The crystallinity of PEEK composites

A. A. Mehmet-Alkan and J. N. Hay*
The School of Chemistry, The University of Birmingham, PO Box 363, Edgbaston, Birmingham B15 2TT, UK

(Received 15 March 1993)

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 poly(ether ether ketone) carbon fibre composite, APC-2, which may contain as much as 70% carbon fibre. A First Law procedure, developed for determining the degree of crystallinity of poly(ether ether ketone) (PEEK), has been outlined previously. It involved direct measurement of the enthalpy changes associated with melting, crystallization and heat capacity changes, and was found to be an effective method for determining the crystallinity of the PEEK matrix. The procedure has been applied to carbon fibre and glass fibre PEEK composites.

(Keywords: PEEK; composites; crystallinity)

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, which has a profound effect on physical and mechanical properties as well as on fracture behaviour. The excellent high temperature properties of poly(ether ether ketone) (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 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 (d.s.c.) 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 evaluates the overall enthalpy change at T_1, which is a measure of the crystallinity of the sample. Furthermore, using the degree of crystallinity as determined by wide angle X-ray scattering (WAXS), or density, the enthalpy of fusion of PEEK was found to be 122.5 J g^{-1}.

The present communication 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, UK. After thorough drying, the granules were compression moulded into plaques 150 mm × 150 mm × 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 plaques were also obtained from ICI.

D.s.c. was carried out on a Perkin-Elmer model DSC 2C interfaced to a BBC Master microcomputer, which controlled the DSC and collected and analysed the heat flow, temperature or time data. The DSC was calibrated from the melting points of ultra-pure metals. A value of 26.45 J g^{-1} was taken for the enthalpy of fusion of indium.

WAXS measurements were carried out using a Picker high resolution automated powder diffractometer, on polished flat specimens. The scattering data were collected by a Phillips PW1710 diffractometer control unit and a Brother AT microprocessor. 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

Degree of crystallinity, X_c. Two average X_c values can be defined. These are the weight, $X_{c,w}$, and the volume, $X_{c,v}$, degree of crystallinity, assuming that only crystalline and amorphous phases exist in the sample. Then:

$$X_{c,v} = (\rho - \rho_c)/(\rho_c - \rho_a) \tag{1}$$

and

$$X_{c,w} = \rho_c(\rho - \rho_c)/[\rho(\rho_c - \rho_a)] \tag{2}$$

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, d.s.c. and i.r. spectroscopy, define the difference between the amorphous and crystalline regions in different ways, and so derive different average values for the same sample.

In crystalline polymer composites, a minimum of three phases are present and the analysis is further complicated by additional density, weight and volume terms. Using

---

*To whom correspondence should be addressed

0032-3861/93/163529-03

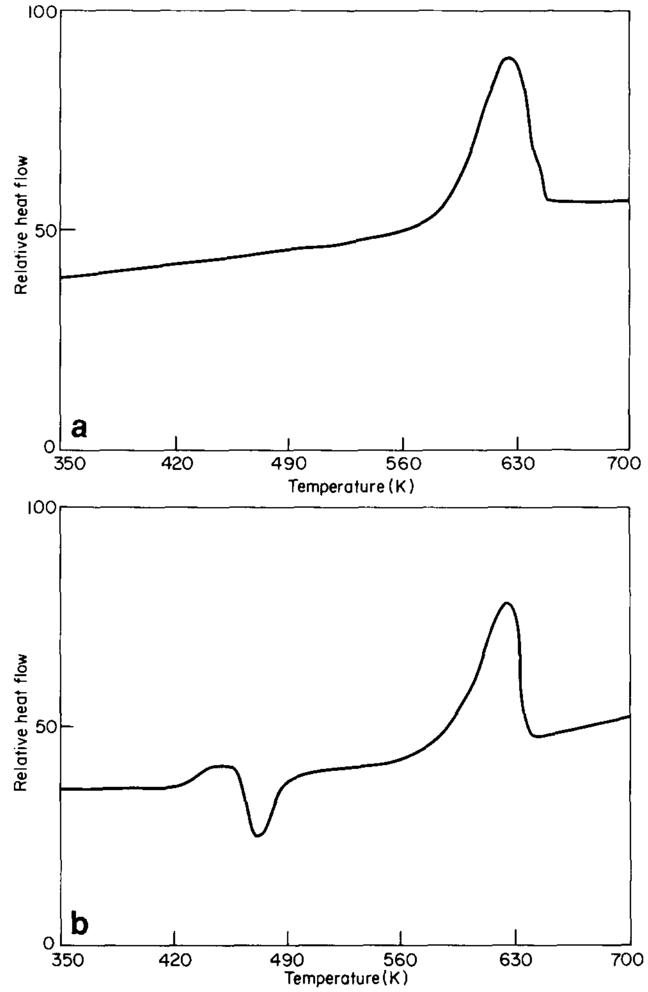

Figure 2 D.s.c. thermographs of plaques of (a) glass fibre reinforced PEEK; (b) APC-2. Heating rate 10 K min^{-1}

the density data listed in *Table 1*, and the fact that the APC-2 composite contained 68±3% carbon fibre by weight, the crystallinity of the PEEK phase is found to be negative, which is clearly untenable. Voids are present which, together with the uncertainties in each parameter, make determination of the degree of crystallinity by density uncertain. Furthermore the WAXS of APC-2 is dominated by the carbon fibre, which swamps the contribution from the crystalline PEEK (see *Figure 1*) and limits the effectiveness of the analysis.

