Routine crystallinity measurements of polymers by d.s.c.

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INTRODUCTION

Determinations of polymer crystallinities from heats of fusion are often based on measuring the area of d.s.c. melting peaks above somewhat arbitrarily chosen baselines. The choice of sensible baselines becomes difficult when the melting peaks are extremely broad as in the case of low density polyethylenes (LDPE), or when crystallization occurs during the d.s.c scan as often is the case with poly (ethylene terephthalate) (PET). A further problem can occur when the heat of fusion derived from the peak area is divided by the heat of fusion of the fully crystalline material in order to calculate the degree of crystallinity, in that the degree of crystallinity value is temperature dependant. Gray[1] and Richardson[2] have separately proposed rigorous methods of treating data which avoid these problems. In this note we report the results of our efforts to apply two methods of these authors to the routine measurements of the crystallinity of PET and polyethylene (PE).

Most of the d.s.c. literature on PE has been exclusively concerned with high density polyethylene (HDPE) where the melting peaks are usually sharp and well-defined. Here we have extended the scope to include branched LDPE and polyethylene copolymers where the crystallinities are lower and where the melting processes are much broader. In the case of PET, we have been particularly interested in the ability of the data treatment routines to deal with amorphous and low crystallinity samples as well as those with higher crystallinity. PET is ideally suited for this since it can be readily quenced from the melt into the amorphous state.

THEORY

We summarize here the main relations and conditions for the methods that have been used.

Total enthalpy method

This approach is recommended by both Gray[1] and Richardson[2]. It requires the data to be fully corrected and calibrated with respect to the true baseline so that the total heat capacity is known, including both specific and latent heat contributions. With this data one can readily integrate to obtain the total enthalpy change between any two temperatures. Referring to *Figure 1* the weight fraction crystallinity at temperature T_1 is given by:

$$\chi(T_1)=\frac{H-H_1}{\Delta H_f(T_1)} \tag{1}$$

where: H is total observed enthalpy change between T_1 and a temperature T_2 above the polymer melting peak. H_1 is the enthalpy change for amorphous polymer between T_1 and T_2. $\Delta H_f(T_1)$ is the enthalpy of fusion at T_1 for fully crystalline polymer.

Peak area method

This alternative method is described by Gray and is specifically recommended by him for use with PE. The procedure is close to the conventional intuitive approaches where interpolated baselines are constructed. Starting from fully corrected data this method involves drawing a straight baseline between the points at temperatures T_1 and T_2 (see *Figures 2* and *3*). The weight fraction crystallinity is then given by

$$\chi(T_1)=\frac{\Delta h}{\Delta H_f(T_2)} \tag{2}$$

where Δh is the net area above the baseline taking into account both positive and negative contributions; $\Delta H_f(T_2)$ is the enthalpy fusion at T_2 for fully crystalline polymer.

Two important conditions must be upheld in order that this method is rigorous.

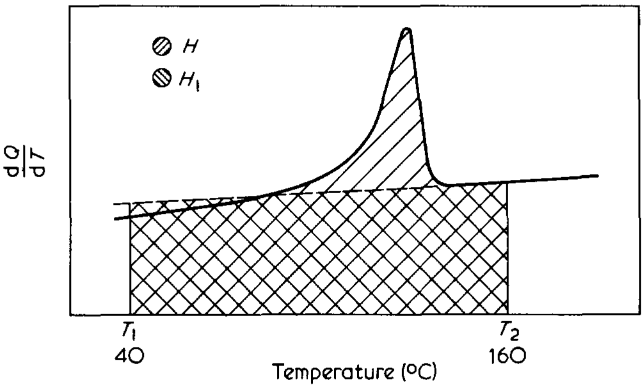

Figure 1 Schematic diagram of a corrected d.s.c. trace for polyethylene, illustrating the total enthalpy method

