Journal of Thermal Analysis, Vol. 51 (1998) 231-236

MODULATED-TEMPERATURE THERMOMECHANICAL ANALYSIS

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(Received May 30, 1997)

Abstract

By employing a 'modulated-temperature' heating programme composed of a series of heat-isotherm stages, it is possible to separate the change in dimensions of an oriented material during heating into two contributions: a thermally 'reversing' component which is due to linear thermal expansion and a 'non-reversing' part arising from relaxation to the disordered state on heating above T_g. Some preliminary results for biaxially drawn poly(ethylene terephthalate) film are presented.

Keywords: modulated-temperature TMA, orientation, shrinkage, thermal expansion

Introduction

Modulated-Temperature DSC is a recent development of the technique whereby an oscillating heating rate is superimposed on the conventional temperature programme [1]. A simple way of relating the response of the heat flow signal (dQ/dt) to the heating rate (dT/dt) is:

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

where C_p is the sample's heat capacity and $f(t, T)$ represents heat flows associated with kinetically limited processes due to physical or chemical changes in the sample that occur both with time and temperature. The latter has been termed 'non-reversing' heat flow and may be caused by such effects as crystallisation, evaporation, degradation, cross-linking *etc.* Several mathematical methods have been described to analyse the data [2–4] – essentially the heat capacity of the sample is derived from the amplitudes of the oscillating heat flux divided by the amplitude of the oscillating heating rate. A sinusoidal temperature modulation is the most commonly applied profile although saw-tooth and stepwise-isothermal programs have been employed.

0368–4466/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Chen and Dollimore have considered the theoretical implications of using a sinusoidal heating rate in simultaneous DSC-TG [5], although, at present, modulated-temperature programming has only been applied to DSC. By analogy to Eq. (1) the rate of change of sample length with respect to time ($\mathrm{d}L/\mathrm{d}t$) measured bydilatometry or thermomechanical analysis (TMA) can be divided into two components:

$$\mathrm{d}L/\mathrm{d}t = \alpha \mathrm{d}T/\mathrm{d}t + f'(t, T) \tag{2}$$

where α is the thermal expansion coefficient ($\mathrm{d}L/\mathrm{d}T$) 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. Previous studies by Sørensen [6] used stepwise-isothermal dilatometry to study the time and temperature dependence of the sintering of inorganic oxides. The duration of every isothermal stage was controlled by the rate of change of sample length; thus this method forms part of the family of Controlled Rate Thermal Analysis techniques [7].

Jaffe has discussed the nature of reversible and non-reversible length changes on heating for oriented polymers [8]. 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 [9]. Thermal expansion is reversible (even if the sign of the coefficient 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. The application of modulated-temperature programming to TMA might afford a means of separating these two effects.

Experimental

Measurements were carried out on a Shimadzu TMA-50. A sample of 125 μm thick poly(ethylene terephthalate) film PET (Melinex®, ICI) was mounted in the film extension clamps under a 1 g load (too low to cause appreciable creep of the specimen at high temperature [10]). Initial sample dimensions were 5 mm wide and 10 mm long. Measurements were started at 30°C followed by a succession of heat/isotherm stages which served to raise the furnace temperature by 2°C at 5°C min^{-1} followed by 2 min isotherm until 180°C was reached. Sample length change and temperature were recorded by a computer every second. Some of the raw data from the instrument for PET film tested along the transverse axis to direction of manufacture is shown in Fig. 1.

