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MODULATED DIFFERENTIAL SCANNING CALORIMETRY
III. Applications to measurements of the glass transition temperature and increment of heat capacity

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Abstract

Modulated-temperature differential scanning calorimetry was used to measure the glass transition temperature, T_g, the heat capacity relaxation in the glassy state and the increment of heat capacity, ΔC_p, in the glass transition region for several polymers. The differential of heat capacity with respect to temperature was used to analyse T_g and ΔC_p simply and accurately. These measurements are not affected by complex thermal histories.

Keywords: glass transition, heat capacity, modulated DSC

Introduction

Complex thermal histories affect the accuracy of glass transition temperature, T_g, measurements. Sometimes it is even difficult to obtain simply a T_g value, or the increment of heat capacity, ΔC_p, in the glass transition region. It is known that the T_g value depends on many parameters, such as the chemical nature of the polymer, its thermal history, different residual stresses and so on. These effects appear in the total heat flow signal from differential scanning calorimetry (DSC) or from modulated-temperature DSC (M-TDSC) [1] . Using the M-TDSC technique [1, 2], it is possible to obtain the value of heat capacity and its differential directly and accurately. A review of M-TDSC has been published by Reading [3]. The non-reversing heat flow signal has already been used to study physical ageing [4].

The aim of this paper is to develop a M-TDSC method which allows the simple and accurate determination of both the T_g and ΔC_p for polymers.

Experimental

Sample

Atactic polystyrene (PS) was obtained from BP Chemicals. Poly(methyl methacrylate) (PMMA), poly(styrene-co-acrylonitrile) (SAN) and poly(vinyl acetate) (PVAc) were obtained from Aldrich. The molecular weights were determined by

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GPC (Waters, model 510) and given in Table 1. The acrylonitrile content (23.9 wt%) of the SAN sample was determined by ^{1}H nmr spectroscopy (Jeol 100).

Table 1 Characterisation data

Sample	$M_w(\times 10^{-5})$	$M_n(\times 10^{-4})$
PS	2.10	9.30
SAN	1.62	8.57
PMMA	1.98	9.75
PVAc	5.20	13.7

Sample preparation

The PS sample was heated at 180°C for 5 min, then annealed at 150°C for 5 min to ensure that it was in its equilibrium state, so as to eliminate the effect of previous thermal history. The sample was cooled from 150°C to liquid nitrogen temperature very fast, and then annealed at different temperatures for one hour.

A SAN/PMMA (50/50, wt/wt) blend was prepared by solvent casting 5 wt% chloroform solutions in glass trays. The blend was dried under vacuum at 50°C for 4 weeks. This sample was initially heated in the M-TDSC module to a temperature of 160°C, approximately 55°C above the T_g, and held there for 10 min. Then the sample was quenched from 160°C to the aging temperature, 80°C, at a cooling rate of 10°C min^{-1}, using a flow of cold nitrogen vapour. The sample was then aged at 80°C in the M-TDSC cell. After aging, the sample was quenched to 30°C, the scan starting temperature.

The PVAc sample was quenched from 100 to 30°C, at a cooling rate of 20°C min^{-1}. It was then annealed at 30°C for different times and the change of heat capacity was measured.

Instrumentation

A TA Instruments M-TDSC was used. See Table 2 for experimental conditions for various polymers.

Table 2 Experimental conditions

Sample	Scanning rate/°C min^{-1}	Amplitude/°C	Period/s
Aged PS	4_h	0.8	60
Cyclic test on PS	$3_{c,h}$	1.5	60
PVAc	0	0.5	80
PMMA/SAN	3_h	1.0	60

c - cooling rate, h - heating rate.

Calibration

The heat capacity calibration was made by running a standard sapphire sample. Comparison of the experimentally determined heat capacity with a reported value [5] was made at the transition temperature. The temperature scale was calibrated using melting of indium.

