polymer respectively and are due to the motion of short lengths of the polymer backbone rather than the large scale increase in mobility that accompanies the glass-rubber transition. It is very difficult to measure this type of behaviour by DSC, but the size and position of these transitions are often very important for a polymer's impact properties since they provide a means of dissipating mechanical energy as heat [3].

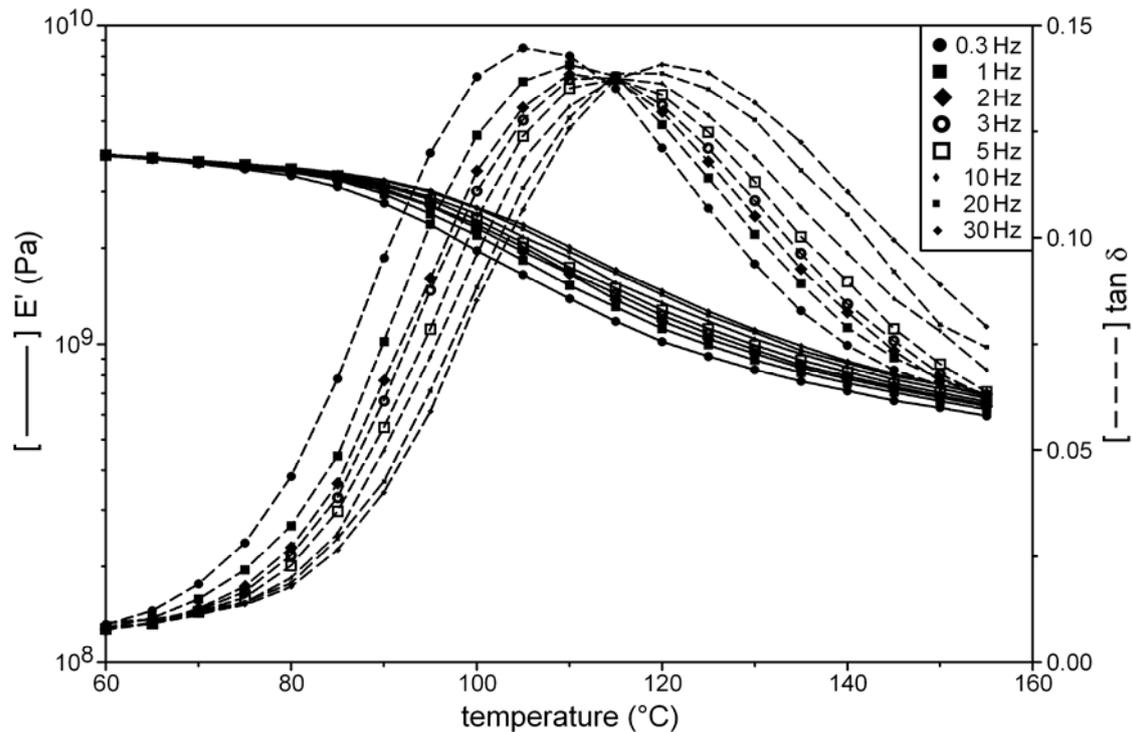
*Step-wise isothermal frequency scans.*

Figure 13. DMA results for poly(ethylene terephthalate) film measured in tension at different frequencies shown. The measurements were performed isothermally in  $5^{\circ}\text{C}$  increments and the apparatus allowed to come to thermal equilibrium for 5 minutes before the sequence of measurements was performed.

Figure 13 shows plots of storage modulus and damping factor for poly(ethylene terephthalate) (PET) film against temperature. The measurements were performed at a number of mechanical oscillation frequencies (0.3 – 30 Hz) and were carried out in a step-wise isothermal fashion with the temperature of the oven being raised by  $5^{\circ}\text{C}$  and allowed to come to equilibrium before each frequency was successively applied to the specimen. It can be seen that the peak in  $\tan \delta$  moves to a progressively higher temperature as the measurement frequency is increased as a consequence of the time dependence of the glass-rubber transition. This maximum reflects the temperature at which the material can deform within the same time frame as the mechanical oscillation. Below this temperature the material is too sluggish to react to the deformation and behaves as a solid, above this temperature the material relaxes faster than the deformation and behaves as a viscous liquid.

*Time-temperature superposition.*

It is well established that the observed temperature at which the glass-rubber transition occurs depends upon the timescale over which one investigates molecular mobility (this applies to all methods of determining this parameter). To a first approximation the process can be treated as a simple thermally activated effect and the relationship between the temperature of maximum mechanical damping ( $T_{\text{peak}}$ ) and the timescale (or

frequency ( $f$ ) of the applied forcing variable (in this case mechanical deformation) can be analysed using a simple Arrhenius expression:

$$\ln(f) = \ln(A) - E_a/(R T_{peak}) \quad (16)$$

where  $E_a$  is the apparent activation energy for the process and  $R$  is the gas constant.

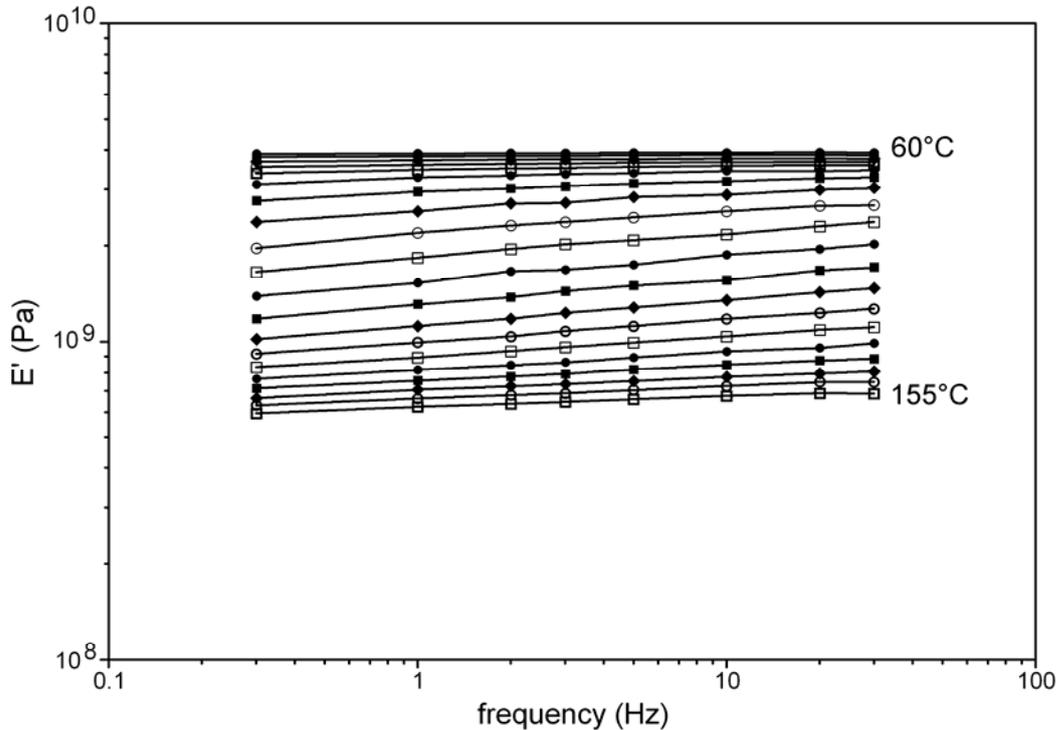


Figure 14. Storage modulus data from figure 13 shown as a function of frequency at different temperatures as indicated.

