A STUDY OF ENTHALPIC RELAXATION OF POLY(ETHYLENE TEREPHTHALATE) BY CONVENTIONAL AND MODULATED TEMPERATURE DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A conventional 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 ageing was measured using conventional and modulated temperature DSC. By conventional DSC the extent of enthalpic relaxation was found to increase with ageing time accompanied by a shift in the apparent glass transition to a higher temperature. Using MTDSC the enthalpic transition could be separated from the glass transition, as it was part of the non-reversing specific heat.

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. As this 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 conventional Differential Scanning Calorimetry (DSC) (*4,5*)

It has been proposed that the relatively new technique of Modulated Temperature DSC (MTDSC) can be used to study physical ageing since it resolves 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 technique to study enthalpic relaxation: the ageing peak is non-reversing superimposed on a reversing glass transition. This enthalpic transition arises as a result of deageing the sample on heating through the T_g

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and is a measure of the extent of enthalpic relaxation (ΔH). While MTDSC has been used to investigate physical ageing, (*8, 9, 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.

EXPERIMENTAL

Poly(ethylene terephthalate) (PET) was provided as moulding pellets by ICI Fibres Ltd.. It had a number average molecular weight of about 20kg mol^{-1}. The pellets were dried prior to compression moulding at 280°C for 3 minutes at 1520 kPa into 150x150x1 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±0.3 mg) were cut directly from the moulded plaques. The DSC 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 (28.42 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 K min^{-1}. The samples were then aged in the DSC at various ageing temperatures, T_a, and for time, t_a.

RESULTS AND DISCUSSION

1. Conventional DSC.

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

The amount of enthalpic relaxation which had occurred was measured by heating the sample through the T_g at an underlying heating rate of 10 K min^{-1} (see figure 2). The sample was then quenched at 40 K min^{-1} and reheated at 10 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 a shift in the apparent glass transition to a higher temperature (see figure 3). The kinetics of this will be described further.

