

Measurement Note

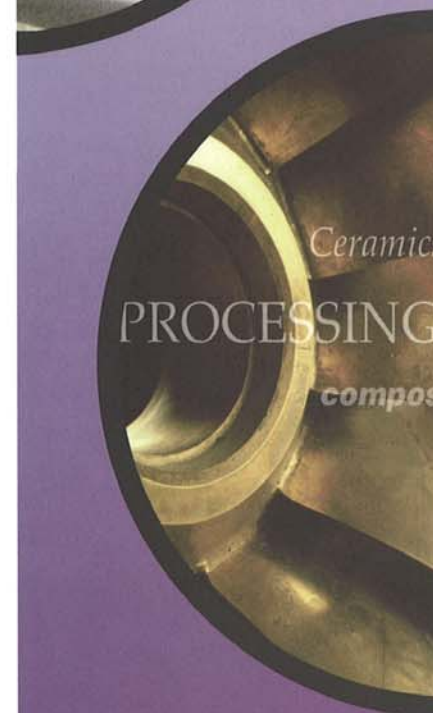
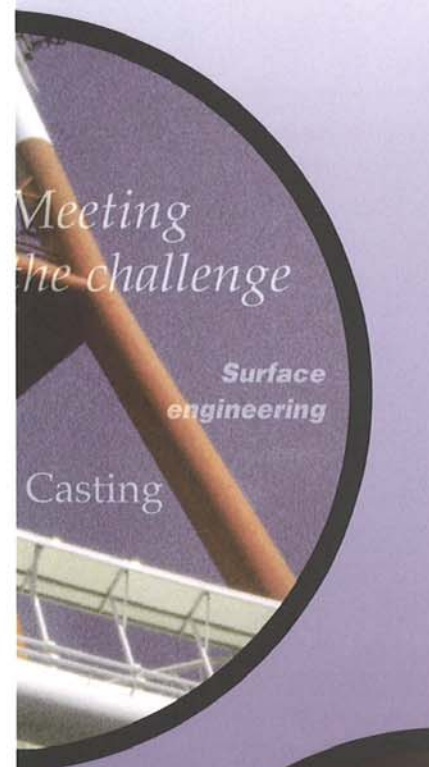
Polymer Composites – Rate Dependent Temperature Calibration of Dynamic Mechanical Analysers (DMA) for T_g measurements

Measurement of the glassy-rubber transition temperature (T_g) provides important data that assist designers in the choice of material for their product depending on its service environment. For composites fabricators, it can ensure the material is correctly cured. Thermal analysis techniques, particularly DSC, DMA (and TMA^[3], DEA) have been widely used to determine the T_g of a material which helps in the QA process for material qualification and supply. All techniques use a controlled temperature profile, which is a built-in programmable feature in the control software of all commercially available instrumentation. DSC generates heat flow data related to transitions as a function of temperature and time, whereas DMA measures the mechanical response of the material as a function of the heating or cooling applied.

DSC uses a small amount of sample placed within a crucible and T_g is denoted as the point of inflection in the step change of the heat flow curve. The temperatures generated in a DSC use well-established calibration procedures, and reference materials (e.g indium, tin), with precisely known melting points.

DMA on the other hand is a versatile technique, which can be used in many deformation modes that are available in most commercially available instrumentation. The data generated indicate the mechanical response of the sample as a result of the temperature ramp. However, it is to be noted that the temperature sensor in a DMA measures the temperature of the environment around the sample. Instrument manufacturers' guidelines recommend that the operator manually adjust the position of the sensor to be as close as possible to the sample, but not touching it. This introduces temperature lag effects depending on where the sensor is positioned relative to the sample. The temperature calibration is therefore an issue. This Measurement Note builds on previous research and seeks to develop a procedure for temperature calibration in a DMA instrument with particular reference for T_g measurements in polymer based material systems.

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Introduction

The glass transition temperature (T_g) denotes a change in the material physical property from a glassy state to a rubbery state. This property is important as it can indicate the maximum service temperature at which the material can be used and for thermoset systems, the degree of cure. Several techniques have historically been used for this measurement and various analysis methods adopted.

