Differential scanning calorimetry and infra-red crystallinity determinations of poly(aryl ether ether ketone)

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The differential scanning calorimetry (d.s.c.) heating thermograms of 12 poly(aryl ether ether ketone) (PEEK) samples of varying degrees of crystallinity have been recorded. The relation found between the degree of crystallinity as determined by specific gravity measurements, and the melting enthalpy of the polymer, shows that recrystallization is occurring during a heating scan rate of 10°C min^{-1}. This implies that d.s.c. is not a convenient technique to assess PEEK crystallinity. The infra-red absorbance spectra of the same samples have also been examined in the range from 1030 to 880 cm^{-1}. The 965 cm^{-1} band, up to now considered as indicative of the PEEK crystallinity, is shown to be practically independent of the degree of crystallinity above 15%. However, there is evidence to support the existence of a true i.r. crystalline band located at 947 cm^{-1}. It is also suggested that the 965 cm^{-1} band is due to a normal vibration mode of a short segmental conformation, whose presence is favoured in the crystalline phase, but also in the amorphous zones nearest to the crystallite surface.

(Keywords: PEEK; thermal analysis; infra-red spectroscopy; crystallinity)

INTRODUCTION

Poly(aryl ether ether ketone) (PEEK) is a high performance thermoplastic semicrystalline polymer which exhibits a high toughness[1], an excellent solvent resistance[2], a low water uptake[3] and a quite satisfactory thermal resistance[4]. These properties make PEEK very attractive as the matrix in high performance carbon fibre composites. Samples with a wide range of crystallinities, from the totally amorphous polymer to samples with ~50% degree of crystallinity, can be obtained[4]. Most of the PEEK properties are more or less sensitive to the level of crystallinity, especially mechanical and thermal properties[5]. It is therefore of paramount importance to assign a correct figure to the degree of crystallinity of a given PEEK sample.

The assessment of polymer crystallinity has been recently reviewed[6]. Differential scanning calorimetry (d.s.c.), one of the most frequently used methods, could be a convenient technique for the evaluation of the degree of crystallinity, provided that PEEK does not experience any recrystallization during the d.s.c. heating scan. There is some controversy in the literature about this last point. The double melting behaviour, frequently observed for PEEK samples isothermally crystallized from the amorphous state, has indeed been interpreted in two different ways. On one hand, some authors[7,8] have attributed the first melting endotherm to the initial trace of melting of the lamellae formed during the previous isothermal crystallization. In that case, a subsequent increase in temperature causes melting and recrystallization during the heating scan, that leads to the formation of thicker lamellae. These thicker lamellae melt at a higher temperature, giving rise to the second melting endotherm. This mechanism is similar to what has been postulated to occur for poly(ethylene terephthalate) by Holdsworth and Turner-Jones[9]. In this interpretation, the d.s.c. trace between the two melting endotherms reflects a subtle combination of heat absorption and production through melting and crystallization. It is then impossible to evaluate the sample crystallinity level by d.s.c., since the amount of recrystallization cannot be determined. On the other hand, other authors[10–12] have suggested that two lamellar populations are formed during the PEEK isothermal crystallization, each population having its own lamellar thickness and consequently its own melting temperature. The first population to be formed would contain the thicker lamellae, the so-called dominant lamellae, whereas the second population would contain the thinner, lately formed and called 'subsidiary' lamellae. With such an interpretation, it would be possible to evaluate the PEEK crystallinity level through d.s.c., because the sum of the two melting endotherms should give a correct idea of the total initial crystallinity, unless some recrystallization would also be present in an important amount. Because the present situation is unclear, we found it interesting to test the relevance of d.s.c. to assess the PEEK crystallinity level.

Infra-red (i.r.) spectroscopy is another method frequently used to determine polymer crystallinity, because of its easy and widespread laboratory use. Attempts to assess the PEEK crystallinity by means of i.r. spectroscopy have been made by various authors. In a first type of approach, a given i.r. band intensity has been correlated to the degree of crystallinity. Note that there is some uncertainty about the exact wave number location of this band, since variations of ~5 cm^{-1} are

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found in the literature concerning its location. For example, Chalmers *et al.*[13] found that the height ratio of the absorbance peaks at 970 and 952 cm^{-1} was a linear function of the PEEK crystallinity. Cebe *et al.*[5] claimed that the area ratio of the same i.r. bands (in this case located at 966 and 952 cm^{-1}) is a better linear estimate of the crystallinity. Another approach has been taken by Nguyen and Ishida[14]. From the measured i.r. spectra of samples of various crystallinity levels, they calculated by an interpolation procedure the spectra of the 100% crystalline polymer and of the totally amorphous one. From these two spectra, and assuming a simple two-phase model to hold for the semicrystalline polymer, they were able to estimate the crystallinity of any PEEK sample by using a fitting procedure. However, the degrees of crystallinity derived in this way were shown to be higher than those obtained from X-ray measurements. This is due to the fact that the technique is sensitive to the crystalline-like conformers and not only to the true crystalline segments. In this paper, the correlation between the 965 cm^{-1} band and crystallinity will also be re-examined.

