

# Measurement Good Practice Guide No. 62

## **Thermal Analysis Techniques for Composites and Adhesives Second Edition**

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### **Abstract:**

This Measurement Good Practice Guide covers five thermal analysis techniques; DSC, TMDSC, DMA, DEA and DTUL. Each technique is described and measurement issues are discussed. Precision statements based on inter-laboratory testing are presented for DSC, TMDSC and DMA. Recommended procedures for each technique are included in the Guide.

Recommendations are made for the choice of technique for the measurement of degree-of-cure and measurement of service temperature for composites and adhesives. Although these measurements are related, they present different measurement challenges and the effectiveness of each technique for these measurements is discussed.

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# Thermal Analysis Techniques for Composites and Adhesives

## Second Edition

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## **Nomenclature**

### **Thermal Analysis Techniques**

DSC	differential scanning calorimetry
DMA	dynamic mechanical analysis
DTUL	deflection temperature under load
HDT	heat deflection temperature (term superseded by DTUL)
DEA	dielectric analysis
TMDSC	temperature modulated differential scanning calorimetry
TGA	thermogravimetric analysis
TMA	thermomechanical analysis

### **Standards Organisations**

ASTM	American Society for Testing and Materials (produce ASTM standards)
BSI	British Standards Institution (produce BS standards)
CEN	Comité Européen de Normalisation / European Committee for Standardisation (produce EN standards)
ISO	International Organisation for Standardisation (produce ISO standards)

### **ISO Standards**

WD	working draft
NWI	new work item
CD	committee draft
DIS	draft international standard
FDIS	formal draft international standard

### **Others**

$T_g$	glass transition temperature
r	repeatability limit at 95 % confidence
R	reproducibility limit at 95 % confidence

## Foreword

The second edition of this Guide presents developments in a number of areas. The range of thermal analysis techniques has been extended to include temperature modulated differential scanning calorimetry and dielectric analysis. Hence, the sections on these two techniques are completely new to the Guide. The other major developments are more detail on the improvement of reproducibility for the measurement of glass transition temperature by dynamic mechanical analysis and explicit guidance on the measurement of degree-of-cure. Although both these topics appeared in the first edition further experimental work has allowed more detailed guidance.

## 1 Scope

- 1.1 This Guide describes thermal analysis measurements relevant to the processing and performance of composites and adhesives. The techniques covered in this Guide are differential scanning calorimetry (DSC), temperature modulated differential scanning calorimetry (TMDSC), dynamic mechanical analysis (DMA), dielectric analysis (DEA) and deflection temperature under load (DTUL).
- 1.2 This Guide specifically relates to the measurement of glass transition temperature ( $T_g$ ) for composites and adhesives.
- 1.3 This Guide provides guidance for selection of the most suitable technique as well as a procedure for the technique. The relationship between these techniques, which are often regarded as equivalent, is clarified. A discussion of the procedures recommended in this Guide is made alongside guidance on the uncertainty that can be expected from each technique.
- 1.4 This Guide is primarily intended for study of composites and adhesives in the temperature range 20 °C (ambient) to 250 °C. However, the procedures may be applied to other materials and temperature ranges, although the precision of the experiments may vary.
- 1.5 The DMA procedure presented here has been produced as an ISO Committee Draft, ISO CD 6721-11, since there is no existing ISO standard for the determination of glass transition temperature by DMA.

## 2 Selection of Thermal Analysis Techniques

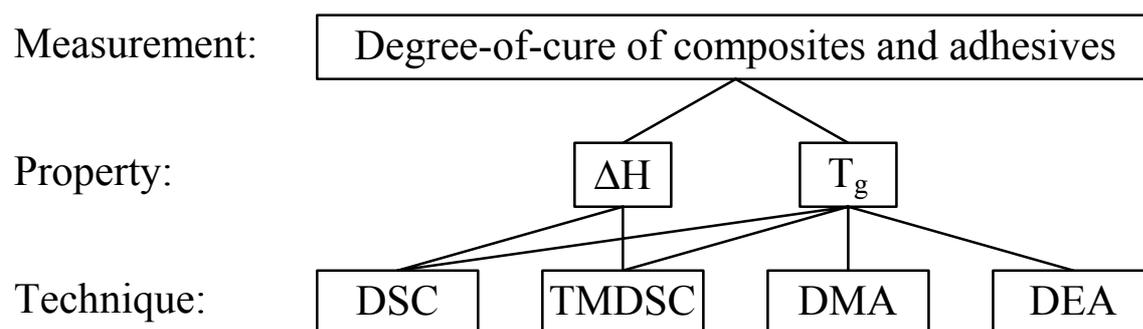
### 2.1 Introduction

Composite materials and adhesives are increasingly being used in demanding applications that require a knowledge of both short-term and long-term service performance. Performance is dependent on the quality of starting materials and the correct processing conditions. Confirmation of correct processing is particularly important for these materials as it is typically undertaken by the end-user rather than the material supplier.

In this section the selection of techniques to solve generic measurement problems is considered. Firstly, measurement of degree-of-cure is considered. This provides information on how far the curing reaction of the composite resin or adhesive has proceeded. Secondly, the measurement of service temperature is discussed.

### 2.2 Guidance for Measurement of Degree-of-Cure

There are a range of thermal analysis techniques that can be used to measure the degree-of-cure of composites or adhesives. The measurement of degree-of-cure by thermal analysis techniques can be achieved by the measurement of two properties; the glass transition temperature ( $T_g$ ) and residual cure, which is indicated by  $\Delta H$ , a change of enthalpy. The use of thermal analysis techniques to measure these properties is summarised in Figure 2.1.



**Figure 2.1.** Properties and techniques for measurement of degree-of-cure.

The measurement of  $\Delta H$  provides a more direct measurement of degree-of-cure since the residual cure of the material is assessed. The glass transition temperature provides an indirect measurement of cure, since the  $T_g$  increases with increasing degree-of-cure, although this relationship is not linear.

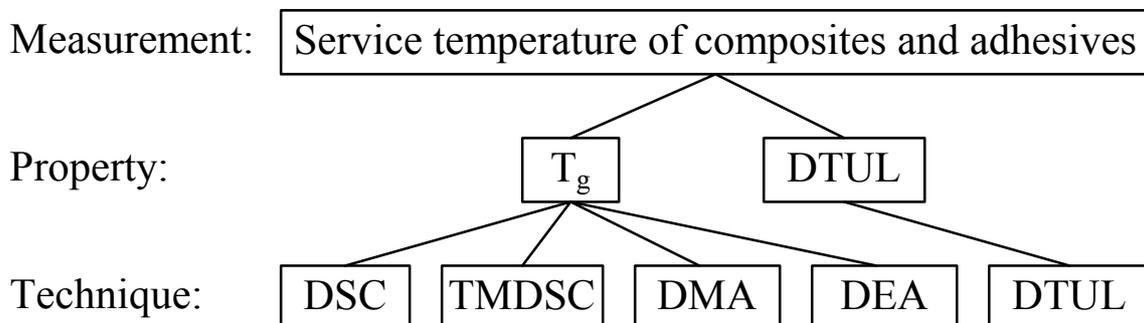
Glass transition temperature can only provide comparative values for the degree-of-cure. This is because the sample is heated during the measurement, which can activate any residual cure in the material. It is not possible to avoid this as it is inherent to the techniques, however it is advantageous to use higher heating rates, since the reduced time above ambient temperature means that there will be less effect on the degree-of-cure of the material. However, uncertainties in  $T_g$  measurement are greater at higher heating rates.

**Table 2.1.** Recommendations for measurement of degree-of-cure.

DSC	<ul style="list-style-type: none"> <li>• Most accessible technique for measurement of degree-of-cure.</li> <li>• Provides good quality information where the reaction is reasonably simple or well understood.</li> </ul>
TMDSC	<ul style="list-style-type: none"> <li>• A more challenging technique to use and interpret effectively.</li> <li>• Can be useful for complex or poorly understood reactions.</li> </ul>
DMA	<ul style="list-style-type: none"> <li>• Widely used technique for measuring <math>T_g</math> to infer degree-of-cure.</li> <li>• Measurement based on mechanical properties, which can be reassuring for some applications.</li> </ul>
DEA	<ul style="list-style-type: none"> <li>• Can be used in a similar way to DMA, but is not widely available and the measurements can be difficult to make.</li> </ul>

### 2.3 Guidance for Measurement of Service Temperature

The maximum service temperature of composite materials have traditionally been assessed by the determination of deflection temperature under load (DTUL). However, thermal analysis techniques are increasingly used for quality control and material selection for composites and adhesives. The use of these techniques for the measurement of service temperature is summarised in Figure 2.2.



**Figure 2.2.** Properties and techniques for measurement of service temperature.

Guidelines for the determination of service temperature can be based on either DTUL or  $T_g$ . DTUL has the advantage that it is a well-established technique and is often preferred by industry users, as they already possess dedicated equipment and perhaps historical data for the technique. However, DTUL is a single-point measurement that does not indicate a fundamental property of the material. For this reason measurement of  $T_g$  can be preferred as it is a material property that can be determined by a number of techniques, although not always with agreement between techniques.

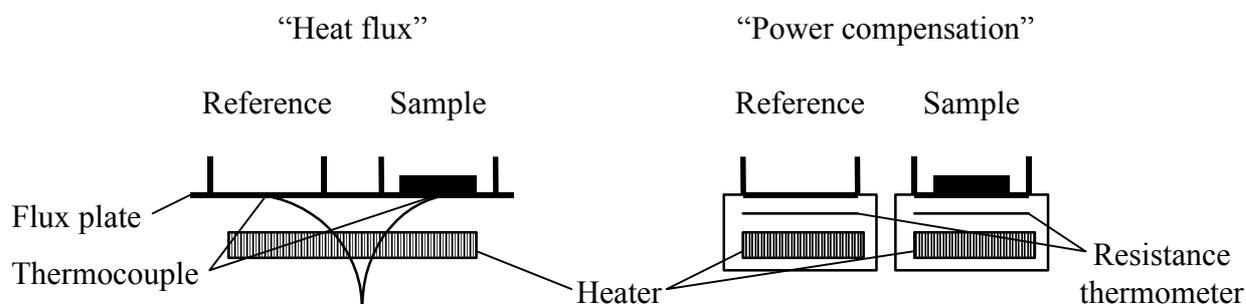
**Table 2.2.** Recommendations for measurement of service temperature.

DSC	<ul style="list-style-type: none"> <li>• Widely used for routine determination of <math>T_g</math> (approximate <math>T_g</math> is known).</li> <li>• Recommended for inter-laboratory comparisons.</li> </ul>
TMDSC	<ul style="list-style-type: none"> <li>• Can be used as an alternative to DSC where reactions obscure <math>T_g</math>.</li> </ul>
DMA	<ul style="list-style-type: none"> <li>• Useful when <math>T_g</math> is unknown or <math>T_g</math> is not detectable using DSC.</li> <li>• <b>Not</b> currently recommended for inter-laboratory comparisons.</li> </ul>
DEA	<ul style="list-style-type: none"> <li>• Can be an alternative to DMA for particular measurements.</li> </ul>
DTUL	<ul style="list-style-type: none"> <li>• Recommended for quality assurance for well-established materials.</li> </ul>

### 3 Differential Scanning Calorimetry (DSC)

#### 3.1 Description of Technique

DSC is a technique in which the difference between the heat flux into a test specimen and a reference specimen is measured as a function of temperature and/or time while the specimens are subjected to a controlled temperature programme. There are two types of DSC instruments currently used; “heat flux” and “power compensation”. A schematic of each type of equipment is shown in Figure 3.1. Although they are fundamentally different in design, the data produced are comparable. DSC is probably the most versatile thermal analysis technique and can be used to study properties such as melting and crystallisation behaviour, glass transition temperature, curing behaviour and specific heat capacity.



**Figure 3.1.** Schematic of “heat flux” and “power compensation” DSC equipment

#### 3.2 Measurement Issues

##### 3.2.1 Instrument and Calibration

Calibration procedures and standard materials are well developed for DSC and appear to be adequate. In general, the differences between instruments from various manufacturers are minor. ISO 11357, Part 1 contains requirements for thermal stability, heating rates, and signal to noise ratio. Most modern instruments should be capable of meeting these requirements and, in practice, any decrease in these qualities will be evident in the quality of data produced. Manufacturer’s procedures are recommended for calibration of an instrument. These are sufficient and also most specific, so reduce the possibility for ambiguity. For temperature calibration, at least two melting point standards should be used and they should be spaced throughout the temperature range required.

### 3.2.2 Specimen

Typical specimen masses used for DSC are in the range 5 to 20 mg. Smaller masses will give sharper peaks, but less response. For “pure” materials a specimen mass of 5 to 10 mg is acceptable. However, for materials containing inert material (such as fibres or fillers), the transition may not be detected. For this reason it is suggested that the specimen mass is increased so there is 5 to 10 mg of active material in the specimen. This is relevant for composite materials or adhesives containing fillers.

