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MODULATED DIFFERENTIAL SCANNING CALORIMETRY OBSERVATION OF PHYSICAL AGEING IN POLYMERS

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Abstract

Modulated-temperature differential scanning calorimetry (M-TDSC) is becoming a useful tool in the characterisation of thermal behaviour of polymers. In this paper, we discuss whether the non-reversing M-TDSC signal can be used, quantitatively and directly, to study the process of physical ageing in polymers. Difference exists between the values of relaxation enthalpy determined by using average heat capacity, $<C_p>$, signal as for conventional DSC and non-reversing heat capacity, C_p^n, signal. When the signal of reversing heat capacity of unaged sample is considered as baseline for $<C_p>$ and C_p^n signals, the difference disappears. It is concluded that non-reversing M-TDSC signal can be used to observe the process of physical ageing semi-qualitatively and directly. With increasing annealing time, the peak of the imaginary part, C_p'', of the complex heat capacity becomes narrow, but peak area changes little. This indicated that C_p'' is not correlated with relaxation enthalpy. It may be related to entropy change during the modulation. However, the entropy change is quite small.

Keywords: entropy, glass transition, modulated DSC, physical ageing

Introduction

The modulated-temperature differential scanning calorimetry (M-TDSC) technique is growing in popularity since its introduction a few years ago [1]. From M-TDSC, one can obtain [2, 3] the following physical quantities.

1. The average heat capacity, $<C_p>$, as for conventional DSC.
2. The complex heat capacity, C_p^*, which can be divided two parts: the real part referred to as the reversing heat capacity, C_p', describes molecular motions and corresponds to the heat capacity in the case of equilibrium, and the imaginary part, C_p''.
3. The non-reversing heat flow or non-reversing heat capacity, C_p^n.
4. The phase angle, which is the phase difference between heat flow and the heating rate.

The non-reversing part has been used to observe physical ageing process [4] in polystyrene. The non-reversing heat flow is only the difference between the total heat

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flow and the reversing heat flow. Some comments indicated that time-dependent events were not correctly described by the non-reversing heat flow [5]. The principal question we wish to raise is whether the non-reversing heat flow or the non-reversing heat capacity can be used for the quantitative study of physical ageing in polymers? We are also concerned with C''_p signal in the glass transition region and whether it can be used to study structure relaxation of glassy polymers.

Experimental

Samples and preparation

Poly(vinyl acetate) (*PVAc*), and polystyrene (*PS*) were obtained from Aldrich. The characterisation data for these polymers are given in Table 1. The average molecular mass and polydispersities were determined using GPC calibrated relative to polystyrene standards.

Table 1 Characterisation data

Polymer	M_m (10^{-5})	M_m/Mn
PS	0.92	1.06
PVAc	0.47	3.1

The *PS* and *PVAc* films were initially heated in the M-TDSC module at 160 and 100°C, approximately 55°C above T_g, for 10 min. Then the *PS* and *PVAc* were quenched from 160 to 40°C and from 100 to 30°C, respectively, at a cooling rate of 20°C min^{-1}. The *PS* and *PVAc* were then aged at 85 and 30°C, respectively, in the M-TDSC cell.

PVAc cyclic experiment: at 100°C for 10 min, the *PVAc* was cooled at a cooling rate of 2°C min^{-1} to –10°C, and then was reheated at a heating rate of 2°C min^{-1} to 100°C.

M-TDSC

A TA Instruments 2920 M-TDSC calorimeter was used. An oscillation amplitude of 1.0°C and an oscillation period of 60 s with a heating rate (also in cooling-heating experiments) of 2°C min^{-1} were used. The calorimeter was calibrated with a standard indium sample. From 2920 M-TDSC, the following important signals can be obtained directly.