Differential Scanning Calorimetry (DSC)

T_g evaluation is performed on the step change in the heat flow curve. The concerns of this technique is the small amount of specimen that is used to generate the data, which may not be representative of the actual component in end-use, and the dilution of the response due to the volume (70% of total) of unreactive specimen fibre in the specimen. In many cases, the step transition is not easily detected and could contribute to the incorrect T_g being reported. Tests are normally conducted in accordance with ISO 11357 (Parts 1 and 2) [1,2].

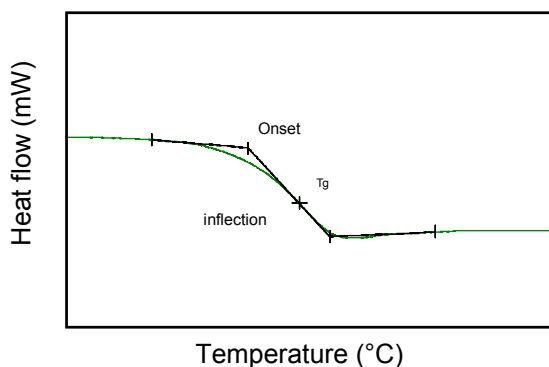


Figure 1: T_g determination by DSC

Dynamic Mechanical Analysis (DMA)

This technique has used different analysis points in several standards [4,5] and other test methods (company in-house) for T_g determination. The analysis points range from the transition onset or inflection point in the storage modulus (vs. temperature curve), the loss modulus peak or the tan delta peak. As a result of previous research at NPL, the inflection point in the storage modulus (linear scale) or peak in the loss modulus curves were the recommended points of analysis. There was generally good agreement between the two points. Whilst the glass transition in a DMA is usually well defined,

there has been concern expressed in the reported temperatures. This is due to several factors

- Design of most commercially available instrumentation where the temperature sensor measures the oven environment around the specimen rather than the specimen itself, leading to problems due to thermal lag between the specimen and the oven.
- The wide range of analysis points used to denote T_g . The differences between the onset and tan delta peak could be as much as 40°C.
- Test parameters used (e.g. heating rate, frequency, mode of deformation etc.).
- Lack of standardised temperature calibration methods.

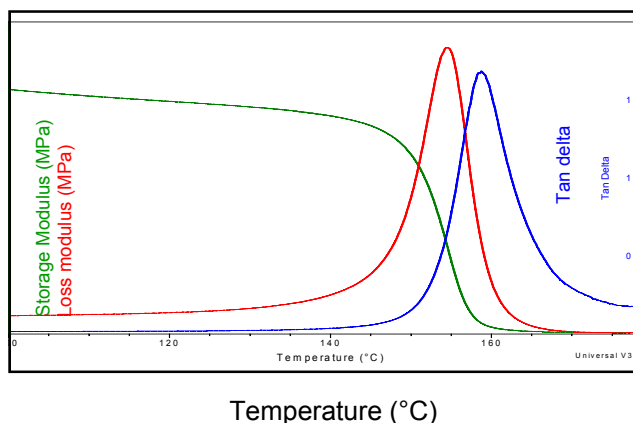


Figure 2: T_g determination by DMA

NPL undertook two DMA round-robin exercises as part of previous research [5] for measurement of T_g . From the analysis, it was evident that the main reason for the differences in reported temperatures was due to the “specimen” temperature measurement made in the instrument. It was found that whilst the repeatability of both techniques was good, the reproducibility of the DMA measurements was much poorer than for DSC.

Development of Temperature Reference Specimens

Initial Trials

In order to address the issue of temperature measurement, three types of reference specimens were developed. Indium was the chosen material for the basis of these specimens, as the melting point is an

established reference. The three temperature reference specimens consisted of indium wire encapsulated within an aluminium tube, a silicone rubber plaque and a glass reinforced composite material.

The calibration procedure developed was based on the melting of indium at 156.62 °C^[1]. The samples were tested in the single cantilever bending mode. Analysis was performed on the part of the loss modulus curve where a sharp deviation related to the melting of indium was observed. The observations are summarised below.

- **Aluminium tube**

There was difficulty detecting the melting point transition and this could be attributed to the relatively high stiffness of the aluminium tube. Heat transfer effects via the metallic clamps was another issue which had to be considered. It is also to be noted that ASTM E1867-97 suggests wrapping indium within aluminium foil.

