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

N. A. Bailey and J N Hay

The School of Metallurgy and Materials, The University of Birmingham, Edgbaston Birmingham B15 2TT, UK

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

* Author to whom all correspondence should be addressed.
superimposed on a linear heating ramp. Three variables are involved – heating rate, \( \beta \), temperature amplitude, \( A \), and modulation period, \( p \), i.e. the inverse of the frequency, \( \omega \). The temperature of the sample and reference, \( T \), accordingly followed the relationship,

\[
T = T_0 + \beta t + A \sin(\omega t)
\]

(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 150x150x0.2 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 moulder 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