A more rigorous approach recognises that the glass-rubber transition is a co-operative effect and does not conform to the simple model described above. A common method for treating such a response is to superimpose data collected at different temperatures and frequencies onto one smooth curve. In Figure 14 the data from Figure 13 are presented on a frequency axis. It can be seen that if a curve at one temperature is chosen as a reference point then data from other temperatures can be shifted in frequency to produce a smooth continuous change in properties spanning a wide frequency range. Ideally both the moduli and damping factor data should produce good overlays (Figure 15). The relationship between the frequency shift ( $a$ ) at a specific temperature ( $T$ ) and the reference temperature ( $T_{ref}$ ) is usually expressed in terms of the Williams-Landel-Ferry (WLF) equation [4]:

$$\log[a(T)] = C_1(T - T_{ref}) / (C_2 + T - T_{ref}) \quad (17)$$

where  $C_1$  and  $C_2$  are constants.

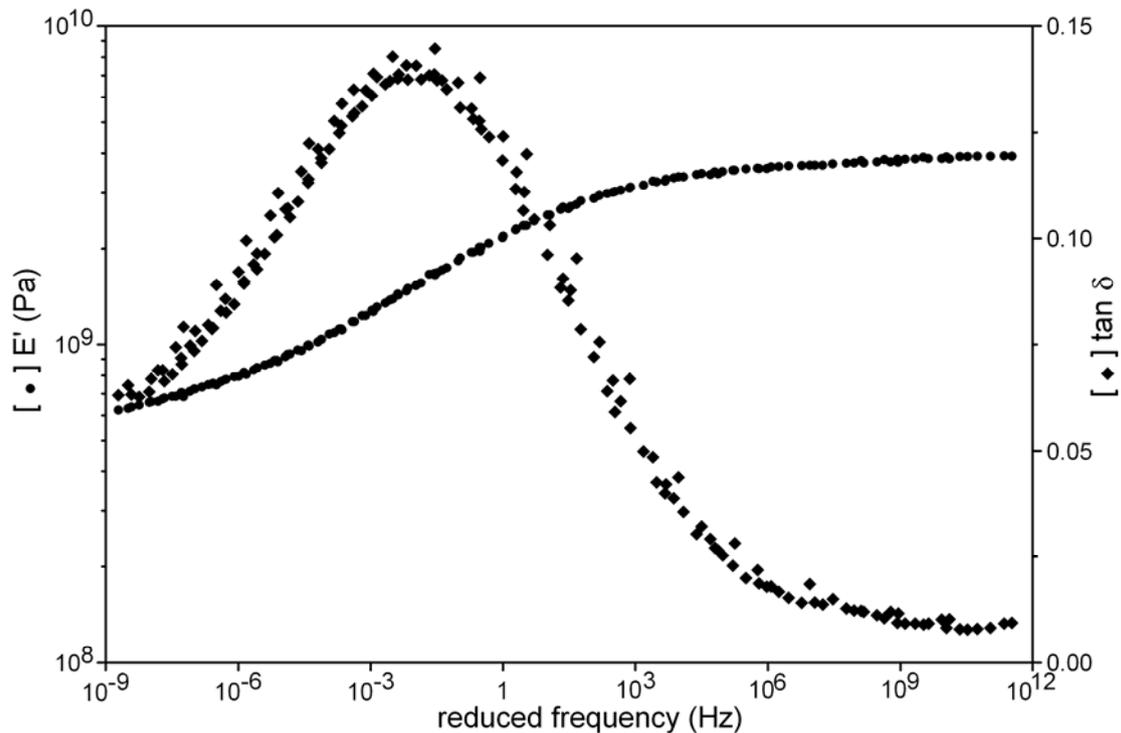


Figure 15. "Master curve" of data from figure 13 with a reference temperature of 100°C.

Time-temperature superposition is a means of extending the frequency range of dynamic mechanical data and has applications for the evaluation of materials for acoustic damping properties.

### Dielectric Techniques

Measurements of electrical properties are particularly sensitive probes of the mobility of ions and dipoles within a specimen. Even non-polar materials like polyethylene often contain polar impurities which give sufficient response for the behaviour of the specimen to be analysed by these methods. The typical experiments described below illustrate the specialised niche occupied by TSCA and DETA in that the measurements are placed in the context of addressing a particular problem. Applications of DETA to remote sensing of sample's properties are described later.

#### *Thermally Stimulated Current Analysis.*

The stability of lyophilized products is crucial in pharmaceutical industry. Freeze-drying a drug formulation is a common way to preserve the active component during the storage until its final use. The active ingredient is diluted and embedded in an excipient formulation during the freeze-drying process. The physical properties of the excipient in the solid state dictate the stability behaviour of the formulation. The knowledge of the glass transition ( $T_g$ ) and melting ( $T_m$ ) temperatures are essential to predict shelf life. If the lyophilised product is stored above one or the other transition, it is likely that the material will change over time and the stability of the active ingredient cannot be guaranteed. The knowledge of  $T_g$  is also very important for the lyophilisation itself. In

particular, the interaction of the system with water is essential to model the freeze-drying process.

DSC is the most appropriate technique to give the best information concerning melting. The data collected are thermodynamic variables such as heat capacity or enthalpy of fusion, etc. However, the change in heat capacity that occurs at the glass transition can often be rather small (particularly for materials with low amorphous content) and there may not be enough sensitivity to detect the glass transition without ambiguity. A feature of the thermally stimulated current technique is that the current flow is directly proportional to the strength of the electric field. Thus it is possible to “magnify” weak transitions by increasing the polarisation voltage.