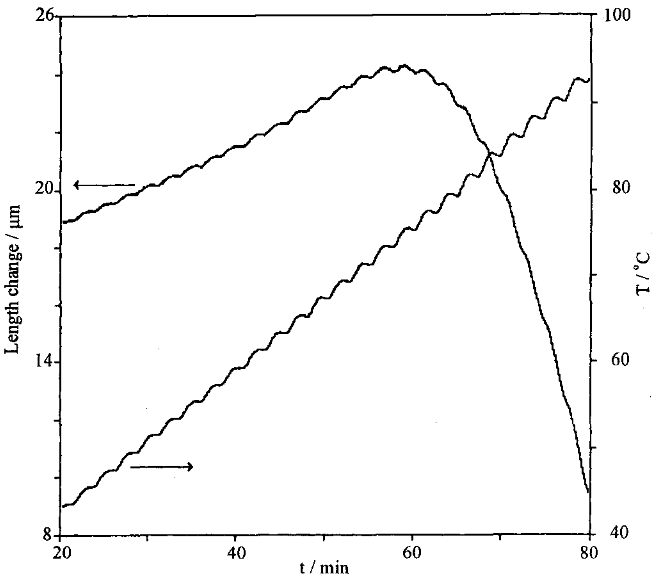

Fig. 1 Raw length change and temperature data from instrument (specimen expansion is shown in a positive direction)

Results and discussion

The first derivatives of the length change and temperature (dT/dt) curves are shown in Fig. 2. The heating rate oscillates about a mean value of 0.83°C min^{-1} within a 2.4 min period and, although the amplitude increased during the experiment due to overshoot of the temperature controller, the data can be deconvoluted by the method disclosed by Reading [11] in order to calculate the average time, temperature, rate of length change (dL/dt), thermal expansion coefficient (α) for each cycle according to Eq. (2) (Fig. 3). The latter two quantities can be integrated with respect to time or temperature, as appropriate, to allow the total length change and length change due to thermal expansion to be determined – results for the temperature range spanning the glass-rubber transition of PET are shown in Fig. 4. The dilatometric T_g of the sample can be estimated by extrapolation of the linear regions of the thermal length change profile above and below the change in thermal expansion coefficient that accompanies devitrification. It is apparent from the total length change curve that some shrinkage begins to occur below this temperature. This effect has been observed by Haworth *et al.* who used conventional TMA to characterise the shrinkage of oriented PET films [10]. These authors were only able to measure the thermal expansion of the film below T_g whereas the present method permits measurement of this parameter through and above the glass transition region. The difference between the two curves rep-

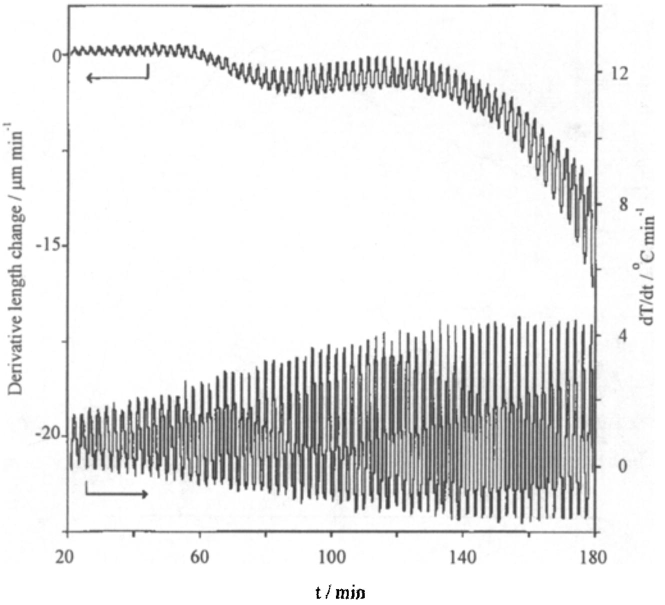

Fig. 2 First derivative of length change and temperature *vs.* time calculated from raw data

