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The crystallinity of poly(ether ether ketone)

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Differences have been observed between the enthalpies of crystallization and fusion of quenched 'amorphous' poly(ether ether ketone) (PEEK) which have been attributed to residual crystallinity produced during quenching. Comparison with samples of PEEK crystallized under well defined conditions reveals that these apparent differences arise from changes in the heat capacity of the crystalline solid and the liquid alone and there is no need to invoke abnormal crystalline structure, or the presence of residual crystallinity produced on quenching to explain the apparent differences. Comparison is made of the degree of crystallinity as measured by d.s.c., WAXS and density from which the enthalpy of fusion of totally crystalline PEEK at 437 K was determined to be $122.5 \pm 1.5\ J\ g^{-1}$.

(Keywords: PEEK; amorphous; crystalline; d.s.c.; enthalpy of fusion; WAXS; density; specific heats)

INTRODUCTION

The excellent high temperature mechanical properties[1] and optimum resistance to solvent stress cracking[2] of poly(ether ether ketone) (PEEK) are not achieved unless it is substantially crystalline, and reproducible mechanical properties are achieved if the degree of crystallinity is precisely controlled[3]. Measurement of this parameter has proved to be difficult, especially in the presence of carbon fibre, since standard techniques such as density measurements have proved to contain complications in that the crystalline unit cell volume varies essentially linearly with crystallization temperature (T_c)[4], making the crystalline density a variable quantity. The procedure also assumes that amorphous material can be obtained. Measurement from the enthalpy of fusion by d.s.c. relies on the value chosen for the totally crystalline sample; only one value has been adopted in the literature[5], namely $130\ J\ g^{-1}$. WAXS has its inherent errors, not least of which is the separation of the crystalline peaks from the amorphous background.

A standard procedure for producing amorphous PEEK has been adopted which involves quenching thin sections (< 1 mm thick) from above the observed melting point into ice/water. On the basis of WAXS and density measurements this material was considered to be non-crystalline. This procedure has been criticized since the observed enthalpy of fusion is greater in modulus to that observed on 'cold' crystallization about 10 K above the glass transition temperature (T_g).

This paper attempts to measure the degree of crystallinity of the quenched material and attempts to resolve the difficulties in measuring the degree of crystallinity by WAXS, d.s.c. and density.

EXPERIMENTAL

PEEK 450 g granules were obtained from ICI P&C plc. It had a melt viscosity of $45\ kN\ sm^{-2}$ at 673 K. The granules were compression moulded, after drying *in vacuo* at 390 K for 16 h, into plaques $150 \times 150 \times 0.5$ mm at 650 K and quenched into ice/water. Discs (3 mm in diameter) were cut from this sheet for thermal analysis, and squares (20×20 mm) for WAXS after crystallizing in a furnace thermostatically controlled to ± 0.5 K.

D.s.c. was carried out on a Perkin-Elmer DSC model 2C interfaced to a BBC Master microcomputer, which collected and analysed the heat flow/temperature data. The d.s.c. was calibrated from the melting points of ultra-pure metals and a value of $28.45\ J\ g^{-1}$ was used for the enthalpy of fusion of indium.

WAXS studies were carried out using a Picker high resolution automated powder diffractometer, on flat specimens. This was achieved by polishing the samples with fine grade emery. WAXS data were collected by a Phillips PW171710 diffractometer control unit and a Brother AT microprocessor. An IBM 4340 series mainframe computer was used to analyse the data. The diffractometer was calibrated using a quartz standard as described elsewhere[6,7] and the degree of crystallinity determined from the relative area under the deconvoluted crystalline and amorphous peaks[4].

The densities of the amorphous and crystalline samples were measured on the square test specimens by weighing in air and n-heptane at 293 K. The measured densities of the samples and the crystallization temperature are listed in *Table 1*.

