polymer communications

Temperature dependence of the melting enthalpy of poly(ethylene terephthalate) and poly(aryl-ether-ether-ketone)

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(Received 13 May 1992; revised 6 October 1992)

The temperature dependence of the melting enthalpy has been determined for poly(ethylene terephthalate) and poly(aryl-ether-ether-ketone) from the experimental heat capacity variations with temperature of the solid and the liquid. A significant depression of the transition enthalpy occurs between the thermodynamic equilibrium melting point and the cold-crystallization temperature. The crystal weight fraction measurements, carried out by taking into account this temperature dependency, is in perfect agreement with the density determinations.

(Keywords: poly(ethylene terephthalate); poly(aryl-ether-ether-ketone); thermal behaviour; melting enthalpy; heat capacity; crystallinity)

Introduction

Semicrystalline stiff chain polymers, having a glass transition well above room temperature, can easily be quenched into the glassy state from the melt. Poly(ethylene terephthalate) (PET) and poly(aryl-ether-ether-ketone) (PEEK) are two stereotypes of this kind of material. Differential scanning calorimetry (d.s.c.) has been largely used to investigate the phase transitions in these semicrystalline polymers and to determine their degree of crystallinity in relation to thermomechanical treatments.

Heating crystallizable polymers from the glassy state generally involves cold crystallization a few degrees above the glass transition temperature, T_g. Reorganization of the crystalline phase takes place during the heating scan, as often revealed by a tenuous but broad exotherm before the final melting[1-7]. Exceptions can be found among polymers having a short temperature gap between the glass transition and the melting point, such as poly(2,6-dimethyl-1,4-phenylene oxide) and poly(4,4'-isopropylidene-diphenylene carbonate)[8]. It is customary to use the difference between the heat of the cold crystallization and the heat of melting to assess the amount of the crystalline fraction in the material prior to the d.s.c. scan[6,9,10]. For that, the melting and crystallization enthalpies are assumed to be independent of temperature and the value taken into account is usually the one determined at the thermodynamic equilibrium melting point, T_f°. This is a rough assumption that can account for the departures reported in the literature between the values of the degree of crystallinity determined from d.s.c. and those obtained from X-ray diffraction or density measurements. As a matter of fact, the phase transition enthalpy involved in the melting is basically temperature dependent, because the heat capacities of the crystalline phase and the liquid do not follow the same dependence on temperature. The enthalpy dependence on temperature for any kind of physical or chemical transformation is given by Kirchhoff's law[11]:

$$\Delta H_f(T_2) - \Delta H_f(T_1) = \int \Delta C_p \, dT \qquad (1)$$

where ΔC_p is the difference of the heat capacities of the final products and initial reactants at the temperature T between T_1 and T_2.

An example of such a calculation has been provided by Wunderlich in the case of polyethylene, which can display a very broad melting temperature range depending on the molecular structure[12]. It provides evidence that the melting enthalpy of highly defective crystals that melt at around room temperature drops by about 15% compared to nearly perfect crystals that melt close to the thermodynamic melting point. Therefore, in the case of PET and PEEK, which crystallize more than a 100°C below the maximum melting temperature when heated from the glass, the assumption of a constant enthalpy for both processes can be seriously questioned. This warning is supported by an experimental estimation by Blundell *et al.*[13] of the PET melting enthalpy, $\Delta H_f = 95\ \mathrm{J\,g^{-1}}$ at 100°C compared with $\Delta H_f = 136\ \mathrm{J\,g^{-1}}$ at 290°C.

The present work is an attempt to assess the temperature dependence of the melting enthalpy of PET and PEEK in order to give more relevance to the crystal fraction determination from d.s.c. data.

Experimental

Isotropic films of PET and PEEK about 100 μm thick were provided by Rhone-Poulenc and ICI respectively.

Thermal analyses were carried out on a Perkin-Elmer DSC-7 Delta apparatus at a heating rate of $20\ \mathrm{K\,min^{-1}}$. Particular care was taken for the electronic adjustment of a linear baseline with empty aluminium pans prior to measurements with the samples. The temperature and heat flow scales were calibrated with the melting peaks of high purity indium and zinc samples, following the standard procedure of the Perkin-Elmer Delta US 6.0 software.