EXPERIMENTAL

Sample preparation

The PEEK powder (commercial grade 150P) was obtained from ICI (Wilton, UK). It was dried overnight at 150°C in vacuum. It was then pressed between aluminium foil at 400°C over 5 min into 200 μm thick films. Some of the films were directly quenched in cold water from the molten state and isothermally annealed in a hot press at a temperature between 150°C and 300°C, for periods ranging from 15 to 30 min, before being quenched again in water. The other films were directly transferred from the molten state to the consolidating hot press, whose temperature was fixed between 120°C and 300°C, and then quenched in water. In the latter case, the samples were not really isothermally crystallized; changing the hot press temperature led essentially to a change in the sample cooling rate from the molten state. The exact thermal history of each of the samples used in this study is presented in *Table 1*.

The aluminium foil was quickly dissolved in concentrated hydrochloric acid. The films were then rinsed in running water, and only void-free regions were retained. The density of these samples was measured by weighing in air and in water at 20°C. The density of water was evaluated using a previously calibrated pycnometer. The volume (X_c) and weight (W_c) crystallinities of the films were then derived from their densities, assuming a value of 1.263 g cm^{-3} for the fully amorphous PEEK[4] and 1.400 g cm^{-3} for the PEEK perfect crystal. Various values for the density of the 100% crystalline PEEK have already been quoted in the literature[2], ranging from 1.341 to 1.415 g cm^{-3}, and are derived from crystalline unit cell determinations. However, it was decided to adopt in this study the published value of 1.4 g cm^{-3} for the 100% crystalline polymer density, because this was the result of a correlation between densities and wide angle X-ray scattering determined crystallinities on a large number of samples covering a wide crystallinity range[4].

Differential scanning calorimetry

The d.s.c. heating scans were recorded on ~7 mg of material in a Perkin-Elmer DSC2 calibrated with indium and zinc. The chosen scanning rate was 10°C min^{-1}. Prior to each experiment, a baseline was recorded with empty pans, which was subtracted from the recorded thermogram of the PEEK sample measured in the next run. Various temperatures and enthalpies were computed from each thermogram: a crystallization peak temperature (T_{ch}) and enthalpy (ΔH_{ch}), which were apparent only for the amorphous or very weakly crystallized samples, a low temperature melting peak (T_{mL}) and enthalpy (ΔH_{mL}), present only for some of the samples isothermally crystallized, and a high temperature melting peak (T_{mH}) and enthalpy (ΔH_{mH}). For the samples crystallized at or above 300°C, it was not possible to separate the low temperature melting peak from the high temperature one; in this case the sum of ΔH_{mL} and ΔH_{mH} was computed.

Infra-red spectroscopy

The 200 μm thick films were polished by means of fine grained sand paper to reduce their thickness to ~50–100 μm. Their absorbance spectra were then recorded in the range from 1030 to 880 cm^{-1} in a

Table 1 Processing conditions, density and crystallinity, as determined by density measurements, of the samples investigated

Sample number	Initial state	T_c (°C)	t_c (min)	Density (g cm^{-3})	X_c (%)	W_c (%)
1	A	–	–	1.2659	2.1	2.3
2	A	150	30	1.2745	8.4	9.2
3	A	150	30	1.2769	10.1	11.1
4	A	180	30	1.2935	22.3	24.1
5	A	220	30	1.2981	25.7	27.7
6	A	260	30	1.2984	25.8	27.8
7	A	300	30	1.3008	27.6	29.7
8	M	120	15	1.2967	24.6	26.6
9	M	150	30	1.2983	25.8	27.8
10	M	180	30	1.3005	27.4	29.5
11	M	300	15	1.3130	36.5	38.9
12	M	Slowly	cooled	1.3177	39.9	42.4

The samples have been quenched from the molten state prior to annealing at T_c during t_c (initial state: A, amorphous), or directly transferred from the molten state to the consolidating press at T_c during t_c (initial state: M, molten)

Perkin-Elmer grating spectrophotometer model 580B, with a resolution of 1.4 cm^{-1} and a relative noise of 0.2.

