PROCEEDINGS OF THE TWENTY-SIXTH CONFERENCE OF THE NORTH AMERICAN THERMAL ANALYSIS SOCIETY, SEPTEMBER 13-15, 1998, CLEVELAND, OHIO

# MODULATED-TEMPERATURE THERMOMECHANICAL ANALYSIS

D. M. Price, IPTME, Loughborough University, Loughborough LE11 3TU U.K.
D.M.Price@lboro.ac.uk

## ABSTRACT

The application of modulated temperature programming to thermomechanical analysis affords a method for separating 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. Measurements may be made under tension (for thin films and fibres) or compression (for self-supporting specimens). The treatment of data is similar to that employed in Modulated Temperature DSC. The superposition of a dynamic load in addition to the modulated temperature program leads to Modulated Temperature Dynamic Mechanical Analysis.

## INTRODUCTION

Modulated Temperature DSC (MTDSC) employs a periodic (usually sinusoidal) heating rate and the resulting heat flow response is analysed to determine the thermally reversible and irreversible (under the conditions of the experiment) components (*1*). The former signal is readily identified with the sample's heat capacity which may be further broken down into thermodynamic and kinetic components by employing the phase lag between the applied heating rate modulation and the sample response (*2*,*3*). A sine wave is the most common heating rate although other waveforms have been used and a variety of data analysis methods have been described (*4*,*5*). Recently, modulated temperature programs have been used in thermogravimetry to determine the degradation kinetics of materials (*6*).

Jaffe has discussed the nature of reversible and non-reversible length changes on heating for oriented polymers (*7*). Whilst all materials generally have a positive coefficient of volume expansion, the inherent anisotropy of ordered polymer chains means that the linear thermal expansion coefficient along the chain axis may be negative. Furthermore, the metastable nature of most oriented polymer structures results in relaxation to the disordered state on heating above $T_g$ hence any change in specimen length with temperature will not be reversible until structural equilibrium is achieved. Trznadel & Krysewski reiterate this concept in a review of thermal shrinkage of oriented polymers (*8*). Thermal expansion is reversible (even if the sign of the coeficient of thermal expansion is negative) but any shrinkage is permanent since it results in an increase in entropy due to loss of order in the matrix. Other irreversible dimensional changes can occur, such as creep under the applied load during a measurement. The application of modulated-temperature programming to TMA affords a means of

separating these two effects.

## EXPERIMENTAL

Experiments were carried out on a Shimadzu TMA-50. Measurements were run either in tension (static 1 g load) or compression (dynamic sinusoidal loading 10±5 g on a 3 mm diameter flat ended probe at 0.1 Hz) starting from 30°C followed by a succession of heat/hold/cool/hold stages which served to alternately raise the oven temperature by 5°C at 5°C/min followed by 1 minute isotherm, and then reduce the oven temperature by 2.5°C at the same rate, again followed by a one minute isotherm. This cycle was repeated until the required upper temperature was reached. Sample length change and temperature were recorded every 0.1 s. Typical raw data from the instrument is shown in figure 1 along with their first derivatives: d$L$/d$t$ and d$T$/d$t$. The heating rate (d$T$/d$t$) and rate of length change (d$T$/d$t$) were computed from the first derivative of the temperature-time data. The heating rate oscillates about a mean value of 0.75°C/min with a 210 second period and amplitude 1.75°C (root-mean-square).

By analogy to equations describing MTDSC (*1*), the rate of change of sample length with respect to time (d$L$/d$t$) measured by thermomechanical analysis (TMA) can be divided into two components:

$$\mathrm{d}L/\mathrm{d}t = dL/dT.\ \mathrm{d}T/\mathrm{d}t + f'(t,T)$$

where d$L$/d$T$ is the thermal expansion coefficient (a) and $f'(t,T)$ encompasses changes in length which occur due to relaxation of stresses in the sample or deformation under the applied load in the case of TMA.

Deconvolution of the TMA signals (time, temperature and length) was carried out according to the method disclosed by Reading (*9*). The algorithm applied a linear least-squares fit to the rate of length change *versus* heating rate data over period in accordance with the equation above. An adjustable parameter, the phase lag, is introduced to accommodate the delay between the heating rate and thermal response of the system. This determined by shifting the heat flow data one point at a time with respect to the heating rate until the best fit is achieved. Since this is an "offline" deconvolution method, the highest resolution is achieved by collecting data at short time intervals although this increases the size of data files and analysis time.