1. Heat flow
2. Complex heat capacity, C^*_p
3. Reversing heat flow (or reversing heat capacity, C'_p, which has been used to analyse interphases in multi-component polymer materials quantitatively [15]
4. Non-reversing heat flow (or non-reversing heat capacity, C^n_p), which has been used to determine relaxation enthalpy for physical ageing of polymers [4]

$$C_p^n = \langle C_p \rangle - C_p'$$

5. Phase angle, $\phi(\tan\phi = C_p'/C_p'')$
6. Dynamic heat capacity C_p'' (imaginary part)

$$C_p^* = C_p' + iC_p''$$

Results and discussion

PVAc cyclic experiment

The post-annealing glass transition of *PS* has been investigated by M-TDSC in the heating mode by Boller *et al.* [6]. The non-reversing component showed a peak in the glass transition region on annealing. Figure 1 shows non-reversing heat flow *vs.* temperature curves for *PVAc* in a cyclic experiment. In the cooling mode, the non-reversing heat flow also showed a broad peak in the glass transition region which was lower by 3°C (peak position) than in the heating mode under these experimental conditions. Figure 2 shows the change of the reversing heat capacity *vs.* temperature in the cyclic experiment for *PVAc*. For the heating and cooling modes, the values of the reversing heat capacity are slightly different in the glass transition region.

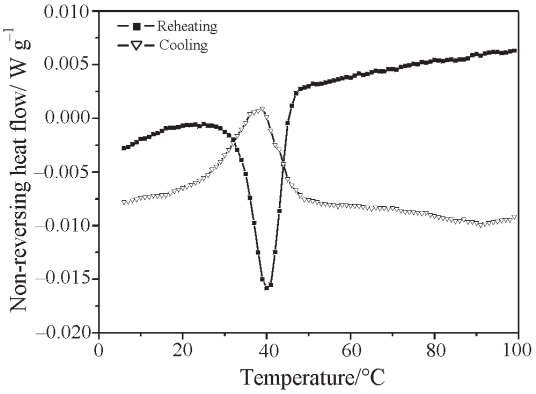

Fig. 1 Non-reversing heat flow *vs.* temperature signals for a cooling-reheating cycle experiment

Each cycle contains structural relaxation in its below T_g part because enthalpy and volume are frozen-in at some value. However, enthalpy relaxation does not exist above T_g. The question arises as to the origin of the peak shown in the cooling mode in the glass transition region? The non-reversing heat flow is determined by subtracting the reversing heat flow from the total heat flow. The total heat flow corresponds to that in a conventional DSC measurement and should be determined at a constant heating rate. The total heat flow depends on heating rate. The underlying constant heating rate can be connected to a certain average frequency, ω_c [5]. The heat capac-

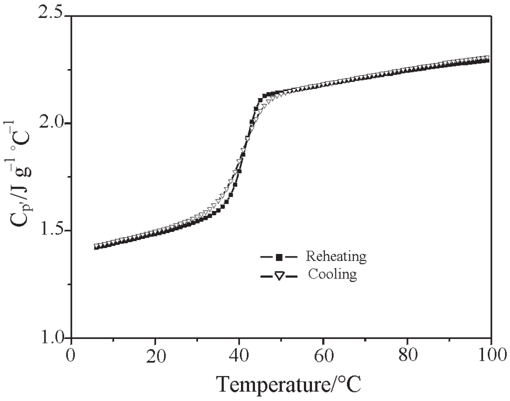

Fig. 2 Reversing heat capacity *vs.* temperature signals for a cooling-reheating cycle experiment

ity, and also the reversing component, is affected by the frequency, ω. Generally, $\omega_c \neq \omega$. The frequency effect on total heat flow and reversing heat flow are different in cooling mode, i.e.,

$$\int <C_p(\omega_c)> \mathrm{d}T \neq \int C_p'(\omega)\mathrm{d}T$$

The difference should result mathematically in a peak formation in non-reversing heat flow in the cooling mode. Thus, the peak in the cooling mode is not enthalpy relaxation.

Measurement of relaxation enthalpy

In amorphous polymers, it is common for an enthalpy relaxation to be present over the glass transition region. This relaxation, which has been described in literature using several names including stress relaxation and volume relaxation, is endothermic and increases in size with longer ageing times and increased ageing temperatures [7]. Hence, measuring the size of this relaxation is of interest. According to the definition of the measurement of non-reversing heat flow, the value of non-reversing signal is affected by frequency. Since frequency is inversely related to period, the reversing heat capacity C_p' is shifting to higher temperatures as modulation period decreases. Figure 3 shows the changes of 'relaxation enthalpy' (peak area in the non-reversing heat flow) with modulation period determined for the unaged *PS*. With increasing frequency, the value increases. Obviously, this is not expected. Thus, the value cannot be used quantitatively for the study of physical ageing in polymers.

