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Modulated-Temperature Thermomechanical Measurements

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Abstract: There are close analogies between DSC (which measures enthalpy changes) and thermomechanical analysis (TMA) (which measures volume or length changes). This naturally leads to the application of modulated temperature programs to TMA as a means to separate the reversible nature of thermal expansion from irreversible deformation arising from creep under the applied load or changes in dimensions due to relaxation of orientation. The effect of experimental variables and calibration are described and the application of the technique to study the glass-rubber transition and melting of polymers is discussed.

Keywords: calibration, glass transition, melting, modulated temperature thermomechanical analysis, thermal expansion, shrinkage, creep

Introduction

The earliest use of modulated-temperature programming in thermal analysis to separate thermally reversible from irreversible processes appears to be the work of Garn and Sharp published in 1982 [1,2]. By employing a small sinusoidal temperature wave superimposed on a constant heating rate they were able to distinguish between rapidly reversible pyroelectric currents and the irreversible discharge which occurs over a longer timescale due to the decay of oriented dipoles in thin dielectric polymer films. Ten years later similar principles were described by Reading to deconvolute heat capacity from heat flow arising from time dependant chemical and physical transformations (e.g., polymerization, crystallization and melting) in differential scanning calorimetry (DSC) [3]. Furthermore, modulated-temperature DSC (MTDSC) offers the advantage of increasing the temperature resolution of thermal events without sacrificing sensitivity by a combination of slow underlying scanning rates and rapid temperature modulation [4].

Thermomechanical analysis (TMA) involves measurement of the response of a material to a constant load or deformation as a function of temperature [5]. Although the technique was first applied to polymers in 1948 there is often difficulty in interpreting the results due to the superposition of creep and stress relaxation upon linear thermal

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expansion [6]. Hedvig has described the use of a differential thermomechanical technique to overcome these effects [7]. Since thermal expansion is due to reversible changes in molecular vibrational modes which occur with temperature (c.f., changes in enthalpy due to the absorption or dissipation of heat in DSC) a simpler approach might be to employ modulated-temperature programs in TMA.

Theory

The theory of modulated-temperature TMA (MTTMA) can be developed by direct analogy to the equations used to describe MTDSC by simply substituting the specimen's length or thermal expansivity for enthalpy and heat capacity in the following equation used for MTDSC [3]:

$$dQ/dt = C_p dT/dt + f(t, T) \quad (1)$$

where Q is the amount of heat evolved, C_p the thermodynamic heat capacity, T the absolute temperature, t the time and $f(t, T)$ some function of time and temperature that governs the kinetic response of any chemical or physical transformation.

For MTTMA this becomes:

$$dL/dt = \mathbf{a} dT/dt + f'(t, T) \quad (2)$$

where L is the sample length, \mathbf{a} is the thermal expansion coefficient and $f'(t, T)$ some function of time and temperature that describes dimensional changes due to deformation under the applied load or relaxation of stresses present in (for example) oriented materials. Over a broad temperature range $f'(t, T)$ — the “non-reversing” component of the length change — can be expected to follow an Arrhenius dependence with temperature reflecting the viscous properties of the sample. Providing the period of the temperature modulation covers a small temperature range then — to a first approximation — $f'(t, T)$ can be assumed constant and \mathbf{a} found from the ratio of the amplitudes of the oscillating components of the rate of length change (dL/dt) and the heating rate (dT/dt) [8]. Alternatively, equation (2) can be expressed in its integrated form whereby:

$$DL = \mathbf{a}.DT + g'(t, T) \quad (3)$$

where DL and DT are the changes in length and temperature respectively, $g'(t, T)$ is the integral of $f'(t, T)$. This form is particularly useful for quasi-isothermal measurements (where the underlying heating rate is zero). \mathbf{a} is determined by the ratio of the amplitude of the oscillating part of the length change $\langle A_L \rangle$ divided by the amplitude of the oscillating part of the temperature change $\langle A_T \rangle$. The same technique can be used in MTDSC by exchanging enthalpy (the integral of heat capacity) for length. A pseudo-isothermal analysis (i.e., when the underlying heating rate is non-zero) according to equation (3) is carried out in the implementation of the online deconvolution procedure by TA Instruments using a discrete Fourier transform. Offline deconvolution has the advantage that a choice of models can be used to describe the sample response. This

requires that data are collected at short time intervals for highest resolution of the phase lag and can become computationally expensive for long experiments.

Practical Considerations

No system is capable of responding instantaneously to changes in temperature. For MTTMA there will be a time difference between the temperature modulation and the response of the specimen. This term (the phase lag, \mathbf{d}) arises from two effects: poor heat transfer from the furnace to the specimen (as occurs in MTDSC [9,10]) and any kinetically controlled events within the sample. Furthermore, again due to poor heat transfer, the sample may not be exposed to the same variation in temperature as that recorded by the temperature sensor (although the underlying change in temperature will be the same). This leads to an underestimate of \mathbf{a} which must be corrected by appropriate calibration [11].