A baseline, linearly drawn through 988 and 900 cm^{-1}, was subtracted from the recorded spectra to flatten the spectra. The experimental spectra were then reconstructed by a fitting algorithm, assuming they were the sum of peaks of lorentzian shape. For the amorphous sample, four peaks were necessary to reconstruct the measured absorbance between 1030 and 900 cm^{-1}. These peaks are centred around 1011 ± 0.5, 967.5, 952 ± 0.5 and 928 ± 0.5 cm^{-1}. Because the samples of higher degrees of crystallinity exhibited a shoulder in the 952 cm^{-1} absorbance peak, it was found necessary to introduce for these samples an additional absorbance peak centred at 947 ± 0.5 cm^{-1}. The 967.5 cm^{-1} peak location was also found to be sensitive to the crystallinity, decreasing to 965 cm^{-1} for the highest crystallinities. The fit parameters were the height and half-width of each peak, and a constant shift of the recorded spectra relative to the zero absorbance. The area of each peak was calculated from the well-known relationship between the area and the half-width and height of lorentzian-shaped peaks.

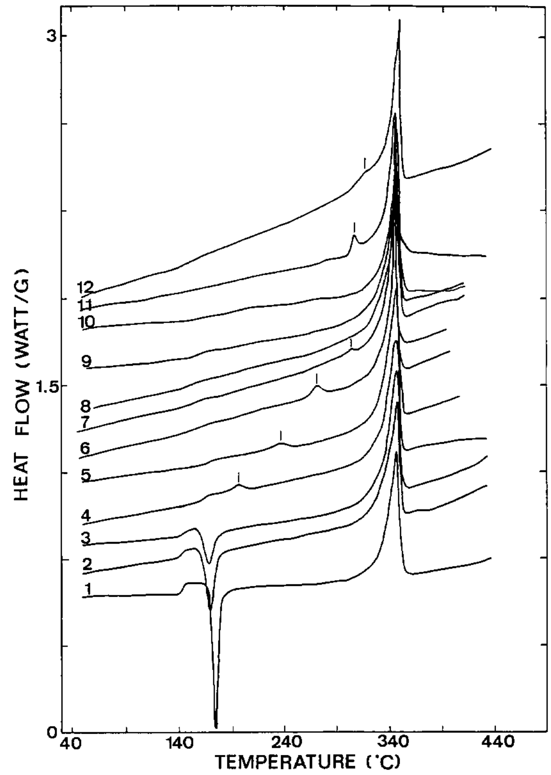

Figure 1 Normalized d.s.c. thermograms of the 12 samples investigated (heating rate 10°C min^{-1}). The exact thermal history and density of each sample are reported in *Table 1*. We report in *Table 2* the peak temperatures and crystallization or melting enthalpies for each sample

RESULTS AND DISCUSSION

Table 1 gives the density and the calculated X_c and W_c for each sample investigated.

In *Figure 1* the recorded thermograms for each sample are reproduced, after normalization to 1 mg of sample. The peak temperatures, along with the associated enthalpies, are given in *Table 2*. Since this paper is mainly devoted to the evaluation of the PEEK crystallinity, we will concentrate only on the crystallization and melting enthalpies. The sum of the enthalpies of the low and high temperature melting endotherms from which we subtract the exothermic crystallization peak enthalpy where applicable, i.e. $\Delta H_T = (\Delta H_{mH} + \Delta H_{mL} - |\Delta H_{ch}|)$, should be directly related to the initial crystallinity of the samples, provided no melting–recrystallization occurs during the heating scan. *Figure 2* is a plot of $|\Delta H_{ch}|$, ΔH_{mL}, $(\Delta H_{mH} + \Delta H_{mL})$ and ΔH_T as a function of W_c. It can be seen that ΔH_{mL} is negligible compared with the total enthalpy ΔH_T, probably because of the short crystallization times of the samples used in this study. The ΔH_T is first rapidly increasing with crystallinity, until crystallinity reaches levels around 40%, where it begins to saturate. Assuming the heat of fusion[4] for the 100% crystalline PEEK to be 130 J g^{-1}, it is possible to compute the enthalpy associated with the melting of the initial crystalline part of each of our samples ($\Delta H_{cryst} = 130 W_c$). The difference between ΔH_T and ΔH_{cryst} is the absolute value of a hidden crystallization enthalpy. This enthalpy is due to the crystals developed

Table 2 Crystallization enthalpy (ΔH_{ch}) and melting enthalpies (ΔH_{mL}, low temperature melting endotherm; ΔH_{mH}, high temperature melting endotherm; $(\Delta H_{mL} + \Delta H_{mH})$; sum of the low and high temperature melting enthalpies, given when the two melting endotherms are not separable) for each of the samples. The corresponding peak temperatures are also given (T_{ch}, T_{mL}, T_{mH}), along with the weight crystallinity (W_c)