The density measurements were performed with a gradient column made of calcium nitrate solutions and calibrated with hollow glass beads having a density accuracy of 10^{-4}.

0032-3861/93/081761-04

Results and discussion

The temperature dependence of the melting enthalpy, which is also the crystallization enthalpy, can be determined from equation (1), provided that the liquid and solid heat capacities can be extrapolated over the temperature range $T_g - T_f^\circ$. With this aim, heat capacities can be computed by the group contribution model[14,15]. Otherwise, experimental data tables or fitted polynomial equations have been provided by Wunderlich and co-workers[8,16–18] for a good number of polymers, including PET and PEEK.

Very good linear relationships as a function of temperature have been derived from the experimental C_p data tables of PET[8,16] for the liquid in the range 350–600 K:

$$C_{p,l} = 1.2344 + 0.001468T (\mathrm{J\,g^{-1}\,K^{-1}}) \qquad (2)$$

and for the solid in the range 100–340 K:

$$C_{p,s} = 0.0720 + 0.003667T (\mathrm{J\,g^{-1}\,K^{-1}}) \qquad (3)$$

Figure 1 shows the heat capacity plot of PET according to equations (2) and (3).

In the case of PEEK, Cheng and Wunderlich[16] showed that the heat capacity of the liquid in the range 420–680 K follows the linear relation:

$$C_{p,l} = 1.0700 + 0.001722T (\mathrm{J\,g^{-1}\,K^{-1}}) \qquad (4)$$

which is very close to that reported by Kemmish and Hay[19].

The heat capacity of solid PEEK does not obey a truly linear relationship at very low temperatures[17,18] but, for reasons of convenience in the following, the linear equation:

$$C_{p,s} = 0.0891 + 0.003412T (\mathrm{J\,g^{-1}\,K^{-1}}) \qquad (5)$$

can be fairly well fitted to the experimental data of Wunderlich *et al.* in the range 190–410 K, with a maximum deviation of only 0.02 J g^{-1} K^{-1}.

It has been generally observed that the heat capacity of semicrystalline polymers below T_g is roughly independent of the degree of crystallinity[15,20]. This is due to the fact that the molecular mobility is essentially the same in the two physical states, although the enthalpy and the density of the crystal are significantly lower than those of the glass at the same temperature. Cheng *et al.*[18] have pointed out that from the standpoint of the addition scheme of skeletal and group vibration modes, very little effect can be expected from the crystal structure. It is, however, worth mentioning that Kemmish and Hay[19] have tried to determine the crystalline heat capacity variation with temperature of PEEK from measurements on a sample of known crystallinity, using the assumption of a two-phase model. They reported a large difference between the crystalline and glassy C_p values, which is in strong contradiction with the general behaviour of semicrystalline polymers mentioned above. Besides, the C_p equation obtained for the crystalline state has a negative ordinate at the origin, which is a physical nonsense. Cheng *et al.*[17] have shown that the heat capacity of solid PEEK is indeed slightly affected by the degree of crystallinity, possibly because of the activation of some local molecular motions in the glass, such as the γ relaxation, which are not allowed in the crystal below T_g. But the C_p depression over the crystallinity range 0–100% is less than 3%.

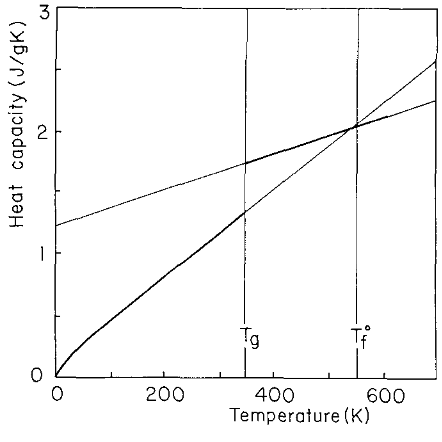

Figure 1 Heat capacity of PET as a function of temperature from experimental data (bold line) and extrapolated (light line)

Assuming that the linear relationships for $C_{p,l}$ and $C_{p,s}$ can be reasonably extrapolated below T_f° and above T_g, respectively, the melting enthalpy at any temperature T between T_f° and T_g can then be written from equation (1), using the data reported in the literature for the melting enthalpy ΔH_f° at the thermodynamic equilibrium melting point T_f°. In the case of PET, the following equation is obtained[12]:

$$\Delta H_f(\mathrm{PET}) = -166.57 + 1.1624T - 0.001099T^2\ (\mathrm{J\,g^{-1}}) \qquad (6)$$

assuming $T_f^\circ = 553$ K and $\Delta H_f^\circ = 140$ J g^{-1}.