- **Silicon plaque**

The melting point transition was sharp and clear. However, the material was rubbery and so did not replicate a typical specimen to be used in subsequent tests. The specimen was also not ideal for the most commonly used test mode (flexure - single cantilever bending).

- **GRP laminate**

The transition relating to the melting point of indium was clear. However the T_g of the GRP material was around the same region as the melting transition. There was a possibility of overlapping transitions which could make any analysis inconsistent.

Figure 3 shows the effect of different heating rates on the determination for the transition temperature.

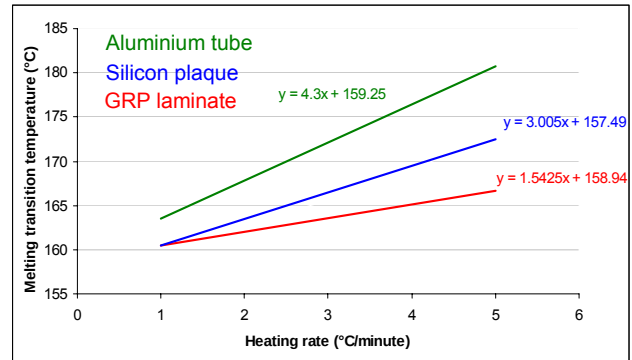


Figure 3: Multiple heating rate effect of three temperature reference specimens

A round-robin testing programme was conducted on the silicon plaque temperature reference specimen at different sites. The scatter in the results (Fig 4) indicate the effect of reported temperature in the different instrumentation. The highest value suggests the thermocouple was not calibrated correctly.

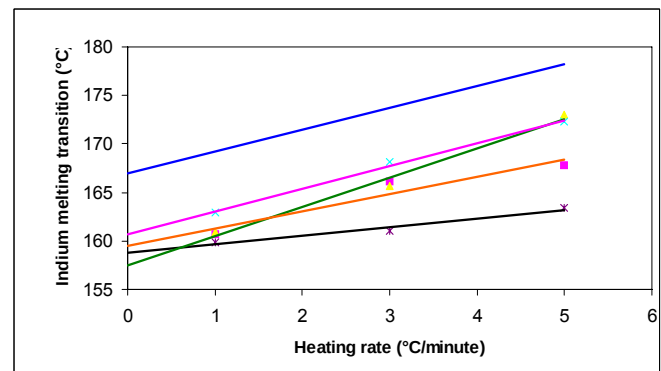


Figure 4: Melting transition analysis on silicon plaque specimen tested at different sites

Improved Temperature Reference Specimen

Because of the shortcomings of the experimental reference specimens, a new type of reference specimen was developed using a woven carbon fibre prepreg. The material for the reference specimen was chosen such that its T_g was higher than the melting point of indium to avoid overlapping transitions.

Temperature Reference Specimen	Lay-up configuration (side view)	Comment
Specimen No 1 (both faces)		Indium encapsulated near both faces of the specimen.
Specimen No 2		Indium encapsulated in the centre of specimen.
Specimen No 3 (one face)		Indium encapsulated near one face of the specimen.

Table 1: Prototype temperature reference specimens
(positioning of indium indicated in red)

The specimens were made in three configurations (see Table 1), by encapsulating indium in different positions within the bar shaped specimen. The encapsulated specimens were cured in an oven before machining them to the required dimensions suitable for test in the DMA instrument. The specimens were manufactured using different lay-up configurations to study the thermal conductivity effects.

All the specimens were tested at heating rates of 1, 3, 5 and 10 °C/minute. Specimen No 3 was tested with the surface near the indium, facing both upwards and downwards in the instrument clamps. Analysis was performed on the loss modulus curve at the point where a sharp drop was observed.

The results indicated (Figure 5) that the sample with indium on both sides gave multiple transitions as expected. This was an indication of the temperature distribution within a specimen during test. The response was less pronounced when the indium encapsulated face was aligned downwards in the clamps. The response for the specimen

with indium encapsulated in the centre was more pronounced than in the other configurations. The specimens were then tested at different heating rates and the peak in loss modulus values were plotted against the heating rate as shown in Figure 6. The “apparent” melt temperature varied between the different configurations. A polynomial fit was derived in order to extrapolate the value to zero heating rate.