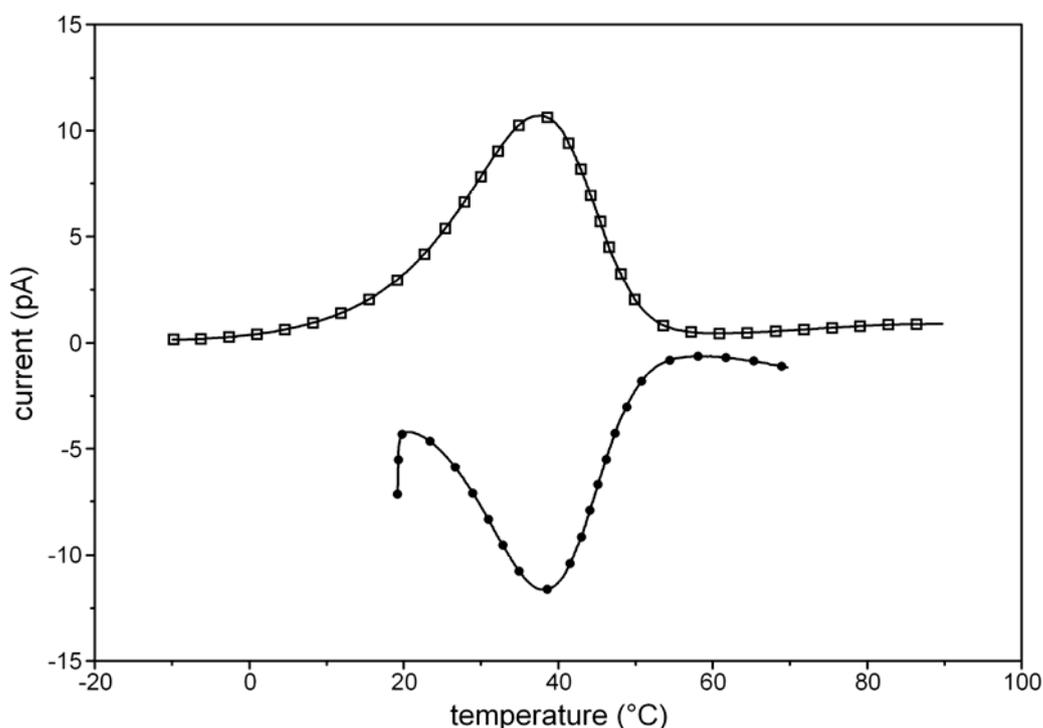


Figure 16. Thermally stimulated current analysis of a freeze dried drug. Lower curve: polarisation current. Upper curve: depolarisation current. Heating rate:  $7^{\circ}\text{C min}^{-1}$  for both experiments.

Figure 16 shows the results from a TSCA of a freeze-dried drug. In essence, two experiments are shown. The lower curve represents the current flow during polarisation under an applied field of 100 V as the sample was heated from  $20^{\circ}\text{C}$  at  $7^{\circ}\text{C min}^{-1}$  to  $70^{\circ}\text{C}$ . The sample was then cooled to  $-10^{\circ}\text{C}$  and the electric field switched off. The upper curve shows the discharge of the sample as it was heated to  $90^{\circ}\text{C}$  at the same rate in the absence of any external field. The peaks in both curves represent the glass transition of the drug. Note that the peak in the polarisation curve occurs at a higher temperature than the discharge curve which is typical of this technique. The discharge curve is known as the “global” discharge curve - a more advanced technique can be used to carry out the polarisation experiment over a narrow temperature window in order to examine the time and temperature dependence of the discharge process.

TSCA is more often applied to polymeric materials [5], but this example illustrates the use of the technique on a system where the detection of small amounts of amorphous material is of critical importance to its stability.

#### *Dielectric Thermal Analysis.*

Measurement of thermal transitions of thin films can be problematic due to the small amount of material that is present. The glass transition temperature of adhesives affects the tack and bonding behaviour, but analysis by DSC can be difficult unless the material is physically removed from any backing. This can be aided by swelling the adhesive in solvent and scraping it off the substrate with a blade. There is a danger that the properties of the sample could be changed by this process even if the adhesive is subsequently dried so as to remove any residual solvent. Dielectric measurements, however, are ideally suited to testing thin films and, so long as the backing undergoes no thermal transitions in the region of interest, the adhesive can be measured in situ without any preparation.

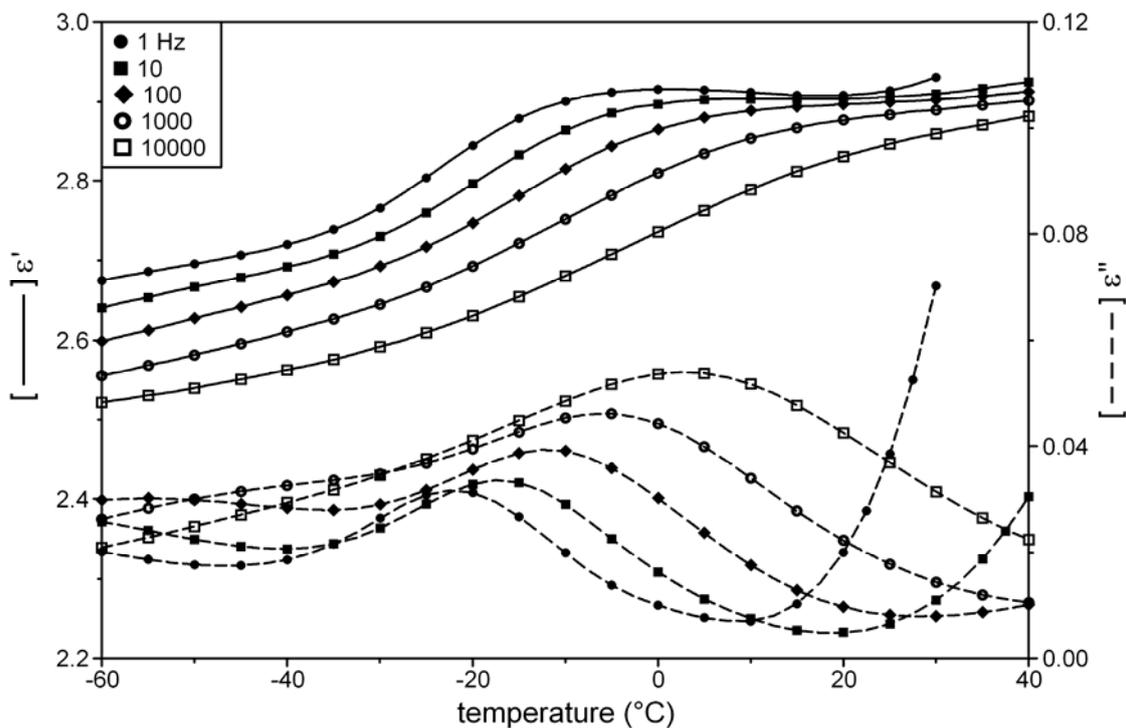


Figure 17. Dielectric analysis of thin layer of pressure sensitive adhesive on poly(ethylene terephthalate) film at different electrical field frequencies shown.. Heating rate:  $2^{\circ}\text{C min}^{-1}$ .