The versatility of DSC means that there is wide variety of materials and forms that may be analysed. This variety creates difficulties in prescribing a standard procedure for specimen preparation without restricting the applicability of the technique. Instead, there are a number of basic requirements that any specimen should fulfil:

- good thermal contact between the specimen and the pan; this is best achieved by having a single piece of specimen with a flat surface in contact with the base of the pan
- the specimen should be representative of the material; there are two aspects to this, firstly, that the specimen composition is representative of the material. For materials that exhibit variation, which is probably true of all composites and adhesives, the number of specimens tested should reflect this. Secondly, the specimen should be unchanged, as far as possible, by the specimen preparation. This is the more challenging aspect since this is dependent on the details of the specimen and the preparation method, so it is not possible to provide general recommendations on techniques for specimen preparation.

The use of powdered specimens is not recommended as they will fail to meet either of the requirements above. There is unlikely to be good thermal contact between the pan and the specimen or within the specimen. The thermal properties of a finely divided specimen will be different to a single piece due to both the higher surface area and the preparation required for such a specimen.

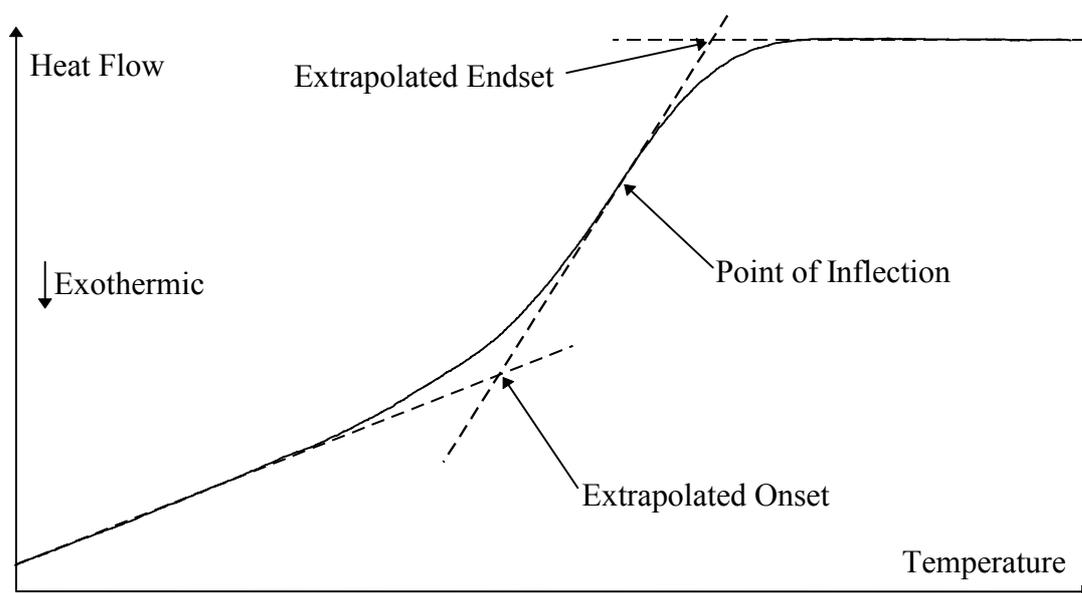
### 3.2.3 Procedure for $T_g$ Determination

Heating rates of 10 °C/minute or 20 °C/minute are typically used for  $T_g$  determination. The use of a higher heating rate increases the sensitivity to the glass transition. The reported  $T_g$  is generally independent of heating rate, however this is not the case for the first order transitions. A higher heating rate will broaden such transitions (e.g. curing or melting) which will reduce the accuracy of analysis. The recommended heating rate has been chosen as 10 °C/minute as it is most suitable for a versatile procedure for detecting  $T_g$  and any first order reactions.

### 3.2.4 Analysis of Results

The glass transition can be poorly defined in this technique, so, the glass transition may not be observed or an incorrect transition may be analysed as the glass transition. To avoid the second case an approximate temperature for the glass transition should be known before the heat flow trace is analysed (for instance, from manufacturer's data or DMA results).

The point of inflection of the change in heat flow is recommended as the analysis point since the definition of this point is unambiguous. Other midpoints (such as the half-height and half-width) and extrapolated points (such as onset and endset) are sensitive to the positions of the tangents before and after the transition, which are determined by the operator. Analysis points are illustrated in Figure 3.2.



**Figure 3.2.** Illustration of analysis points from a DSC trace. (Data presentation according to addendum to ISO 11357-1.)

## 3.3 Uncertainty for Technique

### 3.3.1 Definitions

#### *Repeatability (r) at the 95 % confidence limit*

The difference between two single results found on identical material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability value  $r$  on average not more than once in 20 cases in the normal and correct operation of the method.

**Reproducibility (R) at the 95 % confidence limit**

Single results on identical test material reported by two laboratories will differ by more than the reproducibility value *R* on average not more than once in twenty cases in the normal and correct operation of the method.

(The repeatability and reproducibility values have been calculated according to ISO 5725.)

**3.3.2 Precision Data for DSC**

The precision data for DSC are presented in Table 3.1, these data allow a comparison of the same material with and without glass fibres. It can be seen that the average  $T_g$  from DSC for the polyester resin and composite is similar. However, the reproducibility limit is much greater for the composite than the resin.

**Table 3.1.** Precision data for DSC.

	Number of sites	General Mean (°C)	Repeatability Limit (°C)	Reproducibility Limit (°C)
Unreinforced polyester	8	92.6	3.9	6.1
Glass fibre-polyester	7	92.8	3.7	11.0
Carbon fibre-epoxy	8	137.8	5.2	15.6
Epoxy adhesive	5	55.6	2.9	12.9

The epoxy adhesive material presents an additional problem because the material was not fully cured. This results in a large exotherm in the DSC trace, which in some cases overlaps the glass transition, so it cannot be analysed. Consequently, two sites that tested the epoxy adhesive material were not able to report results. Although, as shown in Table 3.1, the repeatability is good for sites that were able to report a glass transition temperature.

**3.3.3 Precision Statement for DSC**

For materials with a clear transition, such as unfilled resins, a repeatability limit of 4 °C and a reproducibility limit of 7 °C can be expected. For materials with a less distinct transition, such as highly filled composite materials, a repeatability limit of 5 °C and a reproducibility limit of 16 °C can be expected.

## **3.4 Standards**

### **3.4.1 Published Standards**

A list of relevant standards is given in the Bibliography. Preference is given in this Guide to ISO standards, that also form the framework for the database standard ISO 10350-2. All parts of ISO 11357 are listed. ISO 11357 consists of eight parts; part 1 covers the general principles of the technique, while the remaining parts each cover a specific measurement. There are also relevant standards from ASTM and CEN covering the determination of glass transition temperature.

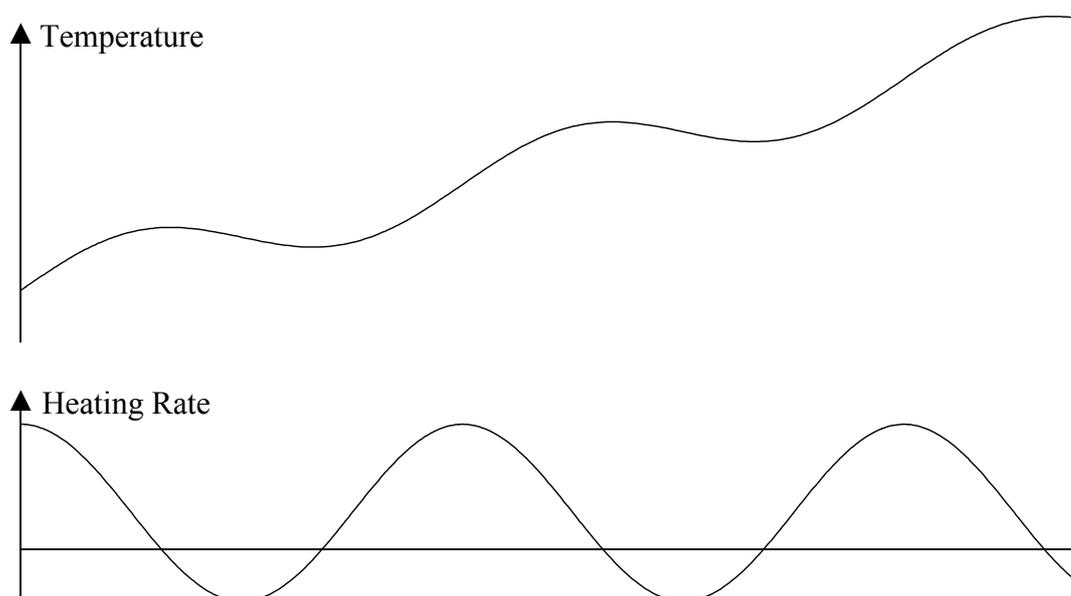
### **3.4.2 Revision of ISO 11357, Part 1**

A revised version of ISO 11357, Part 1 has previously been proposed. This revision was not accepted, but an addendum to the current standard containing the proposed, and additional, text was agreed. NPL is the project leader for this addendum. Particular aspects covered are a new format for the presentation of data (see Figure 3.2), a high precision calibration procedure (probably not required for work on composites and adhesives) and additional information on the interaction between calibrants and specimen pans. However, there was concern that the change in data presentation should not occur through an amendment, but needed full consideration, including consultation with IUPAC. It has now been agreed that with the 5 year review of ISO 11357, Part 1 about to be initiated in early 2003, that the addendum will be considered at the same time.

## 4 Temperature Modulated Differential Scanning Calorimetry (TMDSC)

### 4.1 Description of Technique

A modification of DSC that has become widely available in recent years is temperature modulated DSC, which is also known by a number of trade names. In this technique a modulation is superimposed on a linear heating rate. An example of a temperature profile and heating rate for a TMDSC test is shown in Figure 4.1. The resulting complex heat flow can be resolved into components, which may allow further information to be obtained from a single trace. There is currently some debate over the validity of data obtained from TMDSC and the significance of the components of the signals.



**Figure 4.1.** Example of a temperature programme and heating rate for a TMDSC test.

### 4.2 Measurement Issues

#### 4.2.1 Instrument and Calibration

Generally the equipment is the same as for DSC, except that the instrument should be capable of applying a periodically varying temperature cycle in combination with an underlying heating ramp. For the procedure recommended in this Guide, a maximum heating rate of 10 °C/min and a maximum cooling rate of 5 °C/min is required.

#### 4.2.2 Specimen

The test specimen is essentially the same as a standard DSC sample. For TMDSC it is particularly important that there is good contact between the sample and the pan. For this reason crimped aluminium pans are recommended (but not hermetically sealed) and the height of the sample should not be any greater than necessary.

#### 4.2.3 Procedure

Some of the parameters for a TMDSC procedure are dependent on the properties of the sample. It is recommended that a DSC test be performed on a material before TMDSC tests are attempted. This is to establish if TMDSC testing will be beneficial and also inform the selection of parameters for the TMDSC test.

There are some types of tests for which a “heat only” programme is recommended, that is a modulation in which the heating rate applied to the sample does not become negative, i.e. cooling. For instance, tests that involve melting reactions, however, this is generally not necessary for composites and adhesives testing.

The major difficulty for setting parameters for TMDSC testing is that there are a number of interrelated variables. Typical parameters are a period of 50 to 100 seconds, an amplitude of  $\pm 1$  or  $2$  °C and an underlying heating rate of 1 to 4 °C/minute. It is suggested that these parameters should be selected so that there are a minimum of six modulations across the transition of interest. In the recommended procedure presented in this Guide, the period and oscillation have been set and the underlying heating rate is modified to achieve a suitable number of modulations across the glass transition.

A further complication is that there are a number of different approaches to applying the modulation. Various shapes of waveforms have been proposed and there does not appear to be a consensus on this subject.

#### 4.2.4 Analysis of Results

The suggested analysis point is the point of inflection of the step increase in the heat capacity plotted on a linear scale. This point has been selected as it is analogous to the analysis point selected for DSC. A potential benefit of TMDSC is that there should be less influence of other reactions on the material. For TMDSC it is also possible to detect the glass transition as a peak in the phase angle, which has similarities with  $\tan \delta$  for techniques, such as DMA and DEA.

## 4.3 Uncertainty for Technique

### 4.3.1 Definitions

#### *Repeatability (r) at the 95 % confidence limit*

The difference between two single results found on identical material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability value  $r$  on average not more than once in 20 cases in the normal and correct operation of the method.

#### *Reproducibility (R) at the 95 % confidence limit*

Single results on identical test material reported by two laboratories will differ by more than the reproducibility value  $R$  on average not more than once in twenty cases in the normal and correct operation of the method.

(The repeatability and reproducibility values have been calculated according to ISO 5725.)

### 4.3.2 Precision Data for TMDSC

A study to establish the precision of TMDSC tests has been carried out, this involved six sites, each testing a polymethylmethacrylate (PMMA) material and a carbon-fibre/epoxy composite. Each site tested three samples of each material according to the procedure in Appendix 2. The resulting precision data are presented in Table 4.1.

**Table 4.1.** Precision data for TMDSC.

	Number of sites	General Mean (°C)	Repeatability Limit (°C)	Reproducibility Limit (°C)
PMMA	6	117.6	2.9	4.9
Carbon fibre-epoxy	6	151.0	3.4	24.1

### 4.3.3 Precision Statement for TMDSC

The repeatability for TMDSC measurements is around 3 °C, which is comparable to that for DSC. For the two materials tested there is a wide variation in the reproducibility. An unfilled thermoplastic gave a reproducibility of 5 °C, while a filled thermoset gave a reproducibility of over 24 °C. At this time it is not known to what degree this increase is due to the weaker response of the thermoset, the presence of fibres or residual cure in the material.