Sample	W_c (%)	T_{ch} (°C)	ΔH_{ch} (J g^{-1})	T_{mL} (°C)	ΔH_{mL} (J g^{-1})	T_{mH} (°C)	ΔH_{mH} (J g^{-1})	$(\Delta H_{mL} + \Delta H_{mH})$ (J g^{-1})
1	2.3	175.0	−37.8	–	–	346.4	49.3	–
2	9.2	169.4	−26.6	–	–	347.2	49.2	–
3	11.1	168.7	−20.6	–	–	347.3	47.6	–
4	24.1	–	–	196.3	1.7	347.3	47.4	–
5	27.7	–	–	234.1	2.64	347.4	47.9	–
6	27.8	–	–	271.9	3.54	346.9	48.4	–
7	29.7	–	–	304.4	–	346.3	–	52.4
8	26.6	–	–	–	–	347.5	46.0	–
9	27.8	–	–	–	–	346.7	47.2	–
10	29.5	–	–	–	–	345.6	51.3	–
11	38.9	–	–	309.2	–	348.1	–	56.4
12	42.4	–	–	317.6	–	348.3	–	60.6

For a complete description of the thermal histories of the samples, refer to *Table 1*

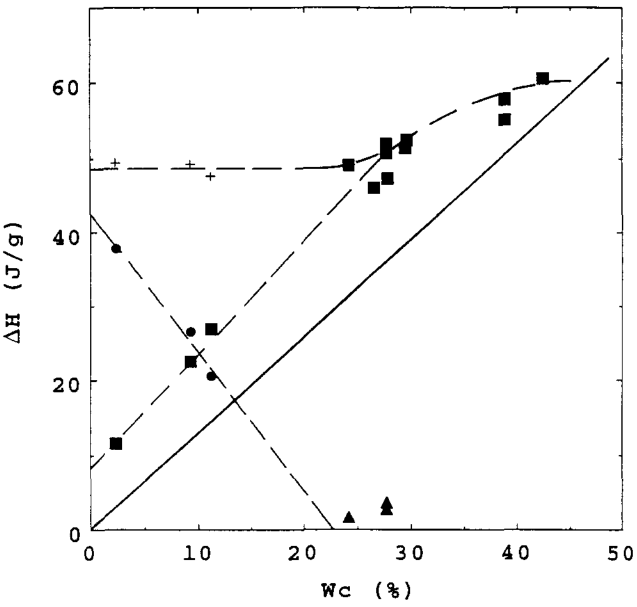

Figure 2 Plot of the melting and crystallization enthalpies of the PEEK samples, as a function of their initial weight crystallinity (W_c), as determined by means of density measurements: ΔH_{ch} (●) is the crystallization enthalpy observed upon heating the less crystalline samples; ΔH_{mL} (▲) represents the enthalpy calculated for the low temperature melting endotherm, where applicable; ($\Delta H_{mL} + \Delta H_{mH}$) (+) is the sum of the low and high temperature melting enthalpy endotherms; ΔH_T (■) is the difference between the sum of the melting enthalpies and the crystallization enthalpy; ΔH_{cryst} (——) represents the melting enthalpy one expects from the initial sample crystallinity, assuming 130 J g^{-1} for the heat of fusion of a 100% crystalline sample[4]

during the scan and that were not revealed through a crystallization exotherm during this scan. This hidden crystallization enthalpy, ΔH_{hidden}, is presented in *Figure 3* as a function of the initial PEEK crystallinity. For the nearly fully amorphous sample, the ΔH_{hidden} is around 10 J g^{-1} (which amounts to 7.5% crystallinity). This crystallization occurs at temperatures higher than the observable crystallization exotherm, i.e. above ~240°C which is the upper integration limit of this exotherm. Below 25% initial crystallinity, the ΔH_{hidden} increases with the initial crystallinity, to reach more than 15 J g^{-1} (~10% crystallinity) around 25% initial crystallinity. This is perhaps due to the parallel increase of very poorly crystallized polymer zones, which reorganize strongly without taking part in the crystallization exotherm. Above 25% initial crystallinity, however, the more crystalline the sample, the less recrystallization it experiences during the heating scan. This may be due to two reasons: either, the higher degrees of crystallinity are obtained with samples crystallized at higher (mean) temperatures; consequently, the scan time between this temperature and the final melting temperature is reduced, and therefore also the amount of recrystallization; or, the amount of material able to recrystallize during the d.s.c. scan diminishes when the initial crystallinity and the crystalline perfection are increased, an obvious assertion.

One could think that the ΔH_{hidden} results from an underestimation of the 100% crystalline PEEK heat of fusion (ΔH_m°). Two values for ΔH_m° have been quoted in the literature, namely 130 J g^{-1}, i.e. the value used above, obtained from the relation between melting points and lamellar thicknesses[4], and 162 ± 20 J g^{-1}, a result derived from the study of the equation of state for PEEK[15]. Indeed, one can increase the ΔH_m° value until ΔH_T is equal to zero for the sample with highest crystallinity. This would mean that no recrystallization occurs during the d.s.c. scan for this sample which was obtained by slow crystallization from the molten state. This would correspond to a value of ΔH_m° of ~145 J g^{-1}. However, even in such a case, there is still a noticeable ΔH_{hidden} of the order of 10 J g^{-1}, for every sample below 30% crystallinity.