The dependence on temperature of the melting enthalpy of PEEK is given by the relation:

$$\Delta H_f(\mathrm{PEEK}) = -118.90 + 0.9809T - 0.000845T^2\ (\mathrm{J\,g^{-1}}) \qquad (7)$$

taking $T_f^\circ = 663$ K, as determined from the Thomson–Gibbs equation by Blundell and Osborn[21] and Lee *et al.*[5], and using an average value $\Delta H_f^\circ = 160$ J g^{-1} borrowed from Zoller *et al.*[22] and Lee *et al.*[5]. This ΔH_f° value for PEEK is significantly higher than the one estimated by Blundell and Osborn[21] to which it is often referred. Our choice is founded on the very good agreement between two independent determinations.

The variation curves with temperature of the melting enthalpy of PET and PEEK between T_g and T_f° are plotted in *Figure 2* according to equations (6) and (7). Both plots exhibit a slight maximum as previously observed by Wunderlich in the case of polyethylene[12]. This maximum simply results from the parabolic shape of the enthalpy variation curves for the solid and the liquid, but its physical meaning is still obscure. The main conclusion from *Figure 2* is that an 8% depression of the enthalpy of fusion can be expected for PET between the thermodynamic melting point and the cold-crystallization temperature. In the case of PEEK, the depression is about 10%.

Calculations can then be applied to the thermal behaviour of PET and PEEK. *Figure 3* shows the d.s.c. heating traces of amorphous PET and PEEK samples. The drawing of a baseline through the thermograms of the samples by linear interpolation from the beginning of the cold-crystallization peak to the end of the melting peak discloses a broad intermediate exotherm relevant to the crystal reorganization process. The densities $d = 1.336$ g cm^{-3} for PET and $d = 1.262$ g cm^{-3} for PEEK

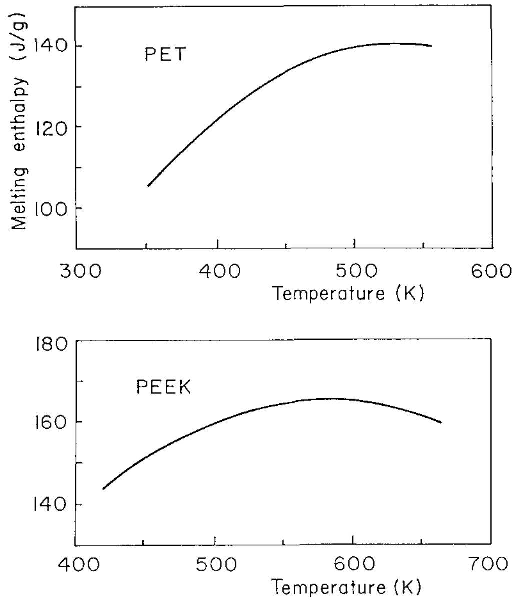

Figure 2 Enthalpy of melting for PET and PEEK as a function of temperature according to equations (6) and (7)

