THE CRYSTALLINITY OF POLYARYL ETHER ETHER KETONE
II. Peek composites

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Measurement of the degree of crystallinity of the polymer matrix in a composite is complicated by the presence of the reinforcing additive. This is particularly the case in APC–2 in which as much as 70% can be carbon fibre. A First Law procedure, developed for determining the degree of crystallinity of PEEK, which involves direct measurement of the enthalpy changes associated with melting, crystallization and heat capacity changes, has found to be an effective method for the determination of the crystallinity of the PEEK matrix. The procedure has been applied to carbon fibre and glass fibre PEEK composites.

Keywords: amorphous, APC–2, crystalline, density, DSC, enthalpy of fusion, glass fibre, PEEK, WAXS

Introduction

High melt viscosity and kinetic effects reduce the development of crystallinity in polymers such that melt crystallized samples are not completely crystalline. The degree of crystallinity, X_c, can be varied by suitable thermal treatment, and this has a profound effect on physical parameters, and mechanical properties as well as fracture behaviour. The excellent high temperature properties of PEEK and its optimum resistance to solvent stress cracking [1] is not achieved unless it is substantially crystalline. Mechanical properties are not reproducible unless the degree of crystallinity is precisely controlled.

Each standard method for determining the degree of crystallinity, X_c, of PEEK has its associated problems [2, 3]. We have recently [2] derived a First Law method of determining the crystallinity of PEEK, which involves integrating the various specific heat changes as determined by differential scanning calorimetry between two standard temperatures, T_1, above the glass transition temperature,

T_g, and T_2, above the last trace of melting, T_m. This procedure evaluated the overall enthalpy change, at T_1, and was a measure of the crystallinity of the sample. Furthermore, using the degree of crystallinity as determined by WAXS, or density, the enthalpy of fusion of PEEK was found to be 122.5 $J \cdot g^{-1}$.

The present report extends the procedure to determining the degree of crystallinity of PEEK glass and carbon fibre composites.

Experimental

PEEK, type 450G, was obtained from ICI Speciality Polymers Group, Wilton. After thorough drying, the granules were compression moulded into plaques 150× 150× 1 mm at 650 K and quenched into ice/water. Test specimens were cut directly from these plaques.

APC–2 samples and short glass fibre filled moulding powder was also obtained from ICI ltd.

Differential scanning calorimetry, DSC, was carried out on a Perkin-Elmer model DSC 2C interfaced to a BBC Master microcomputer, which controlled the DSC, collected and analysed the heat flow-temperature or time data. The DSC was calibrated from the m.pts. of ultra-pure metals.

A value of 26.45 $J \cdot g^{-1}$ was taken for the enthalpy of fusion of indium.

Wide angle X-ray scattering measurements were carried out using a Picker high resolution automated powder diffractometer, on polished flat specimens. The scattering data was collected by a Phillips PW 171710 diffractometer control unit and a Brother AT micro-processor. An IBM 4340 series mainframe computer was used to analyse the data. The diffractometer was used as described elsewhere [4, 5].

Densities were measured by weighing in air and in n-heptane at 293 K.

Results and discussion

The degree of crystallinity, X_c

Two averages X_c can be defined. These are the weight, $X_{c,w}$ and the volume, $X_{c,v}$ degree of crystallinity. If it is assumed that only crystalline and amorphous phases exist in the sample, then the total volume, V_t, is

$$V_t = V_a + V_c \qquad (1)$$

where V_a and V_c are the volumes of the amorphous and crystalline phases, such that

$$X_{c,v} = V_c/(V_c + V_a) = (\rho - \rho_c)/(\rho_c - \rho_a) \qquad (2)$$

Similarly,

$$X_{c,w} = \rho_c (\rho - \rho_c)/[\rho (\rho_c - \rho_a)] \qquad (3)$$

where ρ, ρ_c and ρ_a are the sample, crystalline and amorphous densities, respectively.

Measurement of the degree of crystallinity is complicated by the variability of polymer morphology, and by the fact that the different experimental techniques used to measure the degree of crystallinity, e.g. WAXS studies, density, DSC and IR spectroscopy, defines the difference between the amorphous and crystalline regions in different ways, and so derives different average values for the same sample.