Thus, a typical MTTMA experiment yields the thermal expansivity (\mathbf{a}) and phase lag (\mathbf{d}) during the course of the experiment in addition to the average rate of length change ($\langle dL/dt \rangle$) calculated as a sliding average over one modulation period. The non-reversing rate of length change may be calculated by difference between \mathbf{a} and $\langle dL/dT \rangle$. The phase lag may also be used to divide \mathbf{a} into in-phase (\mathbf{a}') and out-of-phase (\mathbf{a}'') components as for MTDSC. For conventional TMA it is usual to normalize thermal expansivity for the initial sample length (L_0). Since MTTMA determines the thermal expansivity on a continuous basis it is more useful to normalise this signal using the average length over one modulation ($\langle L \rangle$) instead of L_0 . This is a similar procedure to using the instantaneous sample mass to normalize the DSC signal from a simultaneous DSC-thermobalance. The derivatives (\mathbf{a} , $\langle dL/dT \rangle$, etc.) may be integrated with time or temperature to determine the reversible length change, total length change and non-reversible length change. Typical examples of this are presented in references 12 and 13. If the specimen is exposed to heating and cooling as a consequence of the temperature program then a technique known as "parsing" may be employed to break down the data into heat/cool/re-heat segments in order to study the effect of thermal history of the sample response [13].

Although low thermal mass samples (such as thin films and fibers examined under tension) make ideal specimens for MTTMA since long, thin samples can be used to improve the signal-to-noise ratio without unduly compromising heat transfer, measurements may also be made under compression for the examination of bulk polymers. Any periodic modulation of temperature may be employed, as well as non-linear underlying temperature programs although, like MTDSC, sinusoidal, square or triangular heating profiles are the simplest to implement.

Experimental

Thermomechanical measurements were carried out on a TA Instruments 2940 TMA [14]. The instrument was fitted with a modified heater assembly which served to pre-heat the purge gas before circulation through the oven. All measurements were carried out under helium (flow rate: 100 ml/min) so as to ensure good thermal coupling between the oven, thermocouple and sample. Temperature calibration according to

ASTM Test Method for Temperature Calibration of Thermomechanical Analyzers (E 1263) was carried out using gallium, indium, tin, bismuth and lead. All measurements described here were made using a circular flat-ended “macro-expansion” probe (part number: 944123-901 from TA Instruments Inc. New Castle DE) of 6.07 mm contact diameter. Additional firmware was provided by the manufacturer to enable a sinusoidal modulation of the oven temperature over a range of operating conditions. In the absence of forced cooling of the oven, it was only practical to perform measurements above ambient temperature and under conditions where the maximum rate of cooling did not exceed 1°C/min. Addition of a cooling accessory (such as a refrigerated recirculator or liquid nitrogen cooling) would extend the operational range of the instrument.

Calibration

Temperature calibration in MTTMA may be carried out by reference to the melting temperatures of pure metal standards as for conventional TMA described above. Riesen and Schawe have discussed this with particular reference to fibers [15]. An additional calibration must also be made to take into account the effect of temperature modulation in calculating the thermal expansion coefficient by MTTMA from the length change data. This is illustrated for a series of aluminum cylinders examined under quasi-isothermal conditions using a $\pm 1^\circ\text{C}$ amplitude temperature modulation at a fixed isothermal temperature of 100°C . α (normalized for the average length of the specimen at 100°C) was calculated as described above. Results for three specimens of different dimensions are shown in Figure 1 along with the theoretical value calculated from data in ASTM Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis (E 831). It can be seen that at long modulation periods the thermal expansion coefficient measured by MTTMA coincides with the literature value. As the modulation period decreases, poor heat transfer to the specimen reduces the amplitude of the temperature modulation experienced by the sample below that recorded by the temperature sensor. This causes an apparent decrease in α . As the period is reduced from 900 to 150 s, the magnitude of this effect appears to follow the order of the specimen's size, indicating that low thermal mass samples and/or long modulation periods are to be preferred in this technique.

Practical considerations, however, mean that it is not always possible to use ideal conditions — therefore a correction must be applied depending on the thermal resistance of the system. In the absence of any non-reversible changes occurring in the sample (usually at the beginning of the experiment) the average rate of change in length ($\langle dL/dT \rangle$) should equal the reversing rate of length (determined from the ratio of the amplitudes of the modulated length ($\langle A_L \rangle$) and modulated temperature ($\langle A_T \rangle$)). Thus it is possible to derive a calibration factor (K) to correct for poor heat transfer:

$$K = \frac{\langle A_L \rangle / \langle A_T \rangle}{\langle dL/dT \rangle} \quad (4)$$

Although K will be a function of the thermal diffusivity of the specimen (and the efficiency of heat transfer from the furnace to the sample), once determined, K can