Results and discussion

Measurements of the glass transition temperature and heat capacity relaxation

The total heat flow from M-TDSC is given by Eq. (2) [6].

$$dQ/dt = bC'_b + f(t, T) + \omega BC'_\omega \cos(\omega t) + C \sin(\omega t) \tag{2}$$

T is the absolute temperature, b is the heating rate, B is the amplitude of the sine wave, ω is the frequency of perturbation and t is the time. $bC'_b + f(t, T)$ is the underlying signal component, after the cyclic component, $\omega BC'_\omega \cos(\omega t) + C \sin(\omega t)$, has been filtered out by averaging over the period of the perturbation. Single-primed quantities, C'_b, C'_ω, denote reversing heat capacities. C is the amplitude of the change in heat flow due to the effect on $f(t,T)$ of the temperature modulation. Tlus equation may be expressed entirely in terms of heat capacity.

$$dQ/dt = b(C'_b + C_E) + \omega BC^*_\omega e^{j\omega t} \tag{3}$$

Here, C_E, defined as $f(t,T)/b$, is the apparent excess heat capacity as a consequence of the kinetically-hindered response of the sample. $C^*_\omega = C'_\omega + jC''_\omega$. C''_ω defined as $C/\omega B$, is the out-of-phase or kinetic heat capacity. For many processes such as simple irreversible chemical reactions, C''_ω is small [6], and, also,

$$C'_b = C'_\omega \tag{4}$$

Under these conditions, the non-reversing component, C_E, can be found by subtracting C''_ω from the underlying value $C'_b + C_E$. The situation when considering the glass transition is more complex, because C'_b and C'_ω are functions of the heating rate and ω, respectively. Here we have chosen conditions such that

$$C'_\omega >> C''_\omega \tag{5}$$

The glass transition temperature is a very important polymer parameter, since it indicates the limit of the polymer as a solid. Molecular dynamics simulations have shown [7] that for solid polymers (in the glassy state) the time involved to reach a steady-state temperature is in the picosecond range. The solid heat capacity can be written [7] simply as

$$C_p = C_{po} \tag{6}$$

C_{po} represents the vibrational heat capacity. In the liquid state, the equilibrium heat capacity is then given by the change in the number of holes with temperature under equilibrium conditions [8, 9].

$$C_p(\text{liquid}) = C_{po} + \varepsilon_h(dN^*/dT) \tag{7}$$

N^* is the equilibrium number of holes and ε_h is the activation energy for the formation of holes. On the cooling, or on the heating run, the heat capacity changes from Eq. (6) to Eq. (7) during the glass transition.

Most of the hole relaxation will be complete during cooling or heating through the glass transition when slower cooling or heating rates are used. The increment of heat capacity, ΔC_p, at glass transition does not change on the cooling and heating run, or for different thermal histories. Table 3 gives ΔC_p values for different experimental conditions. This can provide a method for the composition analysis of multiphase materials [10].

Table 3 ΔC_p values for different thermal histories

Sample	Thermal history		$\Delta C_p\ K^{-1}$/J(g °C)$^{-1}$
PS	cooling		0.259
	heating		0.257
SAN/PMMA	aged	0 (min)	0.319
		30	0.320
		180	0.325
		1020	0.327
		1800	0.319

K is the calibration constant.

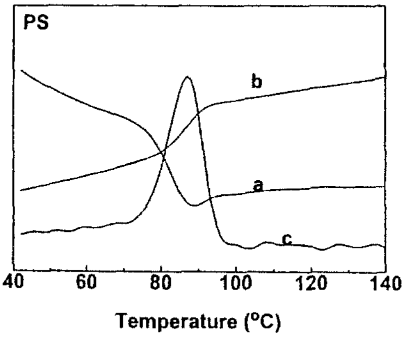

Fig. 1 Variations of total heat flow (a), heat capacity (b) and differential of heat capacity (c) with temperature for polystyrene

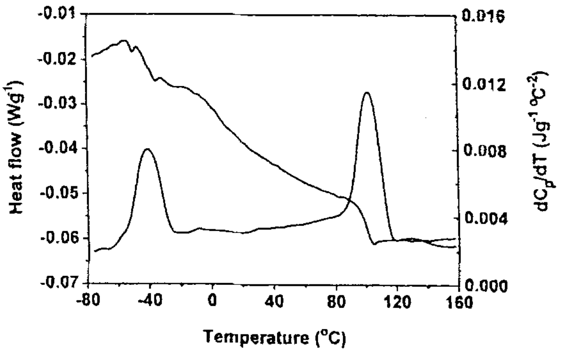

Fig. 2 Variations of total heat flow (a) and differential of heat capacity (b) with temperature for the (60:40) polyurethane-polystyrene IPN

Figure 1 shows the changes of total heat flow, heat capacity and the differential of heat capacity with temperature for PS. The relaxation signal appears in the total heat flow signal. It can be seen that the peak position of the differential of heat capacity corresponds to the point of inflection of the heat flow curve or heat capacity curve. If the peak position is used to determine the T_g, it is very easy and accurate.