The above results clearly indicate that PEEK recrystallization occurs during a 10°C min^{-1} d.s.c. heating scan. The amount of recrystallization being a priori unknown, invalidates the use of d.s.c. to evaluate the degree of crystallinity of PEEK. This does not mean however that the double lamellar population hypothesis can be discarded; it simply means that whatever the hypothesis about the double melting behaviour of PEEK, recrystallization must be taken into account to fully interpret the d.s.c. results.

In *Figure 4*, we present the measured i.r. absorbance, after having subtracted the base line, the deconvoluted absorbance peaks and the recalculated absorbance for the 2.1, 22.3 and 39.9% crystalline samples. It can be seen that the shoulder in the 952 cm^{-1} peak, due to the 947 cm^{-1} peak, is clearly increasing with crystallinity. The fitting procedure can also be seen to be quite satisfactory.

To obtain quantitative results, it is necessary to choose a reference absorbance peak, independent of crystallinity, with which the absorbances of the crystalline-sensitive peaks can be compared. Following the previous published studies[5,13], the 952 cm^{-1} peak was chosen as reference. However, it is worth noting that the same kind of graphs are obtained and the same conclusions can be drawn if the 1011 cm^{-1} absorbance peak is used instead of the 952 cm^{-1} peak as reference in the ratioing process. From a comparison with the normal mode frequencies of various *p*-di-'light'-substituted aromatic rings[16], it

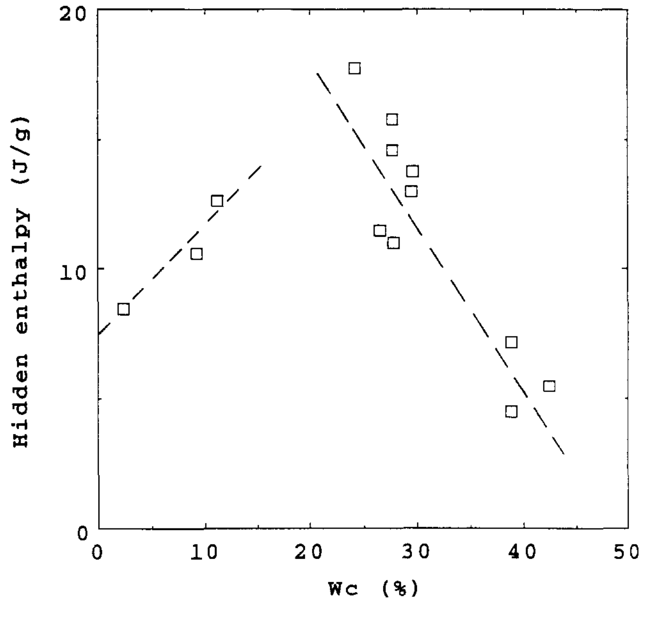

Figure 3 Variation of ΔH_{hidden} with the initial sample crystallinity; ΔH_{hidden} (□) is the difference between ΔH_T and ΔH_{cryst}. It is proportional to the amount of material having recrystallized during the d.s.c. scan, and which was not detected through any endotherm or exotherm

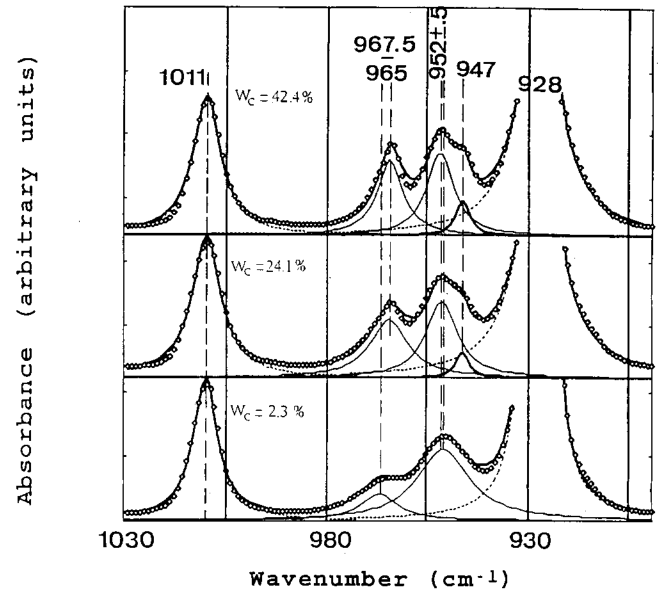

Figure 4 Measured i.r. absorbance (open symbols), deconvoluted absorbance peaks and recalculated absorbance (continuous lines) for three typical PEEK samples. Lower curve: $X_c = 2.1\%$; middle curve: $X_c = 22.3\%$; upper curve; $X_c = 39.9\%$. The 947 cm^{-1} deconvoluted absorbance peak has been drawn as a thicker line for the sake of clarity

