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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 TMA 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 will be 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.

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 usual in the case of 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 MT-DSC) is employed rather than the conventional linear temperature ramp then it is possible to separate the temperature dependent thermal expansion from the time (& temperature) dependent creep or stress relaxation behavior according to the equation:

$$dL/dt = \alpha\ dT/dt + f'(t,T)$$

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 fibers 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 MT-DMA 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 measurements were carried out on a TA Instruments 2940 TMA. The instrument was fitted with a modified heater assembly which served to pre-heat the purge gas before circulation through the furnace. All measurements were carried out under helium (flow rate: 100 ml/min) 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. 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. The addition of a cooling accessory (such as a refrigerated recirculator or liquid nitrogen cooling) would extend the operational range of the instrument.

RESULTS AND DISCUSSION

1. 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 adenda, 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, $\langle dL/dT \rangle$. In the absence of any irreversible dimensional changes (i.e. creep or stress relaxation) $\langle A_L \rangle / \langle A_T \rangle$ should equal $\langle dL/dT \rangle$. Thus it is possible to derive a calibration factor (K) to correct for this effect:

$$K = \frac{< A_L > / < A_T >}{< dL/dT >}$$

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 a is then given by:

$$a = \frac{< A_L > / < A_T >}{K. < L >}$$

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 an almost linear trend results (figure 1). 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 1 also indicates that the phase lag also appears to be a simple function of modulation frequency. Correction of the phase lag for MT-TMA was done by an analogous method to that described by Aubuchon and Gill for MT-DSC *(6)*. 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.

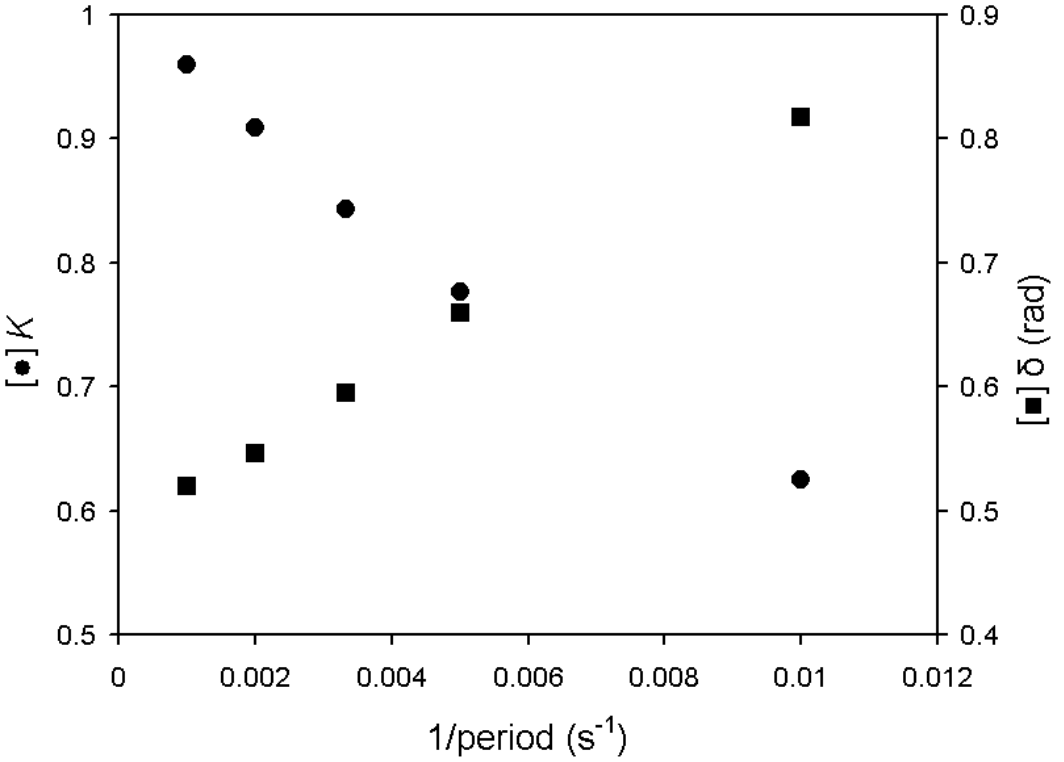

Figure 1. Effect of period on K and d

2. Effect of period on the glass transition.

Figure 2 shows the effect of changing the modulation period on the thermal expansion coefficient of poly(methyl methacrylate) (PMMA) after calibration of the data as described above. As the timescale of the modulation is decreased, the position of the step increase in a 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 for this process (in this case 480±50 kJ/mol) can be calculated from an Arrhenius plot. Such effects have been observed in AC calorimetry *(7)* and MT-DSC - there is potential for overlap of these techniques to provide new insights into the time dependence of vitrification processes.

