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MODULATED-TEMPERATURE THERMOMECHANICAL ANALYSIS OF FIBRES

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Abstract

The application of modulated temperature programming to thermomechanical analysis affords a method for measuring the 'true' thermal expansion coefficients of materials that deform irreversibly during normal TMA. This may arise from creep under the applied load or changes in dimensions due to relaxation of orientation. Acrylic fibres made with various degrees of orientation shrink to different extents on heating but all show the same 'true' thermal expansion coefficients using this approach. The application of modulated temperature programming to Dynamic Mechanical Analysis is also discussed.

Keywords: fibres, modulated temperature TMA, orientation, shrinkage

Introduction

Modulated temperature DSC (MTDSC) employs a periodic 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 heating rate modulation and the sample response [2, 3]. A sine function is the most common heating profile 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].

In a previous paper, the application of modulated-temperature programming to TMA was described with particular reference to the study of orientation in poly(ethylene terephthalate) film [7]. This work examines the effect of thermal history and orientation on acrylic fibres and investigates the application of modulated-temperature programming to dynamic mechanical methods.

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Experimental

Samples of acrylic fibre produced with different draw ratios and regenerated cellulose fibre were kindly supplied by Courtaulds Plc. Experiments were carried out on a Shimadzu TMA-50. Measurements were run under tension with either a static 1 g load or dynamic sinusoidal loading (10±5 g at 0.2 Hz). The temperature program consisted of a succession of heat/hold/cool/hold stages. These served to alternately raise the oven temperature by 5°C at 5°C min^{-1} followed by one 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 from 30°C until the required upper temperature was reached. Sample length change and temperature were recorded every 0.5 s. Typical raw data from the instrument are shown in Fig. 1 along with their first derivatives: dL/dt and dT/dt. The heating rate oscillates about a mean value of 0.75°C min^{-1} with a 210 s 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 (dL/dt) measured by thermomechanical analysis (TMA) can be divided into two components:

$$dL/dt = dL/dT \cdot dT/dt + f(t, T)$$

where dL/dT is the thermal expansion coefficient 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 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 *vs.* heating rate data over period in accordance with the equation above. An adjustable parameter, the phase lag, was introduced to accommodate the delay between the temperature modulation and thermal response of the system. This was determined by shifting the rate of length change data one point at a time with respect to the heating rate until the best fit was achieved. Since this is an 'offline' deconvolution method, the resolution depends on the data sampling rate with consequent penalties in terms of storage requirements and analysis time.

Conventional dynamic mechanical measurements were carried out on a Rheometric Scientific DMTA 3 at 1 Hz and 3°C min^{-1}.

Results and 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 the average rate of length change (av. dL/dt), the reversing rate of length change (rev. dL/dT) and the phase difference (Fig. 2). 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 thermal expansion is largely unaffected by the direction

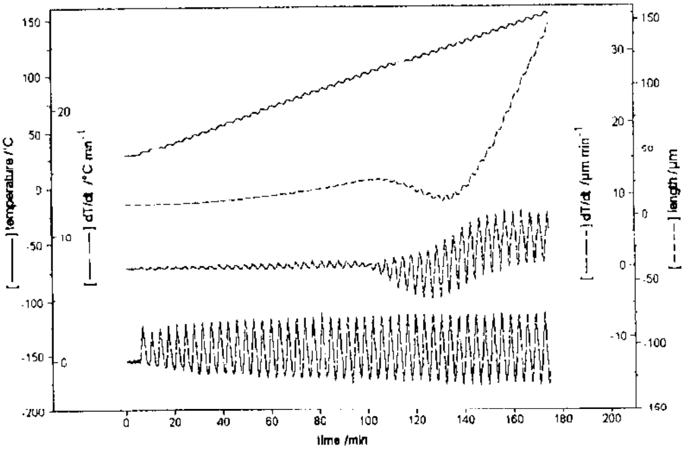

Fig. 1 Raw data from modulated temperature TMA experiment on an acrylic fibre

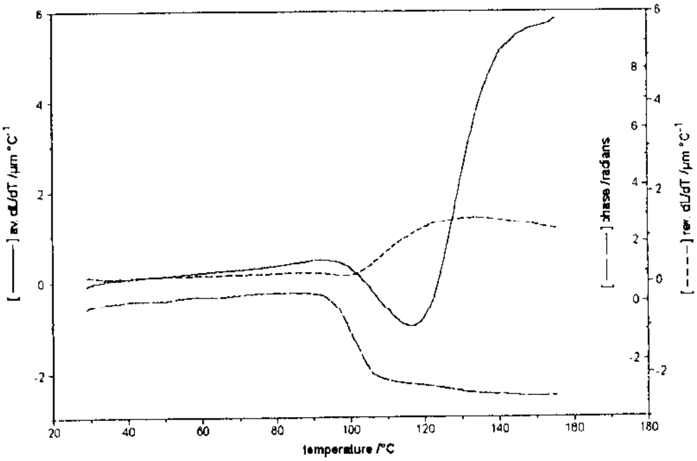

Fig. 2 Deconvoluted data from Fig. 1 (see text)

of the temperature change except in the glass-transition region where the effect of thermal history is evident (Fig. 3).

The total length change and length change due to thermal expansion can be obtained by integrating the above signal with respect to temperature. This is illustrated in Fig. 4 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.