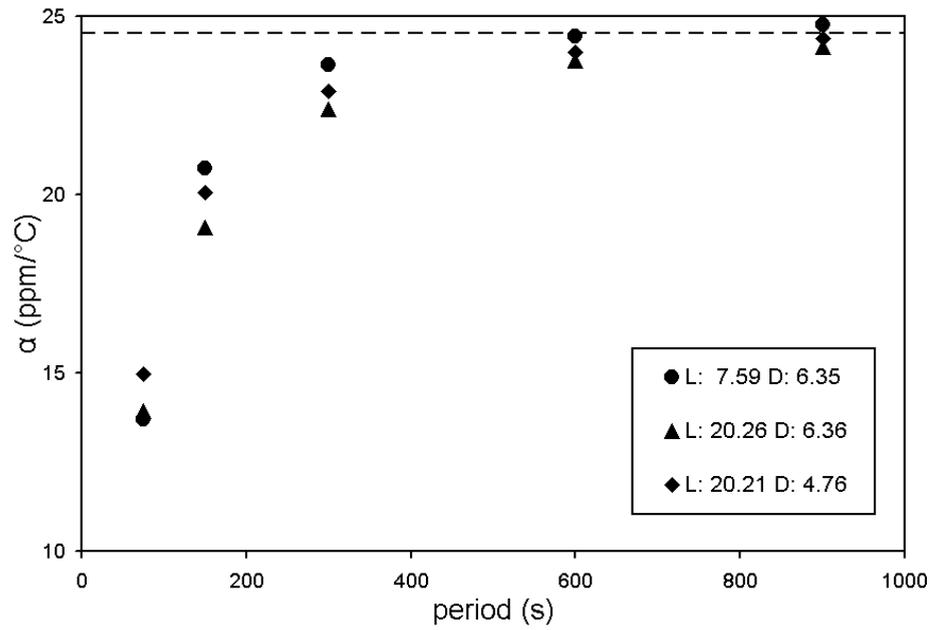


Figure 1 — *Uncorrected thermal expansion coefficient (α) of different cylinders of aluminum of length (L/mm) and diameter (D/mm) indicated as a function of modulation period under quasi-isothermal conditions about a mean temperature of $100^{\circ}C$. Literature value indicated by a dashed line.*

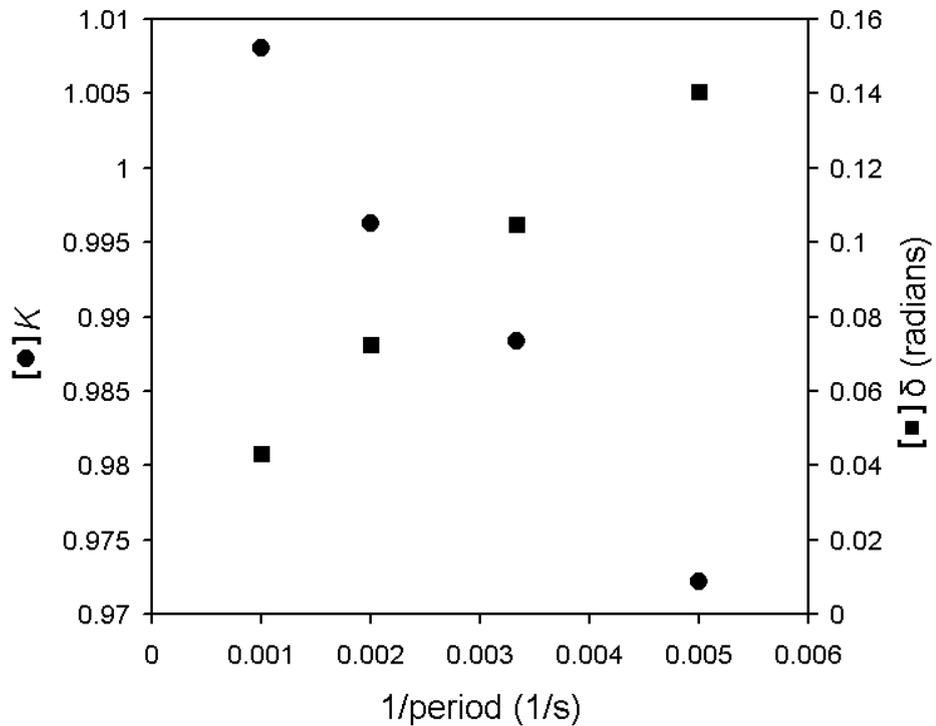


Figure 2 — *Thermal expansion calibration factor (K) and initial phase lag (d) versus the reciprocal of the modulation period for a sample of epoxy resin.*

generally be assumed to be constant during the course of the experiment. The corrected value of \mathbf{a} is then given by:

$$\mathbf{a} = \frac{\langle A_L \rangle / \langle A_T \rangle}{K \cdot \langle L \rangle} \quad (5)$$

In the absence of any irreversible length change occurring then K can be easily recalculated at any time during the experiment. If K is plotted as a function of frequency ($=1/\text{period}$) then an almost linear trend results (Figure 2). This observation suggests that use of a temperature modulation containing several frequencies (or simply scanning in frequency at a constant temperature) might afford an alternative means of calibration. Figure 2 also indicates that the phase lag also appears to be a simple function of modulation frequency. Correction of the phase lag for MTTMA is done by an analogous method to that described by Aubuchon and Gill for MTDSC [16]. Ancillary experiments demonstrate that if the amplitude of the modulation is increased (at the same period) K will decrease and that similar statements can be made concerning the dependence of the phase lag as a function of modulation conditions. Multi-frequency MTDSC experiments have been described by Reading et al. using a combination of two sinusoidal temperature modulations [17]. Recently, Androsch and Wunderlich have described the use of a triangular heating profile with a full Fourier transform to extract the heat capacity correction factor for MTDSC experiments [18]. Both approaches would appear to afford an alternative means of calibration in MTTMA.