The differences in the zero heating rate temperature response for the different temperature reference specimens for the melting of indium ($156.62\text{ }^{\circ}\text{C}^{[1]}$) were between 0.8°C to 1.7°C (Table 2). This variation in the “apparent” melt temperature for the different temperature reference specimens was considered to be acceptable for the application of the rate dependent temperature calibration procedure.

On the basis of the observed results and transition clarity, the design with the indium in the centre was chosen as the ideal specimen configuration for further development as a temperature reference specimen.

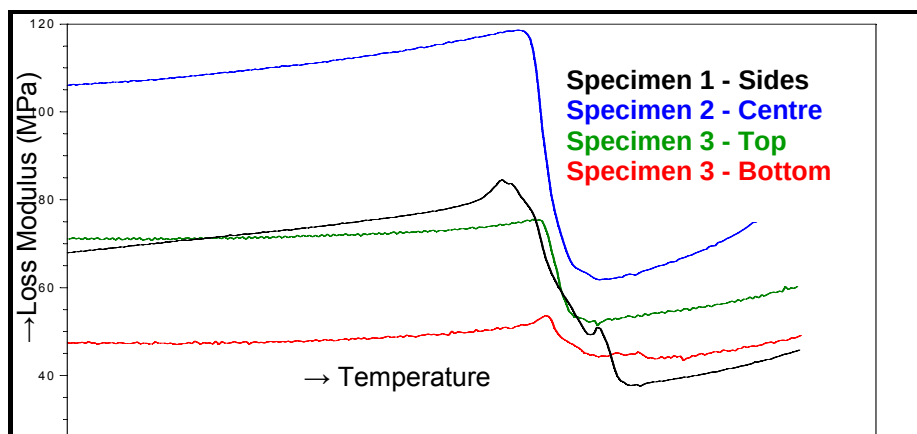


Figure 5: Response due to indium melt for the different configurations of the temperature reference specimen shown in Table 1. Test speed is 3 °C/minute

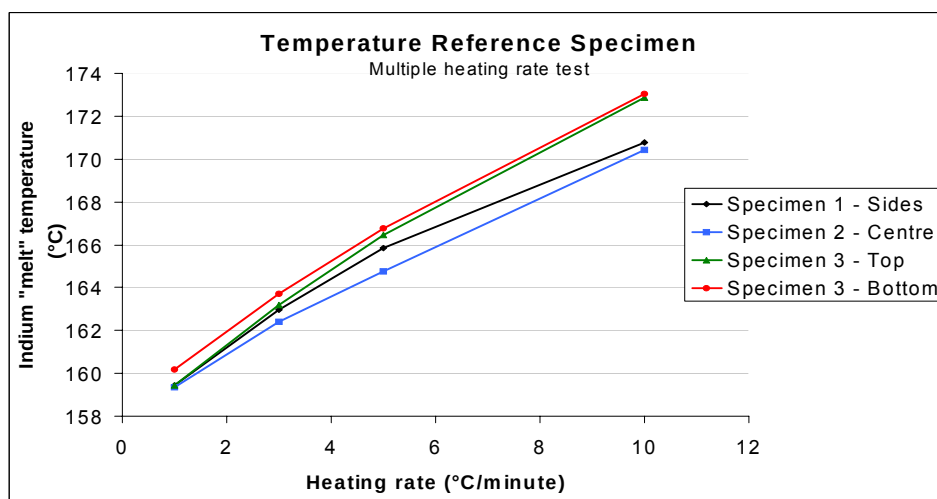


Figure 6: Effect of heating rate on the “measured” melt temperature for the different configuration temperature reference specimens (analysis based on loss modulus peak)

Position of indium within specimen	0 °C/minute heating rate value	Deviation from indium melting point reference
	°C	
Top face	157.44	+ 0.82
Bottom face	158.33	+ 1.71
Centre	157.92	+ 1.3
Side faces	157.53	+ 0.91

Table 2: Indium “melt” temperature* extrapolated for zero heating rate
 (*reference value =156.62 °C)

Measurement was also carried out at multiple heating rates on a plain CFRP specimen. The zero degree heating rate value thus extrapolated was 192.3 °C, which was around 35°C above the reference indium melting point (Figure 7).

