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THEORY AND APPLICATIONS OF MODULATED TEMPERATURE PROGRAMMING TO THERMOMECHANICAL TECHNIQUES

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Abstract

The application of modulated temperature programs to thermomechanical analysis can be used 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. Modulated temperature TMA allows the time-dependent nature of thermal expansivity to be studied. Measurements made under compression afford a means of measuring the thermal expansivity of soft specimens independently of initial load. Application of these principles to scanning thermal microscopy leads to a novel method of generating image contrast based upon local changes thermal expansivity of a specimen.

Keywords: creep, modulated temperature, thermomechanical analysis, thermal expansion

Introduction

When a material is heated, it usually expands. On cooling, it generally returns to its original dimensions. This is reversible thermal expansion and the rate of change of length with respect to temperature is the thermal expansion coefficient of the material. However, if the specimen softens as it is heated and (as is often the case for TMA) it is subjected to a mechanical load, then it will flow and creep. This deformation is permanent and the specimen will not recover its original length on cooling. Alternatively, if the material was stretched when soft and then cooled before the experiment, residual stresses will have been left in the sample. On heating these will relax and the specimen will shrink. It can only be made to return to its original length by the original drawing process. The length changes measured by conventional TMA are therefore a combination of these effects unless the specimen is completely isotropic and measurements are made under zero load (thermodilatometry). If, however, a modulated temperature program (such as those used in modulated temperature differential scanning calorimetry (MT-DSC)) is employed (rather than the conventional linear temperature ramp) then it is possible to separate the temperature dependent

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thermal expansion from the time (and temperature) dependent creep or stress relaxation behaviour according to the equation:

$$\frac{dL}{dt} = \alpha \frac{dT}{dt} + f'(t,T) \quad (1)$$

where L is the sample length, α 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. This technique is known as modulated temperature TMA (MT-TMA) [1–4].

Initial studies by MT-TMA on oriented films and fibres showed that it was possible to measure the underlying thermal expansion of oriented materials whilst they relaxed to the unoriented state [1, 3]. Dynamic load MT-TMA is also possible [3, 4] and modulated temperature dynamic mechanical analysis has also been developed [5]. In this paper, the effect of experimental variables and calibration are addressed as well as describing a new form of scanning probe microscopy, which exploits the principles of MT-TMA to generate image contrast based upon the specimen's thermal expansivity.

Experimental

Thermomechanical analysis

Thermomechanical measurements were carried out on a TA Instruments 2940 TMA. The instrument was fitted with a modified heater assembly, which served to preheat the purge gas before circulation through the furnace. All measurements were carried out under helium (flow rate: 100 ml min^{-1}) so as to ensure good thermal coupling between the furnace, thermocouple and sample. Temperature calibration was carried out according to ASTM test method for temperature calibration of thermomechanical analyzers (E1263) 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. The manufacturer supplied additional firmware to enable a sinusoidal modulation of the oven temperature and perform online deconvolution of the data in a similar fashion to that used for MT-DSC. Surrounding the furnace with a coil through which water was circulated served to provide additional cooling. This made it possible to perform measurements above ambient temperature under conditions where the maximum rate of cooling did not exceed 4°C min^{-1}.

Scanning thermal expansion microscopy

Scanning thermal expansion microscopy (SThEM) was carried out using a Thermo-Microscopes Explorer scanning probe microscope. The instrument was fitted with a silicon nitride cantilever which had a thin palladium strip deposited across the apex of the tip [6]. This functioned as a heater and a resistance thermometer so that measure-

ments of the heat flux from the tip to the surface could be used as a means of mapping the specimen's thermal conductivity from the electrical power required to hold the tip at a constant temperature above that of the sample [7]. Additional electronics were used to modulate the tip temperature by ±3°C about a mean temperature of 40°C at 1 kHz and a lock-in amplifier was used to isolate the resulting *z*-axis displacement corresponding to the same frequency as the temperature modulation [8].

Results and discussion

Correction of thermal expansion coefficient for thermal gradients

The basic equations for MT-TMA calculate the thermal expansivity of the specimen from the ratio $\langle A_L \rangle / \langle A_T \rangle$, where $\langle A_L \rangle$ is the amplitude of the specimen's length change and $\langle A_T \rangle$ is the amplitude of the temperature modulation. In an ideal experiment $\langle A_T \rangle$ experienced by the sample would be the same as that recorded by the temperature sensor placed nearby. Due to the physical size of the specimen and addenda, the sample the temperature modulation is damped due to poor heat transfer. This means that the measured thermal expansivity determined from the ratio of the amplitudes of modulated length and temperature is less than the underlying length change of the sample measured from the slope of the underlying length *vs*. temperature profile, $\langle \mathrm{d}L/\mathrm{d}T \rangle$. In the absence of any irreversible dimensional changes (i.e., creep or stress relaxation) $\langle A_L \rangle / \langle A_T \rangle$ should equal $\langle \mathrm{d}L/\mathrm{d}T \rangle$. Thus it is possible to derive a calibration factor (K) to correct for this effect [9]:

$$K = \frac{\dfrac{\langle A_L \rangle}{\langle A_T \rangle}}{\left\langle \dfrac{\mathrm{d}L}{\mathrm{d}T} \right\rangle} \tag{2}$$