To obtain a measure of the 'relaxation enthalpy' for aged polymers, a series of physical ageing experiments for the *PS* was conducted. Figure 4 shows the values of relaxation enthalpy determined at different periods for *PS* aged at 85°C. The annealing time was 840 min. The uncalibrated values are again affected by frequency.

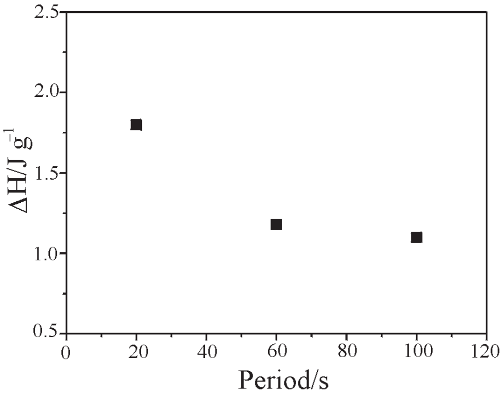

Fig. 3 ‘Relaxation enthalpy’ *vs.* period for the unaged *PS*

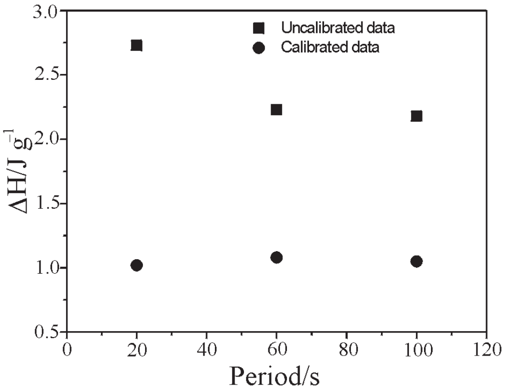

Fig. 4 ‘Relaxation enthalpy’ *vs.* period for the aged *PS*

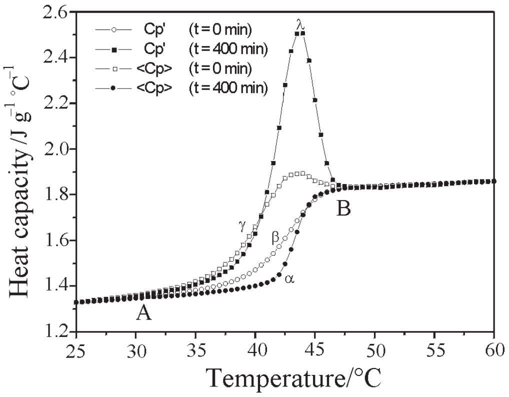

Fig 5 $<C_p>$ and C'_p *vs.* temperature signals for the unaged and aged *PVAc*

When the unaged experimental data are considered as the baseline, the calibrated data are independent of the period used.

However, it is necessary to know whether the value of relaxation enthalpy determined by C_p^n signal is the same as that determined by $<C_\mathrm{p}>$ signal as for conventional DSC. Figure 5 shows a comparison for calibrated heat capacities, C'_p and $<C_\mathrm{p}>$, for unaged and aged *PVAc*. The value of relaxation enthalpy determined by $<C_\mathrm{p}>$ as for conventional DSC equal to the difference of peak area BλA and peak area BγA for the aged and the unaged, respectively. The value of relaxation enthalpy determined by C_p^n, which is the difference of $<C_\mathrm{p}>$ and C'_p, is illustrated and equal to peak area BλAα–peak area BγAβ. Then, we have

$$(\text{area } \mathrm{B}\lambda\mathrm{A}\alpha\text{–peak area } \mathrm{B}\gamma\mathrm{A}\beta)\text{–}(\text{peak area } \mathrm{B}\lambda\mathrm{A}\text{–peak area } \mathrm{B}\gamma\mathrm{A})=\text{area } \mathrm{B}\beta\mathrm{A}\alpha\mathrm{B}\neq 0$$

Obviously, the value of relaxation enthalpy determined by C_p^n signal is different from that determined by $<C_\mathrm{p}>$ signal as for conventional DSC. How to understand the difference? The reversing heat capacity, C'_p, describes molecular motions and corresponds to the heat capacity in the case of equilibrium. With increasing annealing time, volume decreases [8, 9]. Annealing results in perfection of molecular chain packing and reduces the mobility because of decrease of free volume and increases activation energy [10]. With increasing annealing time C'_p is affected, shifting to higher temperature. So non-reversing heat flow or non-reversing heat capacity chooses a variable baseline. Figure 6 gives a comparison of ΔH calculated by using $<C_\mathrm{p}>$, C_p^n and C''_p signals.