## **4.4 Standards**

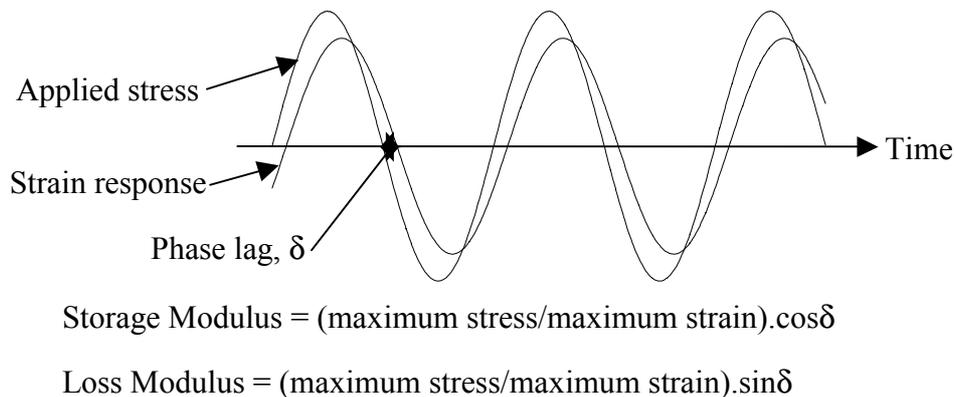
There are currently no directly relevant standards for the measurement of glass transition temperature by TMDSC. At the time of publication there is an ASTM standard for the measurement of thermal conductivity and diffusivity (ASTM E 1952: 1998).

ISO TC16 / SC5 / WG8 has started to produce a new series of test methods for measurement of thermal conductivity. Seven methods have been identified including TMDSC. A part 1 document for TMDSC is proposed, equivalent to the part 1 for DSC (ISO 11357, Part 1) and a part 2 document that presents the method for thermal conductivity. Both these documents are the responsibility of NPL and the UK.

## 5 Dynamic Mechanical Analysis (DMA)

### 5.1 Description of Technique

DMA applies a sinusoidal load to a specimen and the resulting deformation is measured during a controlled temperature programme. The response of the specimen is used to calculate the storage (elastic) modulus and loss (viscous) modulus. Frequently, the ratio of loss and storage moduli,  $\tan \delta$ , is reported. These terms are illustrated in Figure 5.1. The test can be performed in a variety of deformation modes (e.g. flexure, torsion, shear, compression, tension), and so can be applied to a variety of material forms. The most common application of DMA is determination of the glass transition temperature, which is sensitive to many aspects of processing. This technique is also known as dynamic mechanical thermal analysis (DMTA). DMA is far more sensitive to the glass transition than DSC.



**Figure 5.1.** Illustration of the principle of dynamic mechanical analysis.

## 5.2 Measurement Issues

### 5.2.1 Instrument and Calibration

There are two types of calibration that can be applied to DMA equipment; mechanical and temperature. Temperature calibration is a controversial area, which is covered in detail in Section 5.2.2.

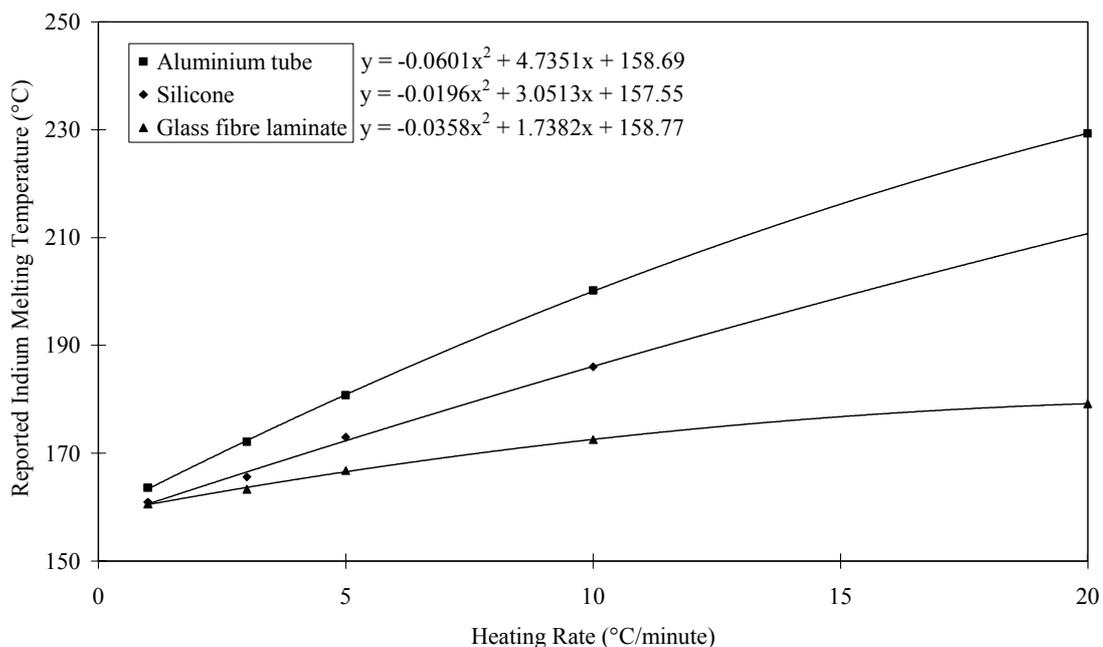
Mechanical calibration will vary from instrument to instrument. The fundamental aim of the calibration will depend on the design of the instrument, while the detailed procedure will depend on the testing mode and clamps being used. Generally, the procedures recommended by manufacturers are satisfactory for a particular instrument. In addition, the determination

of glass transition temperature does not depend on the absolute mechanical properties of the material, but the change in properties.

### 5.2.2 Temperature Correction

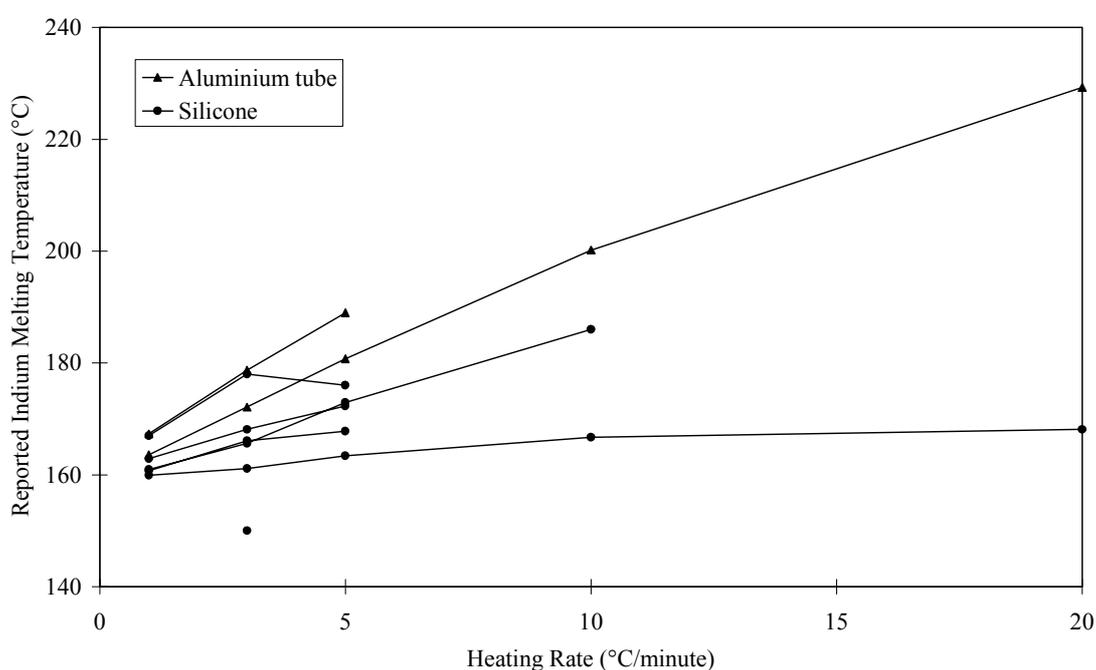
The temperature reported by DMA equipment has long been recognised as a source of error. A number of approaches are currently used to calibrate the equipment with respect to temperature. Manufacturers often recommend methods for calibrating their equipment and other methods have been developed by individual sites. These calibration methods generally involve monitoring the melting transition of a material (for instance indium or water) or the glass transition temperature of a standard polymer.

Three types of calibration specimen have been developed at NPL. All the specimens were based on the indium melt, because this temperature is similar to the temperature of transitions that are usually studied. These fixtures consisted of indium encapsulated in either aluminium tubing, silicone rubber or a composite material. Results of tests at NPL on the three types of specimen are shown in Figure 5.2 together with a second order polynomial curve fitted to the results. It is clear that the material used in the specimen has a major influence on the reported temperature of the melt. An interesting feature is that all the curves extrapolate to a narrow temperature range at zero heating rate and this is close to the expected melting temperature of indium at 156.6 °C. This suggests that the differences in the reported melting temperature of Indium are entirely due to the heating rate. There is no evidence that either kinetic effects or contamination has affected the melting temperature of the Indium.



**Figure 5.2.** Graph showing the effect of heating rate on the reported indium melting temperature for three types of DMA temperature calibration fixtures tested at NPL.

The silicone and aluminium fixtures were supplied for inter-laboratory testing. Six sites reported results for the silicone specimen and two sites reported results for the aluminium specimen. A number of sites reported that they were not able to observe the effect of the indium melt with the aluminium specimen. The results reported for these fixtures are shown in Figure 5.3. Again the results extrapolate to the expected melting point of indium at zero heating rate. It is interesting that a similar trend is observed for the different sites, which include instruments from several manufacturers. The only exception is the single point at 150 °C obtained at a heating rate of 3 °C/minute. It is not possible to establish if this is due to a fundamental difference or erroneous calibration of the temperature sensor in that instrument because there is only a single point.

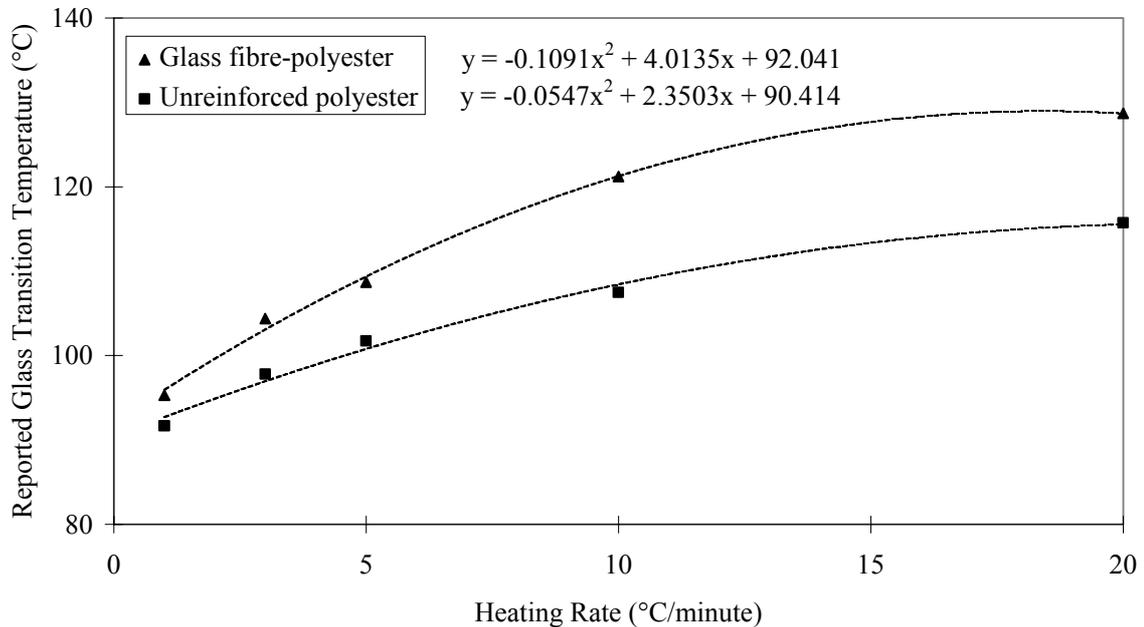


**Figure 5.3.** Graph showing the results of the round-robin testing for the two types of DMA temperature calibration fixtures supplied.

The use of these fixtures to correct temperature from DMA was investigated. It was found that it was not possible to improve the reproducibility by the use of such fixtures. (More details of this investigation are presented in the first edition of this Guide.)

There is a further problem with fixed point calibration. As shown in Figure 5.4, different materials are affected by the heating rate to different extents. Although both materials are based on the same resin, the temperatures reported are significantly different. A fixed point correction would be identical irrespective of the material being tested, and therefore, is not satisfactory. So, it is reasonable to state that the relationship between the temperature measured by the thermocouple and the specimen temperature is complex and cannot be determined with fixed point corrections. It would appear that it is necessary to perform an

extended set of measurements to establish the relationship between reported and specimen temperature, or to monitor the specimen temperature directly.