Figure 2 gives another example of a polyurethane-polystyrene (60:40) interpenetrating polymer network, IPN, made in our laboratory [11]. Obviously, it is very difficult to obtain the T_g values from the total heat flow, because the heat flow signal is very complex. However, it is very easy using the differential of heat capacity signal to obtain them accurately and simply. The dC_p/dT maximum gives a glass transition temperature at half vitrification which is governed only by the time scale of modulation [12].

Figure 3 shows the changes of dC_p/dT *vs.* temperature for a SAN/PMMA (50/50, wt/wt) blend at different aunealing times. The peak position is almost constant. Figure 4 gives another example of PS after annealing at different temperatures for one hour. T_g was 86.5±1.0°C in spite of the different annealing temperatures. The change is small. Figure 5 gives the results for a cyclic experiment with PS. The T_g value is 85°C on cooling, and 86°C on heating.

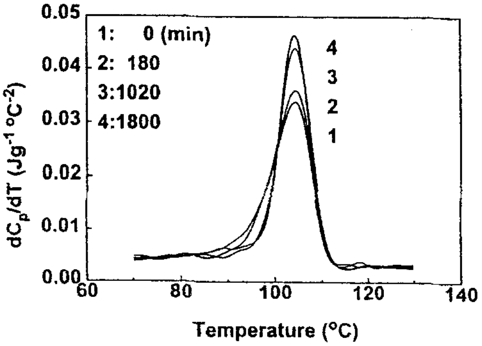

Fig. 3 dC_p/dT *vs.* temperature for the SAN/PMMA (50/50) blend at different annealing times

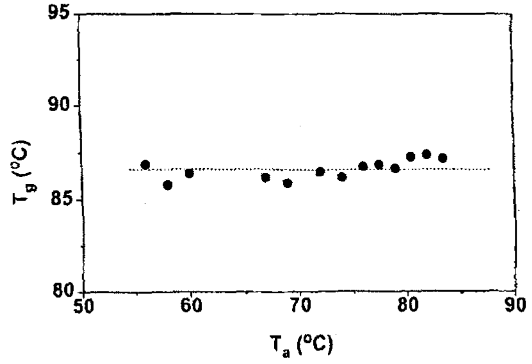

Fig. 4 Variation of the glass transition temperature with ageing temperature for polystyrene

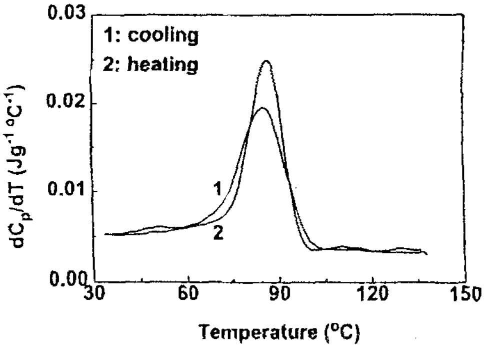

Fig. 5 Differential of heat capacity *vs.* temperature for polystyrene in a cyclic experiment

Figures 3, 4 and 5 show that T_g determined using the M-TDSC differential of heat capacity signal does not give changes which are sensitive to previous thermal history. However, the non-reversing signal showed that the peak position indeed shifted to lower temperatures with decrease in annealing temperature [4]. Figure 6 shows the change of non-reversing heat flow with temperature for the cyclic experi-

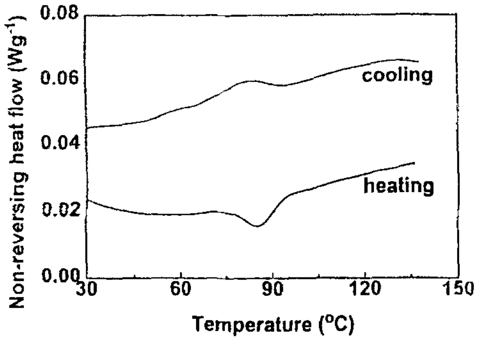

Fig. 6 Non-reversing heat flow *vs.* temperature for polystyrene in a cyclic experiment