MTTMA of the Glass Transition

Typical raw data from a MTTMA experiment on a block of cured epoxy resin (bisphenol-A-epichlorohydrin/triethylene tetramine, Struers "Epofix") are shown in Figure 3. It is possible to discern the modulation in length of the specimen brought about by the modulation in its temperature. Deconvolution of the signals into average length ($\langle L \rangle$), thermal expansion coefficient (\mathbf{a}), $\langle dL/dT \rangle$ (ie. the derivative of the average length vs. temperature) and phase lag (\mathbf{d}) is shown in Figure 4. From the plot of the average length vs. temperature it is difficult to define the glass-rubber transition temperature of the material. The $\langle dL/dT \rangle$ plot does not aid interpretation either. The thermal expansion coefficient, however, clearly shows a step increase at the glass-rubber transition very much like the corresponding change in heat capacity observed for DSC. The glass transition temperature (T_g) may readily be assigned as the extrapolated onset of this process (or some other convenient point on this curve). The phase lag shows a characteristic peak similar to that seen in MTDSC during devitrification. The expansivity and phase lag curves above T_g appear to show a high temperature tail compared the typical shapes that one would expect for a glass transition (a sigmoidal step in \mathbf{a} and Gaussian peak in \mathbf{d} respectively) which might indicate that there is some other process occurring alongside devitrification.

A repeat run on the same sample was performed after allowing the instrument to cool slowly to room temperature. The data from both experiments are overlaid in Figure 5. The glass transition of the specimen has now increased by about 10°C suggesting that the initial material was incompletely cured. The distorted shapes of the plots of \mathbf{a} and \mathbf{d}

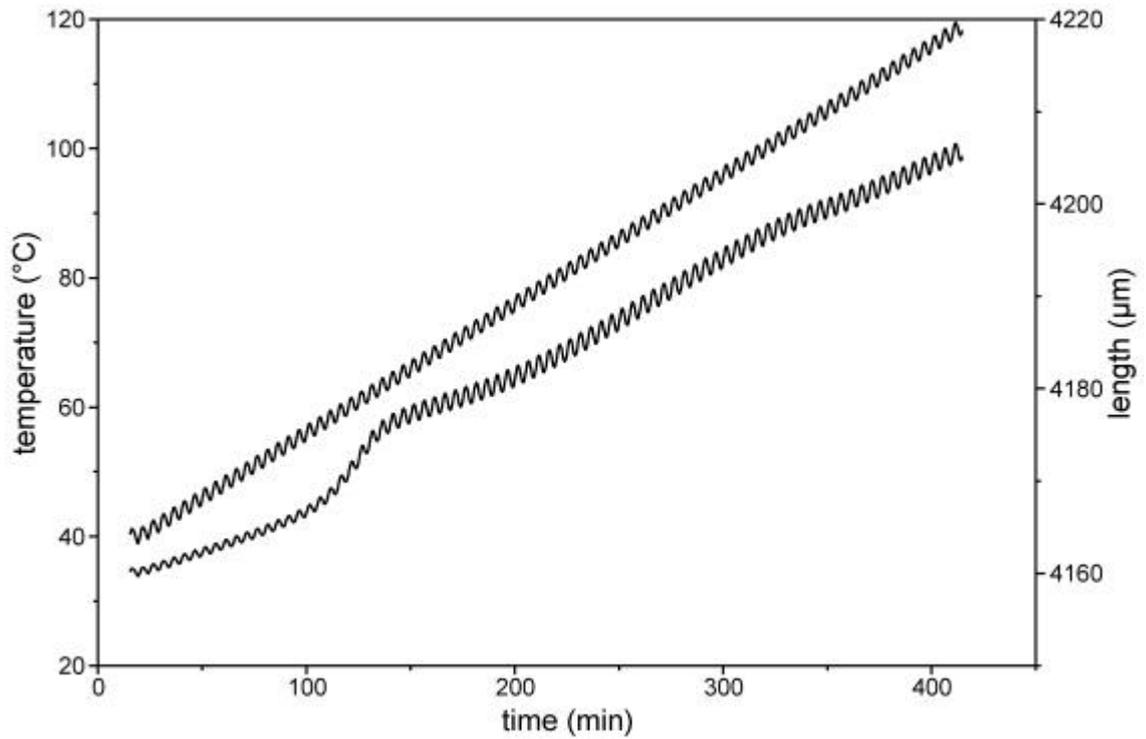


Figure 3 — Raw data for a sample of epoxy resin heated at $0.2^{\circ}\text{C}/\text{min}$ with a 1°C amplitude, 300 s temperature modulation (top: temperature, bottom: length).