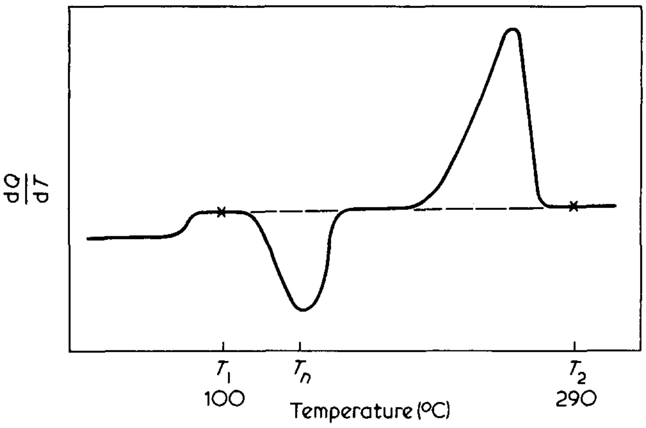

Figure 2 Schematic diagram of a corrected d.s.c. trace for poly (ethylene terephthalate) of low crystallinity. The exotherm at T_n is representative of a crystallization process during the scan

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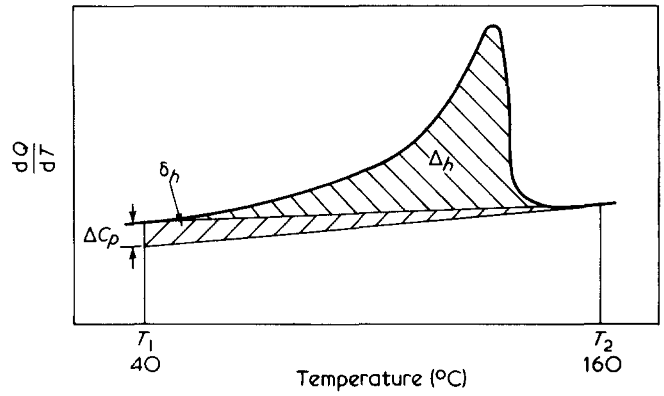

Figure 3 Schematic diagram of d.s.c. trace for polyethylene showing the ethalpy correction δh needed for the peak area method to account for gradual melting at T_1

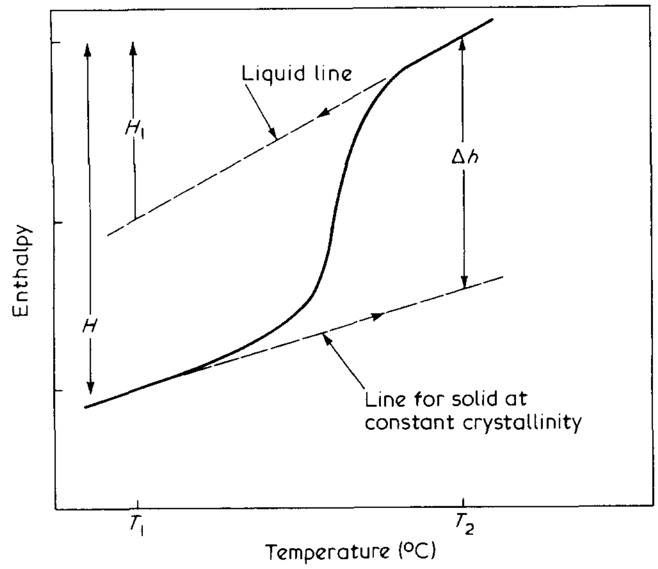

Figure 4 Schematic enthalpy plot illustrating main parameters of the two methods

(i) T_1 must be chosen to be low enough to ensure that no melting is occurring; i.e. the d.s.c. signal at T_1 must be entirely derived from specific heat and there must be no latent heat contribution.

(ii) T_2 must be chosen such that the extrapolated specific heats of pure amorphous and pure crystalline material are identical at this point.

A detailed comparison of the principles of the two approaches has been presented in Gray's article. The basic difference is illustrated by the schematic enthalpy plot in *Figure 4*, where it is seen that the total enthalpy method involves an extrapolation downwards from the melt, while the peak area method involves an extrapolation upwards from the semi-crystalline state.

EXPERIMENTAL

D.s.c.

The data were obtained from a Perkin Elmer DSC2 linked with a PDP11 computer. Traces from the samples were corrected to the true baseline by reference to traces obtained with empty sample pans using the methods described by Gray[1] and Richardson[2]. This involves corrections for instrumental curvature and slope. The data were calibrated in absolute units by comparing with the specific heat of a sample of sapphire. The computer was also programmed with the routines needed to calculate the areas required for equations 1 and 2.

In all cases, 10 mg samples were used. For PE, a heating rate of 20°C min^{-1} was used between 25°C and 180°C. For PET, 40°C min^{-1} was used between 40°C and 300°C.