## RESULTS & DISCUSSION

Figure 1 shows the raw data (temperature and length) and their first derivatives (with respect to time) for an acrylic fibre. The deconvolution procedure gives average rate of length change (d$L$/d$t$), reversing rate of length change (rev. d$L$/d$T$) and phase difference. These quantities can be expressed with respect to time or temperature by multiplying by the average heating rate. Since the heating program exposes the sample to a succession of heat/cool/re-

heat cycles it is possible to separately analyse each part of the temperature profile in order to study the effect of thermal history of the sample response (Reading has termed this "parsing" (*9*)). Treatment of the data in this manner indicates that the bulk of the sample's deformation occurs during the first heating part of the temperature cycle and that thermal expansion is largely unaffected by the direction of the temperature change except in the glass-transition region where the effect of thermal history is evident (*10*). The phase difference can be employed to further separate the reversing rate of length change into its in-phase and out-of-phase components. This becomes important for measurements in compression (where creep occurs) and allows the thermal expansion coefficients of soft materials such as adhesives & sealants to be evaluated independently of loading conditions (*11*).

These rate of length change signals can be integrated with respect to time (for the average d*L*/d*t*) or temperature (for the reversing d*L*/d*T*) to allow the total length change and length change due to thermal expansion to be determined. This is illustrated in figure 2 for three acrylic fibres prepared using different tensions in the processing line. The difference between the families of curves represents the changes in dimensions due to irreversible shrinkage arise from loss of orientation or creep under load. Modulated temperature TMA has also been used to study orientation in PET films (*12*).

When the sample is subjected to a dynamic load this technique becomes modulated temperature Dynamic Mechanical Analysis (MTDMA). Figure 3 shows the results of an experiment performed on a perspex (polymethylmethacylate) rod in compression. The data was first analysed to determine the amplitude and phase difference of the length change due to the applied loading cycle. This yields the complex modulus (from the ratio of the load amplitude divided by the length change amplitude (*13*)) and damping factor (tan delta). The length change response was then deconvoluted to determine the in-phase and out-of-phase reversing d*L*/d*T* response (figure 4 – the complex modulus and tan delta have been averaged over one period for illustration). The in-phase response shows the increase in thermal expansion approaching the $T_g$ whereas the out-of-phase reflects the kinetic component of the creep under load. Schick has used pseudo-isothermal MTDMA to study the melting of polymers (*14*). The author has employed a similar approach to study the cure of cross-linking systems. DMA is more sensitive than DSC to such effects and modulated temperature programming further enhances the technique. It is clear from figure 4 that the modulus and damping factor are also affected by the temperature program and could be treated in a similar fashion to the rate of length change signal. The opportunity for "parsing" the data, not only according to the thermal history, but also the loading cycle is possible.

## CONCLUSIONS

These examples show the potential of modulated temperature programming for the study of dimensional changes using thermomechanical

analysis. The effects of orientation and creep can be studied and the measurements can be made less sensitive to choice of initial load. The application of this approach to dynamic mechanical analysis presents intriguing possibilities.

**ACKNOWLEDGEMENTS**

This work was carried out at the Thermal Methods and Conservation Science Laboratory, Department of Chemistry, Birkbeck College, University of London. The author is grateful to Marianne Odlyha and Gary Foster for their hospitality and to Shimadzu (UK) Ltd. for the loan of equipment.

**REFERENCES**

1. Reading, M.; *Trends Polym. Sci.*, 1 (1993) 248-253
2 Schawe,J.E.K.; *Thermochim. Acta*, 260 (1995) 1-16
3. Reading, M.; *Thermochim. Acta*, 292 (1997) 179-187
4. Schawe,J.E.K.; *Thermochim. Acta*, 271 (1996) 127-140
5. Reisen, R.; Widmann, G; Truttmann, R; *Thermochim. Acta*, 272 (1996) 27-39
6. Blaine, R.; *Am. Lab.*, 30 (1998) 21-23
7. Jaffe, M.; in *Thermal Characterization of Polymeric Materials*, Turi, E.A., Ed.; Academic Press: Orlando, (1981) p.731-750
8. Trznadel, M.; Kryszewski, M.; *J. Macromol. Sci.*, C32 (3&4) (1992) 259-300
9. Reading, M.; *US Patent 5,474,385*, December 12 1995
10. Price, D.M.; *Thermochim. Acta*, 315 1 (1998) 11-18
11. Price, D.M.; *Courtaulds Plc. internal report*
12. Price, D.M.; *J. Thermal Anal.*, 51 (1998) 231-236
13. Price, D.M.; *Thermochim. Acta*, 294 (1997), 127-131
14. Schick, C.; Merzlyakov, M.; Wurm, A.; *Polym. Mat. Sci. Eng.*, 78 (1998) 123-124