RESULTS AND DISCUSSION

The enthalpy of fusion

It can be seen from *Figure 1* that quenched PEEK samples crystallized on heating about 20 K above the T_g, with the evolution of the heat of crystallization ($-\Delta H_c$). This was evaluated from the area under the crystallization curve using a non-linear baseline in the conventional way. At higher temperature, several melting endotherms were observed from 500 to 650 K and the areas under the total endotherms evaluated to determine the enthalpy

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Table 1 Experimental characteristics of the PEEK samples

Sample	Crystallization temperature (K)	Crystalline density[a] (g cm^{-3})	Sample density (g cm^{-3})
1	Quenched		1.261
2	Quenched		1.261
3	Quenched		1.261
4	Quenched		1.261
5	433	1.384_1	1.285
6	438	1.388_0	1.282
7	585	1.380_7	1.298
8	600	1.411_5	1.300

[a]Calculated from equation (3)

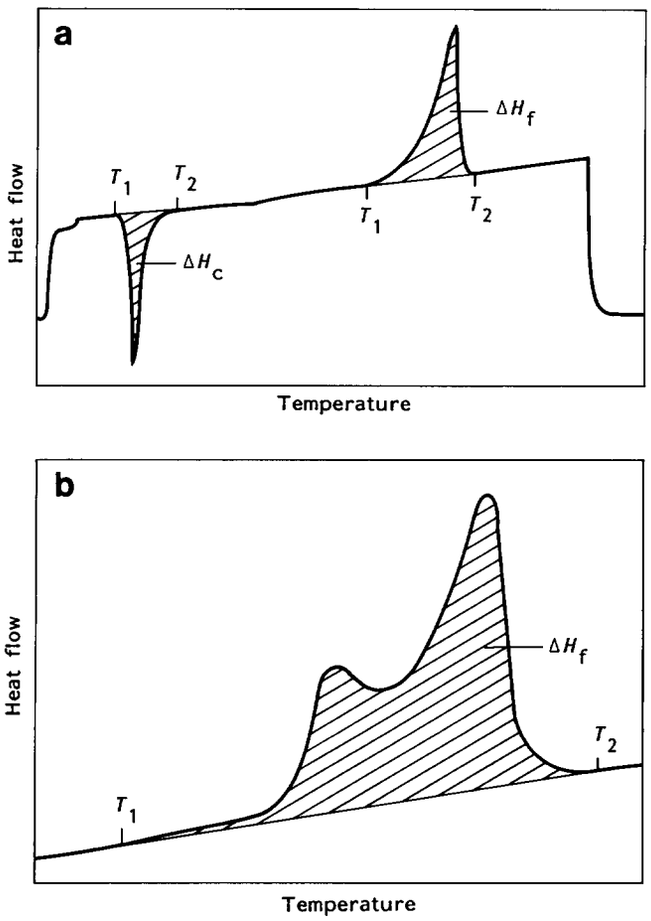

Figure 1 D.s.c. thermograph of PEEK: (a) quenched amorphous PEEK showing the determination of the enthalpies of crystallization and fusion (shaded regions); (b) the multiple melting peaks of PEEK crystallized in the higher temperature region

of fusion (ΔH_f), using the same procedure as above. For quenched samples, ΔH_c values of -23.6 ± 0.7 J g^{-1} were consistently obtained in the region of 450 K, and 41.3 ± 0.8 J g^{-1} for ΔH_f of the as-crystallized sample in the higher temperature region. The data are listed in *Table 2*. There is a marked difference between the two values and there is an apparent implication that the quenched samples are substantially crystalline prior to recrystallization at 450 K, as has been suggested by others[8].

Material crystallized isothermally to different degrees of crystallinity exhibited either a very much smaller enthalpy of crystallization, or none at all[9]. The corresponding enthalpy of fusion varied considerably reflecting crystallization conditions and the initial degree of crystallinity, as measured by WAXS.

Since the enthalpies of fusion and crystallization are measured at different temperatures, they have to be corrected for heat capacity differences, in particular

$$-\Delta H_c(T_1) = \Delta H_f(T_2) + \sum_{T_1}^{T_2} \Delta C_p dT \qquad (1)$$

where ΔC_p is the heat capacity difference between the liquid and the partially crystalline solid.

