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# A study of enthalpic relaxation of poly(ethylene terephthalate) by conventional and modulated temperature DSC

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## Abstract

A standard power-compensation Perkin-Elmer DSC-2 was modified for temperature modulation experiments. Samples of amorphous poly(ethylene terephthalate) were aged in the DSC at temperature,  $T_a$ , for time,  $t_a$  below the amorphous  $T_g$ . The progress of enthalpic relaxation was measured using conventional and modulated temperature DSC (MTDSC). By conventional DSC the extent of enthalpic relaxation was found to increase with ageing time accompanied by an apparent shift in the glass transition to a higher temperature. Using MTDSC the non-reversing enthalpic transition could be separated from the reversing glass transition. By MTDSC the extent of enthalpic relaxation was also found to increase with ageing time. However, by studying the reversing component it was found that there is no increase in the glass transition temperature with increased ageing time. It was found that the kinetics of enthalpic relaxation were more accurately determined by conventional DSC than MTDSC. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Enthalpy relaxation; Physical ageing; Poly(ethylene terephthalate); Glass transition; Modulated temperature DSC

## 1. Introduction

When a polymer is rapidly quenched from the melt, the molecular conformation of the liquid is frozen in and the polymer chains are in a higher energy than the equilibrium conformation. However, the polymer chains still retain some mobility and so with time, relax back towards equilibrium conformation in a process known as enthalpic relaxation or physical ageing. Thus an enthalpic transition (with associated energy change  $\Delta H$ ) arises as a result of annealing the sample on heating through the  $T_g$  and can be used as a

measure of the extent of this process. As ageing occurs, the mechanical and physical properties change with time [1], the polymer becoming more brittle, having a reduced elongation to break, increased yield stress [2] and decreased creep compliance [3]. This process has been extensively studied in the past using differential scanning calorimetry (DSC) [4,5] under conventional, linear heating or linear cooling conditions.

It has been proposed that the relatively new technique of modulated temperature DSC (MTDSC) can be used to study physical ageing since it resolves a transition composed of thermally reversing and non-reversing components [6]. It has also been shown that by including the phase lag in the analysis an in-phase and out-of-phase component of the specific heat can be determined [7]. This makes MTDSC an interesting

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technique to study enthalpic relaxation: the ageing peak is non-reversing superimposed on a reversing glass transition. While MTDSC has been used to investigate physical ageing [8–10], there has been little work reported comparing the kinetics of enthalpic relaxation with those by conventional DSC, and less using a power compensated calorimeter.

## 2. Experimental

Poly(ethylene terephthalate) (PET) was provided as moulding pellets by ICI fibres. It had a number average molecular weight of about  $2 \times 10^4 \text{ g mol}^{-1}$ . The dried pellets were compression moulded at  $280^\circ\text{C}$  for 3 min at 1520 kPa into  $150 \text{ mm} \times 150 \text{ mm} \times 1 \text{ mm}$  plaques. The plaques were then quenched in ice/water to give amorphous material.

DSC measurements were made on a modified power-compensation Perkin-Elmer DSC-2, adapted for modulated temperature experiments as reported elsewhere [11]. All samples were encased in aluminium pans with an empty pan as the reference. Discs of PET ( $13 \pm 0.3 \text{ mg}$ ) were cut directly from the moulded plaques. The DSC temperature was calibrated from the melting temperatures of 99.999% indium, tin, lead and stearic acid and the thermal response from the enthalpy of fusion of indium ( $28.47 \text{ J g}^{-1}$ ), and the heat capacity of sapphire. A

standard glass was formed by cooling the samples in the DSC through the glass transition region at  $40 \text{ K min}^{-1}$ . The glass transition temperature was determined by calculating the value for heating rates of 20, 10, 5, 2.5 and  $1.25 \text{ K min}^{-1}$  and then extrapolating to zero heating rate,  $T_g$  is  $349.7 \text{ K}$ . The samples were then aged in the DSC at various ageing temperatures,  $T_a$ , and for time,  $t_a$ .