This eliminated the possibility of detecting overlapping transitions (i.e. indium melt and Tg) when used as a temperature reference specimen with indium encapsulated.

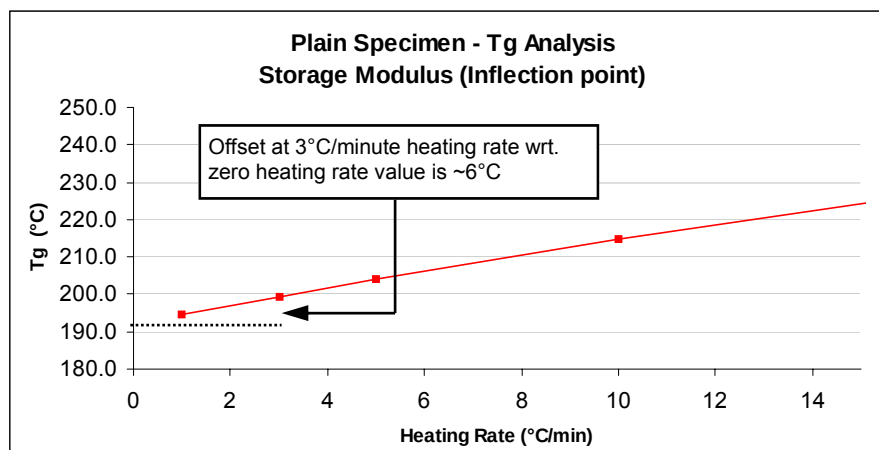


Figure 7: Tg measurement at multiple heating rates - plain specimen without the indium encapsulation

Additional tests were carried out by monitoring the temperature of the plain specimen directly by inserting a thermocouple through a drilled hole in the longitudinal side of the specimen (Fig 8). The thermocouple was connected to a digital data logger and both the DMA temperature readout and the external data logger readout noted. The measurement indicated the effect of temperature lag between the instrument readout and the thermocouple inserted directly into the sample.

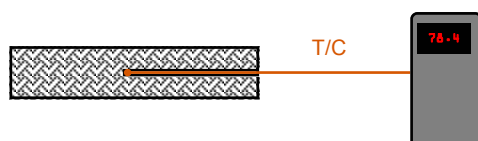


Figure 8: Thermocouple inserted through hole in the specimen

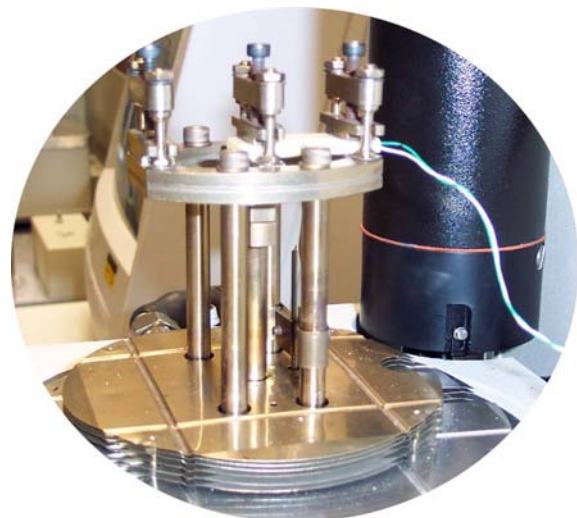


Figure 9: Plain fixture with inserted thermocouple loaded in clamps for direct monitoring of temperature

It was evident that at the stable state ambient condition, there was no significant difference between the readings. The temperature lag is noticeable only while the test is in progress (Fig 10). The heating rate, placement of the temperature sensor by the operator, instrument clamps, the design of the oven chamber and the size and thermal conductivity of the specimen itself are some of

the contributory factors influencing the data generated by DMA. This result confirmed the basis for the development of the temperature reference specimen, which was the only way to narrow some of the differences caused by testing the same materials by different instruments, test parameters and operators.