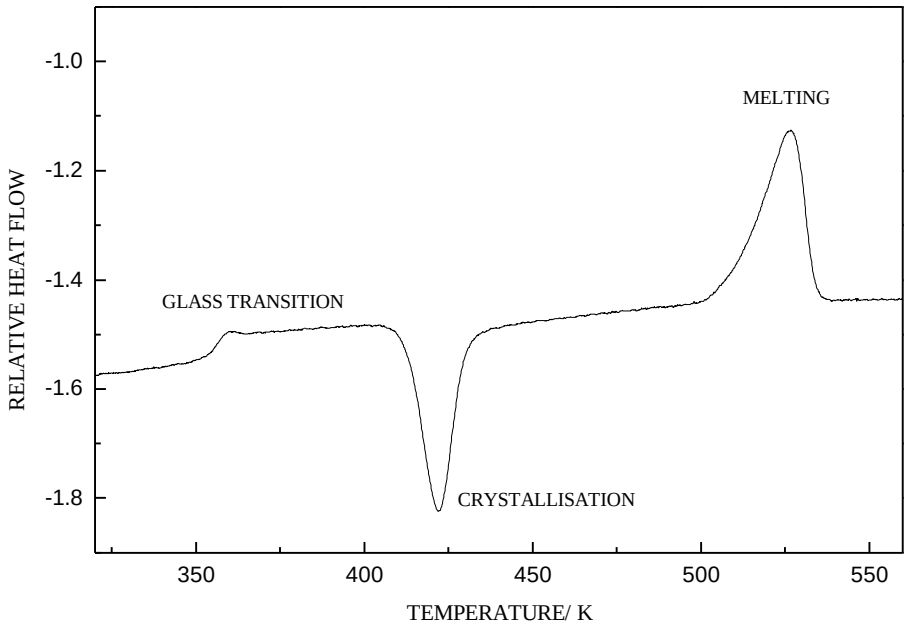

FIGURE 1: AMORPHOUS PET MEASURED BY CONVENTIONAL DSC

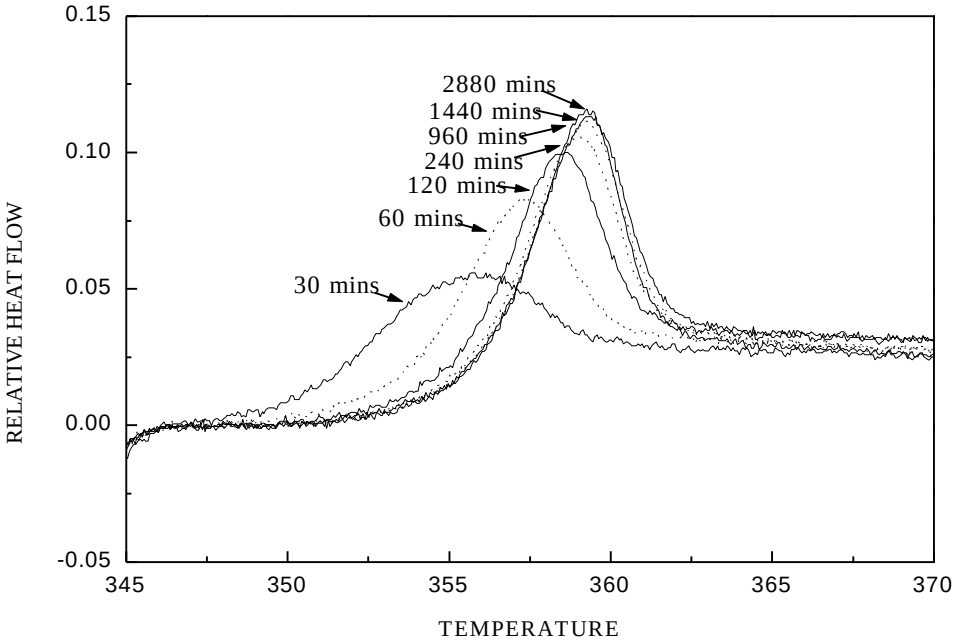

FIGURE 2: ENTHALPIC RELAXATION PEAK SUPERIMPOSED ON Tg OF

2. Modulated Temperature DSC

Amorphous PET samples were heated from 350 to 375 K, with an underlying heating rate of 0.62 K min^{-1}, a modulation period of 60 seconds and modulation amplitude of ±1 K. The raw data was deconvoluted and the total, reversing and non-reversing signals determined (see figure 4).