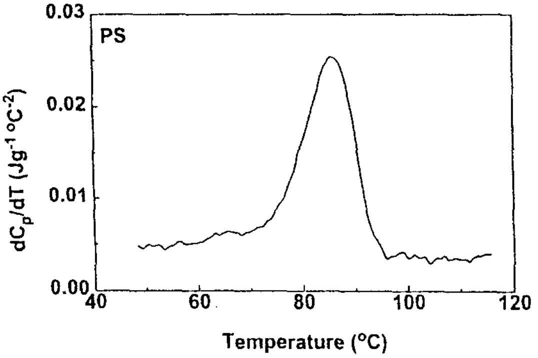

Fig. 7 Differential of heat capacity *vs*. temperature for polystyrene at 0.5°C $\min^{-1}$

ment for PS. In the cooling mode, the peak position of the non-reversing heat flow shifts to lower temperature. The difference between the peak temperatures of the cooling and heating modes is about 4°C.

Recently, Reading *et al.* [6] have indicated that at a slower cooling rate (1°C $\min^{-1}$), the underlying signal is free from any relaxation effects, and, thus, is purely reversing. Figure 7 shows the results for a heating experiment with PS carried out at 0.5°C $\min^{-1}$, where no relaxation occurs. Under these experimental conditions, the T_g is 86°C. This result is the same as that of the cyclic experiment. The glass transition temperature derived from dC_p/dT (also from heat capacity) is almost independent of heating rate. Thus, one can measure it from a heating or a cooling run, as it is largely independent of thermal history. The fact is that T_g hardly changes whether the process is purely reversing or not. In this way, M-TDSC is able to establish a precise glass transition temperature on cooling as well as on heating. Conventional DSC is unable to do this because of the simultaneous recording of heat capacity and enthalpy relaxation.

M-TDSC can also be used to measure the heat capacity change near T_g. Figures 8 and 9 give the results of heat capacity *vs*. time for PVAc at 30°C and for the SAN/PMMA(50/50) blend at 85°C. The dashed lines shown in Figures 8 and 9 are the fitting results. The following C_p-time relationship holds.

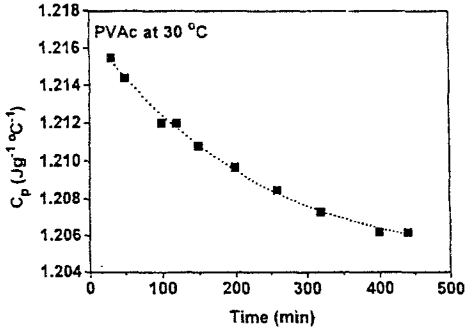

Fig. 8 Heat capacity of PVAc *vs*. annealing time at 30°C

$$C_p(t) = C_p(\infty) + A\exp(-t/\tau)$$

A and t are constants. These results clearly show that the value of heat capacity decreases with annealing time. However, this change is very small. It is only about 1.2% of the heat capacity value at the equilibrium state. This will be the subject of a future paper [13].

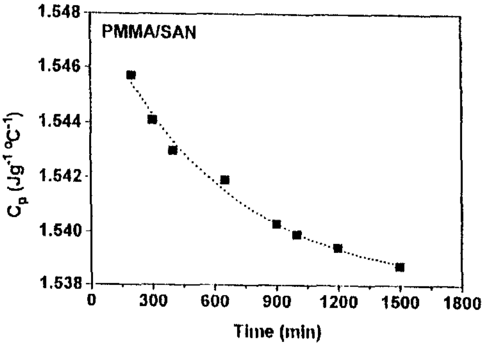

Fig. 9 Heat capacity of (50/50)SAN/PMMA blend *vs*. annealing time at 85°C

ΔC_p *measurements*

The value of the apparent heat capacity, C_p^a (not calibrated) can be presented as follows.

$$C_p^a = A_0 + A + BT + f(T) \tag{8}$$

A_0 is a system state constant. Different state constants result in the shift of the base line. A and B are constants and $f(T)$ is a function of temperature. Outside the transition region, $f(T)=0$.

Consider the value of the differential of the apparent heat capacity with temperature.

$$dC_p^a/dT = B + df(T)/dT \tag{9}$$

To obtain the required value of heat capacity, it is necessary to integrate the signal over the region of interest, which in this case is the glass transition.

$$\Delta C_p^a = \int_{T^a_{p(i)}}^{T^a_{p(e)}} (dC_p^a/dT)dT \tag{10}$$

$T^a_{p(i)}$ and $T^a_{p(e)}$ are the initial and final temperatures in the glass transition region [10]. It is assumed that the integration constant is independent of temperature. Using the above equation to calculate ΔC_p, only requires a one-point calibration for heat capacity, which is selected in the transition region. The reason for this is discussed below.