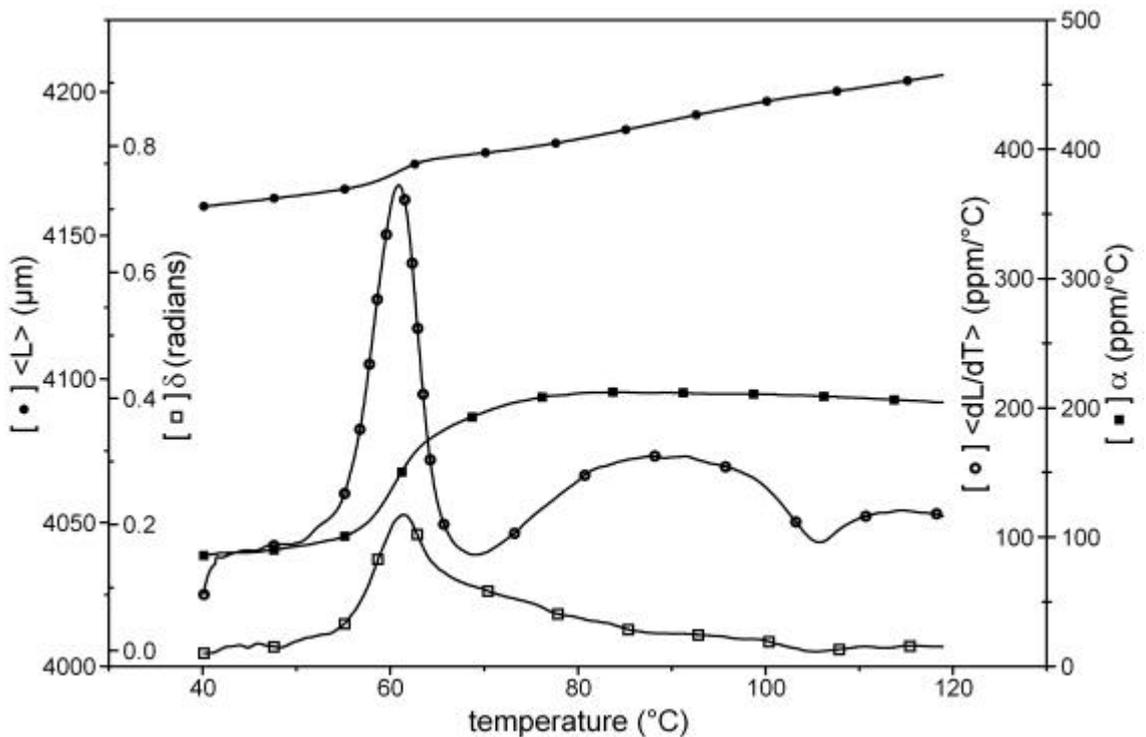


Figure 4 — Deconvoluted data from figure 3 (\circ : average length $\langle L \rangle$), \square : expansion coefficient (α), \circ : average rate of length change $\langle dL/dT \rangle$, \circ : phase lag (δ).

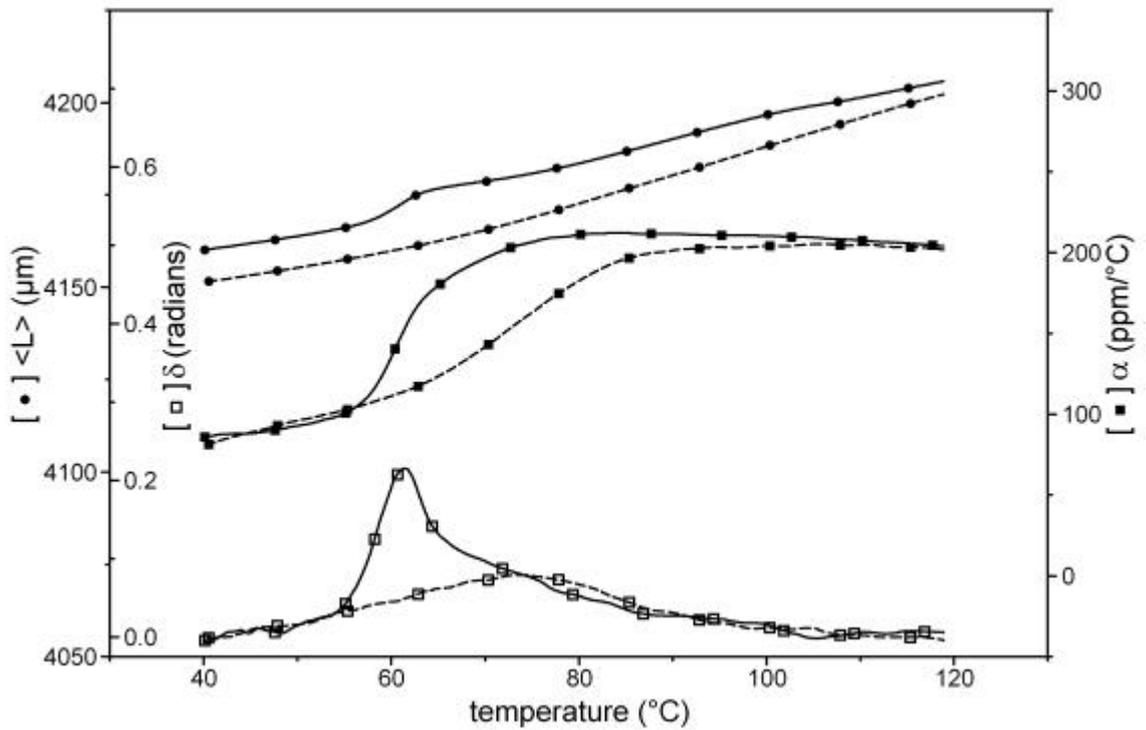


Figure 5 — Initial (solid lines) and repeat (broken lines) scans on epoxy resin (\circ : average length $\langle L \rangle$, \square : expansion coefficient (α), \bullet : phase lag (δ)).

