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THE APPLICATION OF MODULATED TEMPERATURE POWER COMPENSATION DSC TO THE CHARACTERISATION OF POLYMER BLENDS

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Abstract

A modulated temperature power compensated differential scanning calorimeter, MTDSC, has been built from a standard Perkin-Elmer DSC model-2 such that a computer generated voltage has been applied to induce a sinusoidal change in sample temperature superimposed on a linear heating rate. The effect of amplitude of the temperature fluctuation, modulation period and block temperature on the reversibility has been assessed from the Lissajous diagram of heat flow *vs.* sample temperature. From their reproducibility and symmetry the most effective conditions for operating the MTDSC has been deduced. The specific heat of sapphire has been measured using these operational conditions for comparison with conventional DSC.

Phase separated blends of polycarbonate (PC) and polyethylene terephthalate (PET) have been analysed.

Keywords: crystallisation, glass transition, Lissajous diagrams, modulated temperature power compensation differential scanning calorimetry, polyethylene terephthalate/polycarbonate blends

Introduction

The advantages of modulated temperature heat flux differential scanning calorimetry, MTDSC, over conventional DSC have been discussed by Reading *et al.* [1]. Increased sensitivity, better resolution, and improved ability to resolve overlapping transitions have been claimed but it is increasingly apparent that the experimental conditions required for MTDSC are more stringent than those required for conventional DSC. Nevertheless, the technique has been used widely and it is conventionally being used to study polymers, composites, blends etc. In this paper a power compensation DSC has been used since the individual heaters are closer to sample and temperature sensor and the thermal response should be faster. However, the effect of experimental variables on MTDSC measurements needed to be quantified.

Computer temperature profiles were generated to follow a mathematical relationship but for comparison with the original work a sinusoidal heat/cool fluctuation was

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superimposed on a linear heating ramp. Three variables are involved – heating rate, β, temperature amplitude, A, and modulation period, p, i.e. the inverse of the frequency, ω. The temperature of the sample and reference, T, accordingly followed the relationship,

$$T = T_0 + \beta t + A\sin(\omega t) \tag{1}$$

where t is time and T_0 the initial temperature. The effects of these variables on the quality of the reversing and non-reversing specific heats are considered.

Wunderlich *et al.*'s [2] procedure of defining appropriate experiment conditions for pseudo-isothermal MTDSC measurements from the Lissajous diagrams of power against temperature was adopted. These plots were used to determine the maximum heating rates, amplitude and modulation periods for which the calorimeter's response was reversible in heating and cooling. The effect of sample and block temperatures as well as sample size was also considered and a comparison made with a heat flux MTDSC.

A polyethylene terephthalate/polycarbonate, PET/PC, blend has been studied using MTDSC and a comparison made with conventional DSC. This blend system has been extensively studied in the past [3–5].

Experimental

Polyethylene terephthalate, PET, was provided as moulding pellets by ICI Fibres Ltd. with a number average molecular mass of about 20 kg mol^{-1}. Bisphenol-A-polycarbonate, PC, was supplied by ECP Enichem. It had a number average molecular mass of 20 kg mol^{-1}. Pellets of the two polymers were dried at 110°C for 24 h and blended by mass in a twin screw extruder (supplied by APV) with zone temperatures from 285 to 310°C at high torque and shear. The blend extrudate was pelletised after cooling in a water trough at 7°C. The pellets were dried and compression moulded at 280°C for 3 min at 1520 kPa into 150×150×0.2 mm plaques. The plaques were quenched in ice/water. The plaques were amorphous as measured by DSC and X-ray wide-angle scattering. Compositions from 15 to 92 wt% PET were produced.

Measurements were made on a power compensated Perkin Elmer DSC, model 2 adapted for modulated temperature experiments. The heat-cool functions of the DSC were controlled by an IBM compatible PC and the heat flow-temperature data stored as well as displayed directly on the monitor. A multifunctional card with several A to D and D to A ports was used to measure the sample and reference temperatures as well as heat flow *vs.* time. The D to A port was used to generate a voltage, which followed a predetermined time dependence. When applied to the zero calibration potentiometer of the calorimeter the voltage controlled the sample and reference temperatures. Any time dependent voltage could be selected but for the present a sine wave was used for direct comparison with the earlier work of Reading *et al.* [1]. This sinusoidal heat-cool profile was superimposed on a linear heating ramp.

