Reversible melting in poly(butylene terephthalate)

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Abstract

Crystallized samples of poly(butylene terephthalate) (PBT), examined in the melting region by means of temperature modulated differential scanning calorimetry (TMDSC), show reversible fusion. The analysis of the complex heat capacity reveals that the fusion of poor crystallites can follow temperature modulation more easily than perfect crystals, in agreement with the findings recently reported in the literature, and that the amount of reversible melting decreases with increasing the modulation frequency. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Temperature modulated differential scanning calorimetry (TMDSC) is a technique which provides information about the reversible aspects of thermal events [1–4]. It is well known that TMDSC is characterized by a periodic temperature modulation which is applied to the conventional linear DSC temperature programme:

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

where β is the underlying scanning rate, T_a the amplitude of the temperature modulation and ω the angular modulation frequency ($\omega = 2\pi\nu = 2\pi/t_p$, ν and t_p being the frequency and the period, respectively).

The resulting heat flow rate is analysed to obtain an underlying component, corresponding to the heat flow signal available from a conventional DSC, and a periodic component [1,4].

Two different mathematical approaches have been proposed in order to analyse the thermal behaviour under TMDSC conditions and, as a consequence, two different physical interpretations of the heat flow response have been suggested [5–9].

In this paper the method developed by Schawe et al. has been followed and used. According to Schawe's treatment [7–9], the modulus of the complex specific heat capacity $c(\omega)$ can be calculated by means of the following relationship:

$$|c(\omega)| = \frac{\Phi_a}{mT_a\omega}, \tag{2}$$

where Φ_a is the calibrated heat flow rate amplitude of the periodic component [9] and m the sample mass.

The complex heat capacity, which is frequency dependent, is defined as

$$c(\omega) = c'(\omega) - \mathrm{i}c''(\omega) \tag{3}$$

with

$$c'(\omega) = |c(\omega)| \cos(\phi), \qquad (4)$$

$$c''(\omega) = |c(\omega)| \sin(\phi), \qquad (5)$$

where $c'(\omega)$ and $c''(\omega)$ are the real and the imaginary heat capacity, respectively, and ϕ the phase shift between the heat flow signal and the temperature change rate.

Neglecting the contribution due to heat transfer [9], the phase shift ϕ is equal to zero if thermal events do not occur in the sample; as a consequence $c'(\omega)$ and $|c(\omega)|$ are identical and correspond to the equilibrium heat capacity.

The above mathematical treatment is correct only if the system remains close to equilibrium during the temperature modulation; i.e. the change of the heat capacity must be low within a modulation period [7]. For this reason, severe operative conditions have to be respected: small underlying scanning rates and small temperature amplitudes [7,8].

The TMDSC technique is particularly useful in the study of polymeric materials, whose processes, owing to the limited mobility of the chains, are often essentially slow and time-dependent [10]. These thermal events can be easily observed in the complex heat capacity curve when their characteristic times τ are comparable to the period of the temperature modulation. For this reason, the choice of the underlying heating rate and the modulation frequency and amplitude is critical. Glass transition, as well as melting and crystallization, are thermal processes that, in the appropriate conditions, can be reversed during the modulation period [6,8,11–13]. Other thermal events, such as, for example, cold crystallization, enthalpy relaxation, annealing and crystal reorganization, that take place far from equilibrium, occur continuously during the run and are not revealed, except to a very small extent [10], by $|c(\omega)|$, $c(\omega)'$ and $c(\omega)''$ curves.

Several papers dealing with the analysis of the glass transition by modulated differential scanning calorimetry are found in [6,8,11,14–19]. Only recently attention has been devoted to the study of reversible melting and crystallization [5,6,12,13,20–26]. As a matter of fact, problems arise in the interpretation of first-order transitions, owing to relevant kinetic effects [6,12,13].

The present note reports a preliminary study carried out by means of TMDSC on the melting behaviour of poly(butylene terephthalate).