In crystalline polymer composites a minimum of 3 phases are present and the analysis is further complicated by additional density, weight and volume terms. The presence of voids within the composite makes the determination of the degree of crystallinity by density impossible, and additional scattering from the fibre component makes WAXS and IR spectroscopic methods ineffective. Crystallinity studies on the two composites were limited to DSC measurements using the First Law method [2].

Differential Scanning Calorimetry

It has been shown previously [6] that rapidly quenched thin film PEEK samples crystallize on heating in the calorimeter above the glass transition temperature, with the evolution of the enthalpy of crystallization, ΔH_c. The glass filled material exhibited this behaviour, see Fig. 1. Crystalline samples obtained by isothermal crystallization at a high temperature did not exhibit this exotherm. The APC–2 sample behaved in this way, see Fig. 2. Whereas samples crystallized to different extents exhibited the exotherm to a lesser extent.

ΔH_c was evaluated by integrating under this crystallization exotherm using a non-linear baseline for the quenched and crystalline samples, see Table 1. The maximum values measured for the quenched specimens were 24±1 and the minimum 0.0±1.0 J·g^{-1} for the well crystallized samples. On further heating, see Fig. 1, several melting endotherms were observed and integrating over the total endotherms the range of enthapy of fusion values was 30–45 kJ·g^{-1}. This difference between the maximum enthalpy of crystallization and that of fusion, of 25–90% does not imply that the specimens had crystallized on quenching but that
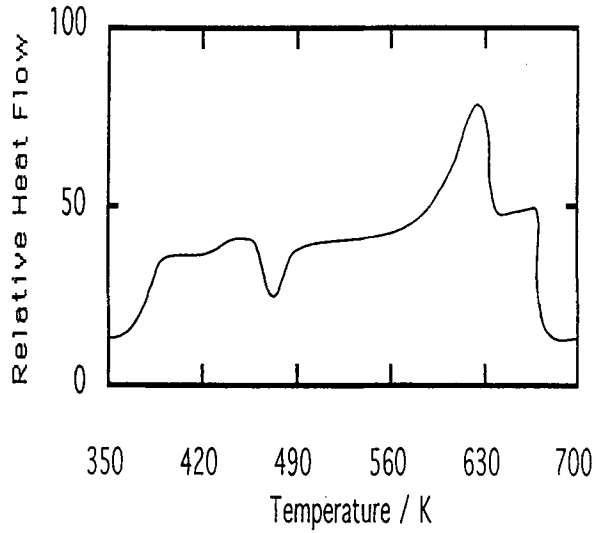
Fig. 1 DSC curve of glass fibre reinforced PEEK moulding powder, showing glass transition, and crystallization exotherm and melting endotherm. Heating rate 10 deg·min^{-1}
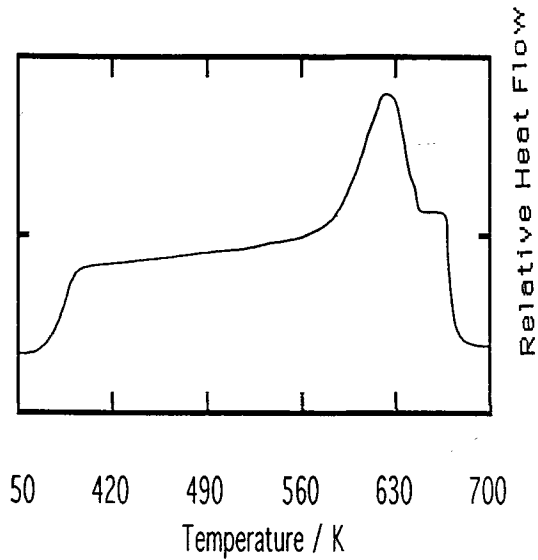

Fig. 2 DSC curve of APC–2 sample. Experimental conditions as above

the enthalpies are measured at different temperatures. Correction has to be made for the heat capacity differences, ΔC_p, between the liquid and partially crystalline solid, i.e.

$$-\Delta H_c\,(T_c\,) = \Delta H_f\,(\,T_m\,) + \sum_{T_c}^{T_m} \Delta C_p\ \mathrm{d}T \qquad (4)$$

DSC was used to measure the specific heats of the liquid and partially crystalline material directly and the various terms of Eq. (4) evaluated directly.