Figure 17 shows plots of  $\epsilon'$  and  $\epsilon''$  obtained at various frequencies for a sample of poly(ethylene terephthalate) film coated with a  $50\ \mu\text{m}$  thick layer of pressure sensitive adhesive. The glass-rubber transition of the adhesive can be observed as a step increase in  $\epsilon'$  and a peak in  $\epsilon''$  which shifts to higher temperatures as the measurement frequency increases. Figure 18 shows the response of the base film itself. The PET has a weak transition due to local movement of dipoles associated with its  $\beta$  transition which has a

much stronger frequency dependence than that of the adhesive. This causes some uncertainty with the assignment of  $T_g$  of the adhesive at 10 kHz where there is expected to be some overlap. At lower frequencies the peak in  $\epsilon''$  due to the substrate is well separated from the  $T_g$  of the adhesive and the latter can be measured more accurately. Measurement of the properties of paints and other coatings can be carried out in the same way. In some cases the film may be put down directly onto a metal substrate which can then be used as one of the electrodes.

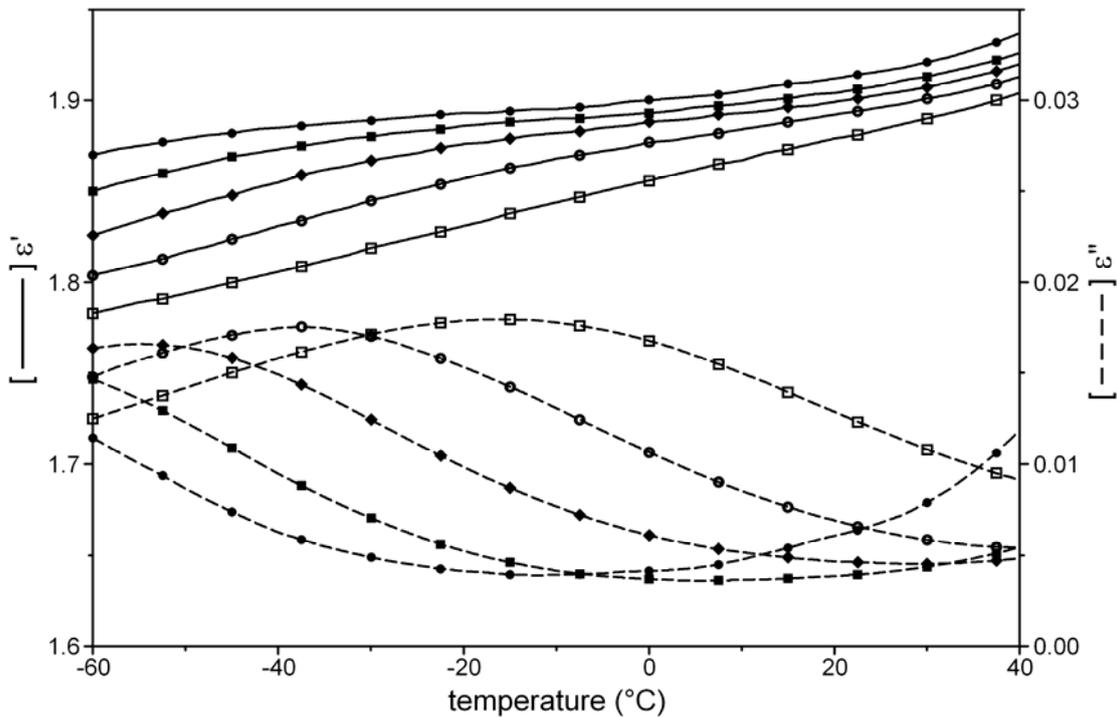


Figure 18. Dielectric analysis of uncoated poly(ethylene terephthalate) film under the same conditions as figure 17.

The principles of time-temperature superposition can be used with equal success for dielectric measurements as well as dynamic mechanical tests. Analysis of the frequency dependence of the glass transition of the adhesive in the system described above shows that it follows a WLF type dependence whereas the  $\beta$  transition of PET obeys Arrhenius behaviour. This type of study can be used to distinguish between different types of relaxation phenomena in materials.

## APPLICATIONS

The following examples are used to demonstrate the broad range of applications of thermomechanical and thermoelectrical measurements. Many of the applications are not typical of the routine types of tests described earlier, but are placed here to show the diversity of these techniques in characterising materials and provide short “case studies” which present the methods in the context of addressing particular problems.

### Thermomechanical Analysis

Whilst thermomechanical measurements are routinely used to investigate mechanical stability and measure thermal expansion coefficients. Two examples are given which illustrate the use of the technique on the small scale as a micro-analytical tool to identify the distribution of two materials within a matrix and also on a larger scale to investigate the firing of a ceramic material.

#### *Localised thermomechanical analysis of pharmaceuticals.*

Micro-thermal analysis is discussed further in Chapter 6. Here the technique is employed to illustrate the use of thermomechanical measurements on small samples to identify different components in a mixture of two materials [6]. Figure 19 shows a