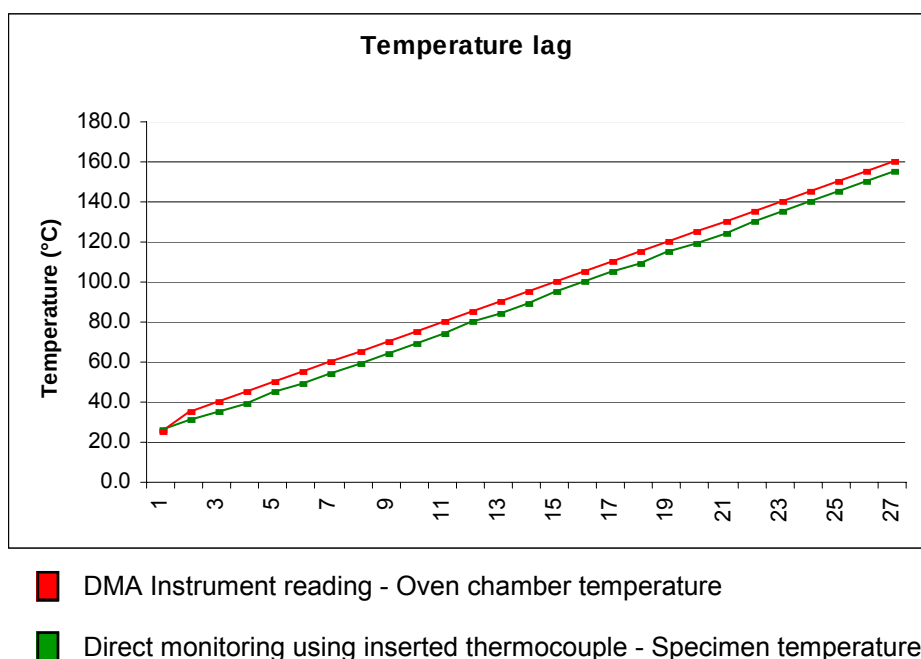


Figure 10: Direct temperature monitoring of the plain specimen using an inserted thermocouple at 3°C/minute heating rate

Based on the above observations, a temperature calibration procedure was developed for T_g measurements by DMA for polymer-based systems.

The procedure is based on the rate dependent response of materials when tested in the DMA and allows for the position of the temperature sensor and other factors mentioned above. Additionally, the temperature reference fixture has also been designed to simulate typical sample dimensions for testing by the single cantilever bending mode in most commercially available instrumentation.

The procedure developed as a result of the research is described in the following pages, and involves testing the temperature reference specimen using multiple heating rates. The measured indium “melt” temperatures are plotted against heating rate

and the zero degree heating rate value determined. This should normally be $\pm 2^{\circ}\text{C}$ from the indium melting temperature. If this condition is satisfied, a similar multiple heating rate test is performed using the actual sample and the zero degree heating rate value determined based on the T_g analysis points determined for the different heating rates.

The T_g is analysed as the inflection point in the storage modulus curve ^[6] (or alternatively the peak in the loss modulus curve). The extrapolated zero heating rate value is reported as the true T_g for the sample on test.

For QA testing purposes an offset for the different heating rates are determined based on the true T_g value. A ‘calibration curve’ is then derived for the different heating rates. Subsequent tests on similar material types can then be tested at any of the heating rates and the offset applied to report T_g.

Manufacture of indium temperature reference specimens

A batch of indium temperature reference specimens was manufactured in the NPL autoclave (Figure 11) using the preferred configuration (indium centrally placed). The X-ray image of the manufactured specimens (Figure 12) was obtained to check for any manufacturing defects caused by the flow of indium during the pressurised curing process.

As part of on-going research a round-robin testing exercise is being planned using a number of materials of known degree of cure, and by applying the temperature calibration procedure. The results will also be compared with T_g values determined by other thermal analysis techniques (DSC, TMA, DEA etc). Possibilities of adopting similar approaches for other deformation modes and materials may be explored.

Following the validation exercises, the authors hope to make the temperature reference specimen widely available through NPL.