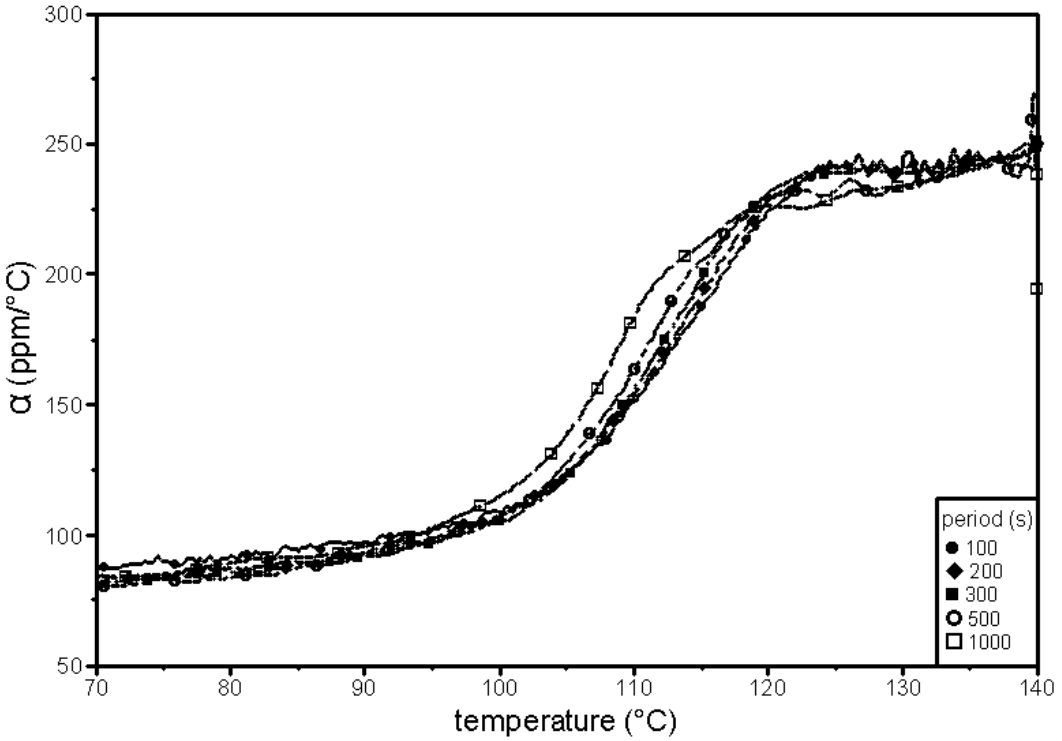

Figure 2. Effect of period on a

3. Effect of load on the MT-TMA curves.

In addition to providing the usual information from a thermomechanical measurement (i.e. length vs. temperature or time), MT-TMA also gives the "true" thermal expansivity of the sample and the phase lag between the temperature modulation and the specimen response. It has been demonstrated that, providing the system response is linear (i.e. in the absence of gross deformation of the sample during the temperature modulation), the thermal expansivity of soft samples (such as a polymer above Tg) can be measured independent of choice of initial load. This is illustrated in figure 3 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 specimen. Above 115°C the ongoing creep of the specimen means that the sample response is no longer linear with temperature over the timescale of the temperature modulation and the curves measured under different loads diverge. This effect can be suppresses 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 in seen in d whereas at a higher load a negative peak is seen. As yet, this effect is unexplained.