2. Experimental

The poly(butylene terephthalate) (PBT) sample (M_n=28 000) was synthesized in the bulk according to the usual two-stage polycondensation procedure. The measurements were carried out by means of a Perkin-Elmer dynamic differential scanning calorimeter DSC 7 (DDSC). The external block temperature control was set at $-20°C$. The instrument was calibrated in temperature and energy with high-purity standards (indium, cyclohexane, *n*-octadecane, zinc) at $2°C$ min^{-1} according to the procedures of standard DSC. Dry nitrogen was used as purge gas at a rate of 35 ml min^{-1}. In order to reduce temperature gradients, the sample mass was kept small and approximately equal to 4 mg.

The following standard test procedure was employed: the samples were heated up to $260°C$, kept at this temperature for 3 min in order to cancel any previous thermal history, then quickly cooled down to $200°C$. At this temperature, PBT crystallization is fast and the levelling off of the DSC trace occurs within 5 min. Nevertheless, the samples were kept at $200°C$ for 30 min to improve crystal perfection as much as possible. Subsequently the crystallized samples were analysed from $200°C$ to $235°C$ using the dynamic programme that in Perkin-Elmer DDSC is obtained through a saw-tooth temperature modulation. The underlying heating rate was set at $0.6°C$ min^{-1}, the temperature modulation amplitude was $0.1°C$ and the frequency ranged from 12.5 to 25.0 mHz. It is worth noting that modulation amplitudes and frequencies were chosen in order to avoid cooling during the dynamic runs. In such a way temperature calibration problems that could arise due to the possible discontinuity at zero heating rate [27] can be totally eliminated. Moreover, taking into account that the measured rate compensation was 0.07 K/(K min)$^{-1}$ [28] and the heating rates ranged from 0.2 to $1.2°C$ min^{-1}, it turns out that the maximum temperature uncertainty was lower than $0.1°C$, a value that can be considered within the experimental error. Very

recently temperature calibration in TMDSC has been widely discussed [29].

The Perkin-Elmer DDSC software analyses the periodic component of the heat flow rate response by means of a Fourier series: the first harmonic, that was found to be generally the prominent term of the series [8,13], is extracted and examined. It is worth noting that the heat flow rate data are corrected by subtracting an empty pan run obtained under the same conditions. In this way the instrumental effects due to the time-dependent heat response of the calorimeter can be removed and the measured phase shift, after correction of phase lag [9,19,24], can be associated with the time-dependent processes that occur in the sample.

3. Results and discussion

The specific heat capacity, c_β, of a crystallized PBT sample, calculated from the underlying component of the heat flow rate, is shown in Fig. 1 together with the modulus of the complex specific heat capacity, $|c(\omega)|$, which, on the contrary, is obtained from the periodic component.

It is well known for PBT that the double melting endotherm, observed by conventional DSC, is due to a mechanism based on fusion of original less perfect crystallites that, after recrystallization into thicker crystals, finally melt at higher temperature [30,31].
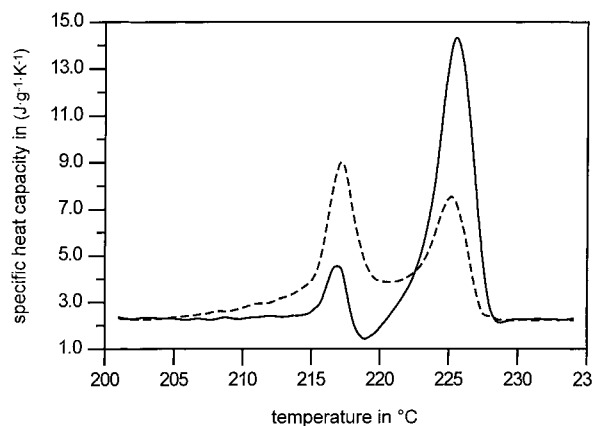
Fig. 1. Specific heat capacity, c_β, (solid line) and modulus of the complex specific heat capacity, $|c(\omega)|$, (dashed line) for crystallized PBT (β=0.6°C min^{-1}, ν=12.5 mHz, T_a=0.1°C).
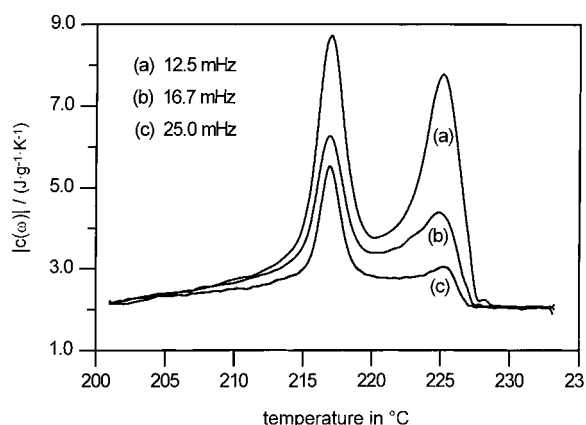
Fig. 2. Modulus of the complex specific heat capacity for crystallized PBT at the indicated frequencies (β=0.6°C min^{-1}, T_a=0.1°C).