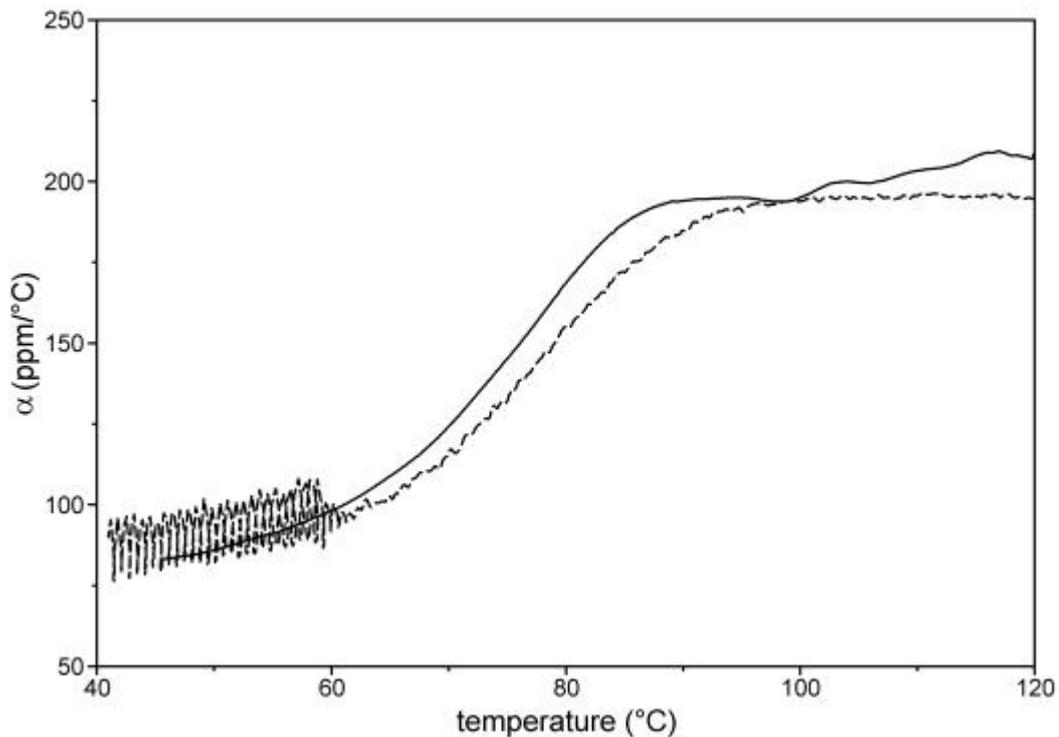


Figure 6 — Cooling scans at different modulation periods of 1000 s (solid line) and 100 s (broken line).

discussed above are presumably a consequence of further cross-linking taking place during the initial temperature scan. Further thermal cycling of the sample resulted in no change in properties.

The effect of modulation frequency on the measurement of the glass transition was investigated by performing cooling scans on the fully cured epoxy resin sample at the same underlying cooling rate but different modulation periods. Plots of thermal expansion coefficient vs. temperature for measurements at 100 s and 1000 s period are shown in Figure 6. The noise in the data obtained at 100 s period below 60°C is due to loss of proper modulation due to insufficient cooling capacity of the instrument. As would be expected by analogy with heat capacity measurements, there is a shift in the position of the T_g to higher temperatures with shorter modulation periods [19]. The apparent activation energy for the glass transition was found to be 459 ± 2 kJ/mol from an Arrhenius plot of the dependence of T_g on modulation period.

MTTMA of Melting

The reorganization of polymers as they are heated through their melting transition has been widely studied by MTDSC [20-23]. Although the melting of flexible macromolecules is an irreversible process, some of the overall melting may be reversible due to inherent annealing and crystal perfection. In order to investigate this phenomenon by MTTMA, identical experiments were conducted on a sample of poly(ethylene terephthalate) (PET) kindly supplied by ICI using the 2940 TMA and a TA Instruments 2920 MDSC operating in standard DSC mode. A temperature program consisting of twenty linear heat-cool ramps at 1°C/min over a temperature range of 5°C was applied in a step-wise isothermal fashion every 5°C. In effect this gives a triangular temperature modulation of $\pm 2.5^\circ\text{C}$ with a period of 600 s. It should be noted that such a waveform can be synthesized by a summation of a series of sine waves of with a fundamental period (p) of 600 s and amplitude (A_T) 2.5°C plus odd harmonics ($p/3 = 200$ s, $p/5 = 120$ s, ...) with decreasing amplitudes ($A_T/9$, $A_T/25$, ...). The data from these experiments were analysed according to equation 3. For the DSC data it was necessary to integrate the heat flow with respect to time to obtain the cumulative enthalpy of the sample. By subtracting a moving average over one modulation the oscillating components of L and T are obtained (H and T for the DSC experiment). \mathbf{a} (and C_p) are then obtained by a linear fitting procedure using the phase lag as an adjustable parameter to shift the data until the best fit is achieved [24].

Plots of \mathbf{a} and C_p are shown in Figure 7 for both techniques. At each isotherm there is a characteristic decay in the parameter with time to reach a steady state value. The shape of the decay curves was fitted to a single exponential decay similar to that used by Schick et al. [25]:

$$y(t) = A + B \exp[-(t-t_0)/\tau] \quad (6)$$

where $y(t)$ is the value of \mathbf{a} or C_p at time (t), t_0 is the start time of the isotherm, A and B are constants and τ is the relaxation time of the decay. It should be noted that Ozaki and Wunderlich have fitted similar C_p data to a double exponential decay and that recent work by Schick et al. use a Kohlrausch-Williams-Watts stretched exponential to describe