Samples

The samples of PE were made by melt pressing plaques, 1 mm thick at 160°C and then either quenching into ice cold water or slow cooling in a press at a constant rate of 1°C min^{-1}. Samples LD 1, 2 and 3 are branched low density polyethylenes; HD 1 is a linear polyethylene; PEC1 and 2 are copolymers with other olefines.

The amorphous PET sample was made by quenching an extruded melt onto a chilled roller. Samples of varying crystallinity were obtained from the amorphous material by annealing using various times and temperatures.

Crystallinities

Crystallinities were estimated from wide angle X-ray diffraction. The amorphous curves for PE were fitted using the criteria similar to those outlined by Pfeisser and Matthews[3]. The PET amorphous curve was fitted in a manner similar to that described by Farrow and Preston[4].

These methods provide crystallinity values that correlate well with specific volumes measured in density columns. In the case of PE, one obtains linear relationships with specific volume that extrapolate to points which are equivalent to the densities for the amorphous and crystalline phases of 0.856 and 1.000 respectively, and which agree well with generally accepted values. For the case of PET, there is a linear relationship with specific volume that extrapolates from an amorphous density of 1.335 to 1.477 for 100% crystallinity based on the above X-ray procedure. This latter value is within the band of crystalline densities quoted in the literature (1.455–1.515). In view of the present uncertainty in the crystalline density of PET, all the following thermal data has been related to our X-ray crystallinity measurements.

RESULTS AND DISCUSSION

Polyethylene

For the analysis of the PE scans (*Figure 1*), T_1 was chosen to be 40°C, this being the temperature at which the d.s.c. response had settled from the initial surge. T_2 was originally chosen to be 140°C, as this was suggested by Gray[1] as being close to the cross-over of the crystalline and amorphous specific heats. For two reasons T_2 was eventually changed to 160°C; first, the tail of the melting peak of some HDPE samples extends past 140°C, and second, the difference in value of Δh in equation 2 between $T_2 = 140$°C and 160°C is not significant.

The values used for the heat of fusion of fully crystalline PE were taken from Richardson's macrocalorimetry data[2], i.e. $\Delta H_f(40°\text{C}) = 284$ kJ Kg^{-1} $\Delta H_f(160°\text{C}) = 308$ kJ Kg^{-1}. A list of samples and the main results are given in *Table 1*. Columns A to D give a comparison of estimates of crystallinity from the various enthalpy relationships together with one from the X-ray method.

Table 1 Results for polyethylene samples

		H (kJ Kg^{-1})	T_p (°C)	Δh (kJ Kg^{-1})	Observed C_p (40) (kJ/Kg/°C)	Calculated C_p (40) Equation 5	Correction to $\Delta h = \delta h$ Equation 6	A χ Equation 1	B χ Equation 2	C χ Equation 3	D χ X-ray
LD1	Quench	402	104	104	2.394	2.032	22	0.40	0.34	0.41	0.46
LD2	Quench	414	113	114	2.371	2.005	22	0.44	0.37	0.44	0.47
LD3	Quench	435	117	139	2.284	1.968	19	0.495	0.45	0.52	0.52
LD1	1°C min^{-1}	409	106	106	2.485	2.005	29	0.44	0.34	0.44	0.50
LD2	1°C min^{-1}	423	113	128	2.355	1.972	23	0.49	0.415	0.49	0.52
LD3	1°C min^{-1}	423	118	149	2.131	1.945	11	0.53	0.48	0.52	0.55
HD1	Quench	478	131	204	1.987	1.854	8	0.665	0.66	0.69	0.66
HD1	1/2°C min^{-1}	524	138	259	1.825	1.744	5	0.83	0.84	0.85	0.84
PEC1	Quench	411	116	117	2.317	2.012	18	0.43	0.38	0.44	0.45
PEC2	Quench	418	125	128	2.259	1.988	16	0.465	0.415	0.47	0.52
PEC3	1°C min^{-1}	374	121	70	2.540	2.079	28	0.33	0.22	0.32	0.33

Columns A and B compare the estimates obtained by the direct application of the total enthalpy and peak area methods using equations 1 and 2. For the two HDPE samples the agreement is good, but for the LDPE and copolymers the peak area method gives systematically lower estimates. The main reason is believed to be the violation of the condition for the peak area method that no melting should be occurring at T_1. This is demonstrated in *Table 1* by comparing the observed specific heat C_p (40°C) with that predicted by the relationship:

$$C_p(40) = \chi\, 1.63 + (1-\chi) . 2.3$$

where χ has been taken to be the value deduced in column A from the total enthalpy method. The values of 1.63 and 2.3 are taken from Wunderlich and Baur[5] and are the specific heats of the crystalline and amorphous phases respectively at 40°C. The difference δC_p between the predicted and observed can be attributed to the latent heat of the gradual melting process that is occuring at T_1.