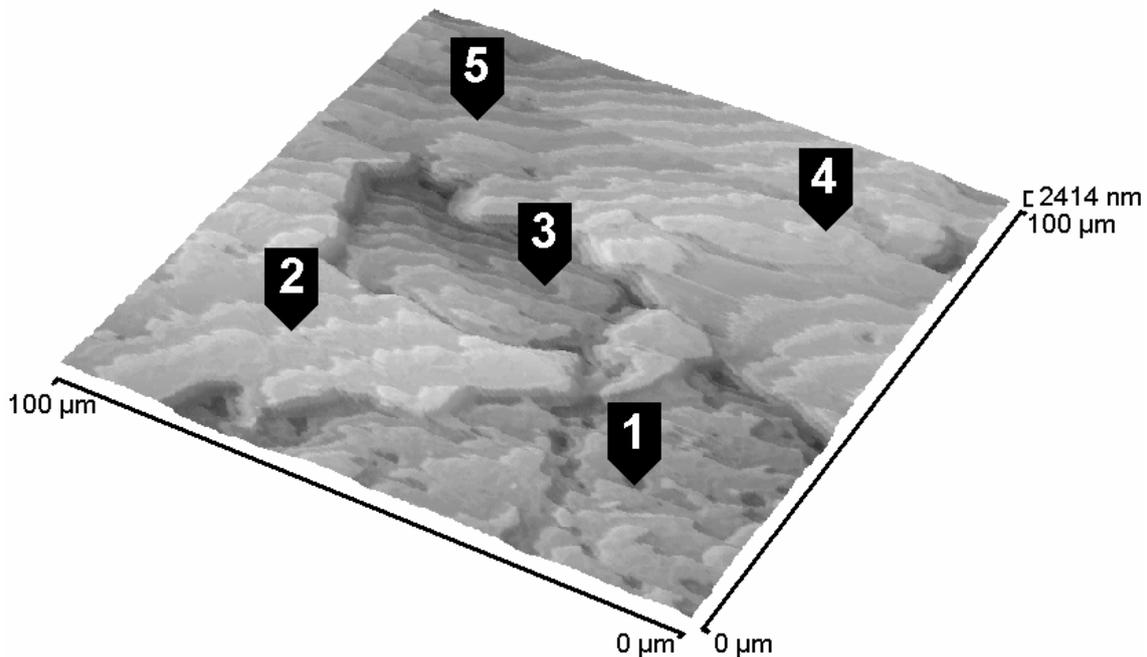


Figure 19. Atomic force micrograph of the surface of a pressed compact containing a mixture of benzoic acid and salicylic acid. Labels indicate positions of localised thermomechanical analysis in figure 20.

micrograph of the surface of a tablet pressed from a mixture of benzoic acid and salicylic acid which is used as a test specimen for dissolution studies to mimic the effect of digestion within the gut. The image was obtained by using an atomic force microscope which uses a fine stylus to measure the height of the sample as the tip of the stylus is scanned over the surface of the specimen. Having obtained the image, the tip may be placed on the sample with a pre-set force and heated by passing a current through it. At the same time its vertical displacement is measured. In this way, thermomechanical analysis of areas less than  $5 \mu\text{m}^2$  may be carried out. Several different locations may be measured consecutively and used to “map” the softening or melting behaviour of a specimen with high spatial resolution.

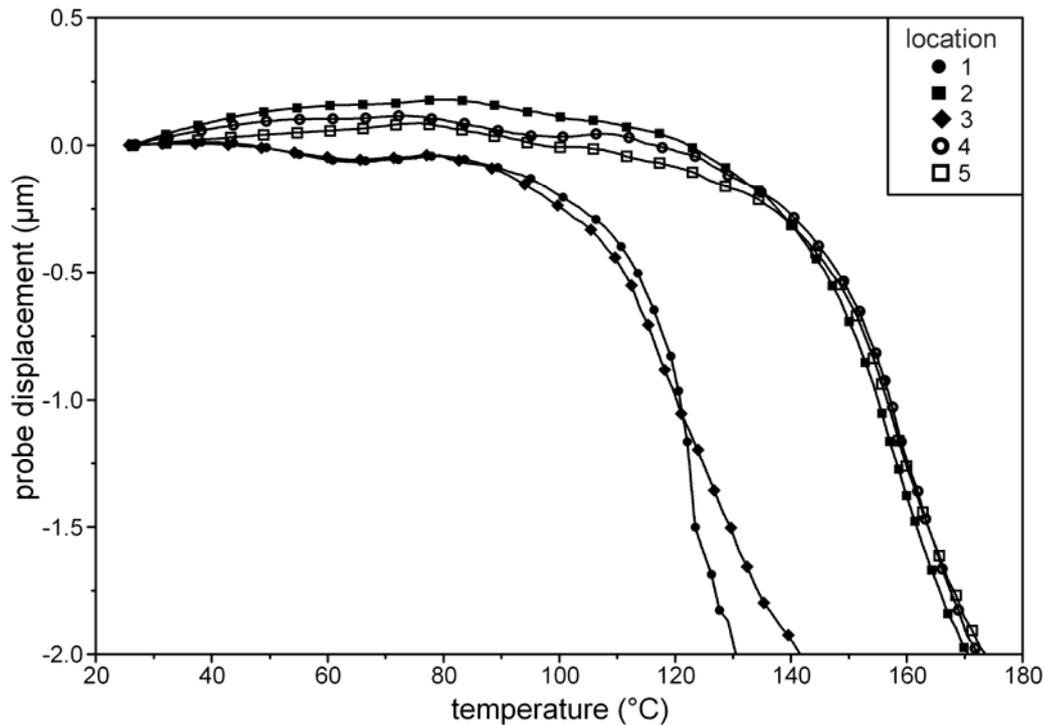


Figure 20. Localised thermomechanical analysis of different areas shown in figure 19. Heating rate  $10^{\circ}\text{C s}^{-1}$ .

Figure 20 shows the results of carrying out such measurements at different points marked in Figure 19. It is evident that the material examined at points 1 & 3 has a lower melting temperature than the other locations. Since benzoic acid melts at  $122^{\circ}\text{C}$  and salicylic acid melts at  $159^{\circ}\text{C}$ , the results from such measurements are sufficient to identify the distribution of these materials within the image.

#### *Rate controlled sintering of ceramics.*

The compaction and sintering of high temperature refractory materials may be studied by thermomechanical analysis. In many cases it is desirable that the ceramic changes in dimensions in a uniform manner. In order to achieve this the rate of heating can be controlled by the rate of change of dimensions of the specimen. This can be done by heating the sample at a fixed heating rate and then stopping heating when the rate of change of length exceeds a certain limit. The process is allowed to continue isothermally until the rate falls below the limit and then heating is recommenced. An alternative approach is illustrated in Figure 21. Here, heating takes place at a maximum fixed rate of temperature rise ( $2^{\circ}\text{C min}^{-1}$ ) until the rate of shrinkage reaches a pre-set value. Thereupon the rate of temperature change is controlled so as to maintain a constant rate of shrinkage. The desired rate of shrinkage may be changed during the experiment between different values (in this case stepped alternately between 1 and  $2\ \mu\text{m min}^{-1}$  during the temperature rise) so as to explore the relationship between the sintering kinetics and temperature [7].