## 3. Results and discussion

### 3.1. Conventional DSC

Amorphous PET, when heated at  $10 \text{ K min}^{-1}$  from 320 to  $580 \text{ K}$ , showed a glass transition at about  $350 \text{ K}$ , a crystallisation exotherm at about  $400 \text{ K}$  and melting above  $500 \text{ K}$  (Fig. 1).

When held at a constant temperature (up to  $50 \text{ K}$  below the glass transition) as the ageing time,  $t_a$ , tends to infinity the equilibrium enthalpic relaxation ( $\Delta H_\infty$ ) is reached. Enthalpic relaxation can then be analysed using the Cowie–Ferguson equation [5]:

$$\Delta H(t_a) = \Delta H_\infty(1 - \phi(t_a)) \quad (1)$$

where  $\phi(t_a) = \exp(-t_a/\tau)^\beta$ ,  $\beta$  is the constant, and  $\tau$  the relaxation time.

The amount of enthalpic relaxation which had occurred was measured by heating the sample through

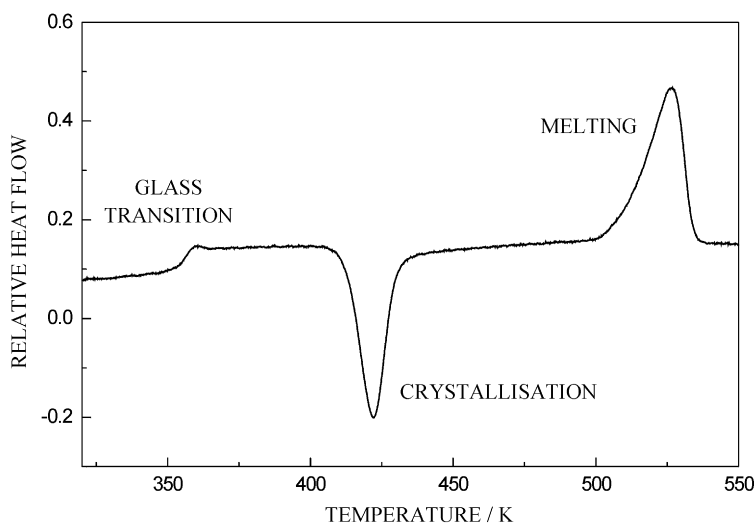


Fig. 1. Amorphous PET by conventional DSC (heating rate =  $20 \text{ K min}^{-1}$ ).

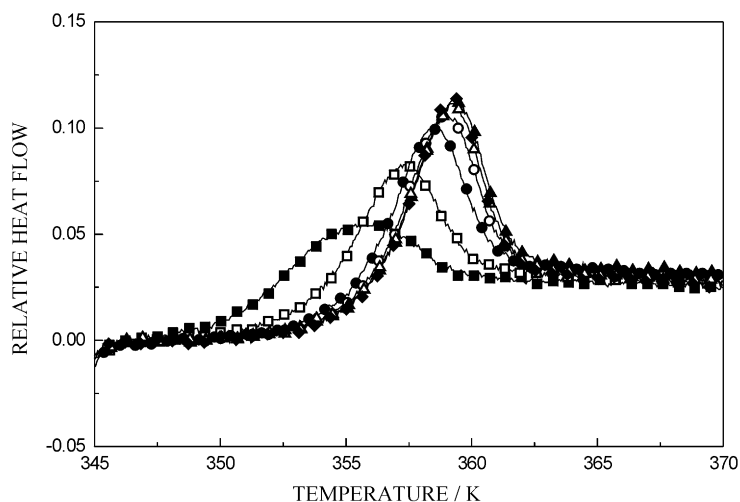


Fig. 2. Enthalpic relaxation peak superimposed on  $T_g$  of PET for ageing time of 30 min (solid square), 60 min (open square), 120 min (solid circle), 240 min (open circle), 960 min (solid triangle), 1440 min (open triangle) and 2880 min (solid diamond).