Thus in order to apply the peak area method rigorously, the baseline should be redrawn to a point at T_1 an amount δC_p below the observed behaviour, as in *Figure 3*. This new baseline will create an enthalpy increment to Δh corresponding to the triangular area

$$\delta h = \delta C_p \frac{(160-40)}{2} \text{ i.e. } \delta h = 60.\ \delta C_p$$

The values of this correction are shown in *Table 1* and are small for the HDPE and significantly larger for the lower density polymers. Column C gives the estimate of χ after taking account of this increment.

$$\text{i.e. } \chi = \frac{\Delta h + \delta h}{\Delta H_{f2}} \tag{3}$$

There is now much better agreement with the total enthalpy estimate (column A) over the whole range of polymers. This confirms the internal consistency of the enthalpy analysis. It also emphasises the weakness of using the peak area approach for samples containing significant low melting material. There are, however, still minor discrepancies with the X-ray crystallinities in column D, which may be significant. Two reasons are proposed:

(i) the X-ray measurement was carried out at room temperature (~20°C) compared with the reference temperature $T_1 = 40$°C. The discrepancy can therefore be due to the removal of low melting crystals between 20°C and 40°C during the preparation for the d.s.c. scan.

(ii) The discrepancies are due to differences in crystal morphology which cause the actual heat of fusion ΔH_f to be reduced from that of a perfect, infinite crystal[6]. This could be due either to defects within the crystal and/or to a reduction in the thickness of the lamellar crystals, which will increase the effect of the surface energy of the lamellar faces. Both these effects will be accentuated in branched LDPE or copolymers. This, in fact, is largely reflected by the observed reduction in the peak melting point, T_p in *Table 1.*

Polyethylene terephthalate

For the PET scans, T_1 was chosen to be 100°C (see *Figure 2*). This is above the glass transition temperature of PET (~77°C) but below the temperature at which amorphous PET usually starts to crystallize significantly during a heating scan. In order to choose a suitable value for T_2 it was necessary to estimate the point at which the specific heats of the amorphous and crystalline phases cross-over.

The specific heat behaviour for amorphous polymer was deduced from the observed specific heat at 100°C and 290°C which were obtained from a heating scan of an amorphous sample. Several sets of observations led to the following relationship for the specific heat of amorphous, liquid polymer.

$$C_1 = 1.530 + 1.72 \times 10^{-3}\, T (\text{kJ/Kg/°C})$$

The behaviour for fully crystalline polymer was deduced by a detailed analysis of the scans for a high crystallinity sample that had been well annealed at 245°C. It was assumed that the crystallinity remained constant up to 150°C and that no crystal melting therefore occurred in the region between 90°C and 150°C. The variation of specific heat of the crystalline phase C was then deduced over this range by assuming that the observed specific heat $= \chi C_c + (1-\chi)C_1$. This analysis gave the following relationship for the crystalline phase:

$$C_c = 0.777 + 4.53 \times 10^{-}3\, T$$

These relationships for C_1 and C_c cross at about 270°C and therefore indicate this as a suitable choice for T_2. However, in practice we used the slightly higher T_2 of