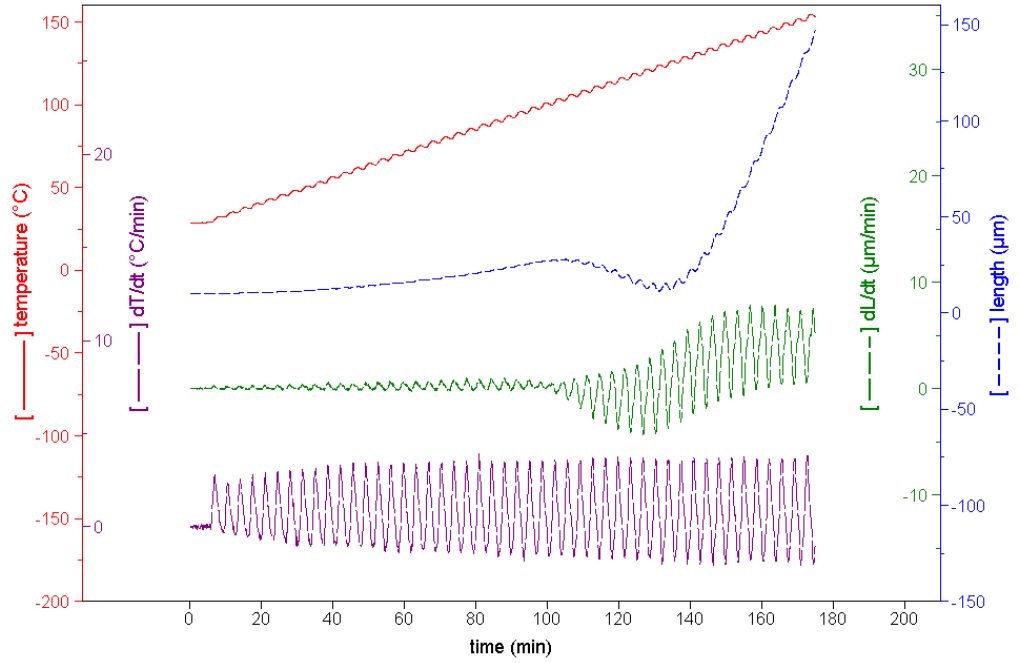


Figure 1. Raw MTTMA data for an acrylic fibre.

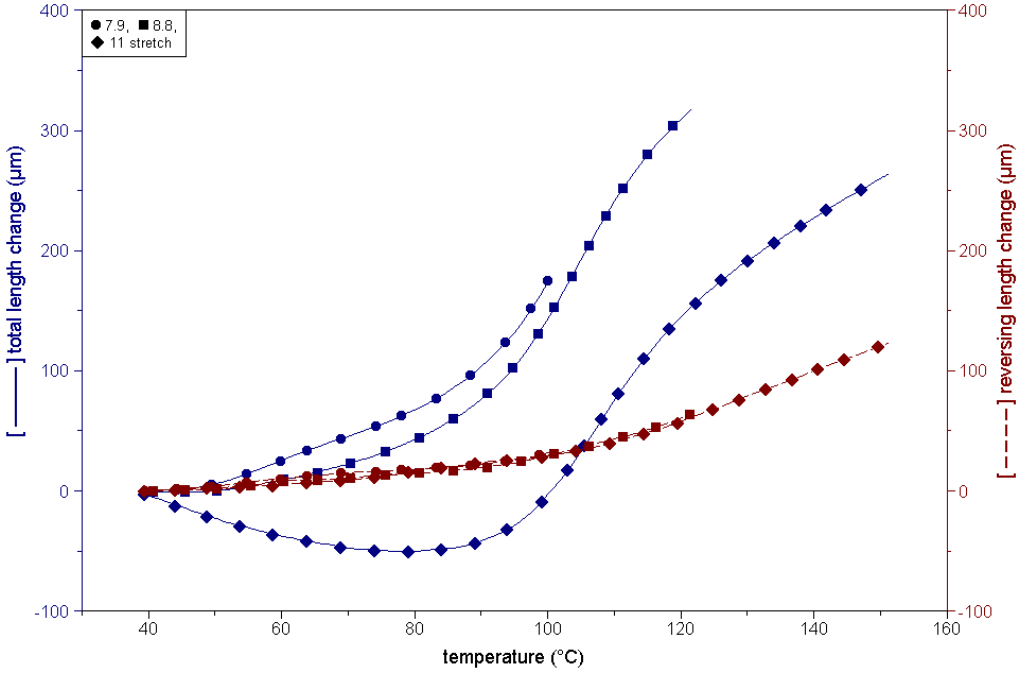


Figure 2. Deconvoluted and integrated data for a series of fibres with different draw ratios (see text).