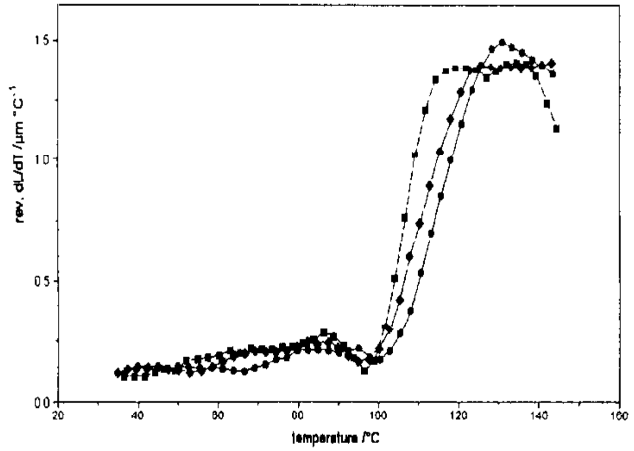

Fig. 3 Reversing dL/dT separated into heat (•), cool (▪) and re-heat (♦) components

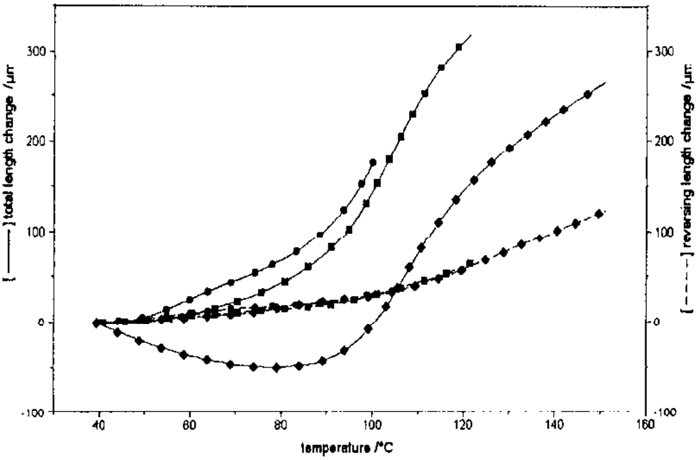

Fig. 4 Total (solid line) and reversing (broken line) length change for acrylic fibres produced with different draw ratios (• 7.9:1, ▪ 8.8:1, ♦ 11:1)

When the sample is subjected to a dynamic load this technique becomes a form of modulated temperature Dynamic Mechanical Analysis (MTDMA). Figure 5 shows the results of an experiment performed on a cellulose fibre. The raw data was first analysed to determine the amplitude of the length change due to the applied loading cycle. This yields the complex tensile modulus (E^*) from the ratio of the load amplitude divided by the length change amplitude [9]. The underlying rate of length change response was the deconvoluted to determine the average and reversing

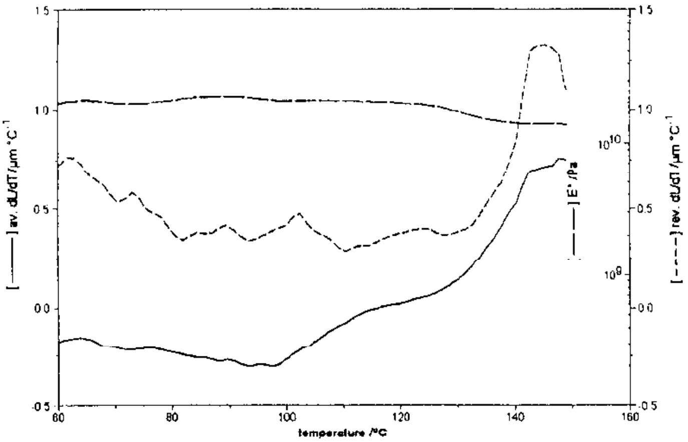

Fig. 5 Average d*L*/d*T* (solid line), reversing d*L*/d*T* (short dashes) and complex tensile modulus (long dashes) obtained by applying a dynamic load in conjunction with a modulated temperature program

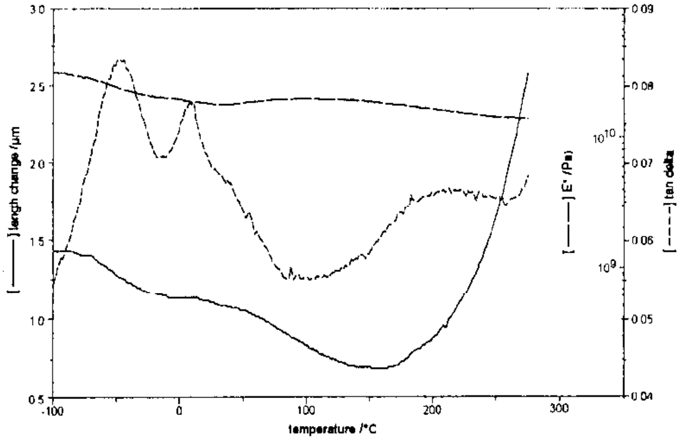

Fig. 6 Conventional dynamic mechanical analysis of a cellulose fibre

components (the complex modulus was averaged over one temperature modulation). It was not possible to measure the damping factor (tanδ) due to the low data sampling rate – thus this experiment should be classified as modulated-temperature dynamic-load TMA. The additional information that this gives can clearly be seen by reference to Fig. 6 which shows the results of a conventional DMA experiment on the same material. Schick has used quasi-isothermal MTDMA to study the melting of polymers [10]. DMA is more sensitive than DSC to such effects and modulated temperature programming further enhances the technique. 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 investigation 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 interesting possibilities.

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