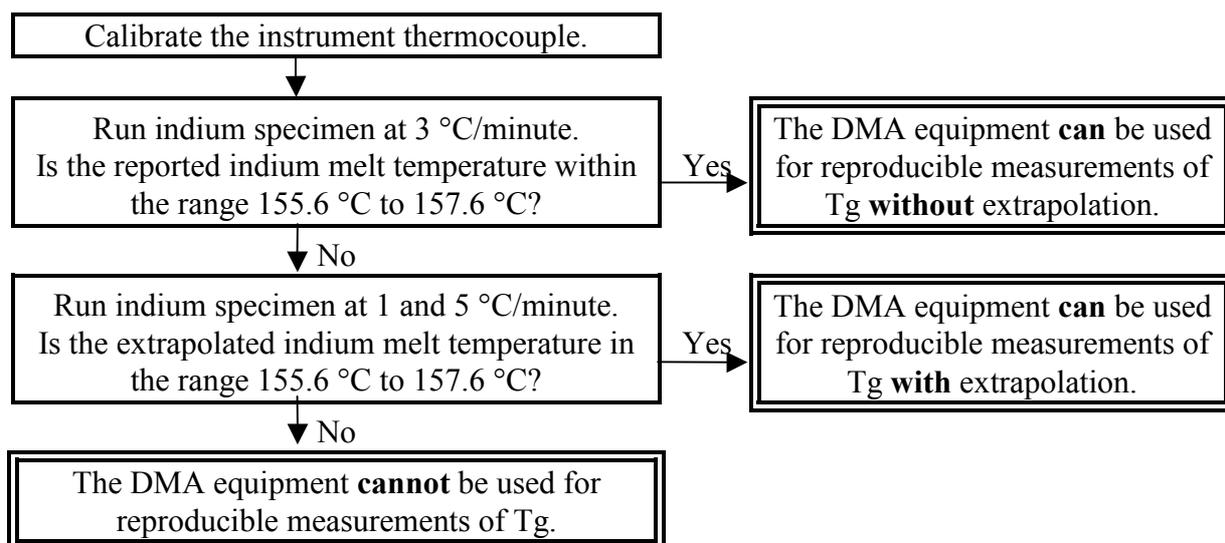
**Figure 5.4.** Graph showing reported glass transition temperatures for a resin and a composite at heating rates of 1, 3, 5, 10 and 20 °C/minute tested at NPL.

### 5.2.3 Extrapolated Temperature Correction

From these findings a procedure has been proposed for the reproducible determination of temperature from DMA equipment. The procedure is described in the flowchart and notes in Figure 5.5.

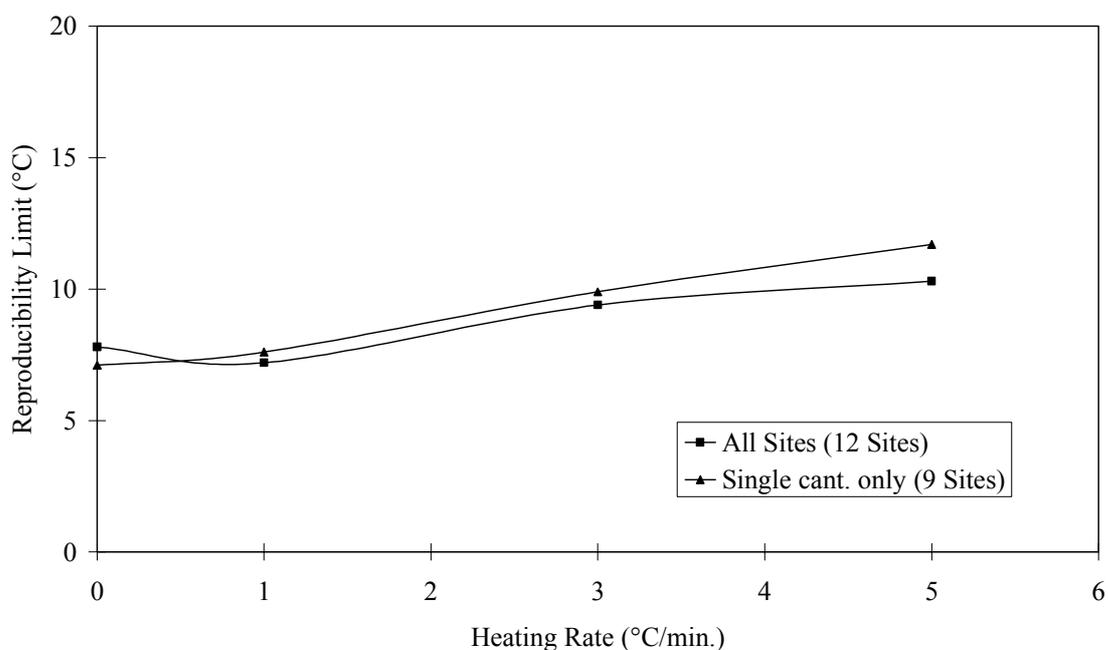
An inter-laboratory testing exercise has been conducted to investigate if this procedure is effective in improving the reproducibility for DMA. Two materials, a polymethylmethacrylate and a carbon-fibre/epoxy composite were tested. Sites were supplied with samples of each material and requested to measure the  $T_g$  by DMA at heating rates of 1, 3 and 5 °C/minute. One set of tests for each material was requested as the aim of this exercise was to investigate the reproducibility, rather than the repeatability.

Inspection of the results revealed that some of the results did not exhibit a monotonic trend in the change of  $T_g$  with heating rate. However, all the monotonic results exhibited an increase in  $T_g$  with increasing heating rate. It was found that all the results that fitted this monotonic trend were measurements which had been made using the single cantilever mode with a span of 12 to 18 mm.



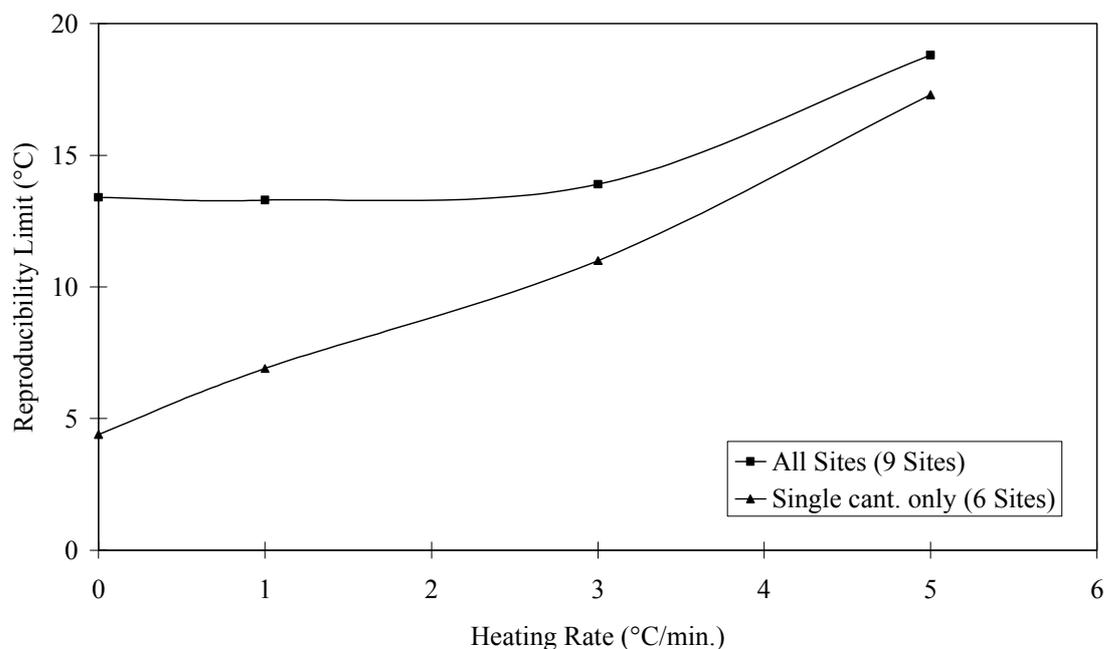
**Figure 5.5.** Flowchart and notes describing the proposed procedure for reproducible temperature determination by DMA equipment

To calculate the  $T_g$ , a linear regression fit was made to the reported  $T_g$  values at 1, 3 and 5 °C/minute. This fit was then extrapolated and the value of the fit at zero heating rate was calculated. This process was repeated for each site giving a single value of  $T_g$  for each site and the reproducibility was calculated based on these values. The reproducibility limits for the PMMA material at each of the three tested heating rates and the extrapolated value is shown in Figure 5.6.



**Figure 5.6.** Graph showing the reproducibility limits for  $T_g$  measurement on PMMA at 1, 3 and 5 °C/minute and extrapolated to zero heating rate.

It can be seen from Figure 5.6 that the reproducibility decreases slightly across the range of heating rates studied. There is some benefit to the use of the extrapolated method for this material, but it is unlikely to justify the extra testing required. It can also be seen that the exclusion of the three sites (which were not single cantilever with a span of 12 to 18 mm) had very little effect on the results for this material.



**Figure 5.7.** Graph showing the reproducibility limits for  $T_g$  measurement on carbon-fibre/epoxy composite material at 1, 3 and 5 °C/minute and extrapolated to zero heating rate.

The reproducibility limits for the carbon-fibre/epoxy material at the three heating rates and extrapolated to zero heating rate are shown in Figure 5.7. It can be seen that the heating rate has a dramatic effect on the reproducibility in this case, particularly for the results from the six single cantilever test sites. In this case the extra testing involved is certainly justified, although it would be useful to gain a better understanding of the reasons for this improvement.

#### 5.2.4 Specimen

As with other aspects of DMA testing, the specimen size is dependent on the particular instrument and testing mode being used. For composites and adhesives, a specimen thickness of 2 mm is recommended. For many instruments a specimen that is 40 mm by 10 mm by 2 mm is suitable. An additional consideration for composite materials is the orientation of fibres within the sample. This has not been investigated in detail, but there is evidence to suggest that preferred fibre direction should be longitudinal within the sample, as this will give more consistent results.

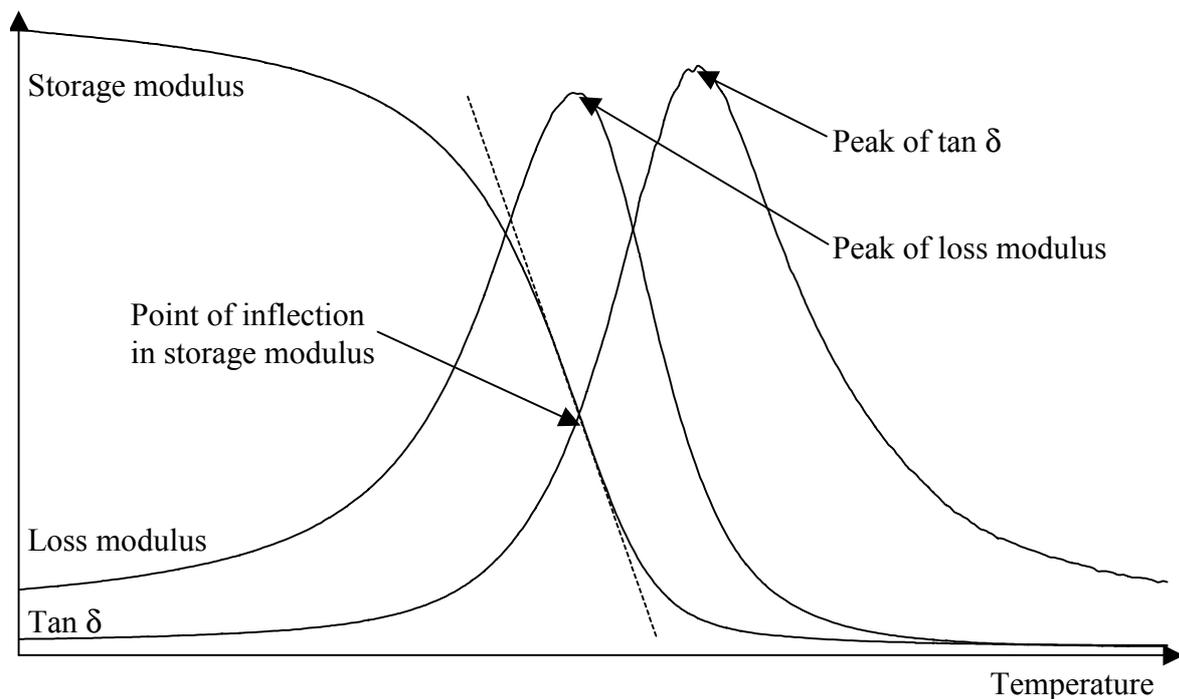
As with preparation of DSC specimens, it is not possible to make general recommendations for the preparation of DMA specimens. Again, the main condition is that the preparation method does not affect the thermal properties of the material.

### 5.2.5 Procedure for $T_g$ Determination

The selection of heating rate often has a significant influence on the results from DMA, as discussed in Section 5.2.2. Generally, procedures recommend 2, 3 or 5 °C/minute heating rate. A lower heating rate reduces temperature variations within the specimen, while a higher heating rate allows quicker testing of specimens. A heating rate of 3 °C/minute and a frequency of 1 Hz is recommended for routine testing.