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 generally be assumed to be constant during the course of the experiment. The corrected value of α is then given by:

$$\alpha = \frac{\dfrac{\langle A_L \rangle}{\langle A_T \rangle}}{K \langle L \rangle} \tag{3}$$

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/period) then it is apparent that at low frequencies K is almost constant (and equal to unity). As the frequency increases there is an approximately linear decrease in K (Fig. 1). Figure 1 also indicates that the phase lag also appears to be a simple function of modulation frequency. Similar behaviour has been observed in MT-DSC [10]. Correction of the phase lag for MT-TMA was done by an analogous

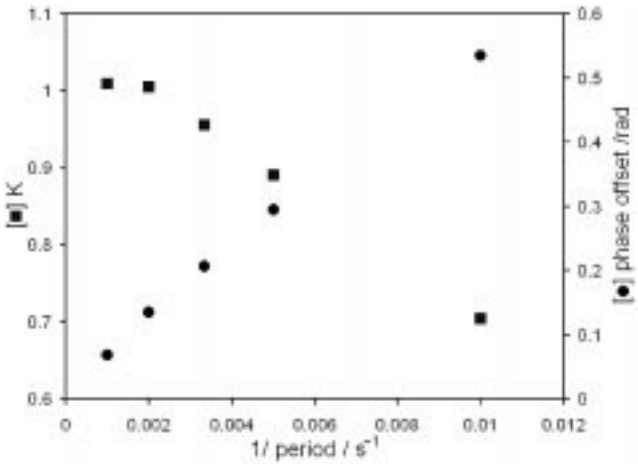

Fig. 1 Effect of period on K and δ

method to that described by Aubuchon and Gill for MT-DSC simply by subtracting the phase lag in a region where no changes in the materials properties are expected [11]. 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.

Effect of period on the glass transition

Figure 2 shows the effect of changing the modulation period on the thermal expansion coefficient of polystyrene (Shell Carinex, M_n=103 kg mol^{-1}, M_w/M_n=2.1) after

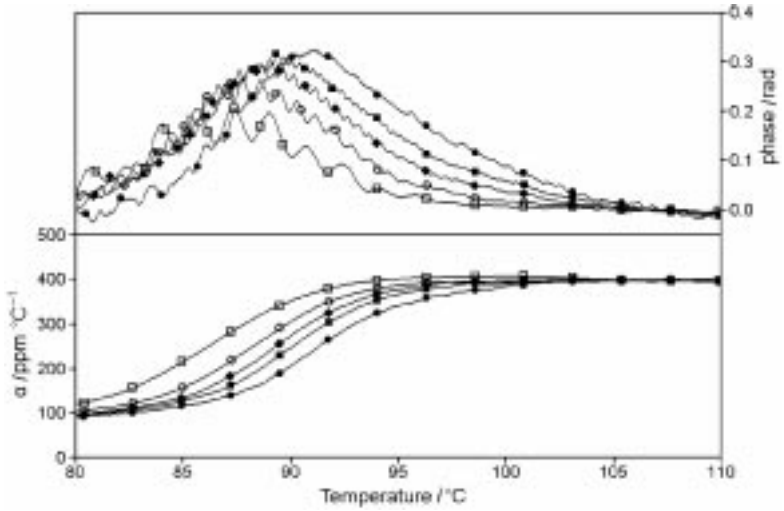

Fig. 2 Effect of period on α for polystyrene, ● – 100 s, ◆ – 200 s, ■ – 300 s, o – 500 s, □ – 1000 s

calibration of the data as described above. As the timescale of the modulation is decreased, the position of the step increase in α moves to a higher temperature. If we take the inflection point of the curves as a measure of T_g then the apparent activation energy (ΔE_a) for this process can be calculated from a plot of $1/T_g$ *vs.* ln(1/period). An analogous effect has been observed in A.C. calorimetry and MT-DSC [12, 13]. Another way of determining ΔE_a is by making measurements at different cooling rates. Results from measurements by conventional TMA and MT-TMA for this material are shown in Fig. 3. Activation energies of 650±60 and 530±50 kJ mol^{-1} were found from cooling rate and modulated temperature studies respectively. A wide variety of thermal methods can be used to determine this parameter, covering different temperature ranges and effective timescales for the measurement [14]. A plot of ΔE_a *vs.* temperature for this material is shown in Fig. 4 – there is an increase in ΔE_a with decreasing temperature which can be fitted to the Vogel–Fulcher–Tamman equation: $\Delta E_a(T)/RT=A/(T-T_0)$ where A=5031 K and T_0=337 K [15].