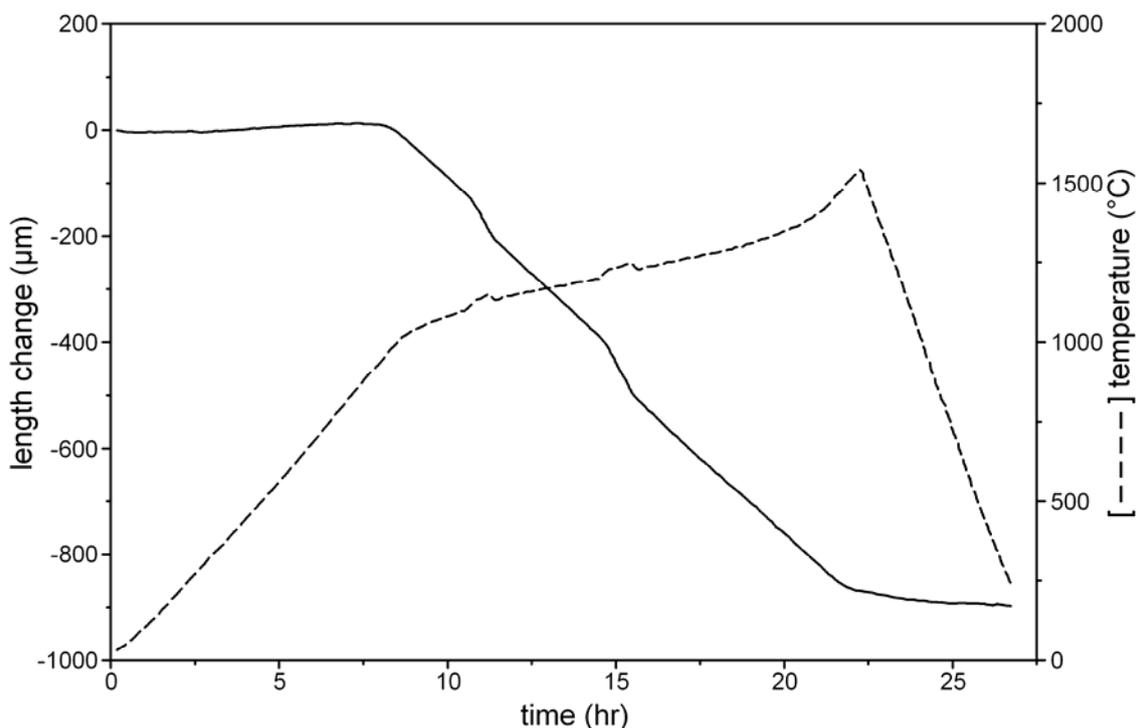


Figure 21. Rate controlled sintering of a ceramic under air. The rate of temperature rise is controlled by the rate of change in length over pre-set temperature ranges with a limiting maximum heating rate  $2^{\circ}\text{C min}^{-1}$ .

A similar technique has been described for DMA whereby the temperature program was controlled by constraining the rate of change of mechanical properties (e.g. storage modulus) to within certain limits. This approach was shown to be effective in resolving the multiple glass transitions of a polymer blend [8].

### Dynamic Mechanical Analysis

Dynamic mechanical measurements are not limited to running experiments on samples in air or inert gases. With care, measurements can be carried out with the test specimen immersed in a liquid or on liquid samples themselves as the following examples demonstrate.

#### *Dynamic mechanical analysis of fibres under dye bath conditions.*

The dyeing and washing behaviour of regenerated and synthetic fibres are markedly dependent upon temperature. For example, acrylic fibres must be dyed above  $T_g$  in order to facilitate dye diffusion; in contrast, the characteristic high wet fastness properties of the resultant dyeings can be attributed primarily to the relative absence of dye diffusion that results from such aqueous treatments (e.g. laundering) being carried out at temperatures below the  $T_g$  of the fibre. Although the effect of temperature on the physical properties of dry fibres is readily performed using conventional thermoanalytical techniques (e.g. DSC), it is less easy to examine the behaviour of fibres under dye bath conditions owing to the presence of water. Of particular interest is the effect of “carriers” - additives to the dye bath which are used to accelerate the rate of dye diffusion within the hydrophobic fibres. The mechanism by which these materials

enhance dye uptake is thought to be by plasticising the fibre by reducing its glass-rubber transition temperature and thus increasing the segmental mobility of the polymer chains.

Using a dynamic mechanical analyser, it is possible to carry out experiments with the sample immersed in a liquid. For this type of measurement, the instrument is fitted with a metal liner which is inserted into the oven so that the sample and clamps can be immersed and the temperature of the bath programmed in the usual way. Results from testing acrylic fibres under different conditions are shown in Figure 22.

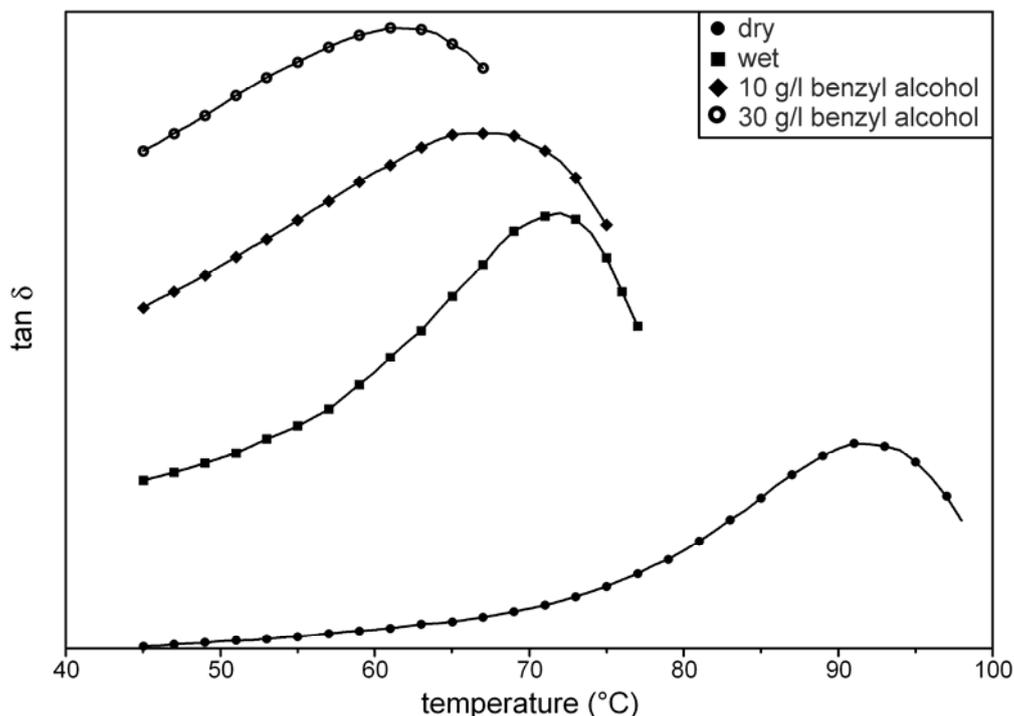


Figure 22. Dynamic mechanical analysis of acrylic fibres in air, water and solutions of benzyl alcohol. Measurements performed in tension at a frequency 1 Hz, heating rate  $1^{\circ}\text{C min}^{-1}$ . Curves shown offset for clarity.

It can be seen that peak in damping factor is reduced from around  $90^{\circ}\text{C}$  to  $72^{\circ}\text{C}$  by the presence of water. Addition of benzyl alcohol to the water bath (as a model “carrier”) further depresses and broadens the peak in  $\tan \delta$  in a fashion typical of the action of a plasticiser thus confirming the nature of carrier activity [9].