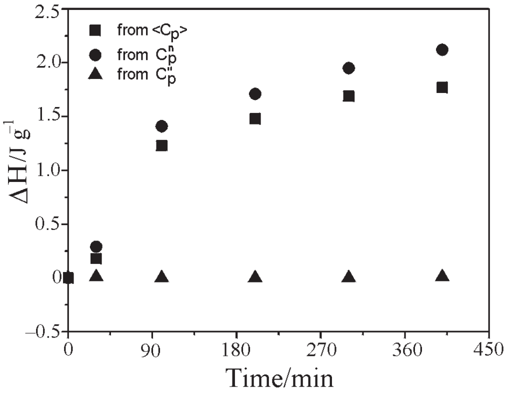

Fig. 6 Comparison for the values of relaxation enthalpy calculated by using $<C_\mathrm{p}>$, C_p^n and C''_p signals

C'_p *physical meaning*

Figure 7 shows C''_p *vs.* temperature at different annealing times for the *PVAc* at 30°C. With increasing annealing time, C''_p is also affected, shifting to higher temperature. Similarly, because the phase angle is small, C''_p is similar to the phase angle itself,

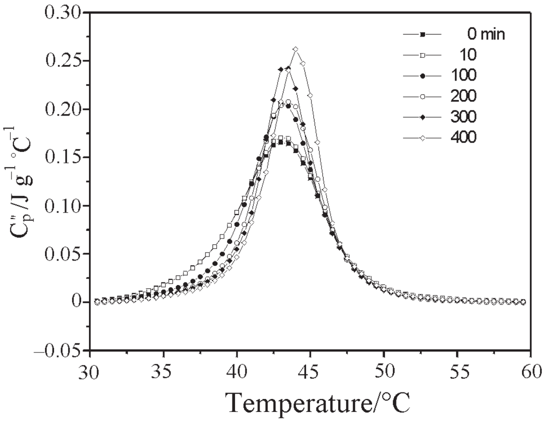

Fig. 7 C_p'' *vs.* temperature signals at different annealing times for the *PVAc*

though modified slightly by the changing value of C_p^* through the glass transition region. C_p'' displays a peak at essentially the same temperature as does phase angle, and is zero before and after the glass transition. The theory developed by Lacey *et al.* [3] indicated an almost invariant peak area and position as the annealing time increases. Experimentally, the peak area changes little, but peak position shifts to higher temperatures with increasing annealing time. Theory model [3] can not describe C_p'' behaviour with annealing time well. C_p'' is not correlated with enthalpy relaxation.

If a system relaxes slowly to equilibrium, the change in enthalpy per unit volume, *H*, can be written as follows [11].

$$H=\{C_{p\infty}+(C_{po}-C_{p\infty})[1-\Phi(t)]\}\delta T \text{ for } t>0 \qquad (1)$$

δT is the change of temperature for calculating the *H* [11]. C_{po} is the equilibrium heat capacity. $C_{p\infty}$ includes all the degrees of freedom that equilibrate very quickly. $\Phi(t)$ describes the time dependence of the relaxation of the system to equilibrium. $\Phi(t=0)=1$ and $\Phi(t\to+\infty)=0$. Heat capacity is determined in the frequency domain as well as in the time domain. Taking a Fourier transform, the following equation for frequency-dependent heat capacity, $C_p(\omega)$, can be obtained [11].

$$C_p(\omega)=C_{p\infty}+(C_{po}-C_{p\infty})\int_0^{\infty}[-\mathrm{d}\Phi(t)/\mathrm{d}t]\exp(\mathrm{i}\omega t)\mathrm{d}t \qquad (2)$$

The static heat capacity is $C_p(\omega=0)=C_{po}$. Then, for slow relaxation processes, $C_{po}-C_{p\infty}>0$. $C_p(\omega)$ must be a complex heat capacity. This reflects the fact that the heat oscillations lag in phase behind the temperature oscillations whenever the inverse of the measurement frequency is comparable to the characteristic relaxation time of the system. Birge and Nagel [11] indicated that one associates the imaginary part of a linear susceptibility of a net absorption of energy by the sample from the application, but a complete cycle of a frequency-domain heat capacity experiment there is no net exchange of energy between the sample and the surrounding heat bath. However, the entropy changes during a complete cycle, by an amount proportional to C''_p.