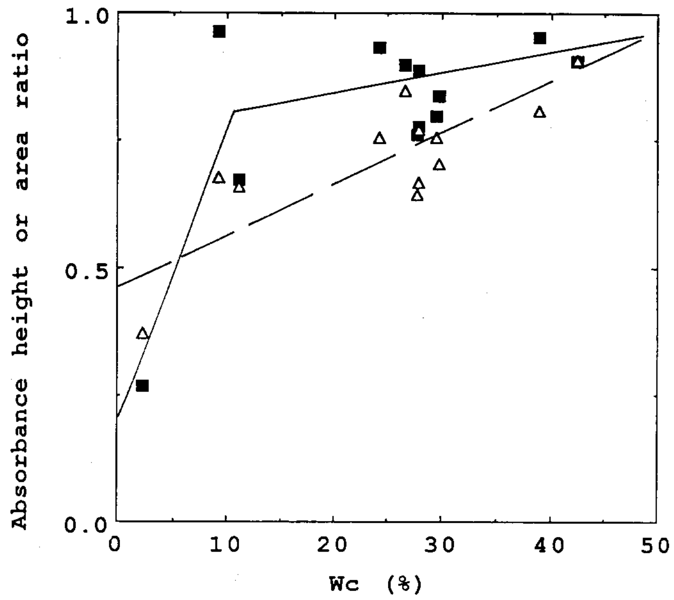

Figure 5 Area ratio between the 965 and 952 cm^{-1} absorbance peaks (—●—), and height ratio of the same peaks (—△—), as a function of the PEEK W_c

seems highly probable that the 1011 cm^{-1} band is one of the aromatic C–H in-plane bending normal vibrations. The situation is less clear for the 952 cm^{-1} band, which probably arises from one of the aromatic C–H out-of-plane vibrations. The equivalence of these two bands with regard to the choice of a reference band, would thus result from their common origin, i.e. aromatic C–H vibration.

In *Figure 5* we present the area ratio between the peaks located at 965 and 952 cm^{-1}. This ratio, according to Cebe *et al.*[5], should be a linear function of the crystallinity. As can be seen from *Figure 5*, a rapid increase in this ratio indeed occurs at the lowest crystallinities. However, the dependence of this ratio on the crystallinity is dramatically reduced above ~15% crystallinity. The 965 cm^{-1} absorbance peak is thus not strictly proportional to the amount of crystalline material. The height ratios of the same peaks are also presented in *Figure 5*. A roughly linear correlation could indeed be drawn between this ratio and the crystallinity, as suggested previously by Chalmers *et al.*[13], but the scatter in the data is very important.

The half-widths of these two lorentzian peaks have been plotted in *Figure 6* as a function of W_c. A strong crystallinity dependence is apparent for these half-widths, the peaks becoming broader for the less crystalline samples. In *Figure 7* the exact 965 cm^{-1} peak position is plotted against W_c. Crystallinity has clearly a strong influence on this peak location, especially at low levels of crystallinity. Finally, it can be seen from *Figure 4* that for a nearly fully amorphous sample, the 965 cm^{-1} peak

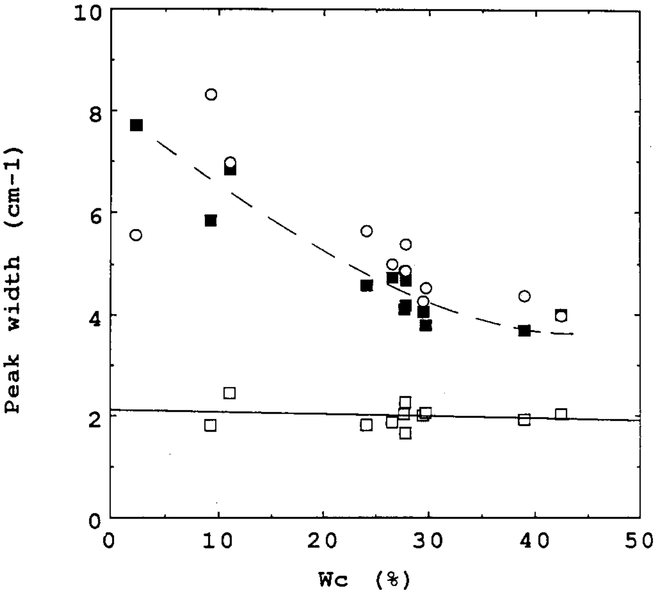

Figure 6 Variation of the half-widths of the 947 (□), 952 (■) and 965 (○) cm^{-1} absorbance peaks, with W_c