It is difficult to make general recommendations for the applied strain on the specimen. The major requirement is that the strain should be in the linear elastic region for the material. Ideally, this should be determined for the material by determining the modulus at a range of strains and determining the elastic limit from the results. In practice, a strain of less than 0.5 % should be suitable for most materials.

### 5.2.6 Analysis of Results



**Figure 5.8.** Illustration of the recommended analysis points from a DMA trace.

A variety of analysis points are used, the most common are the extrapolated onset of the decrease in storage modulus, point of inflection of the decrease in storage modulus, peak of loss modulus and peak of tan delta. Analysis points selected from a curve should be points

that are rigorously defined. In practice this means that the use of peaks and points of inflections is acceptable, but the use of midpoints, onsets and extrapolated onsets is not acceptable. The peak of tan delta has the advantage of being easily identifiable in most traces. However, this point is usually at a temperature significantly higher than either the change in modulus from DMA or the  $T_g$  from DSC. The point of inflection of the decrease in storage modulus has been selected since this point is most meaningful in terms of material properties. The peak of  $E''$  (loss modulus) may be used when there is difficulty in obtaining a value for the point of inflection as there is usually little difference between the two values. The recommended analysis points are illustrated in Figure 5.8.

## 5.3 Uncertainty for Technique

### 5.3.1 Definitions

#### *Repeatability (r) at the 95 % confidence limit*

The difference between two single results found on identical material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability value  $r$  on average not more than once in 20 cases in the normal and correct operation of the method.

#### *Reproducibility (R) at the 95 % confidence limit*

Single results on identical test material reported by two laboratories will differ by more than the reproducibility value  $R$  on average not more than once in twenty cases in the normal and correct operation of the method.

(The repeatability and reproducibility values have been calculated according to ISO 5725.)

### 5.3.2 Precision Data for DMA

The precision of DMA measurements has been investigated with an inter-laboratory testing exercise on four materials. The materials were an unreinforced polyester, glass-fibre reinforced polyester, carbon-fibre reinforced epoxy and an epoxy adhesive. These materials were tested according to the procedure presented in Appendix 3, which used a heating rate of 3 °C/minute. The precision data from this exercise is presented in Table 5.1.

Since the reproducibility limits from these tests were high, further inter-laboratory testing was performed using a method to extrapolate the results to zero heating rate. (This is described in more detail in Section 5.2.3.) The data from this exercise are presented in Table 5.2.

**Table 5.1.** Precision data for DMA.

	Number of sites	General Mean (°C)	Repeatability Limit (°C)	Reproducibility Limit (°C)
Unreinforced polyester	7	93.35	2.92	25.69
Glass fibre-polyester	7	98.62	5.94	24.52
Carbon fibre-epoxy	6	157.95	4.93	15.85
Epoxy adhesive	5	70.38	5.08	17.61

**Table 5.2.** Precision data for extrapolated DMA.

	Number of sites	General Mean (°C)	Reproducibility Limit (°C)
PMMA	9	113.7	7.1
Carbon fibre-epoxy	6	143.7	4.4

### 5.3.3 Precision Statements for DMA

The repeatability can be as low as 3 °C for an unfilled resin and as high as 6 °C for a composite material. Reproducibility limits of 15 to 25 °C can be expected, which is generally accepted to be due to deficiencies in temperature measurement. However, it is possible to obtain much lower reproducibility limits, 4 to 7 °C, by extrapolating results to zero heating rate if the mode of testing is specified.

## 5.4 Standards

### 5.4.1 Published Standards

The ISO standard for DMA, ISO 6721, is composed of ten parts, which are listed in the Bibliography. The form of this standard is rather different to the ISO standard for DSC (ISO 11357). General principles of DMA are covered in Part 1, but the remaining parts cover individual modes of testing. This approach has advantages, but there is no guidance on property determination; a new standard has been proposed to rectify this omission (see Section 4.3.2, below). There are other standards, notably ASTM E 1640: 1994 and prEN 6032, that cover the determination of glass transition temperature by DMA.

### 5.4.2 ISO standard for temperature scanning measurements.

There is currently no ISO standard covering the determination of glass transition temperatures using DMA. An ISO committee draft “ISO 6721 - Part 11 Plastics - Determination of

dynamic mechanical analysis - Glass transition temperature” has been drafted by NPL. The standard is to be advanced to a draft international standard (DIS) during 2003.

### **5.4.3 ISO standard for temperature calibration**

An ISO New Work Item proposal for a procedure for temperature calibration of dynamic mechanical analysers was successful. However, the procedure, based on an ASTM E 1640: 1999, was not accepted. An alternative procedure is being developed to form part 12 of ISO 6721. This part will cover all the required calibrations; temperature, load and displacement. The draft will be prepared by NPL and include the approaches outlined in this Guide. As it is shown that temperature calibration difficulties give rise to the poor reproducibility of  $T_g$  measurements, it is important that part 12 is advanced before part 11 can be confirmed at DIS or FDIS level.

## 6 Dielectric Analysis (DEA)

### 6.1 Description of Technique

DEA measurements are made by the application of a sinusoidally varying voltage and the monitoring of resultant current, which exhibits a phase lag  $\delta$ , as illustrated in Figure 6.1. As should be clear from this figure, DEA can be regarded as analogous to DMA, but with dielectric, rather than mechanical, properties. The quantities usually determined by DEA are the relative permittivity and loss factor. There are a wide variety of electrodes available for DEA, ranging from parallel plate sample holders to interdigitated electrodes on a single substrate.

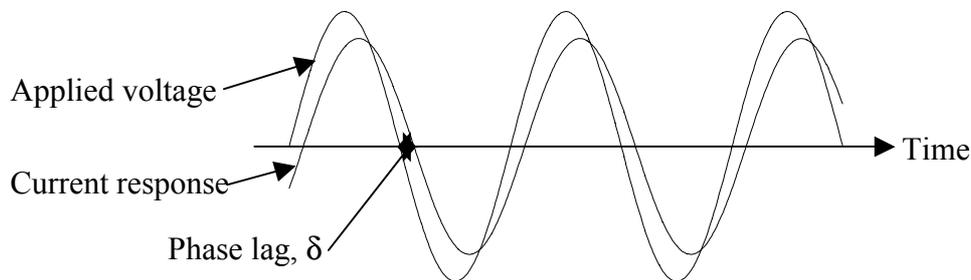


Figure 6.1. Illustration of the principle of dielectric analysis.

### 6.2 Measurement Issues

#### 6.2.1 Instrument and Calibration

The two calibrations required are temperature calibration of the sensor and calibration of the dielectric bridge. If the temperature sensor is in direct contact with the sample then it is only necessary to calibrate the sensor. If the sensor is not in direct contact with the sample, then temperature calibration of DEA equipment is covered in ASTM E 2038. It is recommended that this standard be used with caution as it is a fixed point calibration that may not be applicable to all systems. However, the method in the standard is certainly acceptable as a means of checking the accuracy of a system. The dielectric calibration will be specific to the system being used and manufacturer's recommendations should be followed.

#### 6.2.2 Specimen

The specific requirements for the specimen are mainly dependent on the sample form and type of electrode used. The general requirements are that the specimen covers the surface of the electrodes, that the thickness of the specimen is appropriate for the electrode and that there is good contact between the electrode and the specimen. In addition, it is important that the

sample has very low conductivity and there are no conductive components in contact with the electrodes.

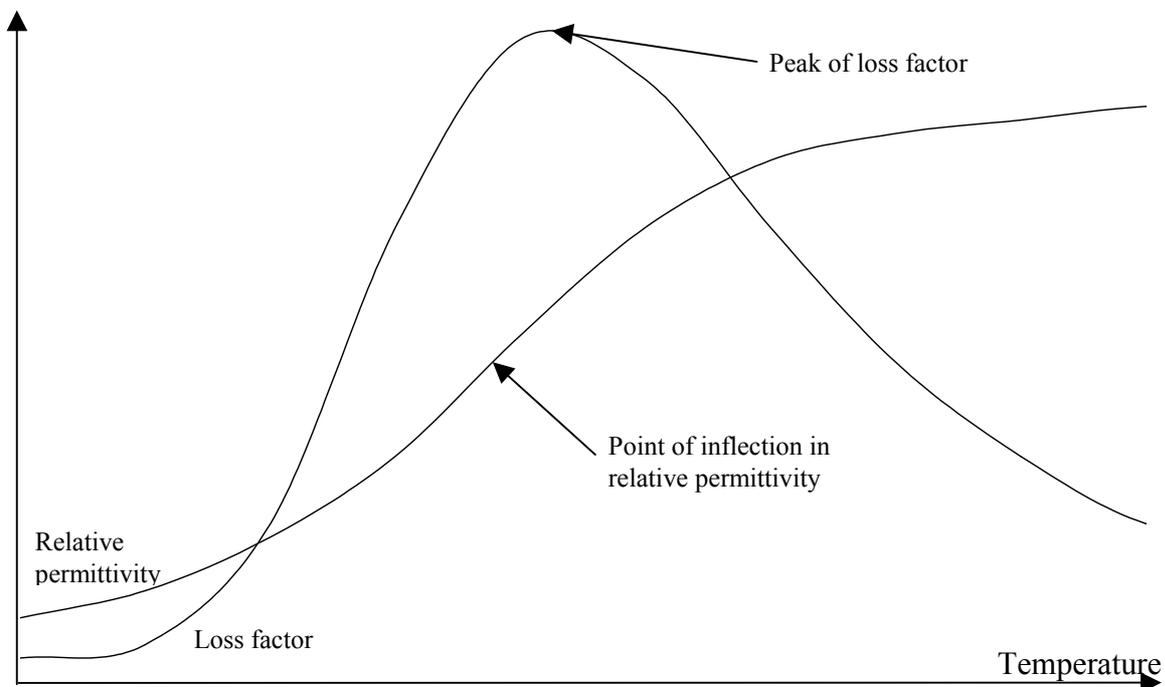
### 6.2.3 Procedure for $T_g$ determination

The comparison with DMA can also be made in terms of the procedure for  $T_g$  determination. The size of the furnace is comparable, so a similar range of heating rates is used for DEA. However, for DEA, since there are no moving parts during the test, it is possible to place the temperature sensor closer to, or in contact with, the specimen.

DEA offers a wide range of frequencies for testing, for example a typical analyser covers frequencies between 0.1 Hz and 100 kHz. This range of frequencies is excessive for measurements with temperature as the independent variable. A frequency of 1 kHz is a good choice for most dielectric analysers and performance is often best around this frequency. Alternatively, a frequency of 1 Hz can be selected to align the procedure with the DMA method. Ideally, measurements should be taken at both frequencies from the same run.

The choice of voltage is specific to the system used, the main criterion is that the voltage is sufficiently small that there is no permanent change to the specimen.

### 6.2.4 Analysis of Results



**Figure 6.2.** Illustration of the recommended analysis points from a DEA trace.

The choice of analysis points is illustrated in Figure 6.2. Again the similarity with DMA is clear. By analogy with other techniques the point of inflection of the step change in the increase in relative permittivity is recommended as the analysis point. The most commonly used alternative analysis point is peak in the loss factor.

## **6.3 Standards**

### **6.3.1 Published Standards**

There are a variety of standards from ASTM relating to the measurement of dielectric properties. The two most relevant are ASTM E 2038 - Standard test method for temperature calibration of dielectric analysers and ASTM E 2039 - Standard practice for determining and reporting dynamic dielectric properties. These provide reasonably complete guidance that can be applied to the measurement of glass transition temperature for composites and adhesives.

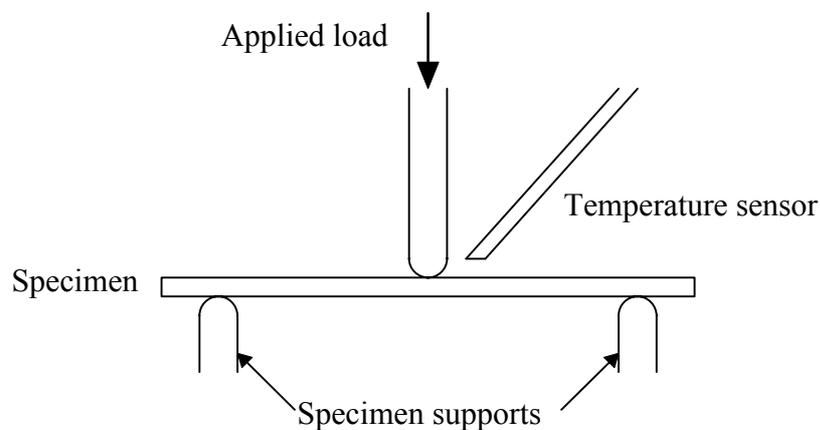
### **6.3.2 Standard for $T_g$ determination.**

There is currently no guidance specifically for the measurement of the glass transition temperature. A useful standard would bring together the aspects of the technique relevant to this measurement. However, it is difficult to see how such a standard would fit into the current range of standards.