Recently, Schawe [12] and Hutchinson and Montserrat [13] discussed physical meaning of C''_p. Schawe [12] indicated that C''_p is connected to the time-dependent processes which includes information about the internal entropy change. From a thermodynamic viewpoint, the minimal entropy change during modulation is given by [14]

$$\Delta S = -\int_{t=0}^{t=2\pi/\omega} \mathrm{d}Q/T \tag{3}$$

dQ is the heat transferred from the heat bath to the sample. According to Reading *et al.* [2, 3], for a complete cycle, the heat flow, d$Q(\omega)$/dt can be rewritten as follows.

$$\mathrm{d}Q(\omega)/\mathrm{d}t = \omega A_\mathrm{T}[C'_\mathrm{p}(\omega)\cos(\omega t) + C''_\mathrm{p}(\omega)\sin(\omega t)] \tag{4}$$

with

$$T = T_\mathrm{o} + A_\mathrm{T}\sin(\omega \mathrm{t}) \tag{5}$$

T_o is the starting temperature.

The following relation holds.

$$\Delta S = -\int_{t=0}^{t=2\pi/\omega} \omega A_\mathrm{T}[C'_\mathrm{p}(\omega)\cos(\omega t) + C''_\mathrm{p}(\omega)\sin(\omega t)]/[T_\mathrm{o} + A_\mathrm{T}\sin(\omega t)]\mathrm{d}t = \pi(A_\mathrm{T}/T_\mathrm{o})^2 C''_\mathrm{p} \tag{6}$$

For a complete cycle, the C''_p is correlated with ΔS.

According to Jones *et al.* [3], the C''_p formula has been obtained [15].

$$C''_\mathrm{p} = \Delta C_\mathrm{p}\omega\tau_\mathrm{g}\exp[-\Delta h^*/(RT_\mathrm{g}^2)(T-T_\mathrm{g})]/\{1+\omega^2\tau_\mathrm{g}^2\exp[-2\Delta h^*/(RT_\mathrm{g}^2)(T-T_\mathrm{g})]\} \tag{7}$$

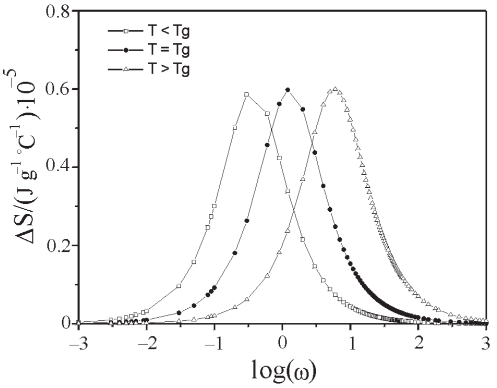

Fig. 8 ΔS *vs.* frequency for the *PS* theoretically

τ_g is the relaxation time at T_g, Δh^* is the activation energy, T_g is the glass transition temperature, ΔC_p is the increment of heat capacity at T_g. We have

$$\Delta S=\pi(A_T/T_o)^2\Delta C_p\omega\tau_g\exp[-\Delta h^*/(RT_g^2)(T-T_g)]/\{1+\omega^2\tau_g^2\exp[-2\Delta h^*/(RT_g^2)(T-T_g)]\} \qquad (8)$$

Figure 8 shows ΔS *vs.* ω for the *PS* theoretically. Generally, $A_T \ll T_o$, $\Delta S \approx 0$.

Conclusions

Difference exists between the values of relaxation enthalpy determined by $<C_p>$ and C'_p signals. The non-reversing M-TDSC signal can be used to observe the process of physical ageing semi-qualitatively and directly. The relaxation peak in the cooling mode in the glass transition region does not result from enthalpy relaxation, only from the difference between effects of heating rate and frequency on segmental motions. With increasing annealing time, C''_p peak becomes narrow, but peak area changes little. C''_p is not correlated with relaxation enthalpy. It may be related to entropy change during modulation. However, the entropy change is quite small.

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