#### *Variable temperature oscillatory rheometry of food additives.*

Cellulose ethers, such as methyl cellulose, are widely used as thickening agents in a variety of foodstuffs such as pie fillings and potato croquettes. These substances possess the unusual feature of forming a reversible gel structure on heating which serves to maintain the mechanical integrity of the product during baking. On cooling, the gel structure breaks down and the original texture of the mixture is regained.

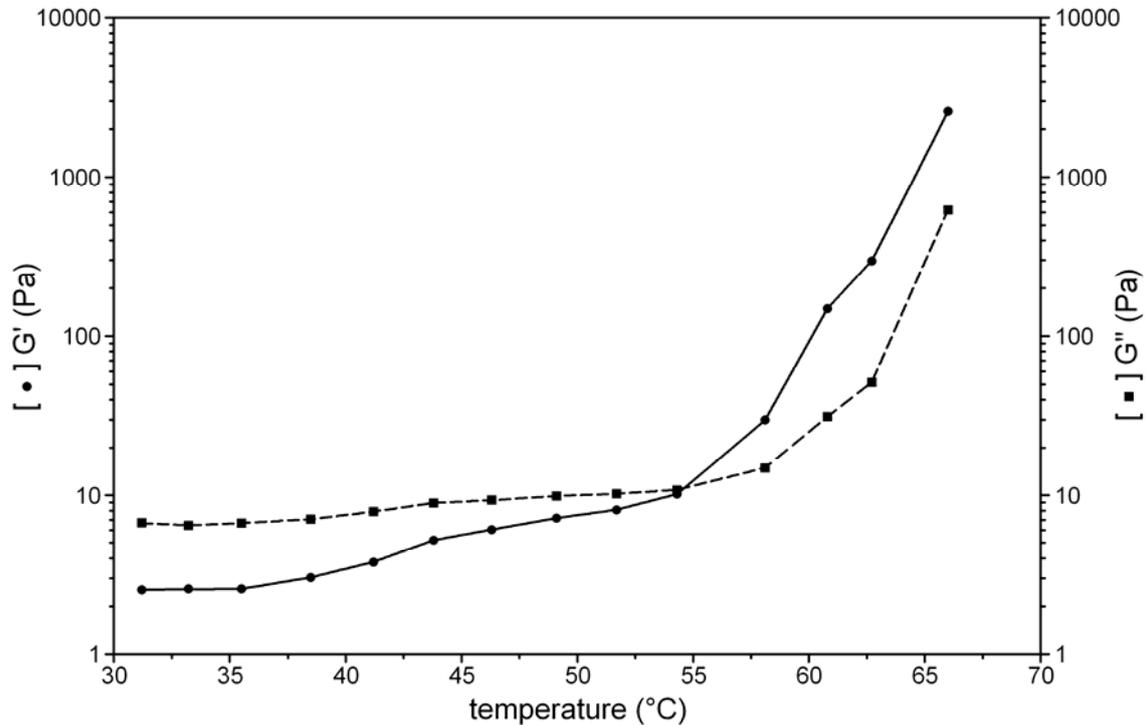


Figure 23. Storage and loss shear modulus for a 10% solution of methyl cellulose in water as a function of temperature. Measurement frequency 1 Hz, heating in steps with 5 mins dwell time between steps.

Measurements on a 10% solution of methyl cellulose in water were carried out using an oscillatory rheometer. Plots of storage and loss moduli ( $G'$  and  $G''$  respectively) against temperature are shown in Figure 23. Below 55°C the loss modulus is higher than the storage modulus indicating that the specimen is responding more like a liquid than a solid. Above this temperature, the situation is reversed and the specimen has predominantly solid-like characteristics. The cross-over between  $G'$  and  $G''$  corresponds to the formation of a cross-linked gel network and the transition between the two types of behaviour [10]. The effect of different additives on gel formation can be a useful indicator of synergistic (lowering of gel temperature) or antagonistic (raising of gel temperature) interactions between materials.

DMA is regularly used to study the chemical reactions which lead to cross-linking of thermosetting resins, such as those used in the manufacture of composites. At high degrees of network formation the rubbery cross-linked gel will vitrify into hard glassy material and the storage modulus will increase by several orders of magnitude. Plotting gel point and vitrification point against temperature and time leads to a Time-Temperature-Transformation (or Gillham-Enns [11]) diagram which can be used to map out the curing of thermosetting polymers. The use of dielectric analysis in the following section will show how this technique can also be used to follow chemical cross-linking and the reverse effect of breakdown of molecular structure brought about by exposure to UV radiation.

### Dielectric Thermal Analysis

Dielectric thermal analysis involves monitoring the viscosity of a system via its ability to store or transport electrical charge. Changes in the degree of alignment of dipoles and the ion mobility provide information pertaining to physical transitions in the material and to material properties such as viscosity, rigidity, reaction rate and cure state. By use of remote dielectric sensors, the measurements can be made in actual processing environments such as presses, autoclaves, and ovens.

#### *In-situ cure monitoring of composites.*

In dielectric cure monitoring, the ion mobility (electrical conductivity) of the material is of greatest interest. Almost all materials contain current carriers, which are charged atoms or charged molecular complexes. The application of a voltage between a set of electrodes will create an electric field that forces those ions to move from one electrode toward the other. Ions encounter something analogous to viscous drag as they flow through a medium filled with molecules, and their mobility through this medium determines the conductivity. Conductivity is inversely proportional to viscosity. Ions moving through very fluid, watery materials have high mobility and conductivity - resulting in low resistivity that correlates with low viscosity. Conversely ions moving through very rubbery materials have low mobility and conductivity corresponding to the high viscosity. It is important to note that beyond some point in the cure the physical viscosity will climb so high that it is no longer measurable, even though the cross-linking reaction has not reached completion. Because increasing polymerisation continues to affect ionic motion, dielectric measurements retain sensitivity past the time when ionic and physical viscosity deviate. Consequently, with proper interpretation, dielectric measurements are useful throughout the entire curing process for determining changes in viscosity and rigidity, and are extremely sensitive in determining the end of cure.

Figure 24 shows the conductivity of a glass fibre reinforced epoxy resin composite during curing in a heated press. An interdigitated electrode was embedded in the sample during lay-up of the specimen, and a resistance thermometer in the electrode monitors the temperature of the sample directly during processing. Initially the conductivity of the specimen increases as it is heated to the cure temperature and the resin becomes less viscous. Cross-linking causes the viscosity to increase and as a consequence, the conductivity decreases. Towards the end of the reaction the material forms a highly cross-linked network and shows a strong frequency dependence in conductivity. Dielectric measurements readily lend themselves to being carried out simultaneously with dynamic mechanical analysis when experiments are performed in compression or torsion. The sample is usually mounted between parallel plates which are used to apply the mechanical stress – electrical connections can be established to these and used to make a dielectric measuring cell [12].