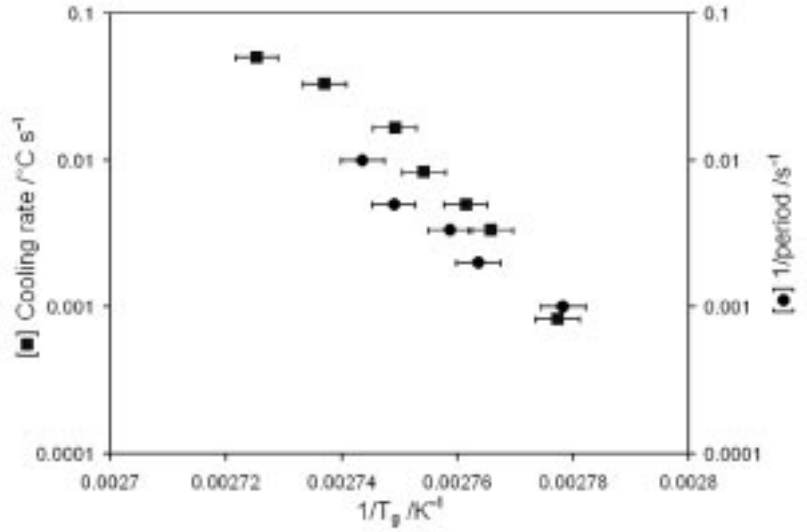

Fig. 3 Plot of reciprocal glass transition temperature *vs*. cooling rate (■) and reciprocal modulation period (●) for polystyrene. Data corrected for thermal lag and other instrumental effects

Effect of load on MT-TMA data

In addition to providing the usual information from a thermomechanical measurement (i.e., length *vs.* temperature or time), MT-TMA also gives the thermal expansivity of the sample and the phase lag between the temperature modulation and the specimen response [16]. It has been demonstrated that, providing the system response is linear – in the absence of gross deformation of the sample during the temperature modulation – the thermal expansivity of soft samples (such as a polymer above T_g)

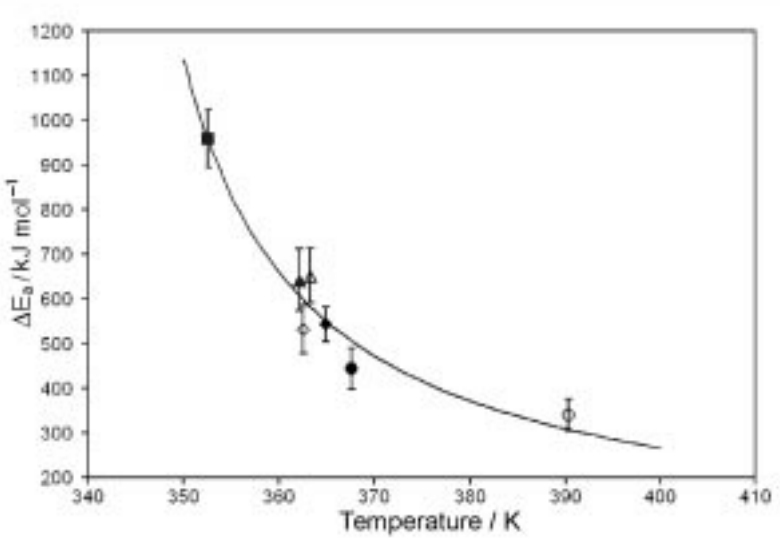

Fig. 4 Plot of apparent activation energy for the glass–rubber transition (ΔE_a) *vs.* temperature for polystyrene measured by a variety of techniques (■ – enthalpy relaxation, ▲ – DSC cooling, ◆ – MT-DSC, Δ – TMA cooling, ◊ – MT-TMA, ● – mechanical spectroscopy and o – dielectric spectroscopy). Solid line indicates fit to the Vogel–Fulcher–Tamman equation (see text)

can be measured independent of choice of initial load. This is illustrated in Fig. 5 for cylindrical samples of PMMA measured under different loads. In this case the phase lag information is employed to resolve the thermal expansivity into in-phase and out-of-phase components. The former represents the 'true' thermal expansivity of the