The procedure implicit in using Eq. (4) in DSC measurements is outlined diagrammatically in Fig. 3 as changes in enthalpy. The overall change in entropy in heating a sample from below T_1 to T_2 is associated with changes in enthalpy, crystallization at T_c, ΔH_c, changing the partially crystalline material from T_c to T_m, ΔH_2, and melting at T_m, ΔH_f. If the original sample is completely amorphous the overall change should be equivalent to the heat change in cooling the liquid from T_m to T_c, ΔH_4, i.e. in general,

$$-\Delta H_c + \Delta H_2 + \Delta H_f - \Delta H_4 = 0 \qquad (5)$$

if the sample is amorphous. If the sample is crystalline the lhs of Eq. (5) is equal to the enthalpy of the crystallization of the sample at T_1, and so reflects the degree of crystallinity of the initial sample prior to heating. This equation is valid even if the sample crystallizes or melts on heating if the net changes in enthalpy are evaluated.

Several quenched samples, and others which had been crystallized isothermally were analysed with this procedure, see Table 1. The quenched samples had a residual entropy which was within experimental error zero, i.e. -0.70 ± 1.20 J·g^{-1}. The quenched samples are accordingly amorphous.

A similar analysis by DSC was applied to APC–2 and glass fibre filled PEEK samples. The DSC trace of the two as-received materials differed substantially in that the glass filled sample behaved as poorly crystallized PEEK in exhibiting a small crystallization exotherm on heating through its T_g. The DSC trace of the APC–2 sample on the other hand was characteristic of a well crystallized PEEK sample, see Fig. 2. The degree of crystallinity of the samples were determined by integrating the DSC trace of heat capacity against temperature between the fixed temperatures T_1 and T_2 and correcting for the composition of PEEK in the composite, see Table 1. From this it can clearly been seen that the PEEK component of APC–2 is substantially crystalline with a degree of crystallinity consistent with it having crystallized at a high temperature and to $33 \pm 4\%$. Annealing at elevated temperatures for extended periods did not substantially improve the degree of crystallinity attained.
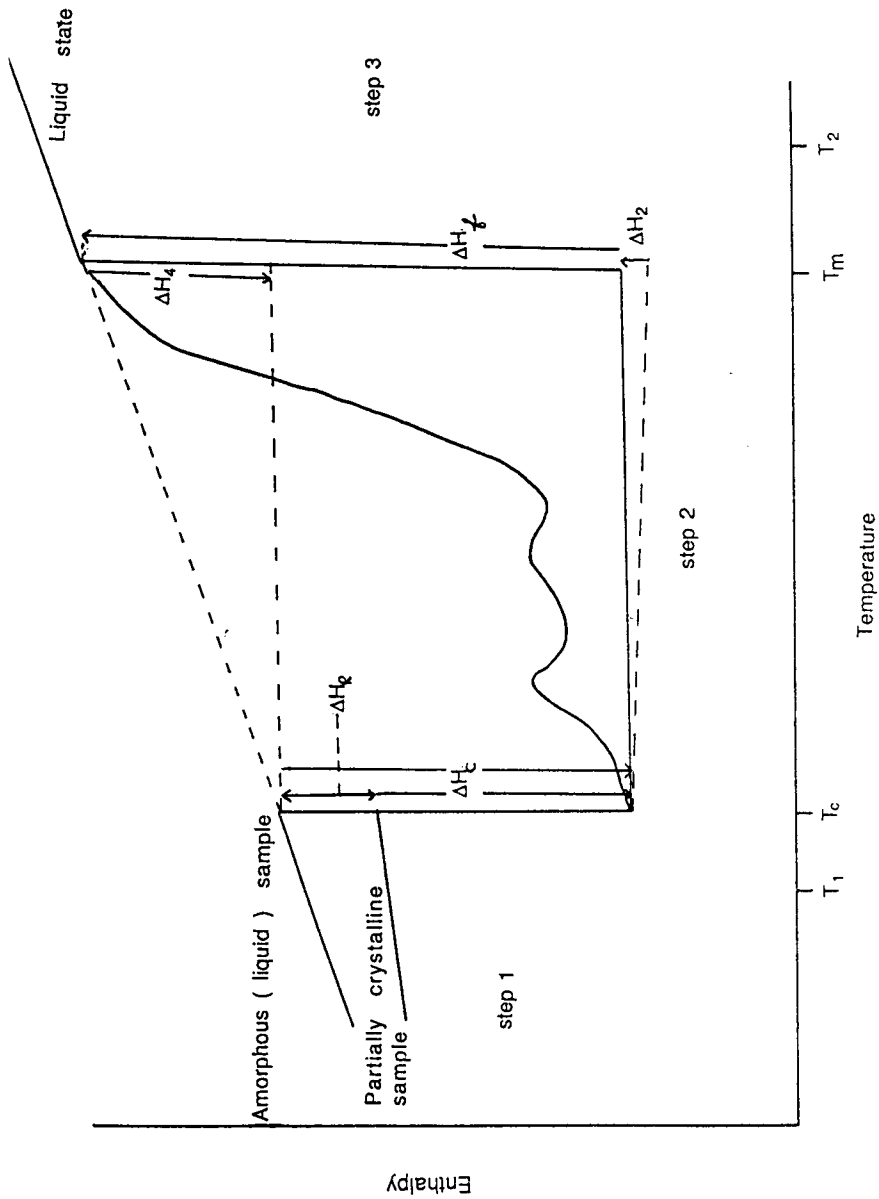
Fig. 3 Schematic representation of enthalpy changes on heating from T_1 to T_2 showing the various contributions to the enthalpy changes