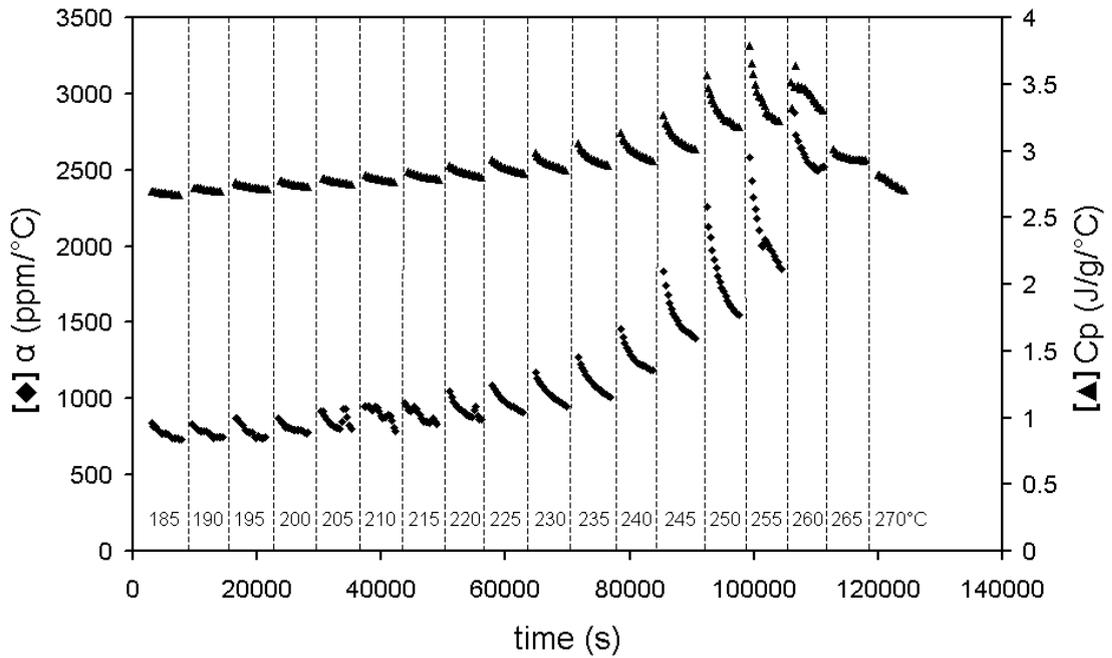


Figure 7 — Heat capacity (C_p (\blacktriangle)) and thermal expansion coefficient (α (\blacklozenge)) for PET during stepwise isothermal melting from 185 to 270°C in 5°C increments.

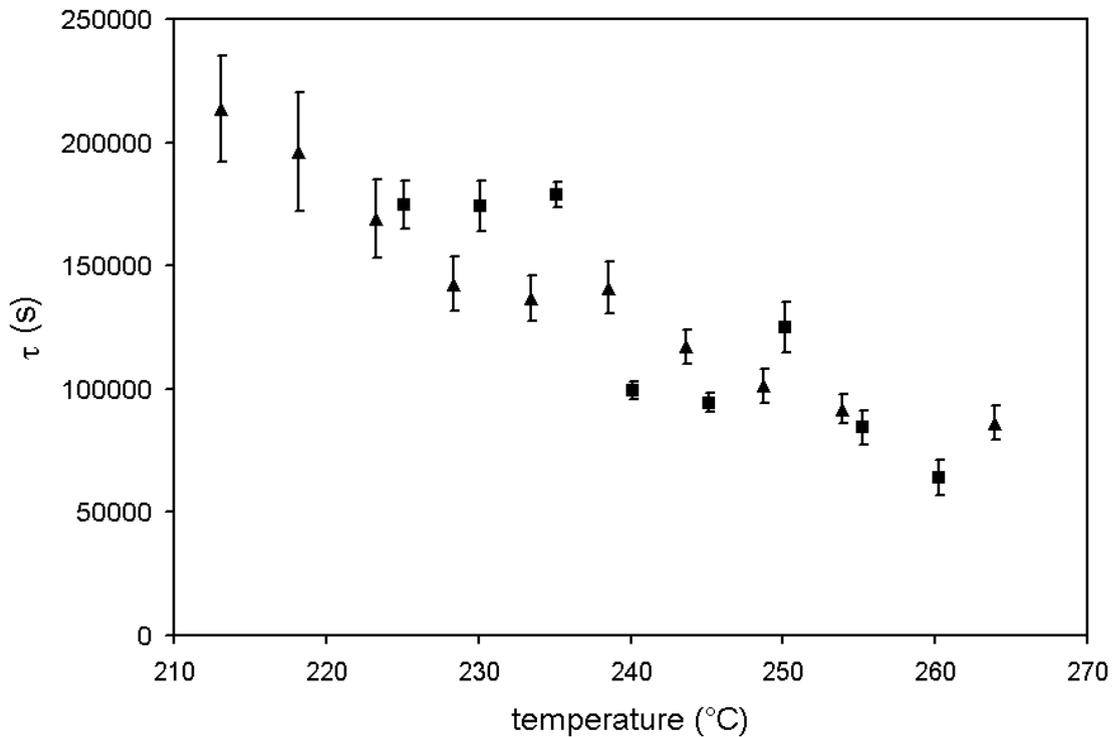


Figure 8 — Relaxation times from TMA (\blacksquare) and DSC (\blacktriangle) studies of PET melting.

the same process [20, 23]. In the present study, little improvement in fitting quality was achieved by using a more sophisticated expression. No attempt has been made to extract the frequency dependence of α and C_p through the melt although such information is contained in the raw data due to the use of a triangular waveform as discussed above.