Differential scanning calorimetry. It has been shown previously[6] that rapidly quenched thin film PEEK samples crystallize on heating in the calorimeter above T_g, with the evolution of the enthalpy of crystallization. The glass-filled material exhibited this behaviour (see *Figure 2a*). Crystalline samples obtained by isothermal crystallization at high temperature did not exhibit this exotherm. The APC-2 sample behaved in this way (see *Figure 2b*).

The enthalpy of crystallization (ΔH_c) was evaluated by integrating under this crystallization exotherm using a non-linear baseline for the quenched and crystalline samples (see *Table 2*). The maximum value of ΔH_c measured for the quenched specimens was $24 \pm 1\ \mathrm{J\,g^{-1}}$ and the minimum was $0.0 \pm 1.0\ \mathrm{J\,g^{-1}}$ for the well crystallized samples. On further heating, several melting endotherms were observed and, integrating over the total endotherms, the range of enthalpy of fusion (ΔH_f) values was 30–45 $\mathrm{J\,g^{-1}}$. This difference between the maximum values of ΔH_c and ΔH_f, 25–90%, does not imply that the specimens had crystallized on quenching but that 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.

$$-\Delta H_c(T_c) = -\Delta H_f(T_m) + \sum_{T_c}^{T_m} \Delta C_p \, \mathrm{d}T \qquad (3)$$

D.s.c. was used to measure the specific heats of the liquid and partially crystalline material directly and the various terms of equation (3) were evaluated directly.

The procedure implicit in using equation (3) in d.s.c. measurements has been outlined previously[2]. The overall change in entropy on 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:

$$-\Delta H_c + \Delta H_2 + \Delta H_f - \Delta H_4 = \Delta H_5 \qquad (4)$$

If the sample is amorphous, ΔH_5 is zero. If the sample is crystalline then the value of ΔH_5 is equal to ΔH_c 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 that had been crystallized isothermally were analysed with this procedure (see *Table 1*). The quenched samples had a residual entropy which was, within experimental error,

Table 1 Densities of materials at 298 K

Material	Density ($\mathrm{kg\,m^{-3}}$)
Carbon fibre (high strength)	1760
Carbon fibre (high modulus)	1870
APC-2 prepreg	1533
APC-2 plaque	1525
PEEK (amorphous)	1240
PEEK (crystalline)[a]	1384–1411
Calculated PEEK density in APC-2 assuming 3 phases	949–1088

[a] Crystallization temperature dependent

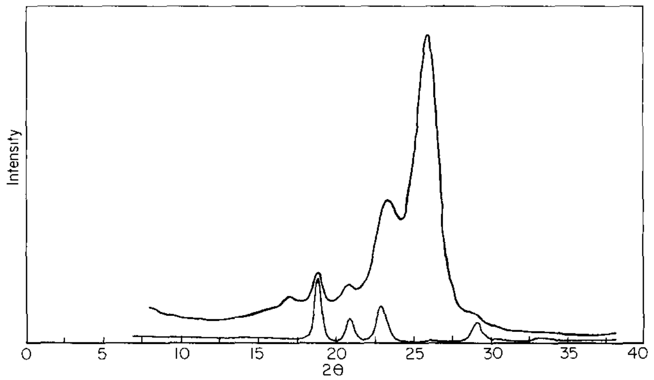

Figure 1 WAXS of APC-2 film; PEEK diffraction lines superimposed

Table 2 Degree of crystallinity and enthalpy changes

Sample	Enthalpy of fusion, ΔH_f (J g^{-1})	Enthalpy of crystallization, ΔH_c (J g^{-1})	Difference, $\Sigma C_p \Delta T$ (J g^{-1})	Residual enthalpy (J g^{-1})	Crystallinity (%)
(a) Amorphous PEEK					
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 (%)	Maximum crystallinity 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	

zero, i.e. -0.70 ± 1.20 J g^{-1}. The quenched samples are accordingly amorphous.

A similar analysis by d.s.c. was applied to APC-2 and glass-fibre-filled PEEK samples. The d.s.c. 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 d.s.c. trace of the APC-2 sample, on the other hand, was characteristic of a well crystallized PEEK sample (see *Figure 2*). The degree of crystallinity of the samples was determined by integrating the d.s.c. 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 be clearly seen that the PEEK component of APC-2 is substantially crystalline with a degree of crystallinity consistent with crystallization at a high temperature to $33 \pm 4\%$. Annealing at elevated temperatures for extended periods did not substantially improve the degree of crystallinity attained.

The opposite situation was observed for the glass-filled composite. The as-received material was poorly crystalline ($12 \pm 2\%$) 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 applications. 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 recrystallization 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; these must have a marked effect on the reproducible properties of the composites.

Acknowledgements

A. A. M.-A. is grateful to the SERC and to ICI Speciality Polymers Ltd for the award of a studentship during the tenure of this work.

References

1 Barton, J. M., Goodwin, A. A., Hay, J. N. and Lloyd, J. R. *Polymer* 1991, **32**, 260
2 Mehmet-Alkan, A. A. and Hay, J. N. *Polymer* 1992, **33**, 3527
3 Hay, J. N., Langford, J. I. and Lloyd, J. R. *Polymer* 1989, **30**, 489
4 Hay, J. N., Kemmish, D. J., Langford, J. I. and Rae, A. I. M. *Polym. Commun.* 1984, **25**, 175
5 Hay, J. N., Kemmish, D. J., Langford, J. I. and Rae, A. I. M. *Polym. Commun.* 1986, **27**, 283
6 Kemmish, D. J. and Hay, J. N. *Polymer* 1985, **26**, 905