D.s.c. measures C_p directly and the terms in equation (1) can be evaluated directly by integrating between two temperatures, below T_c and above the melting temperature (T_m). The overall change in enthalpy (ΔH) measured by d.s.c. is associated with the four terms shown diagrammatically in *Figure 2*. Term 1 involves the

Table 2 Enthalpy changes

Sample	Conventional enthalpy of fusion (J g^{-1})	Conventional enthalpy of crystallization (J g^{-1})	Difference (%)	Residual enthalpy (J g^{-1})
1	41.6 ± 0.3	-24.3 ± 0.3	42	-0.65 ± 1.2
2	40.9 ± 0.3	-23.2 ± 0.3	45	-0.61 ± 1.2
3	40.5 ± 0.3	-23.0 ± 0.3	43	-0.82 ± 1.2
4	42.2 ± 0.3	-22.9 ± 0.3	45	-0.56 ± 1.2
5	32.4 ± 0.3	-2.3 ± 0.3	—	-23.0 ± 0.9
7	45.6 ± 0.3	0	—	-43.8 ± 0.9
8	35.9 ± 0.3	0	—	-30.3 ± 0.9

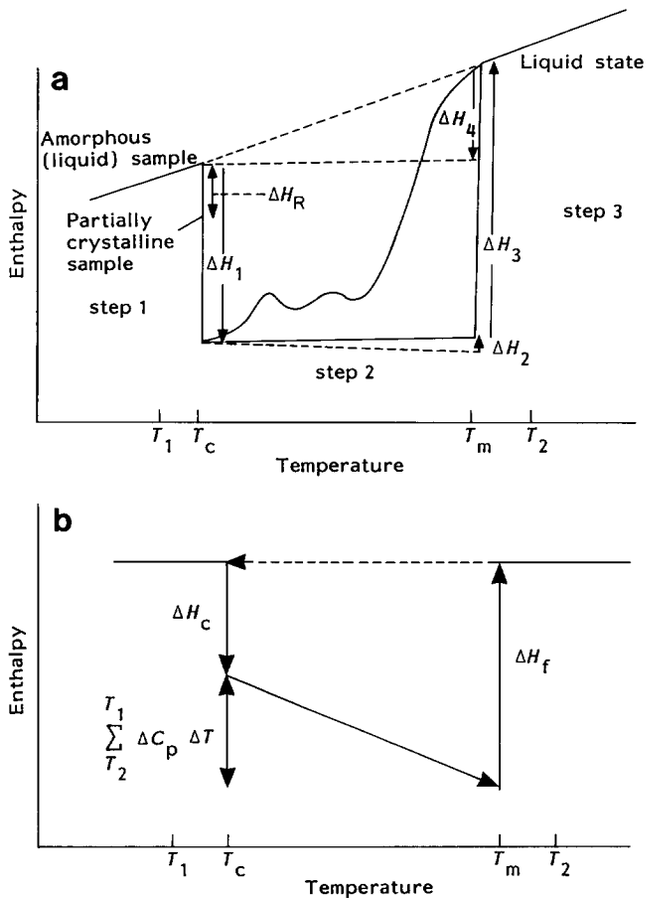

Figure 2 Schematic representation of the enthalpy changes undergone by quenched PEEK on (a) heating from T_1 to T_2 and (b) eliminating the specific heat/temperature dependence

enthalpy change in heating from T_1 to T_c, and that of crystallization at T_c. These have been incorporated into ΔH_1 in *Figure 2a*. Term 2 is the enthalpy change in heating the partially crystalline material from T_1 to T_m, i.e. ΔH_2, and will incorporate any further melting or recrystallization which occurs during the heating. Term 3 is the enthalpy of melting at T_m and that associated with heating the liquid from T_m to T_2, i.e. ΔH_3. The final term, ΔH_4, is that of cooling the liquid from T_2 to T_1. If the initial sample is completely amorphous then by the First Law of Thermodynamics, the overall heat change measured should be zero, i.e.

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = 0 \qquad (2)$$

If, however, the initial sample was partially crystalline then the left-hand side of equation (2) is equal to the residual heat of crystallization of the sample at T_1 (ΔH_R) and reflects the residual degree of crystallinity of the sample.

The value of ΔH_4 has to be evaluated indirectly, as the sample crystallizes on cooling at any relevant rate, from interpolated values of the specific heat determined close to the T_g and above the melting point. However, a mathematical procedure was adopted in the integration of the d.s.c. data which eliminated the necessity to do this. This involved setting the specific heats of the liquid at T_1 and T_2 equal, and desloping the corresponding specific heat/temperature trace (see *Figure 2b*).