All samples were encased in aluminium pans. Pan and lid were used as reference, but were matched by mass. 15–20 mg samples were cut directly as discs from the moulded plaques. The DSC was calibrated from the *m.p.* of 99.999% indium, tin, zinc and lead and the thermal response from the melting endotherm of indium, (28.47 J g^{-1}).

Results

Quasi-isothermal experiments

In the following experiments a zero heating rate was used, i.e $\beta=0$.

Proof that the modulation of the sample and reference temperatures was occurring at the required modulation period and that these temperatures were following the generated voltage was obtained by attaching thermocouples to the underside of the calorimeter cells. The thermocouple readout, which was independent of the DSC, followed the temperature-time relationship and was the same as that measured by the individual platinum resistance thermometers with only a small lag that varied with modulation period. The platinum resistance thermometers were subsequently used to measure the sample, T_s and reference temperatures, T_r. The heat flow of the calorimeter was observed to lag behind the sample temperature and the size of the thermal lag depended on modulation period.

In order to establish under what experimental conditions the calorimeter was reversible in heating and cooling the relative heat flow was plotted *vs.* temperature as Lissajous diagrams (Fig. 1), and averaged over 30–40 cycles. Deviations from the elliptic response from cycle to cycle became obvious in the scatter around and irreproducibility of the ellipse such that the diagrams gave a ready indication as to whether the calorimeter was controlling or not. The amplitude and the modulation period was varied in a systematic way at different quasi-isothermal temperatures and also for a range of block temperatures and atmospheres, flowing nitrogen and helium. From the Lissajous diagrams the range of modulation periods available for a fixed temperature amplitude at each sample temperature could be determined.

For a fixed imposed amplitude of ±1.0 K the measured amplitudes which could be achieved at each modulation period and for different sample temperatures was determined. This is shown in Fig. 2. At the lower sample temperature the imposed am-

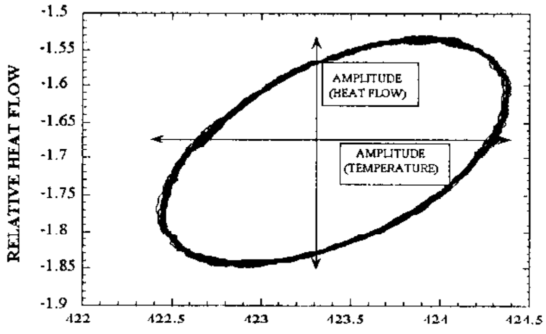

Fig. 1 Lissajous diagram

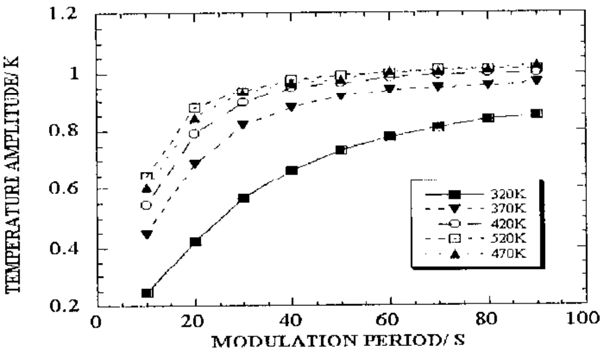

Fig. 2 Variation in amplitude for a sapphire sample, block=283 K, imposed amplitude=1 K