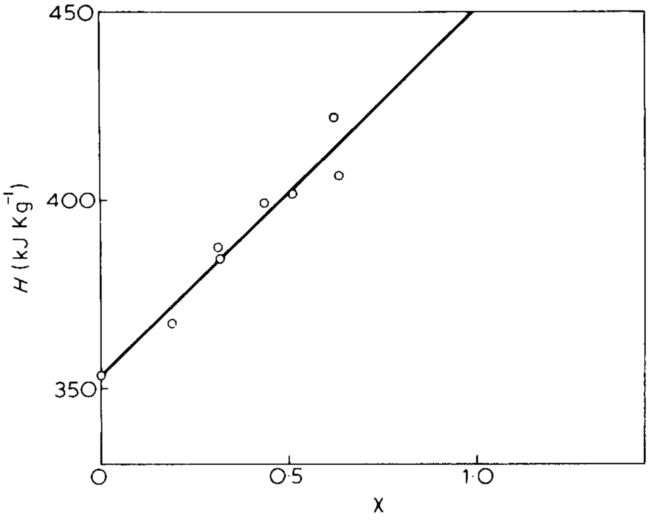

Figure 5 Plot of total enthalpy *H versus* X-ray crystallinity for PET

290°C for reasons similar to those in the selection of the higher T_2 for PE. (The choice of baseline between 100°C and 290°C for the peak area method is close to the baseline used in a recent paper by Illers[7]. When plotted against specific volume our values for Δh agree almost exactly with the data of Illers).

The value taken for the H_1 in equation 1 between 100°C and 290°C was 354 kJ/Kg and was obtained by integrating the relationship for C_1.

The results for $(H - H_1)$ and Δh are plotted in *Figures 5* and *6* respectively. The slopes of straight line fits through these plots indicate the following values for the heats of fusion. $\Delta H_f(100°\mathrm{C}) = 95$ kJ Kg^{-1} $\Delta H_f(290°\mathrm{C}) = 135$ kJ Kg^{-1}. The value at 290°C is slightly higher than the 126 kJ Kg^{-1} at the melting point quoted by Wunderlich[8] but is consistent with the data of Illers[7] who used a similar baseline construction. Our two values are consistent with the relationship for a first order phase change:

$$\frac{\mathrm{d}(\Delta H_f)}{\mathrm{d}T} = C_1 - C_c$$

Integration of this using the above relationships for C_1 and C_c give:

$$\Delta H_f(290) - \Delta H_f(100) = 39\,\mathrm{kJ\,Kg^{-1}}$$

which is consistent with above deduced values.

The experimental scatter for PET is significantly worse than for PE. This is partly due to the lower heat of fusion of PET and partly because the range $T_2 - T_1$ is larger so that the results are more susceptible to instrumental fluctuations that cannot be corrected by the computer. Since the enthalpy of fusion is higher at 290°C, the effect of the scatter is more pronounced in the results for the total enthalpy method than for the peak area method.

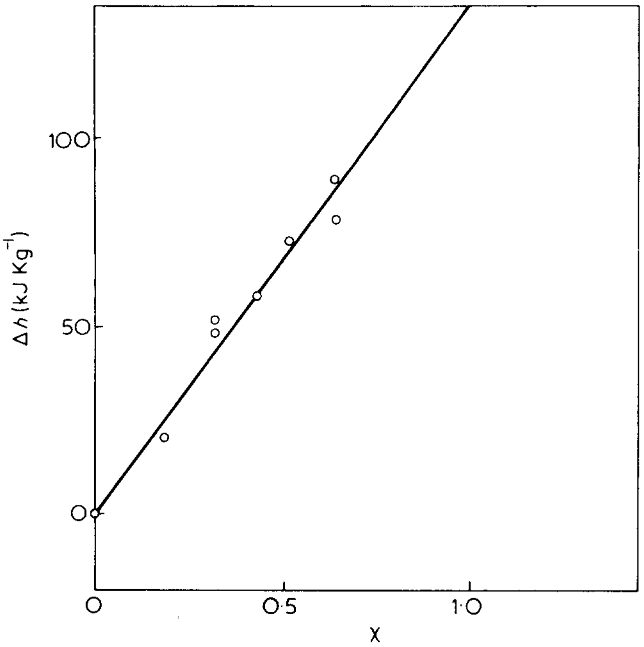

Figure 6 Plot of peak area Δh *versus* X-ray crystallinity for PET

CONCLUSIONS

Using routine on-line facilities, both the total enthalpy and 'net peak area' methods can be made to give measures of crystallinity that are consistent among themselves and which agree well with estimates from other techniques. In PET they can be applied to amorphous or low crystallinity samples, despite the crystallization effects that occur during the heating scan. Of the two approaches, the peak area method gives slightly less experimental scatter and is thus the preferred method for the routine analysis of PET. However for PE, the peak area method can only be made to give consistent results by correcting for the effects of the low melting tail which varies significantly between samples. For this reason, we believe the total enthalpy approach is better for PE.

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