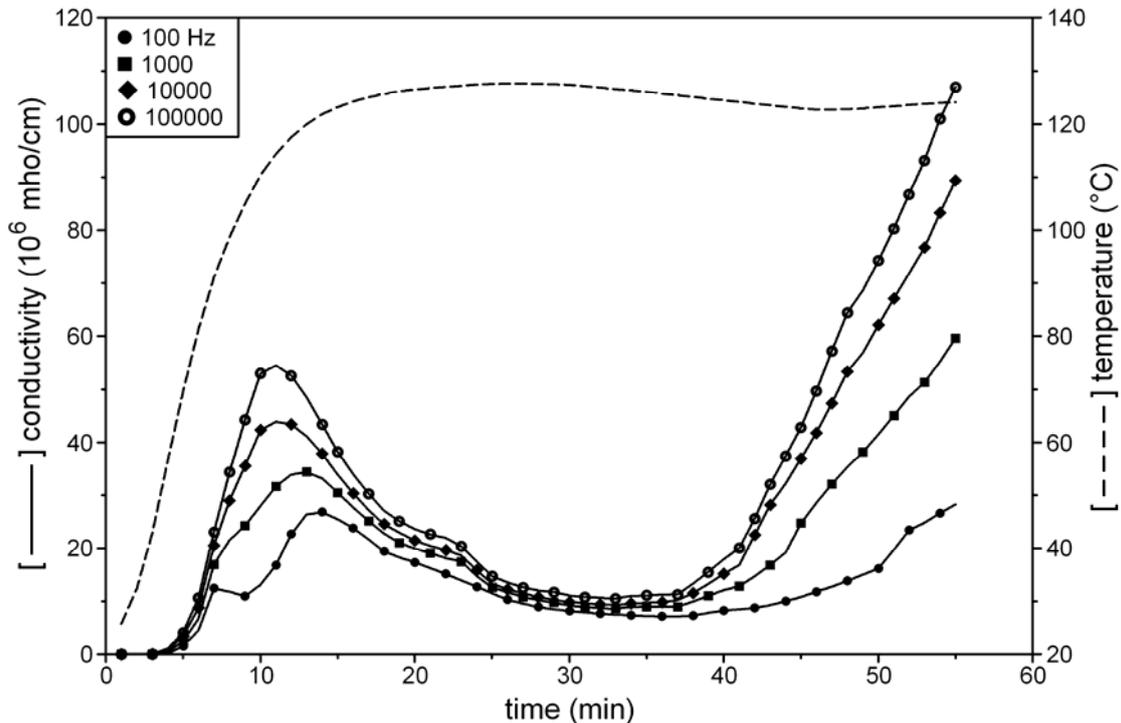


Figure 24. Plots of ionic conductivity against time during the cure cycle of a glass fibre reinforced epoxy resin panel using an interdigitated sensor. Temperature profile measured by sensor indicated.

*In-situ monitoring of the UV degradation of adhesives.*

Tinted self-adhesive plastic films are a popular means of limiting the effects of sunlight on the interiors of buildings and vehicles. Stuck to the inside surfaces of windows, these are used to filter infra-red and ultra-violet (UV) radiation, thereby avoiding heat build-up in offices and vehicles, and fading of interior upholstery. After the glass itself, the adhesive is first to receive solar radiation and must be stabilised against photodegradation by an appropriate choice of polymer and stabiliser package. This not only protects the adhesive but, by blocking short wavelength radiation, suppresses fading of the dyes used to colour the film. The performance of candidate systems is assessed by exposure to intense radiation equivalent to the solar spectrum in a hot, humid environment during accelerated ageing. Measurements of the UV transmission of the film are made at regular intervals in addition to critical evaluation of the optical appearance of the plate by eye. Since these products are to be used in vehicles, any blemishes in the film brought about by degradation of the adhesive are extremely undesirable.

In such a study [13], test panels of window film were mounted on glass plates for accelerated ageing. A small window was cut in the plastic film and an interdigitated single surface dielectric sensor applied to the exposed surface of the adhesive after chilling the plate in a freezer to aid removal of the backing. Measurements of dielectric loss and permittivity were carried out from 0.1 Hz to 100 kHz in decade steps at ambient temperature before and after 600 & 1200 hr exposure.

Table 1. Dielectric loss factor,  $\epsilon''$  (0.1 Hz) for adhesive with different stabiliser packages during accelerated weathering

Sample	“standard”	“poor”	“good”
initial	3.00	2.86	3.14
after 600 hr	8.59	12.6	3.18
after 1200 hr	10.4	71.0	6.45

Values of dielectric loss ( $\epsilon''$ ) at 0.1 Hz for the same adhesive containing three candidate stabiliser packages are given in Table 1 at different stages of weathering. The data indicates that, of the three stabiliser formulations, the “poor” package showed the largest increase in  $\epsilon''$ . UV transmission measurements showed that, although starting with the same value (ca. 0.4%), the transmission of “standard” package rises to 5.7% compared to around 2.5% for both adhesives containing the “good” and “poor” formulations after 1200 hours weathering. The “poor” sample exhibited severe optical distortion of the film, but remained light fast, the “good” sample (the same formulation as the “poor” sample with an additional stabiliser) maintained good UV absorption and showed no blemishes. Even after 600 hours exposure, it was apparent that changes in adhesive behaviour could be detected by this technique before deterioration in appearance could be seen by eye [13].

### **MODULATED TEMPERATURE THERMOMECHANICAL AND DIELECTRIC TECHNIQUES**

In the same way that applying a temperature modulation to DSC can be used to separate thermally reversing thermal events (such as the glass transition) from thermally non-reversing ones (e.g. crystallisation and curing), the same principles can be applied to TMA. This approach enables one to separate reversible dimensional changes due to thermal expansion from irreversible effects such as creep or stress relaxation [14]. Modulated temperature DMA has been developed as a means of investigating the reversible melting of polymers [15]. A sinusoidal heating program has also been employed in TSCA to separate reversible pyroelectric currents from non-reversible thermally stimulated discharge of heated dielectric materials [16].

### **CONCLUDING REMARKS**

The description of thermomechanical and thermoelectrical measurements in a modest chapter such as this is an ambitious exercise. The author has attempted to cover a wide range of methods and applications with the intention of illustrating the diversity of this field whilst emphasising the relationships between the static techniques (such as TMA and TSCA) and the dynamic techniques (dynamic force TMA, DMA and DETA). With the exception of TMA, these methods are often promoted as some of the more “advanced” thermal analysis techniques. It is hoped that the preceding pages help to dispel this myth without belittling their ability to measure useful properties.

## ACKNOWLEDGEMENTS

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