## 7 Deflection Temperature Under Load (DTUL)

### 7.1 Description of Technique

DTUL is a less sophisticated, single point, technique for the evaluation of the effect of temperature on a material. A cantilever beam of material is supported within a temperature controlled environment and a fixed stress is applied. The specimen is then heated at a constant rate. The DTUL is the temperature at which the specimen further deforms by a distance equivalent to a specified strain (0.2 % for plastics, 0.1 % for composites). This temperature value used to be described as heat deflection temperature (HDT), and many users still prefer this terminology.



**Figure 7.1.** Schematic of equipment for determination of DTUL.

### 7.2 Measurement Issues

#### 7.2.1 Instrument and Calibration

The equipment for determining DTUL is relatively simple and consists of a loading apparatus, weights, heating equipment, a temperature sensor and a deflection measuring device. It is possible to confirm the accuracy of the weights and temperature sensor individually. The measurements must account for the thermal expansion of the loading apparatus and the weight of the probe must be included in the calculation of load applied to the specimen.

#### 7.2.2 Specimen

The specimen size required by ISO 75, Part 2 (for unreinforced materials) is 80 mm by 10 mm by 4 mm placed on supports with a span of 64 mm. For ISO 75, Part 3 (for composites) the specimen should be between 9.8 and 12.8 mm wide and the thickness should be between 2

and 7 mm. There is an additional requirement that the span should be 30 times the thickness, so the span of the specimen will be between 60 mm and 210 mm, and the specimen must be 10 mm longer than the span.

### **7.2.3 Procedure for DTUL Determination**

A heating rate of 2 °C/minute is required by ISO 75, Part 1 and this appears to be satisfactory. As with DMA, the temperature in DTUL is monitored by a remote sensor. It was seen in Section 5.2.2 that remote temperature measurement can introduce errors. For DTUL there should be less possibility of error because the frame is totally immersed in the heat transfer medium. So, at this time, remote temperature measurement is acceptable for DTUL.

The applied load for testing of unreinforced materials is determined by selecting a fixed stress of either 0.45 MPa, 1.8 MPa or 8 MPa (ISO 75, Part 2). The database standard, ISO 10350-2, requires that the material is tested at 1.8 MPa and one of the other two stresses. A lower load gives a higher DTUL, so three significantly different values can be determined by this standard. As 1.8 MPa is the most commonly used stress, it would be clearer if the DTUL is determined at only this fixed stress.

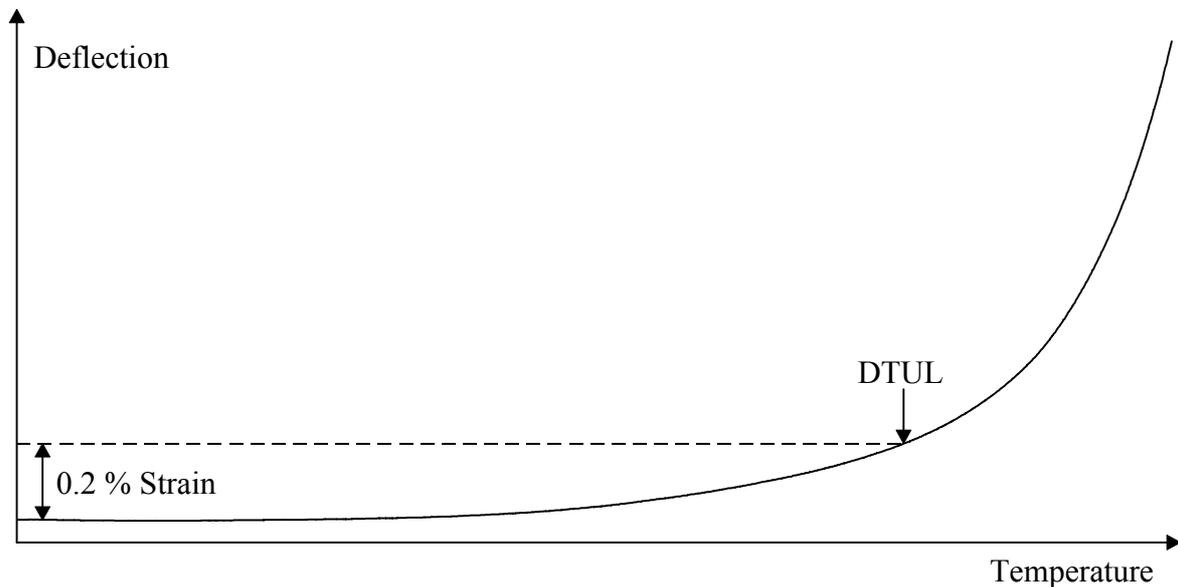
The selection of applied stress for testing of composites is rather different in approach. The current ISO standard, ISO 75, Part 3, requires that the applied stress is 10 % of the failure stress of the material. This is illogical as the deflection is not related to the strength, but the applied load is selected based on the strength of the material, which needs to be measured or known. The resulting strains are generally higher than those for unreinforced materials by ISO 75, Part 2, resulting in a lower DTUL for the composite material. In addition, a 0.1 % strain increase is used which further reduces the DTUL. Consequently, the DTUL for a composite is generally lower than that for a resin which is inconsistent, that is, the addition of carbon or glass fibres appears to reduce the temperature capability of the material.

An alternative approach has been developed at NPL for determining the applied stress for reinforced materials. The applied stress should be a function of the modulus of the material rather than the strength, since DTUL follows the change in modulus. The applied stress shall be one thousandth of the modulus of the material. This modification has been adopted by ISO during the current revision of the standard (see Section 7.3).

### **7.2.4 Analysis of Results**

The DTUL is typically reported as a single result, although a plot of deflection against temperature may be supplied as well. For unreinforced materials (ISO 75, Part 2), the DTUL is determined at a deflection of 0.2 % (illustrated in Figure 7.2), while for composite materials (ISO 75, Part 3) the DTUL is determined at a deflection of 0.1 %. It would improve the

correspondence between the tests for the unreinforced and reinforced materials for the increase in strain in Part 3 to be 0.2 %.



**Figure 7.2.** Typical deflection against temperature curve for DTUL determination.

## 7.3 Standards

### 7.3.1 Published Standards

The key standard for DTUL is ISO 75. As with DSC and DMA, Part 1 contains the general principles, while the remaining parts describe procedures for the determination of DTUL of classes of materials. Part 2 covers plastics and ebonite, while Part 3 covers high strength thermosetting laminates and long-fibre reinforced plastics.

### 7.3.2 Revision of ISO 75

A proposal in 1998 to redraft the current Parts 1, 2 and 3 in a single part 1 was not successful. Instead, the current parts 1 and 2 are being slightly amended and part 3 is to be modified to address the problems with DTUL for composite materials. The amended part 3, proposed by NPL, requires an applied stress of 0.1 % of the modulus of the material. The modulus of the material is not necessarily required since the load can be determined by loading the specimen to a deflection equivalent to 0.1 % strain using the equation in the existing standard. NPL also proposed, and had accepted, that the same strain (0.2 %) used in part 2, be adopted for part 3. The three revised parts of this standard, including the NPL proposal, are now in preparation for publication.

## 8 Demonstration of Techniques

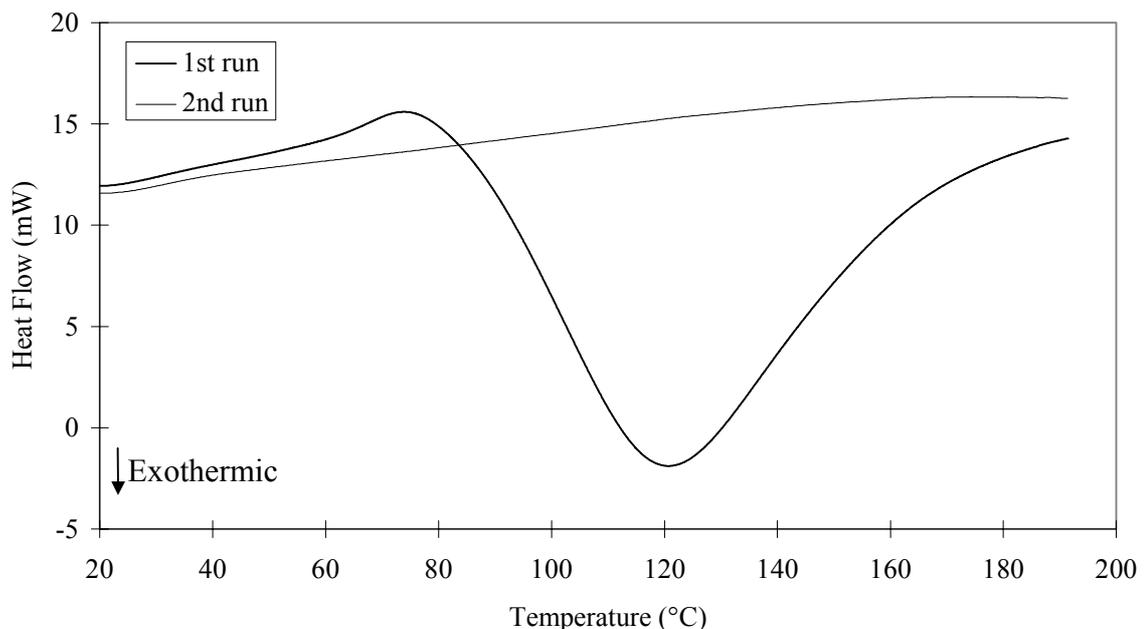
### 8.1 Introduction

This section presents examples of thermal analysis techniques applied to composites and adhesives. These demonstrations illustrate the expected change in properties. Thermal analysis techniques can be used in many other situations, which are not covered here.

### 8.2 Demonstration of Measurement of Degree-of-Cure

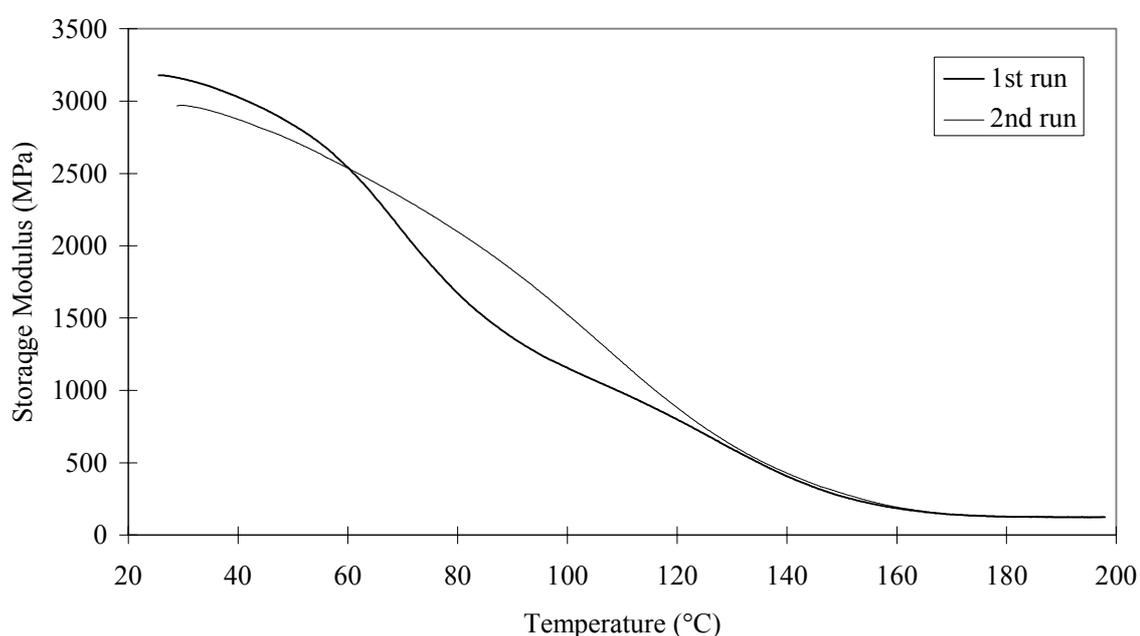
The materials considered in this Guide are all nominally fully cured. In practice, materials that appear to be cured can, in fact, be under-cured. The epoxy adhesive provided for the inter-laboratory testing is an example of such a material. Thermal analysis of this material presents additional problems because the material cures during the experiment. This results in unusual effects during the first run and the repeat run giving a different trace.

The heat flow trace from DSC for two runs on the same specimen are shown in Figure 8.1. It can be seen on the first run that there appears to be a glass transition at 68 °C, at higher temperatures there is a large exotherm (in some cases the exotherm can obscure the glass transition). The second run has a very different appearance, there is no exotherm and the glass transition is now broad and at a higher temperature.



**Figure 8.1.** Graph showing the effect of further curing on the heat flow trace from DSC for the epoxy adhesive.

Figure 8.2 shows storage modulus traces for the same specimen run twice by DMA. Again, the second run has a different appearance to the first, but the differences are more subtle. The first run appears to show two glass transitions, a more distinctive transition at around 70 °C and a less distinctive transition around 130 °C. The second run shows a single transition at around 110 °C. For the first run it is reasonable to assume that the lower temperature, more distinctive, transition is the glass transition. The higher temperature “transition” is not actually a transition, but an artefact of the curing process. The effect of curing is to increase the modulus, while the effect of the increase in temperature on a cured material is a reduction in modulus. The result is that there is a less than expected decrease in modulus for the epoxy adhesive at temperatures for which it is curing, approximately 80 °C to 140 °C. This produces a second point of inflection at around 130 °C.