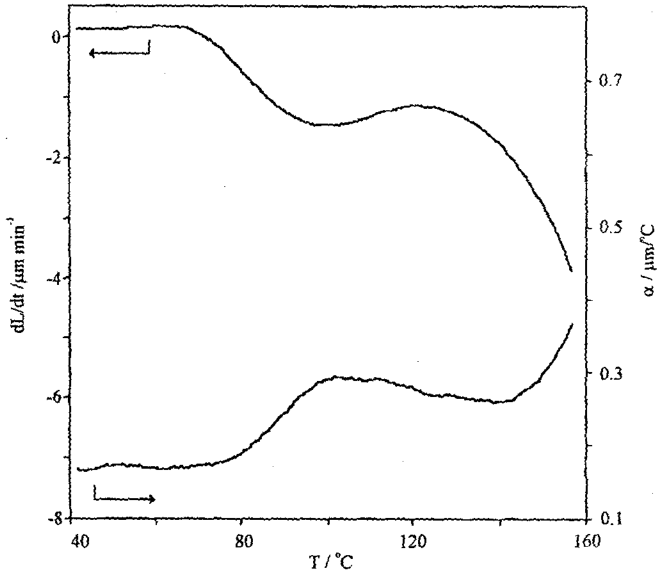

Fig. 3 Deconvoluted data from Fig. 2 showing the underlying rate of change of sample length (d*L*/d*t*) and the contribution from thermal expansion (α)

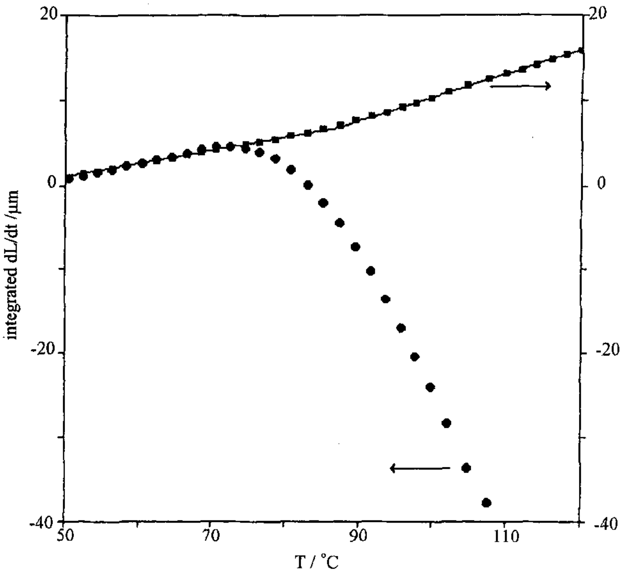

Fig. 4 Cumulative integrals of d*L*/d*t* (with respect to time) and α (with respect to temperature) in region 50 and 120°C

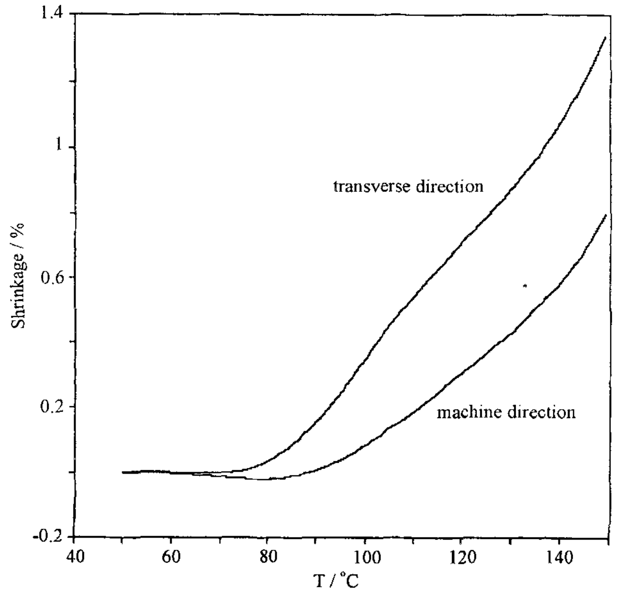

Fig. 5 Difference in thermal shrinkage according to sample geometry

resents the amount of shrinkage due to relaxation of orientation that takes place (i.e. the cumulative integral of $f'(t, T)$ in Eq. (2)). Results for film tested along the transverse and machine direction are shown in Fig. 5. There is roughly twice as much shrinkage in the transverse direction, a result which is in agreement with the common manufacturing conditions for this product [12].

Conclusions

The application of modulated-temperature programming to thermomechanical analysis (TMA) allows changes in sample dimensions due to shrinkage arising from relaxation of imposed stresses and conventional thermal expansion to be distinguished. Results for biaxially oriented PET film indicate that the method has practical applications for the study of oriented polymers. This approach may also be useful for specimens which soften and flow under the applied load during TMA experiments.

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

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