If it is assumed that the calibration constant of heat capacity is K_1 at the onset point of the glass transition and is K_2 at the final point, then the increment of heat capacity at glass transition region is as follows.

$$\Delta C_p = K_2 C^a_{p(e)} - K_1 C^a_{p(i)} \tag{11}$$

In this paper, the value of the one-point calibration constant, K, is approximately

$$K = (K_1 + K_2)/2 \tag{12}$$

Consider that

$$K = K_1 + \delta = K_2 - \delta \tag{13}$$

where δ is a small increment. Then Eq. (11) can be rewritten as follows:

$$\Delta C_p = K[\Delta C^a_p + \delta/K(C^a_{p(e)} + C^a_{p(i)})] \tag{14}$$

According to our experimental results, $\delta/K \sim 10^{-3}$. Thus, Eq. (15) holds.

$$\Delta C_p = K \Delta C^a_p \tag{15}$$

The difference between the results from Eq. (14) and those from Eq. (15) is about 3%.

There is considerable interest in numerical values of ΔC_p at the T_g and various generalisations have been suggested [14, 15] either for ΔC_p or the product $\Delta C_p T_g$.

Conventionally, ΔC_p measurement is labour intensive [16]. Based on this new method, the task becomes very simple. It is only necessary to calculate the integral of the differental signal of heat capacity over the glass transition region. Figure 10 shows the changes of calculated ΔC_p data for PS for different ageing temperatures at same ageing time. The average value of ΔC_p is about 0.30 J(g °C)$^{-1}$. Comparison of the value with literature [17], shows a difference of about 3%. The average value of the product $\Delta C_p T_g$ is 109 J g^{-1}.

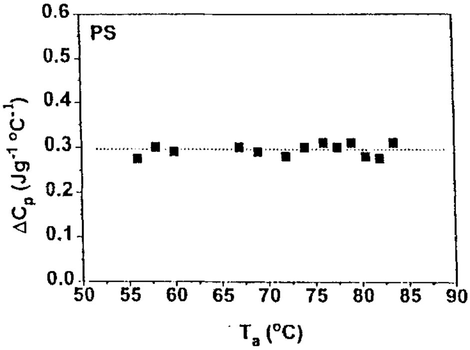

Fig. 10 ΔC_p *vs.* ageing temperature for polystyrene

Conclusion

The differential of heat capacity *vs.* temperature signal has been developed. It can be used to determine the glass transition temperature and the increment of heat capacity during the glass transition accurately and simply.

References

1 M. Reading, B. Hahn and B. Crow, US patent 5224775.
2 P. S. Gill, S. R. Sauerbrunn and M. Reading, J. Thermal Anal., 40 (1993) 937.
3 M. Reading, Trends in Polymer Science, 1 (1993) 249.
4 D. J. Hourston, M. Song, A. Hammiche, H. M. Pollock and M. Reading, Polymer, 37 (1996) 243.
5 D. A. Ditmars, J. Res. Nat. Bur. Stand., 87 (1982) 159.
6 M. Reading, M. Jones and H. M. Pollock, to be submmitted for publication.
7 G. L. Liang, D. W. Noid, B. G. Sumpter and B.Wunderlich, Makromol.Chemie, 2 (1993) 245.
8 N. Hirai and H. Eyring, J. Appl. Phys., 29 (1958) 810.
9 N. Hirai and H. Eyring, J. Polymer Sci., 37 (1959) 51.
10 D. J. Hourston, M. Song, A. Hammiche, H. M. Pollock and M. Reading, Polymer, in press.
11 D. J. Hourston, unpublished work.
12 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 227.
13 M. Song, A. Hammiche, H. M. Pollock, D. J. Hourston and M. Reading, to be submitted for publication.
14 B. Wunderlich and L. D. Jones, J. Macromol. Sci. (B), 3 (1969) 67.
15 R. F. Boyer, J. Macromol. Sci. (B), 7 (1973) 487.
16 M. J. Richardson and N. G. Savill, Polymer, 16 (1975) 753.
17 B.Wunderlich, Polymer Handbook, 1992.