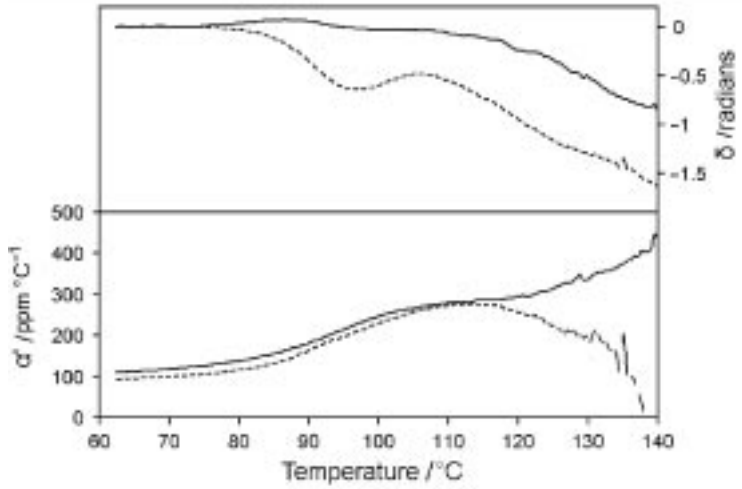

Fig. 5 Effect of load on α′ (in-phase reversing dL/dT) and δ (phase lag) (solid line – 3.4 kPa, broken line – 34 kPa)

specimen. Above 115°C the ongoing creep of the specimen means that the sample response is no longer linear with temperature over the time-scale of the temperature modulation and the curves measured under different loads diverge. This effect can be suppressed until higher temperatures by the use of shorter period and/or lower amplitude temperature modulation as for MT-DSC. The effect of load on the phase lag is interesting – at low load a positive peak is seen in δ whereas at a higher load a negative peak is seen. As yet, this effect is unexplained.

Scanning thermal expansion microscopy

The principles behind MT-TMA can be applied to scanning thermal microscopy so as to generate image contrast based upon the specimen's surface thermal expansivity. In this case an actively heated tip is employed (like those used for micro-thermal analysis [17]). An A.C. temperature modulation is applied to the probe and the resulting expansion and contraction of the surface due to the applied thermal wave is detected via the microscope feedback loop. The amplitude of this movement is used to build up an image of the surface [17, 18]. An example of this is illustrated in Fig. 6 for a sample of metal foil (higher thermal conductivity and lower thermal expansivity) embedded in a cross-linked epoxy resin. Similar measurements have been reported by Varesi and Majumdar who employed a conventional AFM to detect the thermal expansion of Joule-heated elements as a means of mapping temperature distributions [19]. Some advantages of using an active thermal probe to inject heat into the sample are that electrically conductive substrates are not required and that topographic, thermal conductivity and thermal expansivity images may be acquired simultaneously. Localised modulated-temperature thermomechanical measurements (i.e., point measurements, where the modulation is superimposed upon a linear temperature ramp) have also been carried out [20].

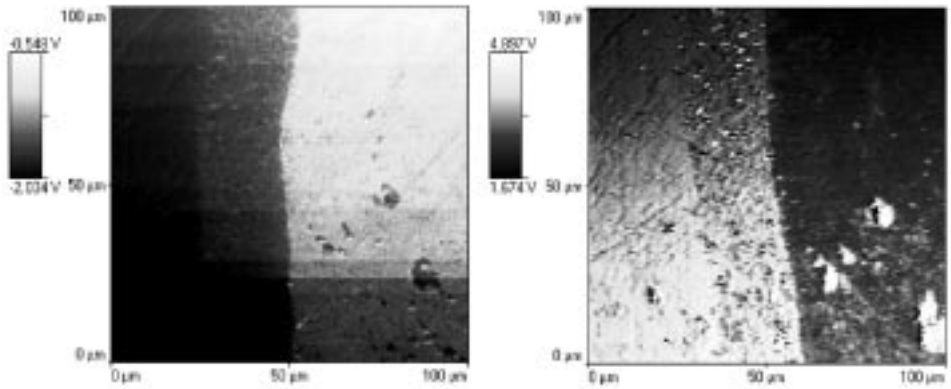

Fig. 6 Thermal conductivity (left) and expansivity (right) of polymer/metal interface – metal is on the right

Conclusions

Modulated temperature thermomechanical analysis provides additional insights into time and temperature dependent dimensional changes that occur in materials. The calibration procedures are similar to MT-DSC where the effects of heat transfer need to be taken into account. The effect of modulation period on the glass–rubber transition of polymers shows the same behaviour as that observed in MT-DSC although the effect of initial loading conditions remains to be investigated further. Modulated temperature programming may be used in scanning thermal microscopy to generate image contrast based upon localised differences in the specimen's thermal expansivity.

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