**Figure 8.2.** Graph showing the effect of further curing on the storage modulus trace from DMA for the epoxy adhesive.

The transition temperatures for both the DSC and DMA experiments are shown in Table 8.1. It appears from the DMA trace that the curing reaction is complete by 140 °C, because there is no difference between the two runs above this temperature. This appears to contradict the DSC, which indicates there is still some exothermic reaction as high as 180 °C. However, this can be accounted for by the higher heating rate in the DSC experiment, since the curing reaction is a function of time as well as temperature.

**Table 8.1.** Data on state-of-cure for the epoxy adhesive.

	T <sub>g</sub> from DSC (°C)	T <sub>g</sub> from DMA (°C)
1 <sup>st</sup> run	67.5	68.7 / 126.8
2 <sup>nd</sup> run	108.9 (broad)	107.4

### 8.3 Demonstration of Measurement of Service Temperature

The traditional method for assessing service temperature is by DTUL. Although this technique has limitations, it is used widely and is required by many specifications and procedures. DSC and DMA both determine the “ $T_g$ ” of a material according to standardised procedures and would be expected to produce the same results for a given material. The results of the three techniques for the three fully-cured materials tested in the inter-laboratory testing are shown in Table 8.2. The DSC and DMA results are from measurements at NPL, while the DTUL result is from an external site according to ISO 75, Part 2. No results are presented for DTUL on the two composite materials, as the site was not able to test according to ISO 75, Part 3, because of the higher loads required.

**Table 8.2.** Service temperature data.

Material	$T_g$ from DSC (°C)	$T_g$ from DMA (°C)	DTUL (°C)
Unreinforced polyester	$91.5 \pm 0.4$	$98.7 \pm 0.3$	$76.1 \pm 1.2$
Glass fibre-polyester	$94.5 \pm 1.1$	$102.8 \pm 0.4$	-
Carbon fibre-epoxy	$132.8 \pm 1.9$	$159.9 \pm 2.0$	-

It can be seen that the reported values of  $T_g$  from DSC and DMA are not comparable.  $T_g$  is well known to be frequency dependent and so would be expected to vary between techniques. However, the frequency dependence of  $T_g$  is often well-defined and the experimental results vary by a magnitude far greater than the anticipated frequency dependence. It is possible that the discrepancy is a result of either a fundamental difference in the glass transition or differences in the instrumentation. In Section 5, results were presented showing that for DMA there can be a large variation in reported temperature between sites. There is no doubt that the thermal contact between the specimen and the thermocouple is superior in DSC equipment and that the temperature variation within the specimen is smaller. It is quite possible that there is a fundamental difference between the techniques, and the difference is constant and reproducible, but this can only be an assumption until  $T_g$  can be measured reproducibly by DMA equipment with suitable temperature calibration.

The DTUL is rather lower than  $T_g$  from either DSC and DMA, and for most materials this would be the case, as DTUL is essentially the temperature at which the modulus of the material has decreased by a fixed amount. The fact that  $T_g$  is usually higher than DTUL should not be a barrier to the acceptance of  $T_g$  as an indication of service temperature. The use of DTUL in design guidelines is based on the DTUL within a formula. There is no reason why a similar approach cannot be developed for  $T_g$ . In the long term this would have the advantage that there are a number of methods to determine  $T_g$ . However, this would require consistent methods for  $T_g$  determination for each of the techniques concerned.

## 9 Concluding Remarks

This Measurement Good Practice Guide describes the development of standardised procedures for DSC, TMDSC, DMA, DEA and DTUL, which are presented in the Appendices. These procedures were developed in collaboration with equipment manufacturers, material suppliers and end users of composites and adhesives. For three of the techniques, DSC, TMDSC and DMA, precision statements have been produced based on inter-laboratory testing.

From these precision statements and expertise from users, guidance has been developed on the application of these techniques for the measurements of degree-of-cure and service temperature for composite materials and adhesives. Demonstrations of the typical results for such studies are also presented to support the guidance.

This Guide covers the major thermal analysis techniques applied to the processing and characterisation of composites and adhesives. The procedures developed have contributed to the development of standards in this area. In addition, the inter-laboratory testing for TMDSC is believed to be the first exercise of this type.

## **Bibliography of Standards**

*(Status as December 2002)*

### **Differential Scanning Calorimetry**

#### **ISO 11357. Plastics. Differential Scanning Calorimetry (DSC).**

ISO 11357. Part 1: 1997. (BS EN ISO 11357-1: 1997.)

*General principles.*

ISO 11357. Part 2: 1999. (BS ISO 11357- 2: 1999.)

*Determination of glass transition temperature.*

ISO 11357. Part 3: 1999. (BS ISO 11357- 3: 1999.)

*Determination of temperature and enthalpy of melting and crystallisation.*

ISO 11357. Part 5: 1999. (BS ISO 11357- 5: 1999.)

*Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion.*

ISO 11357. Part 6: 2002 (BS ISO 11357- 6: 2002.)

*Determination of oxidation induction time.*

ISO 11357. Part 7:2002 (BS ISO 11357- 7: 2002.)

*Determination of crystallisation kinetics.*

ISO WD 11357. Part 8.

*Determination of amount of absorbed water.*

#### **Other Selected Standards**

ASTM D 3417: 1999.

*Standard test method for enthalpies of fusion and crystallization of polymers by differential scanning calorimetry (DSC).*

ASTM D 3418: 1999.

*Standard test method for transition temperatures of polymers by differential scanning calorimetry.*

ASTM D 5028: 1996.

*Standard test method for curing properties of pultrusion resins by thermal analysis.*

ASTM E 967: 1997.

*Standard practice for temperature calibration of differential scanning calorimeters and differential thermal analysers.*

ASTM E 968: 2002.

*Standard practice for heat flow calibration of differential scanning calorimeters.*

ASTM E 1356: 1998.

*Standard test method for glass transition temperature by differential scanning calorimetry or differential thermal analysis.*

prEN 6041 (AITM 3.0002) *Aerospace series. Non-metallic materials.*

*Thermal analysis by differential scanning calorimetry.*

prEN 6064 (AITM 3.0008) *Aerospace series. Non-metallic materials.*

*Thermal analysis for the extent of cure by differential scanning calorimetry.*

## **Temperature Modulated Differential Scanning Calorimetry**

ASTM E 1952: 2001.

*Standard test method for thermal conductivity and thermal diffusivity by modulated temperature differential scanning calorimetry.*

## **Dynamic Mechanical Analysis**

### **ISO 6721. Plastics. Determination of Dynamic Mechanical Properties.**

ISO 6721. Part 1: 2001. (BS EN ISO 6721-1: 2002.)

*General principles.*

ISO 6721. Part 2: 1994. (BS EN ISO 6721- 2: 1996 / BS 2782-3: Method 342B: 1996.)

*Torsion-pendulum method.*

ISO 6721. Part 3: 1994. (BS EN ISO 6721-3: 1996 / BS 2782-3: Method 338A: 1996.)

*Flexural vibration. Resonance curve method.*

ISO 6721. Part 4: 1994. (BS 2782-3:Method 323A:1996.)  
*Tensile vibration. Non resonance method.*

ISO 6721. Part 5: 1996. (BS 2782-3:Method 323B:1996.)  
*Flexural vibration. Non resonance method.*

ISO 6721. Part 6: 1996. (BS 2782-3: Method 323C: 1996.)  
*Shear vibration. Non resonance method.*

ISO 6721. Part 7: 1996. (BS 2782-3: Method 323D: 1996.)  
*Torsional vibration. Non resonance method.*

ISO 6721. Part 8: 1997. (BS 2782-3: Method 323E: 1997.)  
*Longitudinal and shear vibration. Wave propagation method.*

ISO 6721. Part 9: 1997. (BS 2782-3: Method 323F: 1997.)  
*Tensile vibration. Sonic pulse propagation method.*

ISO 6721. Part 10: 1999. (BS ISO 6721-10: 1999.)  
*Complex shear viscosity using a parallel plate oscillatory rheometer.*

ISO CD 6721. Part 11.  
*Glass transition temperature.*

ISO WD 6721. Part 12.  
*Temperature calibration of dynamic mechanical analysers.*

### **Other Selected Standards**

ASTM E 1640: 1999.  
*Standard test method for assignment of glass transition temperature by dynamic mechanical analysis.*

ASTM E 1867: 2001.  
*Standard test method for temperature calibration of dynamic mechanical analyzers.*

prEN 6032 (AITM 1.0003) *Aerospace series. Fibre reinforced plastics.*  
*Test method for determination of the glass transition temperature.*

## **Dielectric Analysis**

ASTM D 150: 1998.

*Standard test methods for AC loss characteristics and permittivity (dielectric constant) of solid electrical insulation.*

ASTM E 2038: 1999.

*Standard test method for temperature calibration of dielectric analysers.*

ASTM E 2039: 1999.

*Standard practice for determining and reporting dynamic and dielectric properties.*

## **Deflection Temperature Under Load**

**ISO 75. Plastics. Determination of temperature of deflection under load.**

ISO 75. Part 1: 1993. (BS EN ISO 75-1: 1996. / BS 2782-1: Method 121: 1994.)

*General test method.*

ISO 75. Part 2: 1993. (BS EN ISO 75-2: 1996. / BS 2782-1: Method 121A to 121C: 1994.)

*Plastics and ebonite.*

ISO 75-3. Part 3: 1993. (BS EN ISO 75-3: 1996. / BS 2782-1: Method 121D: 1994)

*High strength thermosetting laminates and long-fibre reinforced plastics.*

## **Inter-Laboratory Testing**

**ISO 5725. Accuracy (trueness and precision) of measurement methods and results.**

ISO 5725. Part 1: 1994. (BS ISO 5725-1: 1994)

*General principles and definitions.*

ISO 5725. Part 2: 1994. (BS ISO 5725-2: 1994)

*Basic methods for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 5725. Part 3: 1994. (BS ISO 5725-3: 1994)

*Intermediate measures of the precision of a standard measurement method.*

ISO 5725. Part 4: 1994. (BS ISO 5725-4: 1994)

*Basic methods for the determination of the trueness of a standard measurement method.*

ISO 5725. Part 5: 1998. (BS ISO 5725-5: 1998)

*Alternative methods for the determination of the precision of a standard measurement method.*

ISO 5725. Part 6: 1994. (BS ISO 5725-6: 1994)

*Use in practice of accuracy values.*

## Introduction to Appendices

The following Appendices are presented:

Appendix 1: Procedure for Differential Scanning Calorimetry

Appendix 2: Procedure for Temperature Modulated Differential Scanning Calorimetry

Appendix 3: Procedure for Dynamic Mechanical Analysis

Appendix 4: Procedure for Dielectric Analysis

Appendix 5: Procedure for Deflection Temperature Under Load

The procedures are intended to provide accessible procedures for users of these techniques. For this reason, the procedures only contain the basic requirements that have been identified as critical to the technique. The procedures are not intended as replacements for ISO standards but to be used alongside them. For details not included in these procedures, it is advised that the following standards are referred to:

ISO 11357, Part 1 for differential scanning calorimetry

ISO 6721, Part 1 for dynamic mechanical analysis

ISO 75, Part 1 for deflection temperature under load

(There are no suitable standards available for temperature modulated differential scanning calorimetry and dielectric analysis.)

## **Appendix 1: Procedure for Differential Scanning Calorimetry**

### **1 Principle**

The difference between the heat flux into a test specimen and that into a reference specimen is measured as a function of temperature and/or time, while the test specimen and the reference specimen are subjected to a controlled temperature programme under a specified atmosphere [ISO 11357-1: 1997].

### **2 Equipment**

#### **2.1 Differential Scanning Calorimeter**

The instrument shall be capable of a constant heating rate of 10 °C/min.

#### **2.2 Pans**

Aluminium pans shall be used. These may be open or closed (see Clause 4.2).

#### **2.3 Balance**

The balance shall be capable of measuring the specimen mass with an accuracy of  $\pm 0.01$  mg.

#### **2.4 Standard Reference Materials**

The recommended reference materials are sapphire, indium and tin. Gallium and lead may be used in addition.

#### **2.5 Gas Supply**

The recommended gas is dry nitrogen.

### **3 Calibration**

#### **3.1 Procedure**

The instrument shall be calibrated according to the manufacturer's procedures. Where suitable procedures are not available the procedures contained in ASTM E 967: 1997 and ASTM E 968: 2002 shall be used.

#### **3.2 Reference Materials**

Temperature calibration shall be performed using indium and tin. Gallium and lead may be used in addition for temperature calibration. Sapphire and indium shall be used for the heat flow calibration.

### **4 Test Specimen**

#### **4.1 Specimen Mass**

The mass of the specimen shall be such that there are 5 to 10 mg of resin or adhesive present. In other words, the mass of any inert fibre or filler shall not be included when determining the mass.

## **4.2 Specimen Pans**

Pans can be open or closed. If they are closed there shall be a pinhole in the lid of the pan. The use of hermetically sealed pans is not recommended for composite or adhesive specimens.