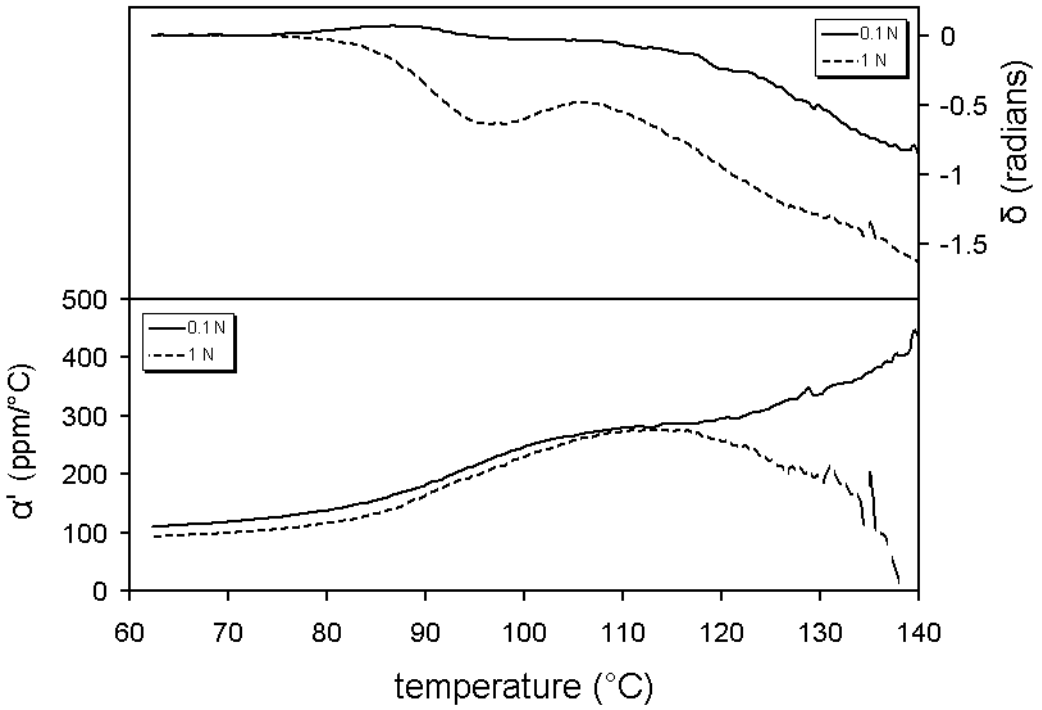

Figure 3. Effect of load on a' (in-phase reversing dL/dT) and d (phase lag)

4. 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). An A.C. temperature modulation is applied to the scanning 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 *(8)*. An example of this is illustrated below for a sample of metal foil (higher thermal conductivity and lower thermal expansivity) embedded in a cross-linked epoxy resin.

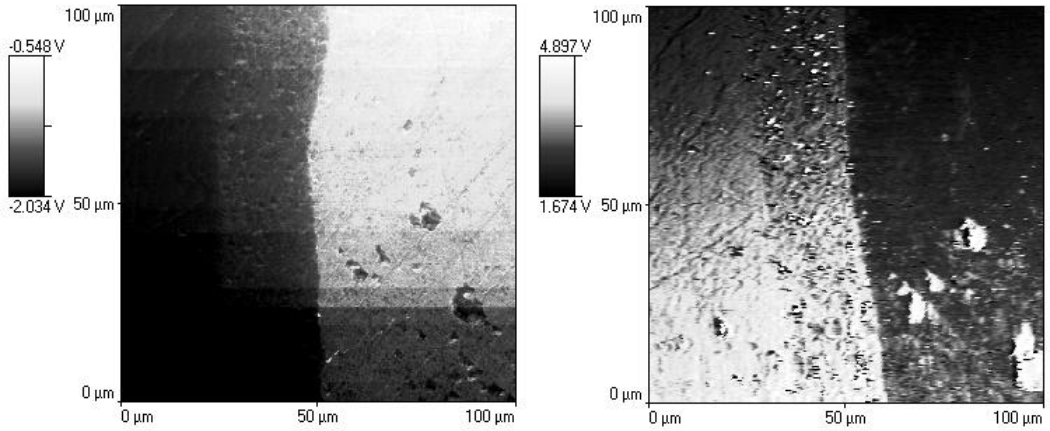

Figure 4. Thermal conductivity (left) & expansivity (right) of polymer/metal interface - metal is on the right.

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. Superposition of a dynamic load in addition to a modulated temperature program yields a form of MT-DMA and the technique may be used in Scanning Thermal Microscopy to generate image contrast based upon localized differences in the specimen' s thermal expansivity.

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