Table 1 Degree of crystallinity and enthalpy changes

Sample	Enthalpy of fusion $\Delta H_f / J \cdot g^{-1}$	Enthalpy of crystallization $\Delta H_c / J \cdot g^{-1}$	Difference $\sum c_p \Delta T / J \cdot g^{-1}$	Residual enthalpy/ $J \cdot g^{-1}$	Crystallinity/ %
		a. Amorphous PEEK samples			
1	41.6	−24.3	17.9	−0.6	−0.5
2	40.9	−23.2	18.3	−0.6	−0.5
3	40.5	−23.0	16.3	−0.8	−0.7
4	42.2	−22.9	20.1	−0.6	−0.5
		b. Crystalline PEEK			
5	32.4	−2.3		−23.0	18.7
6	45.6	0		−43.8	35.8
7	35.9	0		−30.3	24.7
		c. Composites			
Sample	% Crystallinity as received		max. attained		
APC-2					
1	31.5		35.0		
2	33.0		35.0		
3	32.0		36.0		
Glass fibre					
1	12.5		38.0		
2	12.1				
3	13.1				

The opposite was observed with the glass filled composite. The as-received material was poorly crystalline, 12±2% but annealing substantially raised this to 38%, in-line with the APC−2 sample. Since control of the degree of crystallinity is important in maintaining the material properties of PEEK, the marked differences in the degree of crystallinity of the glass fibre filled material on different thermal treatments must limit its application in use. While in contrast, the degree of crystallinity of APC−2 appears to be substantially independent of thermal treatment.

Conclusions

Thermal analysis can be used to determine the degree of crystallinity of PEEK and its composites, but allowances must be made for melting and re-crystallization which may occur on heating. Direct measurement of the overall enthalpic change must be made.

Substantial differences in the degree of crystallinity attained after different thermal treatments have been observed between the glass and carbon fibre filled composites which must have a marked effect on the reproducible properties of the composites.

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References

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Zusammenfassung — Wegen der Gegenwart von Verstärkungszusätzen ist die Messung des Kristallinitätsgrades einer Polymermatrix in einem Gemisch recht kompliziert. Dies ist besonders bei APC-2 der Fall, wo der Kohlenstoffiberanteil bis zu 70% ausmachen kann. Zur Bestimmung der Kristallinität der PEEK Matrix fand man ein geeignetes Verfahren, welches zur Bestimmung des Kristallinitätsgrades von PEEK entwickelt wurde und eine Direktmessung der Enthalpieänderungen bei Schmelzen und Kristallisation sowie der Wärmekapazitätsänderungen umfaßt. Das Verfahren wurde bei Kohlenstoffiber- und Glasfiber- PEEK-Mischungen angewendet.