the  $T_g$  at an underlying heating rate of  $10 \text{ K min}^{-1}$  (Fig. 2). The sample was then quenched at  $40 \text{ K min}^{-1}$  to below room temperature and reheated at  $10 \text{ K min}^{-1}$  so that a baseline of unaged material could be obtained. This was subtracted from that of the aged sample. The enthalpic relaxation peak, so determined, was found to increase in magnitude with

increased ageing time accompanied by an apparent shift in the glass transition to a higher temperature (see Fig. 3). The extent of enthalpic relaxation was plotted against ageing time and a curve fitting procedure applied (see Fig. 4) so that

$$y = a \left( 1 - \exp\left(-\frac{x}{b}\right) \right)^c \quad (2)$$

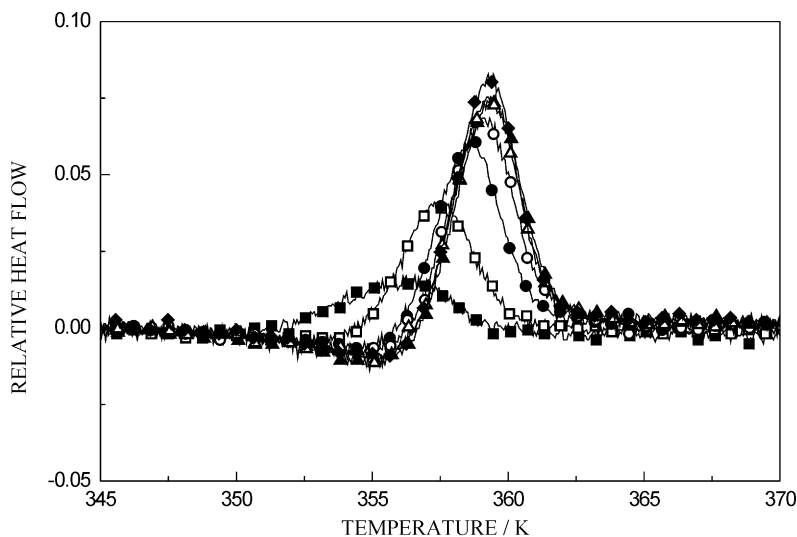


Fig. 3. Development of enthalpic peak with time for ageing time of 30 min (solid square), 60 min (open square), 120 min (solid circle), 240 min (open circle), 960 min (solid triangle), 1440 min (open triangle) and 2880 min (solid diamond).