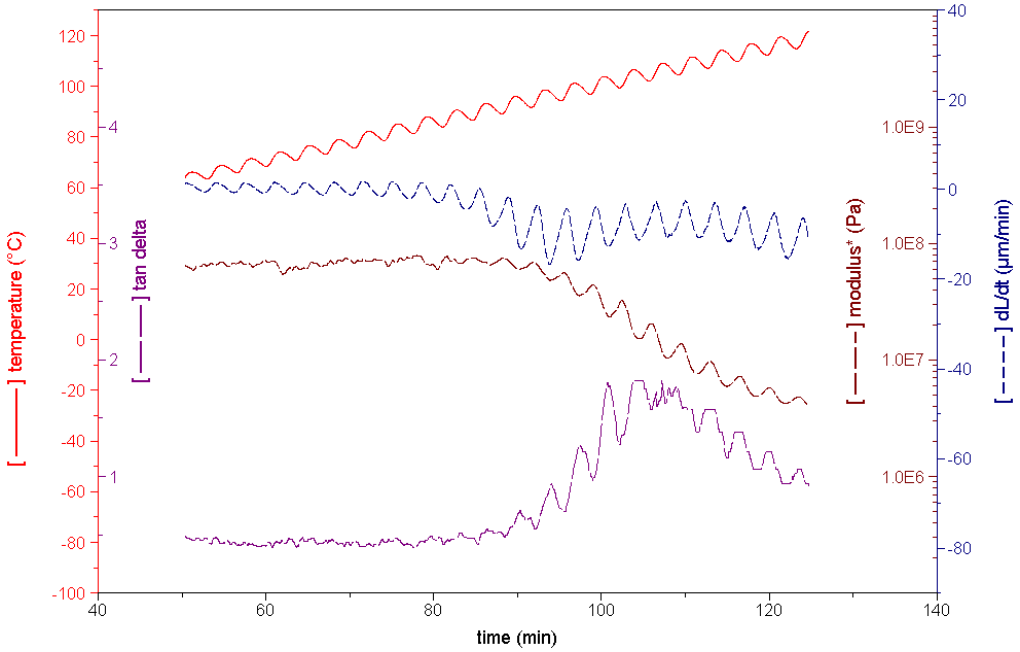


Figure 3. Raw MTDMA data for perspex rod in compression.

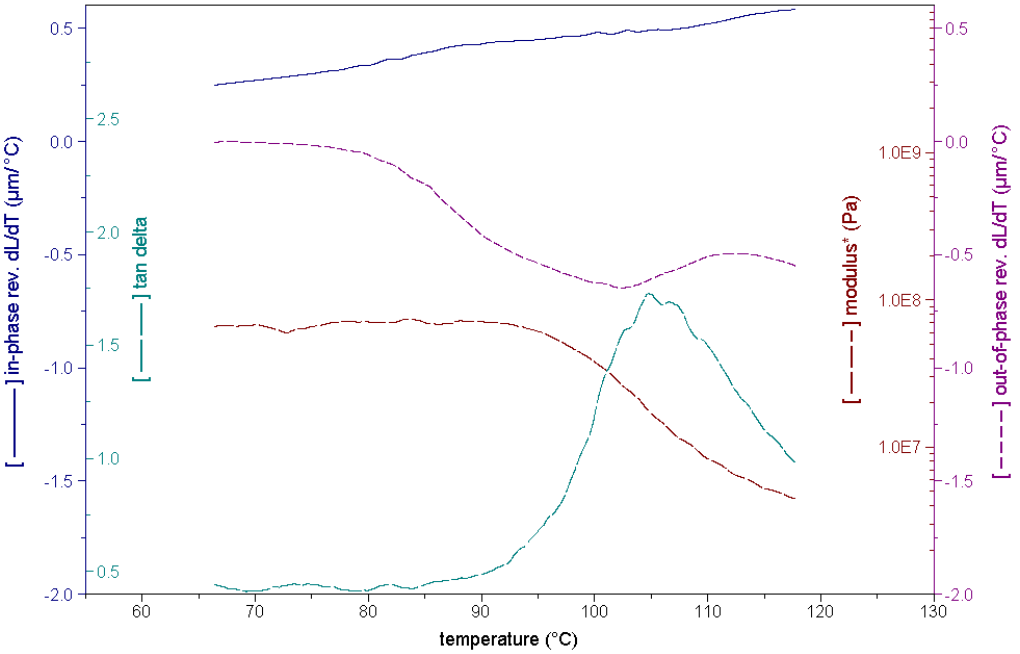


Figure 4. Deconvoluted MTDMA data from figure 3 (see text).