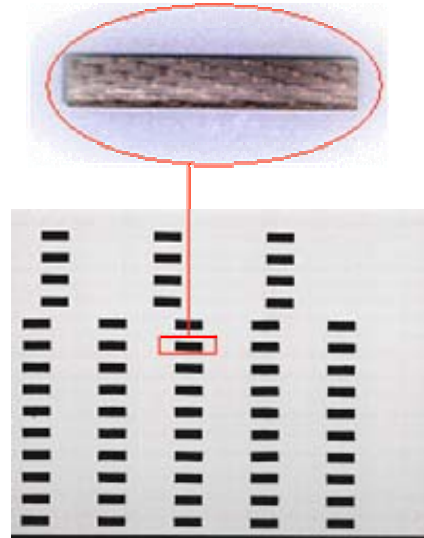


Figure 12: X-ray image of manufactured temperature reference specimens



Figure 11: Temperature reference specimen manufacture in the NPL autoclave

Tg Determination by DMA using Rate Dependent Calibration Process**Equipment Calibration**

1. Calibrate the load and displacement measuring devices of the instrument according to manufacturers' guidelines
2. Check ambient temperature reading of the instrument with a calibrated thermocouple.
3. If the temperature difference between the instrument and calibrated thermocouple at ambient is not within $\pm 1^\circ\text{C}$, check the instrument thermocouple and return to step 2.
4. Test indium temperature reference specimen at four different heating rates (1, 3, 5 and $10^\circ\text{C}/\text{min}$) and plot the melting transition point (loss modulus peak) against the heating rate. This is termed the 'calibration curve'.
5. If the analysis is **not** rate dependent (i.e. less than 2°C variation), test material specimens at $3^\circ\text{C}/\text{minute}$ and report Tg as the inflection point of the storage modulus curve (preferred analysis point). No further calibration is necessary.
6. If the analysis is rate dependent, extrapolate the melting transition values (loss modulus peak) for the different heating rates analysed in step 4 in order to determine the zero heating rate value.
7. (a) If the value determined in step 6 is **not** within $\pm 2^\circ\text{C}$ of 156.6°C , there could be a problem with the measurement device(s) and further investigation is necessary.
(b) If the value determined in step 6 is within $\pm 2^\circ\text{C}$ of 156.6°C , go to step 8.

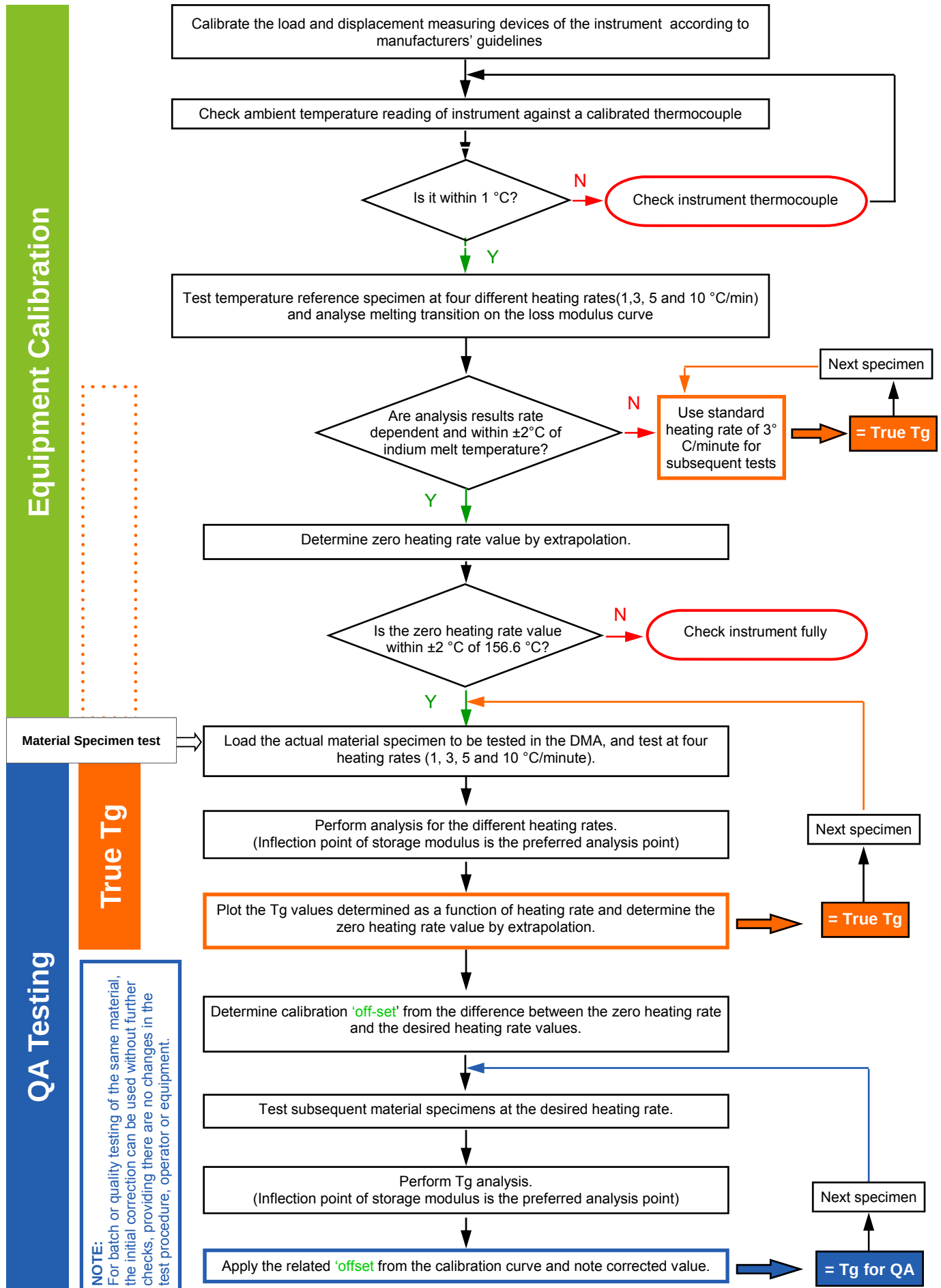
Material Specimen tests**True Tg determination**