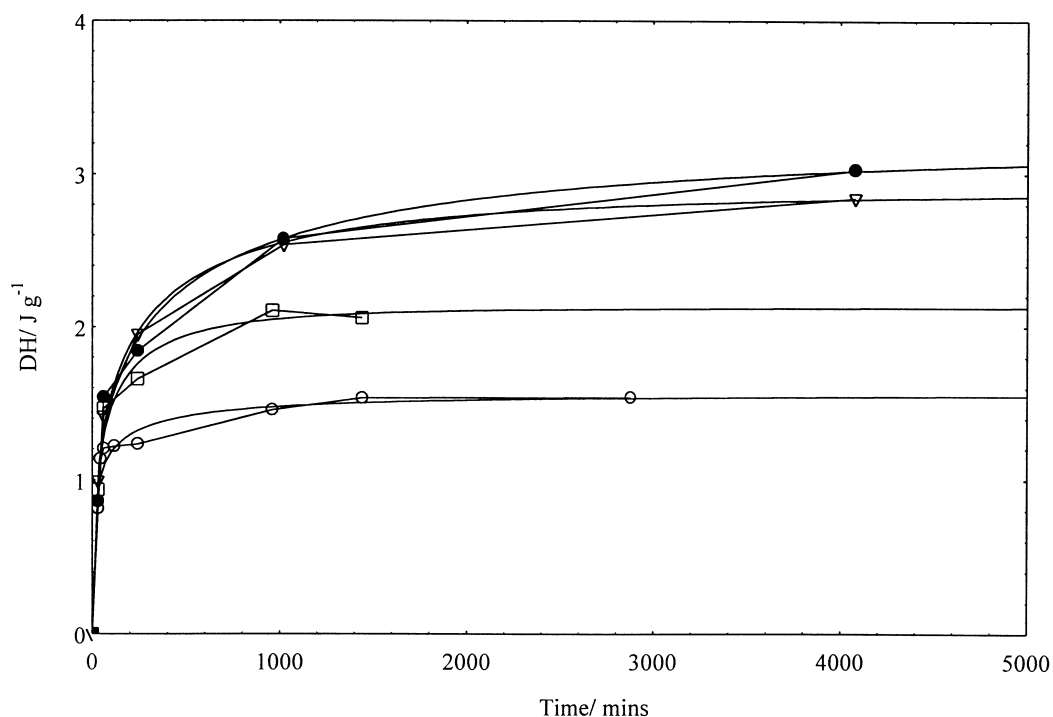


Fig. 4. Curve fitting procedure as analysed by conventional DSC for  $\Delta T$  (where  $\Delta T = T_g - T_a$ ) of 2.7 K (open circle), 5 K (open square), 7.7 K (open triangle) and 10 K (solid circle).

where  $a = \Delta H_\infty$ ,  $b = \tau$  and  $c = \beta$ . From this  $\Delta H_\infty$ ,  $\tau$  and  $\beta$  could be determined (Table 1).

These results were found to correlate well with earlier reported values [4]. From this it can be shown that  $\Delta H_\infty$  increases linearly with increasing  $\Delta T$ . The average relaxation time also increased with  $\Delta T$ . The data also correlated well with values calculated from a log–log plot (Table 2), where  $\log(-\ln(1 - (\Delta H_t/\Delta H_\infty)))$  is plotted against  $\log t_a$ . The slope of the line is  $\beta$  and intercept at  $\log t_a = 0$  is  $\beta \log(1/\tau)$ .

### 3.2. Modulated temperature DSC

An amorphous PET sample was initially heated from 310 to 550 K, with an underlying heating rate of  $2.5 \text{ K min}^{-1}$ , a modulation period of 60 s and amplitude of  $\pm 1 \text{ K}$ . The raw data was deconvoluted and the total, reversing and non-reversing signals determined (Fig. 5).

Amorphous PET samples were held at an ageing temperature,  $T_a$ , for a time,  $t_a$ . The samples were then

Table 1  
Enthalpic relaxation kinetics analysed by curve fitting procedure — conventional DSC

$\Delta T$	$\Delta H_\infty$ (J/g)	$\tau$ (min)	$\beta$
3.7	1.56	33.7	0.322
6.0	2.13	69.6	0.452
8.7	2.89	178	0.437
11	3.20	301	0.403

Table 2  
Enthalpic relaxation kinetics analysed using a log–log plot — conventional DSC

$\Delta T$	$\Delta H_\infty$ (J/g)	$\tau$ (min)	$\beta$
3.7	1.56	35.3	0.340
6.0	2.13	70.4	0.474
8.7	2.89	178	0.448
11	3.20	304	0.417

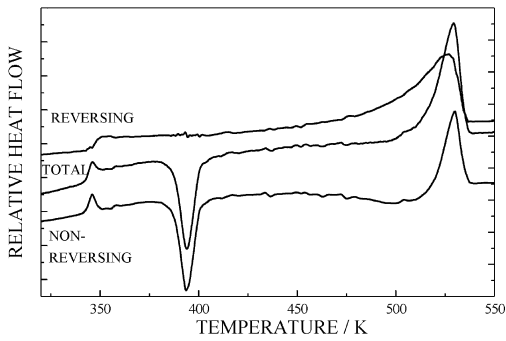


Fig. 5. PET aged at room temperature.

heated from 350 to 375 K, with an underlying heating rate of  $0.62 \text{ K min}^{-1}$ , a modulation period of 60 s and modulation amplitude of  $\pm 1 \text{ K}$  (see Fig. 6). The raw data was deconvoluted and the total, reversing and non-reversing signals determined.