## **4.3 Specimen Form**

Solid specimens shall consist of a single piece with a large area in contact with the pan. A cutting process is recommended for the preparation of specimens. Other processes are allowable providing they do not significantly alter the thermal properties of the material. Powdered specimens shall be avoided where possible.

# **5 Procedure**

## **5.1 Purge Gas**

A dry nitrogen purge gas shall be used. The manufacturers recommended flow rate shall be used, where there is no recommendation a flow rate of 50 ml/minute shall be used.

## **5.2 Heating Rate**

A heating rate of 10 °C/minute shall be used for all experiments.

## **5.3 Temperature Range**

The temperature range of the test shall be at least 50 °C above and below the temperature range of interest (i.e. the approximate glass transition temperature).

# **6 Analysis of Results**

## **6.1 Glass Transition Temperature**

The glass transition temperature shall be taken as the point of inflection of the step change in heat flow plotted on a linear scale.

## **6.2 Other Analysis Points**

The extrapolated onset and endset of the step change in heat flow plotted on a linear scale may be determined in addition to the glass transition temperature.

# **7 Report**

The report shall include the following information:

- a reference to this Measurement Good Practice Guide and any standard used;
- identity of the specimen;
- specimen mass;
- glass transition temperature;
- any additional analysis results;
- the date of the test;
- any deviations from this procedure.

## **Appendix 2: Procedure for Temperature Modulated Differential Scanning Calorimetry**

### **1 Principle**

The difference between the heat flux into a test specimen and that into a reference specimen is measured as a function of temperature and time, while the test specimen and the reference specimen are subjected to an oscillatory or periodically repeating temperature programme under a specified atmosphere [Adapted from ISO 11357-1: 1997 and ASTM E 1952: 2001].

### **2 Equipment**

#### **2.1 Differential Scanning Calorimeter**

The instrument shall be capable of applying periodically varying temperature cycle together with an underlying temperature ramp. A maximum heating rate of 10 °C/minute and a maximum cooling rate of 5 °C/minute are required.

#### **2.2 Pans**

Crimped aluminium pans shall be used (see Clause 4.2).

#### **2.3 Balance**

The balance shall measure the specimen mass with an accuracy of  $\pm 0.01$  mg.

#### **2.4 Standard Reference Materials**

The recommended reference materials are sapphire, indium and tin. Gallium and lead may be used in addition.

#### **2.5 Gas Supply**

The recommended gas is dry nitrogen.

### **3 Calibration**

#### **3.1 Procedure**

The instrument shall be calibrated according to the manufacturer's procedures. Where suitable procedures are not available the procedures contained in ASTM E 967: 1997 and ASTM E 968: 2002 shall be used.

#### **3.2 Reference Materials**

Temperature calibration shall be performed using indium and tin. Gallium and lead may be used in addition for temperature calibration. Sapphire and indium shall be used for the heat flow calibration.

### **4 Test Specimen**

#### **4.1 Specimen Mass**

The mass of the specimen shall be 5 to 10 mg.

#### **4.2 Specimen Pans**

The specimen shall be crimped inside closed pans. If the pans are sealed there shall be a pinhole in the lid of the pan. The use of hermetically sealed pans is not recommended for

composite or adhesive specimens.

#### **4.3 Specimen Form**

Solid specimens shall consist of a single piece with a large area in contact with the pan. A cutting process is recommended for the preparation of specimens. Other processes are allowable providing they do not significantly alter the thermal properties of the material. Powdered specimens shall be avoided where possible.

### **5 Procedure**

#### **5.1 Purge Gas**

The manufacturers recommended flow rate shall be used; else a flow rate of 50 ml/minute shall be used.

#### **5.2 Test Parameters**

A heating cycle of period 100 seconds shall be used and the magnitude of the oscillation shall be plus and minus 1 °C (giving a 2 °C variation in total). The underlying heating rate shall be between 1 and 4 °C/minute. Within this range the underlying heating rate shall be selected such that there are at least 6 cycles across the transition of interest.

#### **5.3 Temperature Range**

The temperature range of the test shall be at least 30 °C above and below the temperature range of interest (i.e. the approximate glass transition temperature).

### **6 Analysis of Results**

#### **6.1 Glass Transition Temperature**

The glass transition temperature shall be taken as the point of inflection of the step change in heat capacity plotted on a linear scale.

#### **6.2 Other Analysis Points**

The extrapolated onset and endset of the step change in heat capacity plotted on a linear scale may be determined in addition to the glass transition temperature.

### **7 Report**

The report shall include the following information:

- a reference to this Measurement Good Practice Guide and any standard used;
- identity of the specimen;
- specimen mass;
- underlying heating rate;
- glass transition temperature;
- any additional analysis results;
- the date of the test;
- any deviations from this procedure.

## **Appendix 3: Procedure for Dynamic Mechanical Analysis**

### **1 Principle**

A specimen of known geometry is placed in mechanical oscillation at fixed frequency and changes in the viscoelastic response of the material are monitored as a function of temperature. The glass transition of the material is marked by a rapid decrease in the storage modulus, a peak in loss modulus and a peak in tan delta. [Adapted from ASTM E 1640: 1999].

### **2 Equipment**

#### **2.1 Dynamic Mechanical Analyser**

Capable of heating at 1 to 5 °C/minute and testing at a frequency of 1 Hz. The load capability of the analyser shall be sufficient for the specimens to be tested.

#### **2.2 Vernier Callipers**

Capable of measuring lengths to an accuracy of 0.05 mm.

#### **2.3 Standard Reference Materials**

A steel bar is required for the compliance calibration of the analyser.

### **3 Calibration**

#### **3.1 Mechanical Calibration**

The instrument shall be mechanically calibrated according to the manufacturer's recommendations. The mechanical calibration will generally involve measurement of the compliance of the instrument using a stiff, usually steel, bar.

#### **3.2 Temperature Calibration**

No method of temperature calibration shall be used, as there is currently no method of temperature calibration that is satisfactory for all types of instrument. (This aspect of measurement is considered in detail in Section 5.2.2 in the main text of this Guide.)

### **4 Test Specimen**

#### **4.1 Specimen Dimensions**

The specimen dimensions will vary depending on the testing mode and the particular instrument being used. A specimen thickness of 2 mm is recommended.

### **5 Procedure**

#### **5.1 Heating Rate**

A heating rate of 3 °C/minute shall be used.

#### **5.2 Frequency**

A frequency of 1 Hz shall be used.

### **5.3 Strain**

The strain on the specimen shall be selected so that it is within the linear elastic range of the material being tested.

### **5.4 Temperature Range**

The temperature range of the test shall be at least 50 °C below to 50 °C above the region of interest.

## **6 Analysis of Results**

### **6.1 Analysis Point**

The glass transition temperature shall be taken as the point of inflection of the decrease in storage modulus plotted on a linear scale.

### **6.2 Other Analysis Points**

The peak of loss modulus and peak of tan delta associated with the glass transition may be determined in addition to the glass transition temperature.

## **7 Report**

The report shall include the following information:

- a reference to this Measurement Good Practice Guide and any standard used;
- identity of the specimen;
- specimen dimensions;
- testing mode;
- glass transition temperature;
- any additional analysis results;
- date of the test;
- any deviations from this procedure.

## **Appendix 4: Procedure for Dielectric Analysis**

### **1 Principle**

An oscillatory electric potential (voltage) is applied to a test specimen by means of an electrode of known geometry. An electric current is measured at a sensing electrode separated from the transmitting electrode by the specimen under test. From the amplitude and the phase shift of the measured current relative to the applied voltage, and from known geometrical constants, desired dielectric properties of the specimen under test may be obtained. The desired properties may be obtained as a function of frequency, temperature or time. [Adapted from ASTM E 2039: 1999].

### **2 Equipment**

#### **2.1 Specimen Chamber and Heater**

Capable of holding a solid or liquid sample in contact with the sensing electrodes and heating the specimen at a rate of 3 °C/minute.

#### **2.2 Oscillatory Voltage Source and Detector**

Capable of applying a sinusoidally varying voltage to the sample and detecting the resulting current. The voltage source shall be able to operate at frequencies of 1 Hz and/or 1 kHz.

### **3 Calibration**

#### **3.1 Dielectric Calibration**

The instrument shall be calibrated according to the manufacturer's recommendations.

#### **3.2 Temperature Calibration**

The temperature sensor should itself be calibrated. If the temperature sensor is in direct contact with the specimen no further calibration is required. If not, then a procedure is described in ASTM E 2038: 1999.

### **4 Test Specimen**

#### **4.1 Specimen Dimensions**

The specimen dimensions will be specific to the type and size of electrodes and specimen chamber used.

#### **4.2 Conductivity of Specimen Components**

Conductive components in the sample may short the electrodes. It is important that no conductive components in the sample are in contact with the electrodes.

### **5 Procedure**

#### **5.1 Heating Rate**

A heating rate of 3 °C/minute shall be used.

## **5.2 Frequency**

Frequencies of 1 Hz and/or 1 kHz shall be used. Ideally, measurements shall be made at both frequencies.

## **5.3 Voltage**

The voltage on the specimen shall be sufficiently small that the response of the sample is linear with respect to voltage.

## **5.4 Temperature Range**

The temperature range of the test shall be at least 50 °C below to 50 °C above the region of interest.

# **6 Analysis of Results**

## **6.1 Analysis Point**

The glass transition temperature shall be taken as the point of inflection of the increase in permittivity associated with the glass transition plotted on a linear scale.

## **6.2 Other Analysis Points**

The peak of loss permittivity and peak of tan delta associated with the glass transition may be determined in addition to the glass transition temperature.

# **7 Report**

The report shall include the following information:

- a reference to this Measurement Good Practice Guide and any standard used;
- identity of the specimen;
- specimen form;
- specimen dimensions;
- type of electrodes;
- glass transition temperature (with frequency);
- any additional analysis results (with frequency);
- date of the test;
- any deviations from this procedure.

## **Appendix 5: Procedure for Deflection Temperature Under Load**

### **1 Principle**

A standard test specimen is subjected to a bending stress to produce a nominal surface stress, given in the relevant part of the procedure. The temperature is raised at a uniform rate, and the temperature at which a specified deflection occurs is measured [Adapted from ISO 75-1: 1993].

### **2 Equipment**

#### **2.1 Bending Apparatus**

The span available (the distance between the lines of contact with the specimen) should be between 60 mm and 210 mm.

#### **2.2 Heating Bath**

The heating bath should be capable of heating at a rate of 2 °C/minute.

#### **2.3 Weights**

A set of weight that covers the full range of applied loads to a resolution of 1 g.

#### **2.4 Temperature Sensor**

A temperature sensor covering the full temperature range (ambient to 250 °C) placed close to, but not touching, the specimen.

### **3 Calibration**

#### **3.1 Weights**

The accuracy of the weights should be checked against known standards or on a calibrated balance.

#### **3.2 Temperature Sensor**

The accuracy of the temperature sensor can be confirmed by a standard thermocouple or with a suitable range of melting standards.

### **4 Test Specimen**

#### **4.1 Specimen Dimensions for Unreinforced Materials**

The required specimen dimensions are  $80 \pm 2$  mm by  $10.0 \pm 0.2$  mm by  $4.0 \pm 0.2$  mm with a span of 64 mm.

#### **4.1 Specimen Dimensions for Reinforced Materials**

The required thickness is between 2 mm and 7 mm and the span should be at least 30 times the specimen thickness. The length of the specimen should be 10 mm greater than the span and the specimen thickness should be between 9.8 mm and 12.8 mm.

## 5 Procedure

### 5.1 Heating Rate

A heating rate of 2 °C/minute shall be used.

### 5.2 Applied Stress for Unreinforced Materials

For unreinforced materials a fixed stress of 1.8 MPa shall be applied.

### 5.3 Applied Stress for Reinforced Materials

For unreinforced materials a stress of one thousandth of the flexural modulus shall be applied, (this stress corresponds to the stress required to produce a strain of 0.1 % in the specimen).

## 6 Analysis of Results

### 6.1 Deflection Temperature Under Load for Unreinforced Materials

The deflection temperature under load shall be determined as the temperature at which the specimen has deflected by a further 0.2 % from the initial deflection.

### 6.2 Deflection Temperature Under Load for Reinforced Materials

The deflection temperature under load shall be determined as the temperature at which the specimen has deflected by a further 0.1 % from the initial deflection. (A deflection increase of 0.2 % has been proposed for use for reinforced materials.)

### 6.3 Other Results

A plot of the deflection of the specimen against temperature can be determined additionally.

## 7 Report

The report shall include the following information:

- a reference to this Measurement Good Practice Guide and any standard used;
- identity of the specimen;
- specimen dimensions;
- deflection temperature under load;
- a plot of deflection against temperature, if required;
- date of the test;
- any deviations from this procedure.

## Equations

$$\text{Applied Force} = \frac{2 \times \text{Stress} \times \text{Width} \times (\text{Thickness})^2}{3 \times \text{Span}}$$

where the applied force is in N; the stress is in MPa; the span, width and thickness are all in mm.

$$\text{Deflection Increase} = \frac{(\text{Span})^2 \times \text{Strain Increase}}{6 \times \text{Thickness}}$$

where the deflection increase, thickness and span are in mm; the flexural strain increase is 0.002 (unreinforced materials) or 0.001 (reinforced materials)