8. Load the material specimen to be tested in the DMA, and test at four heating rates (1, 3, 5 and 10°C per minute).
9. Determine the "apparent" Tg for each heating rate using the inflection point (storage modulus curve).
10. Plot the derived data as a function of the heating rate to generate the 'calibration curve'.
11. Determine the zero heating rate value by extrapolation.
12. Report the value determined in step 11 as the true Tg.

Tg determination for QA testing

13. Determine the off-set value from the difference between the true Tg and the Tg at the desired heating rate from the 'calibration curve' obtained in step 10.
14. Test the material specimens at the desired heating rate.
15. Determine the apparent Tg from the inflection point in the storage modulus curve.
16. Apply the off-set value for the heating rate used, as determined in step 13
17. Report the value determined in step 16 as the Tg of the material for QA purposes.

Tg determination by DMA using rate dependent temperature calibration process



FURTHER READING

1. BS EN ISO - 11357 - 1:1997: Plastics – Differential Scanning Calorimetry - General principles
2. BS ISO 11357 - 2:1999 - Plastics – Differential Scanning Calorimetry - Determination of Glass Transition Temperature
3. BS ISO 11359 - 2 :1999 - Plastics - Thermomechanical analysis (TMA) - Determination of linear thermal expansion coefficient and glass transition temperature.
4. BS EN ISO 6721 - 1:2002 - Plastics - Determination of Dynamic Mechanical Properties - General Principles
5. ISO/CD 6721 – 11 - Plastics - Determination of Dynamic Mechanical Properties - Determination of Glass Transition Temperature
6. Thermal Analysis Techniques for Composites and Adhesives, NPL Measurement Good Practice Guide 62:2002 - Mulligan D.R., Gnanih S.J.P., Sims G.D
7. Temperature Calibration of a Dynamic Mechanical Thermal Analyser - - Polymer Testing vol.17, no. 7 p.523-30:1998 Lotti C., Canevarolo S.V.,
8. Comparison of Dynamic Mechanical Measurements and Tg Determinations with Two Different Instruments. Hagen R., Salmen L., Lavebratt H, Stenberg B.
9. Analysis of the Thermal Environment Inside the Furnace of a Dynamic Mechanical Analyser. Alves N.M., Mano J.F., Gomez Ribelles J.L.

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For information on possible future interlaboratory round-robin exercises and research, please contact:

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