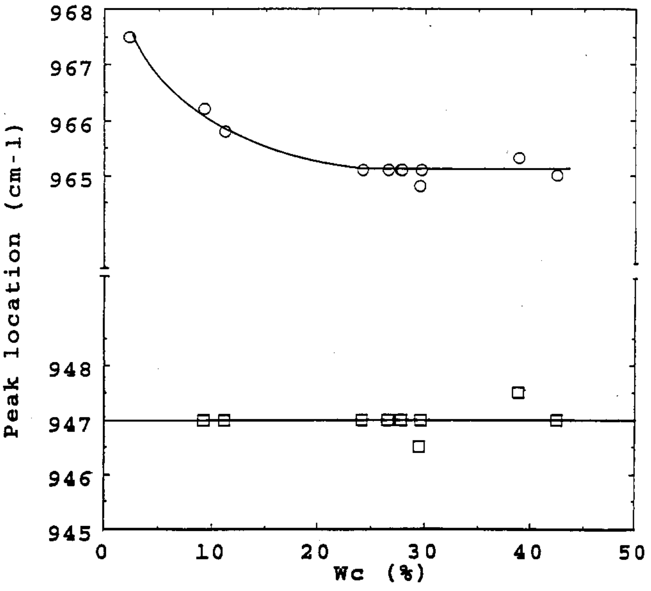

Figure 7 Exact wavenumber peak location of the 965 (○) and 947 (□) cm^{-1} i.r. band, as a function of W_c

is far from being negligible; actually, it does not vanish for amorphous samples.

The direct conclusion of the previous observations is that the 965 cm^{-1} peak is not a crystalline lattice normal mode. Its intensity and location are however strongly influenced by crystallinity (for degrees of crystallinity $< \sim 15\%$). It could therefore be related to a vibration normal mode associated with a given segmental conformation which would be enhanced by the presence of crystallites.

By contrast, *Figure 6* shows that the half-width of the 947 cm^{-1} band is constant whatever the polymer crystallinity. Next, the exact position of this peak (947 ± 0.5 cm^{-1}) is also independent of crystallinity. Moreover, as can be seen from *Figure 8*, the area ratios of this band to the 952 or 1011 cm^{-1} bands are linear functions of the W_c fraction, and a zero absorbance corresponds to a fully amorphous sample. Finally, when extrapolating linearly through zero these absorbance ratios, as a function of the density, a density value of 1.261–1.263 g cm^{-3} is obtained. This compares quite well with the amorphous PEEK density value of 1.263 g cm^{-3}.

These observations suggest that the 947 cm^{-1} i.r. band is a true crystalline band lattice mode which can be used to evaluate the PEEK crystallinity. The observed dispersion of experimental points could be quite certainly reduced by using Fourier transform infra-red spectroscopy instead of the grating spectrophotometer used in this study. However, the need for a deconvolution procedure to calculate the 947 cm^{-1} peak area is an unavoidable source of scatter in the data. Better precision could perhaps be gained through the use of a deconvolution procedure taking into account instrumental broadening.

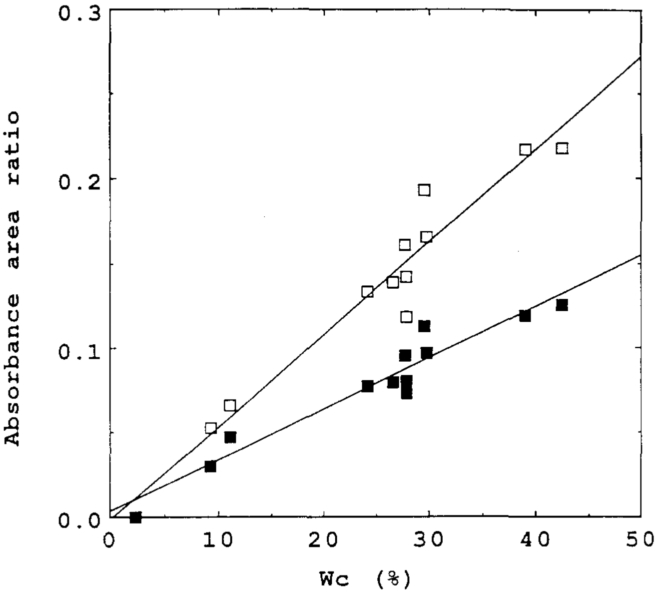

Figure 8 Area ratio between the 947 and 952 cm^{-1} peaks (□), and area ratio between the 947 and 1011 cm^{-1}, peaks (■), as a function of W_c