Deconvolution of the DSC data (time, temperature and heat flow) was carried out according to the method disclosed by Reading [12]. The heating rate was computed from the first derivative of the temperature–time data. The period of the temperature modulation was determined by counting successive minima or maxima in the heating rate profile. The

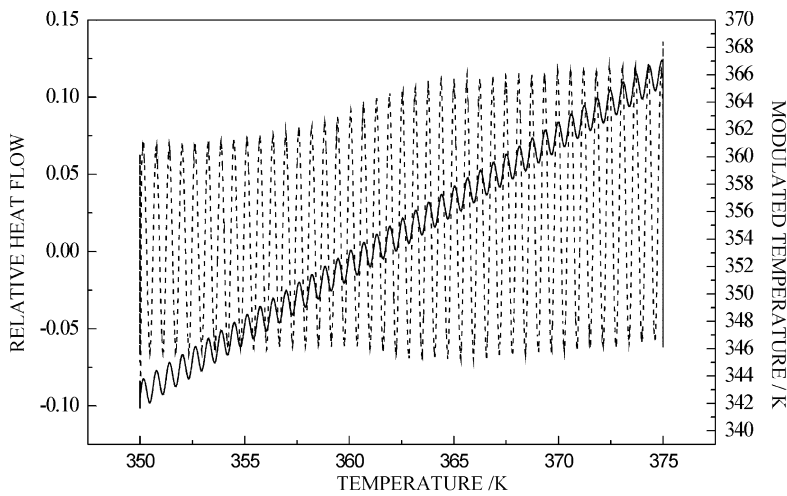


Fig. 6. Modulated temperature for aged amorphous PET showing modulated temperature (solid line) and modulated heat flow (broken line).

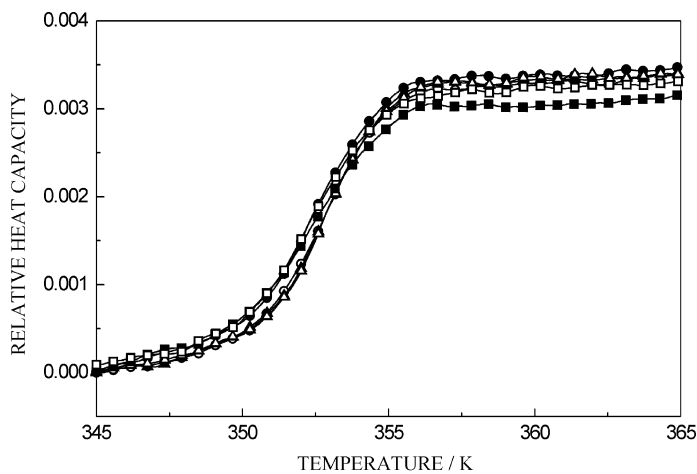


Fig. 7. Reversing trace for ageing times of 15 min (solid square), 45 min (open square), 120 min (solid circle), 240 min (open circle), 960 min (solid triangle) and 1440 min (open triangle).

algorithm applied a linear least-squares fit to the heat flow versus heating rate data over one period. The reversing signal was obtained from the slope of  $dQ/dT$  versus  $dT/dt$  over one modulation and the non-reversing signal from the difference between the total (average) signal and reversing signal. An adjustable parameter, the phase lag, is introduced to accommodate the delay between the heating rate and thermal response of the system. This was 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. If the modulation conditions are such that  $dT/dt$  becomes negative during part of the period it is possible to split each modulation into heat, cool and reheat segments and analyse these separately (Reading has termed this “parsing”). Another advantage of the “linear fitting” approach over the Fourier transform algorithm described by Baur and Wunderlich [13] is that the period need not be predetermined or constant, thus allowing a form of sample controlled MTDSC to be carried out [14].