A plot of the relaxation times to reach equilibrium is shown in Figure 8. There is reasonable agreement between both techniques given the crude nature of these measurements. Schick et al. have used modulated-temperature dynamic mechanical analysis (MTDMA) to follow reversible melting and crystallization in a number of polymers [25-28]. MTDMA would appear to be more sensitive to the final stages of these processes than MTDSC.

Conclusions

The benefits of applying a temperature modulation to the conventional linear change in temperature commonly employed in thermomechanical analysis have been illustrated by reference to the study of the glass-rubber transition of a thermosetting resin and the melting process of a semicrystalline thermoplastic polymer. Modulated-temperature TMA permits the measurement of coefficients of linear thermal expansion under quasi-isothermal conditions and allows the time dependence of relaxation phenomena to be studied. The irreversible effects of creep and stress relaxation may also be examined independently of reversible changes in dimensions that occur due to thermal expansion, thus simplifying the interpretation of such experiments.

References

- [1] Garn, L. E., and Sharp, E. J., *Journal of Applied Physics*, Vol. 53, 1982, p. 8974.
- [2] Sharp, E.J., and Garn, L. E., *Journal of Applied Physics*, Vol.53, 1982, p. 8980.
- [3] Reading, M., *Trends in Polymer Science*, Vol. 1, 1993, p. 248.
- [4] Golbrecht, H., Hammann, K, and Willers, G., *Journal of Physics E: Scientific Instruments*, Vol. 4, 1971, p. 21.
- [5] Neag, C. M., *Material Characterization by Thermomechanical Analysis*, STP 1136, A. Riga and C.M. Neag, Eds., American Society for Testing and Materials, Philadelphia, 1991 pp. 3-21.
- [6] Wetton, R.E., *Handbook of Thermal Analysis and Calorimetry. Vol. 1: Principles and Practice*, M. E. Brown, Ed., Elsevier Science B.V., Amsterdam, 1998 pp. 363-399.
- [7] Hedvig, P., *Applied Polymer Analysis and Characterization: Recent Developments in Techniques, Instrumentation, Problem Solving*, J. Mitchell Jr. (Ed.), Hanser, Munich, 1987 pp. 297-312.
- [8] Price, D. M., *Thermochimica Acta*, Vol. 315, 1998, p. 11.
- [9] Schawe, J. E. K., and Winter, W., *Thermochimica Acta*, Vol. 298, 1997, p. 9.
- [10] Cser, F., Rasoul, F., and Kosier, E., *Journal of Thermal Analysis*, Vol. 50, 1997, p. 727.
- [11] Price, D. M., US Patent 6,007,240, 28 Dec. 1999.
- [12] Price, D. M., *Journal of Thermal. Analysis*, Vol. 51, 1998, p. 231.

- [13] Price, D. M., and Foster, G. M., *Journal of Thermal Analysis and Calorimetry*, Vol. 56, 1999, p. 649.
- [14] Sauerbrunn, S. R., and Gill, P. S., *Material Characterization by Thermomechanical Analysis*, STP 1136, A. Riga and C.M. Neag, Eds., American Society for Testing and Materials, Philadelphia, 1991 pp. 120-125.
- [15] Riesen, R., and Schawe, J. E. K., *Journal of Thermal Analysis and Calorimetry*, Vol. 59, 2000, p. 337.
- [16] Aubuchon, S. R., and Gill, P.S., *Journal of Thermal Analysis*, Vol. 49, 1997, p. 1039.
- [17] Reading, M., Wilson, R., and Pollock, H. M., *Proceedings of the 23rd North American Thermal Analysis Society Conference*, Toronto (1994) pp. 2-11.
- [18] Androsch, R., and Wunderlich, B., *Thermochimica Acta*, Vol. 333, 1999, p. 27.
- [19] Birge, N. O., and Nagel, S. R., *Physical Review Letters*, Vol. 54, 1985, p. 2674.
- [20] Okazaki, I, and Wunderlich, B., *Macromolecular Rapid Communications*, Vol. 18, 1997, p. 313.
- [21] Schawe, J. E. K., and Bergmann, E., *Thermochimica Acta*, Vol. 304/305, 1997, p. 179.
- [22] Toda, A., Tomita, C., Hikosaka, M., and Saruyama, Y, *Polymer*, Vol. 39, 1998, p. 5093.
- [23] Schick, C., Merzlykov, M., and Wunderlich, B., *Polymer Bulletin*, Vol. 40, 1998, p. 297.
- [24] Reading, M., US Patent 5,474,385, 12 Dec. 1995.
- [25] Schick, C., Merzlyakov, M., and Wurm, A., *Proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering*, Vol. 78, 1998, p. 123.
- [26] Wurm, A., Merzlyakov, M., and Schick, C., *Colloid and Polymer Science*, Vol. 276, 1998, p. 289.
- [27] Wurm, A., Merzlyakov, M., and Schick, C., *Journal of Thermal Analysis and Calorimetry*, Vol. 56, 1999, p. 1155.
- [28] Wurm, A., Merzlyakov, M., and Schick, C., *Thermochimica Acta*, Vol. 330, 1999, p. 121.