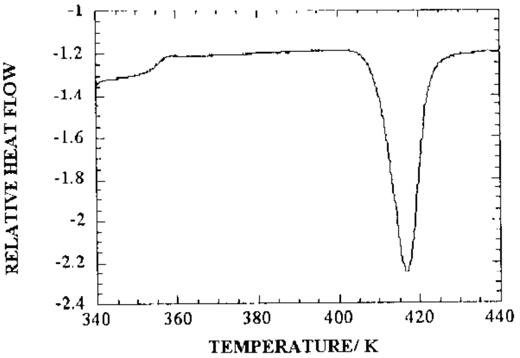

Fig. 3 15/85 PC/PET blend measured by conventional DSC

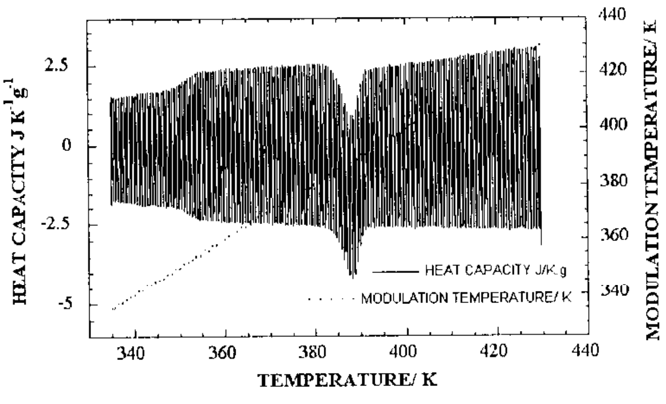

Fig. 4 15 PC/85 PET blend, HR=0.62°C min^{-1}

plitude could not be attained and indeed unless the modulation period was above 40 s this amplitude was not achieved even at the higher temperatures. However, by lowering the block temperature to 183±1 K cycling could be obtained at a sample temperature of 320 K.

Quasi-isothermal specific heat measurements were made on sapphire from the Lissajous diagrams measured at every 10 K from 320 to 580 K. The heat capacity was the ratio of the heat flow to temperature amplitudes. A linear correlation was obtained between the measured and NBS values for the specific heats with an R-value of 0.9985. Clearly using the standard method of calibrating the power response of the calorimeter from the specific heats of sapphire, there was a one to one correlation. These values had an uncertainty of 0.3% and this is more accurate than is normally quoted for conventional DSC, ±2%.

Non-isothermal measurement on polymer blends

A conventional DSC analysis of 85:15 PET/PC blend is shown in Fig. 3. It shows a glass transition at about 350 K and a crystallisation exotherm for PET at 415 K. The blend is heterogeneous but the crystallisation of the PET masks the glass transition of the PC phase at about 416 K. Figure 4 shows the corresponding MTDSC analysis for the same blend at a modulation of ±0.5 K, modulated frequency of 60 s and heating rate of 0.62 K $\min^{-1}$. This also clearly shows the glass transition and the crystallisation of PET and no glass transition for PC. However, deconvoluting the underlying reversing component of the specific heat shows two steps in the specific heats at about 350 and 410 K (Fig. 5). These are the Tgs of PET and PC.

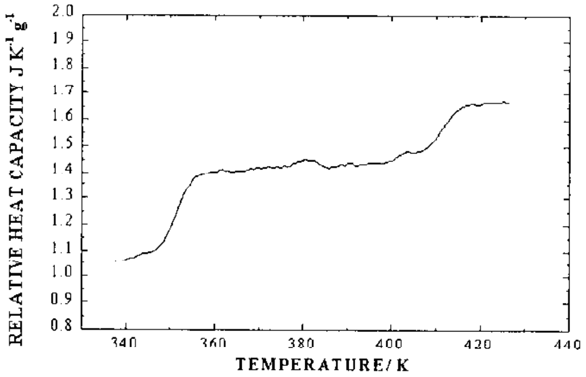

Fig. 5 15/85 PC/PET blend reversing trace

Conclusions

Temperature modulation has been achieved on a power compensated DSC. The effect of temperature amplitude and modulation period in limiting its effect range of use has been measured from Lissajous diagrams. It is apparent that it is more limited than conventional DSC but used under reversible conditions is more accurate in measuring specific heats. When applied to polymer blend systems, the reversible component of the specific heat is useful in resolving overlapping transitions and has been used to confirm the presence of the glass transition temperature of PC in a blend which was hidden by the presence of a crystallisation endotherm.

While more restricted than conventional DSC we consider that MTDSC has its place in conventional thermal analysis but great care has to be used in its application, particularly to polymer systems.

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