Obviously, the melting behaviour depends on the scanning rate, the area of the first peak decreasing with decreasing the heating rate [30].

What is observed from Fig. 1 is that a multiple behaviour is displayed also by the complex specific heat capacity. As described above, $|c(\omega)|$ gives informations about the processes that follow the temperature modulation. Being calculated from the periodic component of the heat flow rate according to Eq. (2), $|c(\omega)|$ data are associated with half of the reversible signal, i.e. a corresponding crystallization process, that takes place during the second half of the modulation period, has to be assumed.

Fig. 2 provides some $|c(\omega)|$ curves obtained at different frequencies. It can be observed that at a given frequency, the first peak, which is associated with the fusion of crystals grown at 200°C during the isothermal crystallization [30], is higher than the second endotherm, which is related to the melting of more perfect recrystallized material. Moreover, the intensity of both the peaks decreases with increasing the modulation frequency.

As far as linearity is concerned, it has to be pointed out that the first harmonic was found to describe with good approximation the heat flow signal in the whole melting region.

In addition, it is worth noting that the complex specific heat capacity in the molten state (for example $|c(\omega)|$=2.05 J g^{-1} K^{-1} at 230°C) is in excellent agree-

ment with the reference ATHAS databank (c_p=2.09 J g^{-1} K^{-1} [32]).

It has been reported that in scanning ($\beta \neq 0$) TMDSC measurements the latent heat of melting may contribute to the measured complex specific heat capacity [21,24]. However, taking into account that the melting enthalpy of defective crystals is smaller than that of more perfect crystals [33], one can affirm with confidence that the decrease of $|c(\omega)|$ in the higher temperature melting region is a real phenomenon, being opposite to the temperature dependence of the latent heat.

The curves shown in Fig. 2 indicate that the fusion of less perfect crystallites is revealed by the TMDSC technique more easily than the successive melting process, a finding which is in agreement with other literature results [20,22]. With respect to more perfect crystallites, poor crystals are characterized by a smaller difference between fusion and crystallization temperature [22], since the folding of the chains is subjected to lesser restrictions. As a consequence, melting and crystallization can occur more easily within the modulation temperature range. As explained in [20–22], reversible melting is originated by melted segments of polymeric chains that, still joined onto higher-melting crystallites, can be 're-attracted' and undergo a new crystallization when temperature is reduced.

Owing to the wide distribution of crystallites with different perfection degree, a large variety of characteristic times τ is expected. The dependence of the peaks intensity on frequency (Fig. 2) can be explained by considering that, with decreasing the period, the amount of crystalline material that can follow the modulation is reduced.

The real and the imaginary parts of PBT specific heat capacity, that can be obtained according to Eq. (4) and Eq. (5) from $|c(\omega)|$ and the phase angle ϕ, are not considered in this short communication for the reason that the correction of the measured phase angle is still uncertain. As a matter of fact, in order to obtain the phase shift connected only to the process occurring in the sample, the effects due to heat transfer have to be quantified and subtracted [5,9,19,24]. The question has already been settled for the glass transition [19]; on the contrary, the problem has not been clarified and a solution has not been found up to now for the melting process [24].

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