To confirm the above interpretation of the nature of the 965 and 947 cm^{-1} PEEK i.r. bands, the i.r. spectra of some highly crystalline model compounds (i.e. similar to some PEEK repeating unit fragments) and PEEK oligomers were recorded in KBr pellets. A full description of the synthesis and thermal properties of these oligomers will be published elsewhere[17]. Because the i.r. spectra were recorded in KBr, no attempt was made to quantify the absorbance values. *Table 3* gives the frequency positions of the i.r. peaks found between 1020 cm^{-1} and 900 cm^{-1} together with their intensities. The 965 cm^{-1} absorbance band is observed even for the short PEEK repeating unit fragments; in contrast, the 947 cm^{-1} absorbance band is observed only for molecules containing at least one complete PEEK repeating unit, which crystallizes in a crystallographic lattice very similar to the PEEK polymer[17]. The 947 cm^{-1} band is therefore related to the existence of the PEEK lattice; this is another argument in favour of the previous assignment of this band to a lattice normal mode.

However, the 965 cm^{-1} band could be associated with the vibration of a short length segmental conformation, since it can already be observed in quite short aromatic molecules. This conformation is obviously present in the PEEK crystalline phase, since the 965 cm^{-1} band is also observed for the nearly fully crystalline PEEK oligomers. However, it has been pointed out above that this peak is observable even in the fully amorphous PEEK. This seems logical, since the probability of finding any given short length segmental conformation in the amorphous phase is not expected to be zero.

With such an interpretation, one would expect the 965 cm^{-1} band to increase proportionally with crystallinity, because the given segmental conformation would be favoured by the increase of crystalline zones. To justify the initial abrupt increase of the 965 cm^{-1} band with crystallinity, followed by a quite weaker dependence (*Figure 5*), one has to postulate that the presence of crystallites enhances also the probability of finding the given segmental conformation in the amorphous phase. Such an increase in this probability could result from the constraints that the amorphous phase experiences due

Table 3 I.r. absorption bands of some highly crystalline ($\sim 100\%$) model compounds or PEEK oligomers

Compound	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	ν_4 (cm^{-1})	ν_6 (cm^{-1})
ΦOΦOΦ	1010.5 (m)	976.5 (w)	964 (w)	954 (vw)	–	930 (vw)
FΦ(CO)ΦF	1011 (w)	–	968 (w)	950 (w)	–	930 (s)
$F\Phi CO(\Phi O\Phi O\Phi CO)_1\Phi F$	1011 (w)	–	965 (w)	952 (w)	948 (vw)	928 (s)
$F\Phi CO(\Phi O\Phi O\Phi CO)_2\Phi F$	1011 (w)	–	964 (w)	951 (w)	946 (sh)	928 (s)

Intensities: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. In the chemical formulae, Φ represents a *p*-disubstituted phenyl to the presence of crystallites; it could be thought to be related to the presence of folds, tie molecules, loose loops, etc.

The increase of the 965 cm^{-1} band with crystallinity is then the result of the decrease of amorphous zones unaffected by the crystallites, of the increase of the crystalline regions, and also of the evolution of the total surface between crystalline regions and amorphous zones. This last parameter is itself a function of the lamellar thickness, which is dependent on both crystallization temperature and time. Because the highest crystallinities are obtained through high temperature crystallization, they are related to more important lamellar thicknesses, that is to a less important total surface between crystalline zones and amorphous zones. This could explain the lower dependence of the 965 cm^{-1} band on the degree of crystallinity, when this degree is increased above a given value.

CONCLUSIONS

From the above analysis, it is demonstrated that PEEK undergoes an important recrystallization during 10°C min^{-1} d.s.c. heating scans. This recrystallization, which can reach more than 10%, is strongly dependent on the initial crystallinity, and cannot be detected in the d.s.c. thermograph. This questions the use of d.s.c. to assess PEEK crystallinity.

On the other hand, the above result leads to the conclusion that the PEEK i.r. band located at 947 cm^{-1} is a true crystalline i.r. band, i.e. which corresponds to a lattice normal mode. This band can therefore be used to calibrate the crystallinity of PEEK, and perhaps even of its composites, after deconvolution of the i.r. spectrum in the range from 1030 to 900 cm^{-1}. By contrast, it has been shown that the 965 cm^{-1} band, previously claimed as indicative of crystallinity, is only very weakly sensitive to the degree of crystallinity above 15%, and is by no means a true crystalline band. We suggest that its presence is possibly due to the normal mode vibration of a short length segmental conformation. The probability of the presence of this conformation would be higher in crystalline regions, and in the amorphous regions near the crystallite surface, than in the unconstrained pure amorphous polymer.

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