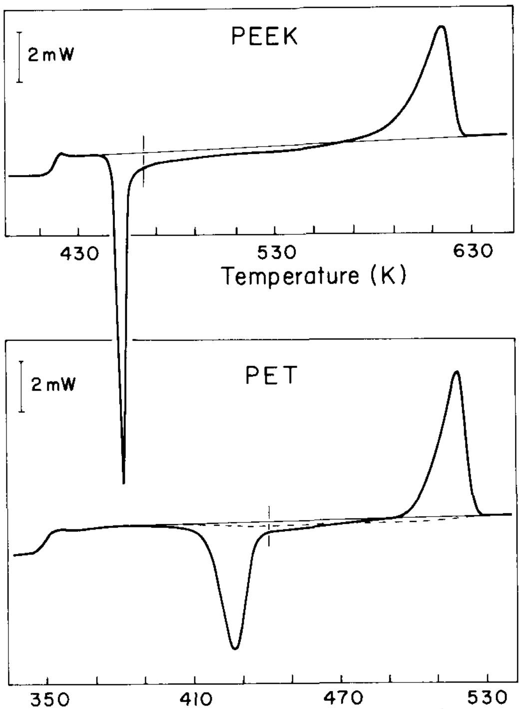

Figure 3 D.s.c. heating traces of glassy PET and PEEK. Sample weight: 7.82 mg (PET) and 7.24 mg (PEEK)

Table 1 Enthalpies of transition for the cold crystallization, ΔH_c, the intermediate reorganization, ΔH_{int}, and the melting, ΔH_f, and crystal weight fractions, X_c

	ΔH_c ($J g^{-1}$) [X_c (%)]	ΔH_{int} ($J g^{-1}$) [X_c (%)]	ΔH_f ($J g^{-1}$) [X_c (%)]
PET	−36.8	−3.2	43.2
	[28.3]	[2.4]	[30.8]
PEEK	−26.6	−11.4	40.3
	[17.6]	[7.1]	[24.5]

are close to the usually reported amorphous density values[23,24], indicating that no crystal is present in both samples. However, in the case of PEEK, the area of the two exothermic processes (i.e. the cold crystallization and the crystal reorganization) is smaller than the area of the melting endotherm. The situation is somewhat different in the case of PET, which gives nearly equal values for the enthalpies of the overall exotherm and the endotherm, within experimental errors. In fact, this equality is only apparent because the linear interpolation of the baseline, which is quite a common assumption, is an approximation. Indeed, although the baseline before the cold-crystallization peak and that after the melting peak should be in the same linear relationship because they both refer to the heat capacity of the amorphous state above T_g, the baseline in the mean temperature range cannot be linear because of the change of physical state of the material. The actual baseline should obey the heat capacity variation given by the relation:

$$C_p = C_{p,s} X_c + C_{p,l}(1 - X_c) \qquad (8)$$

where X_c is the crystal weight fraction. Considering that the solid, which grows during the cold-crystallization step, has a lower heat capacity than the liquid from which it forms, the actual baseline deviates downwards from the linear interpolation in the cold-crystallization temperature range, then draws back to linearity in the melting temperature range. The drawing of the baseline according to equation (8) requires a previous estimation of the crystal weight fraction as a function of temperature using an approximated linear baseline. The baseline thus determined in the case of PET is shown by a dotted curve in *Figure 3*. A similar calculation for PEEK is not necessary because of the lower crystallinity and lower heat capacity difference between the solid and the liquid, compared with PET.

The enthalpies of transition assessed from the peak areas of the cold-crystallization exotherm, ΔH_c, intermediate reorganization exotherm, ΔH_{int}, and final melting endotherm, ΔH_f, are recorded in *Table 1*. Calculations of the crystal weight fractions, X_c, involved in the various transitions have been carried out by using the value of the specific enthalpy at the temperature of the transition peak, for the crystallization and the melting, and the mid-range temperature in the case of the crystal reorganization. *Table 1* shows that the amount of crystal that melts in the high-temperature peak of the PET and PEEK samples is very close to the sum of the amounts of crystal formed during the cold crystallization and the reorganization steps. This is in perfect agreement with the density measurements, indicating that the samples are thoroughly amorphous prior to the d.s.c. scan. The standard method, assuming that the melting enthalpy is independent of temperature, would have led to the conclusion that both samples are initially 2–3% crystalline.

Conclusion

Because of the large difference of temperature between the cold crystallization and the melting of stiff-chain semicrystalline polymers, the specific enthalpy of transition cannot be taken as a constant as it is usually assumed. Indeed, the enthalpy depression between the two processes can be estimated to about 8% and 10% in the case of PET and PEEK, respectively. Although the effect on the measurement of the crystal weight fraction is weak, the agreement with the density determination is much better compared with the standard method, assuming a constant transition enthalpy.

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