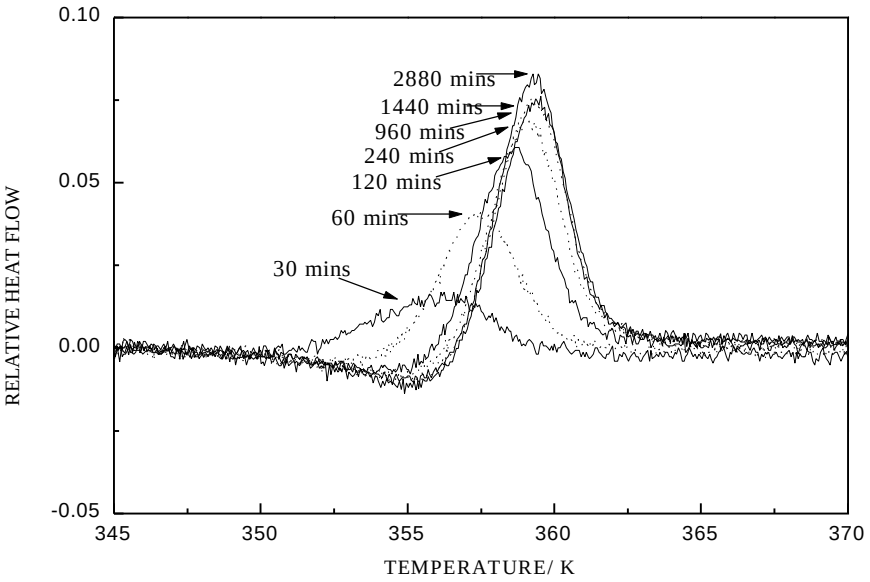

FIGURE 3: DEVELOPMENT OF ENTHALPIC PEAK WITH AGEING TIME IN M

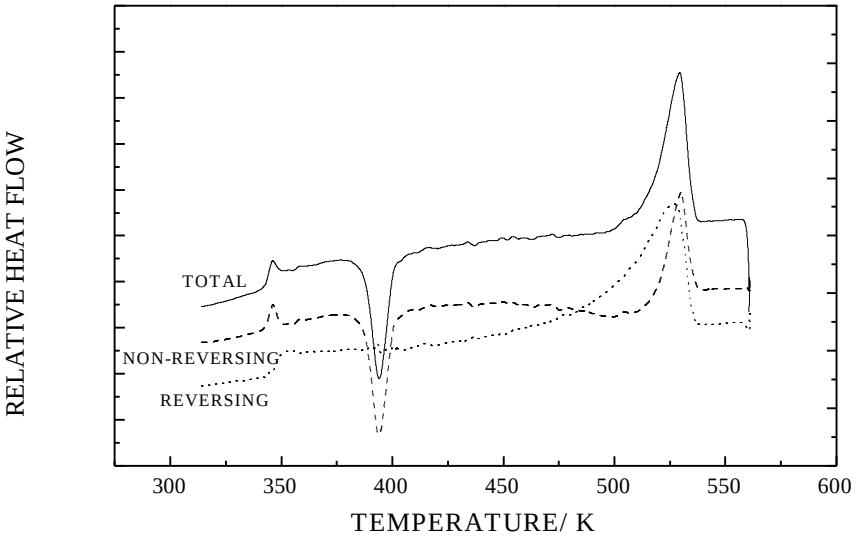

FIGURE 4: PET AGED AT ROOM TEMPERATURE

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 mimina or maxima in the heating rate profile. The 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 *vs.* 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 d*T*/d*t* 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 & Wunderlich (*13*) is that the period need not be predetermined or constant, thus allowing a form of Sample Controlled MT-DSC to be carried out (*14*).

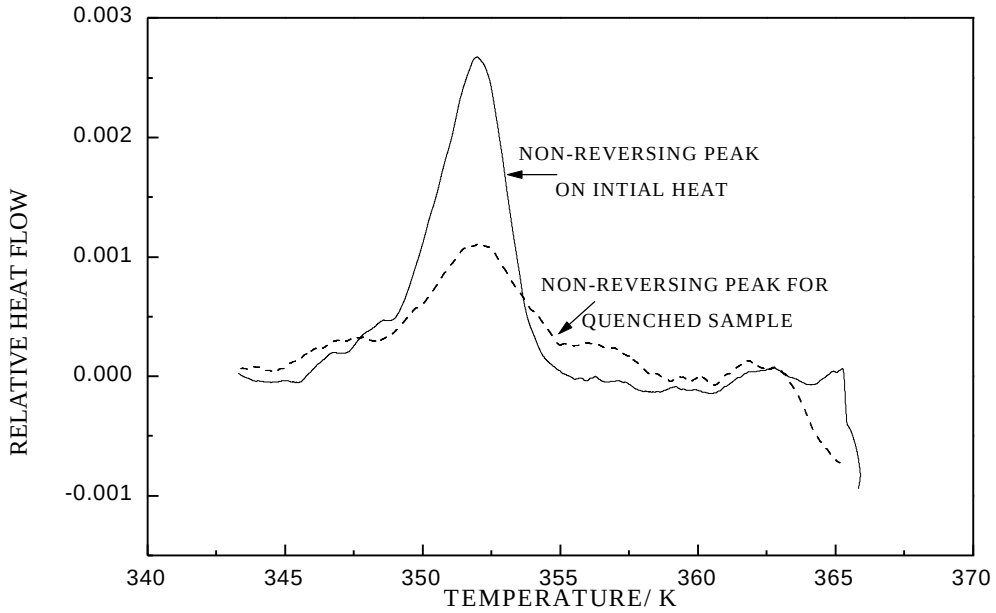

FIGURE 5: NON-REVERSING SIGNAL FOR INITIAL HEAT AND QUENCHED SAMPLE

The deconvoluted data was smoothed to correct for the uniform ripple superimposed on the heat flow 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 (see figure 4). It was found that residual peak arises in the non-reversing component of quenched PET as a result of the temperature program (see figure 5). This can then be subtracted from the peak on the initial heat so any enthalpy change is due solely to relaxation processes. The kinetics of enthalpic relaxation as studied by MTDSC will be presented and compared with those of conventional DSC.

CONCLUSIONS

It is possible to separate a reversing glass transition from a non-reversing enthalpic relaxation process. However a residual peak develops in the non-reversing peak as a result of the sample complex thermal history. This can be corrected for by quenching and re-running the sample. The kinetics of enthalpic relaxation will be compared in a later paper but initial results indicate that it is more accurate to study enthalpic relaxation using conventional DSC.

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