Crystallization and melting enthalpies are unchanged by this procedure but the observed temperature dependence of the specific heat of the partially crystalline solid now reflects the difference between the solid and liquid values, i.e. ΔC_p. Since ΔH_4 has been set to zero by this procedure, the integration of the desloped thermograph between T_1 and T_2 measures $\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$ and as outlined above this is equal to the residual enthalpy of fusion, ΔH_R, of the sample.

Any crystallization or melting of the sample during the heating of the sample above T_1 is accounted for in this procedure, since the integration of apparent specific heats is carried out on the d.s.c. data directly.

Several quenched samples, and others which had been crystallized isothermally to different degrees of crystallinity as measured by WAXS, were heated under standard conditions in the differential scanning calorimeter. The instrument baseline was subtracted from the heat flow/temperature response and the specific heats of the liquid equated at T_1 and T_2. The resulting thermograph was integrated between the limits T_1 and T_2, set below and above the crystallization and melting temperatures. This evaluated ΔH_R, and the values are listed for the various samples in *Table 3*.

The residual enthalpy of the quenched PEEK samples was zero to within experimental error, i.e. -0.70 ± 1.20 J g^{-1} and there was little variation observed between quenched samples. Also partially crystalline samples exhibited a large ΔH_R which increased linearly with weight fraction degree of crystallinity, as measured separately. The corresponding dependence gave a value of 122.5 ± 1.5 J g^{-1} for the enthalpy of fusion of the totally crystalline PEEK at 437 K. This implies that the quenched samples were 0.5 ± 1.0% crystalline. Consistent with the view that the quenched samples were essentially amorphous is the linearity of the specific heat with temperature for the liquid above the melting point and those measured on the quenched glass immediately above the T_g.

Table 3 Weight fraction degree of crystallinity

Sample	by WAXS	Residual enthalpy (J g^{-1})	by d.s.c.[a]	by density
1	0	-0.65 ± 1.2	0.005 ± 0.01	0
2	0	-0.61	0.005	0
3	0	-0.82	0.007	0
4	0	-0.56	0.005	0
5	0.18 ± 0.01	-23.00	0.187	0.18 ± 0.01
6	0.18	—[b]	—[b]	0.18
7	0.35	-43.80	0.358	0.31
8	0.25	-30.30	0.247	0.23

[a]Assuming 122.5 ± 1.5 J g^{-1} for 100% crystallinity
[b]Not determined

The First Law procedure measures the residual crystallinity of the sample and even if the samples had been poorly crystallized such that some further crystallization, annealing or melting occurs during subsequent heating to the melting point the integration incorporates all these changes. It measures the net change in enthalpy between the two temperature limits and it does not rely on evaluating the specific heats as a function of temperature of the partially crystalline material, which would be altered if partial melting or recrystallization were occurring. It does require the temperature dependence of the specific heat of the liquid to be reasonably well defined at the set temperatures.

It is apparent, however, that quenched PEEK is amorphous.

The density degree of crystallinity

Since the crystallographic unit cell of PEEK varies with T_c, the crystalline density was calculated from the dependence of the crystalline specific volume, V, on T_c.

$$V = 0.7584(\pm 4.69 \times 10^{-4}) - 8.327(\pm 0.8994) \times 10^{-5} T_c \text{ cm}^3 \text{ g}^{-1}$$

i.e. equation (3) (T_c values are listed in *Table 1*). From the measured density, the weight fraction degree of crystallinity was calculated, using a value for the amorphous density of 1.261 g cm^{-3} and compared with the weight fraction determined by WAXS and also by the residual enthalpy of fusion.

Wide variations were observed between similar samples and also with the values obtained by the other methods. However, light microscope examination of the crystalline PEEK samples, showed that polishing exposed extensive amounts of voids within the specimens. Since the PEEK had been extensively dried, the voids were attributed to trapped air or solvent residue not extracted. Subsequently samples were carefully examined for the presence of voids on progressive polishing and if present the density data were then rejected.

With this degree of care, good agreement was achieved between the weight fraction degree of crystallinity as measured by d.s.c., WAXS and density (*Table 3*).

CONCLUSIONS

The residual enthalpy of crystallization of PEEK at 437 K has been determined as 122.5 ± 1.5 J g^{-1}, and an integration procedure has been adopted which enables

the crystallinity of PEEK to be evaluated unequivocably even in the presence of annealing and low melting endotherms.

Problems have been observed in the use of density to evaluate the fractional extent of crystallinity due to the presence of voids in the samples.

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