The deconvoluted data was smoothed to correct for the uniform ripple superimposed on the heat flow

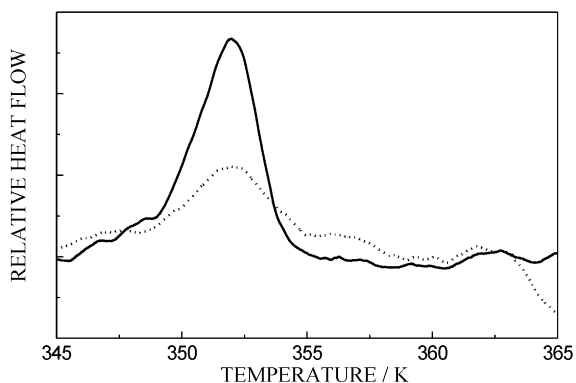


Fig. 8. Non-reversing signal for aged (solid line) and quenched sample (broken line).

traces as a result of the analysis windowing procedure, as has been reported elsewhere [15]. This was found to correspond to the modulation period. The glass transition appears in the reversing signal as the usual increase in heat capacity and the enthalpic relaxation peak is seen in the non-reversing signal (Fig. 5). The glass transition in the reversing signal was found to be unaffected by ageing time (Fig. 7). It was found that residual peak arises in the non-reversing component of quenched PET as a result of the temperature program (Fig. 8). This can then be subtracted from the peak on the initial heat so any enthalpy change is solely due to

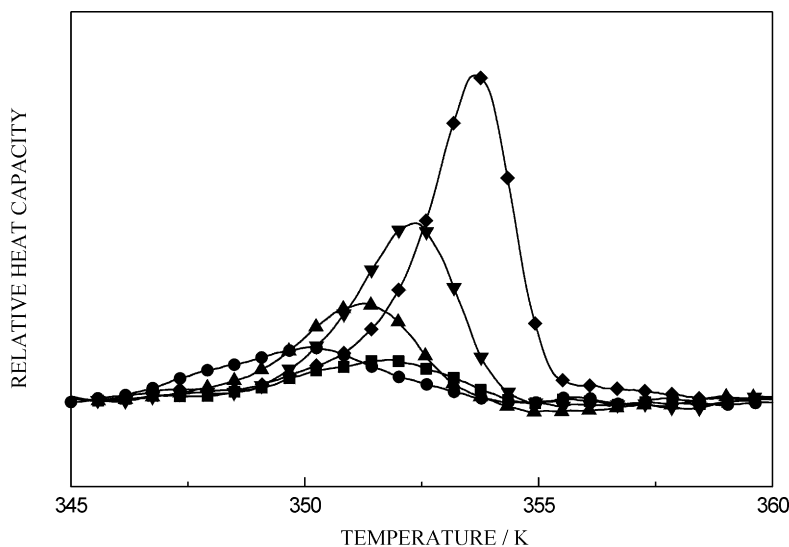


Fig. 9. Enthalpic relaxation of amorphous PET by MTDSC ( $\Delta T = 10$  K) for ageing times of 30 min (square), 60 min (circle), 240 min (triangle up), 1020 min (triangle down) and 4080 min (diamond).

relaxation processes. The enthalpic relaxation peaks can then be compiled as for conventional DSC (Fig. 9). The peaks were found to be well-resolved and the baselines superimposed.

The areas under the peaks were then analysed and the kinetics studied by applying the Cowie–Ferguson equation. The MTDSC data was analysed in an equivalent manner to the conventional DSC data, by curve fitting procedures and log–log plots. By the curve fitting procedure it was impossible to calculate a value for  $\Delta H_{\infty}$  as there was too much scatter in the data. The log–log plots were carried out using experimentally determined values of  $\Delta H_{\infty}$ . These were also found to have a much larger degree of error than the kinetics as calculated by conventional DSC. Since the average heating rates are much faster by conventional DSC and the kinetic data obtained by this method is accurate, it is better to study enthalpic relaxation by conventional DSC rather than the more time-consuming MTDSC.

#### 4. Conclusions

It is possible to separate a reversing glass transition from a non-reversing enthalpic relaxation process using MTDSC. However, a residual peak develops in the non-reversing peak as a result of the sample's complex thermal history. This can be corrected for by quenching and re-running the sample. The parameter for enthalpic relaxation to equilibrium,  $\Delta H_{\infty}$ , was determined by conventional DSC and found to correlate well with published results. It was difficult to determine the kinetic parameters by MTDSC and

further work at longer ageing times is required before conclusive results can be given. To-date it is more accurate and convenient to study enthalpic relaxation by conventional DSC.

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