The effect of molecular weight and crystallinity on the mechanical properties of injection moulded poly(aryl-ether-ether-ketone) resin

R. A. Chivers and D. R. Moore*

ICI Wilton Materials Research Centre, PO Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, UK

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Samples of injection moulded poly(aryl-ether-ether-ketone) (PEEK) resin with molecular weights covering the range, $M_w = 15\,000$–$50\,000$, have been subjected to a variety of thermal treatments, and the resulting material properties measured. It was found that crystallinity could be increased by annealing the mouldings, but also that an effective ceiling value depended on the molecular weight, i.e. the higher the M_w, the lower the maximum crystallinity. Tensile modulus and yield strength of the moulded polymer increased with increasing crystallinity, but the molecular weight had no detectable effect in these cases. In contrast, both crystallinity and molecular weight independently influenced the toughness. Toughness was found to increase with increasing molecular weight, and to decrease with increasing crystallinity. Implications of these effects on the injection moulding of components of PEEK are discussed.

(Keywords: PEEK; crystallinity; modulus)

INTRODUCTION

Poly(aryl-ether-ether-ketone) (PEEK) is a high-performance aromatic thermoplastic. Its molecular structure, in which benzene rings are joined by ether and ketone linkages, confers on it excellent thermal and solvent resistant properties and also a considerable toughness[1]. These properties have led to the successful use of PEEK in a variety of engineering applications in the aerospace industry, as well as in electrical components and as a high temperature bearing material.

The crystallization kinetics of PEEK are such that it is possible to obtain a very wide range of crystallinities in samples of the material simply by adjusting the thermal processing conditions[2–4]. In particular, it is possible to quench PEEK sufficiently fast from the melt so that crystallization is suppressed and an amorphous product is obtained. At the other extreme, a slow cooling cycle from the melt can give rise to uniformly crystalline material with a crystallinity approaching 50%.

Typical injection moulding conditions will lead to crystallinities of 20–30%, depending on the mould temperature and the thickness of the section. Raising the temperature of solid PEEK, whether amorphous or of low crystallinity, above $\approx 200°C$ will give rise to an increase in the crystallinity up to an apparently limiting value[5]. In this respect, PEEK shows similarity with, for example, the behaviour of poly(ethylene terephthalate) (PET), only at somewhat higher temperatures: the melting point of PEEK is $\approx 335°C$[2].

Most of the previous work on the mechanical properties of PEEK has concentrated on material with a single molecular-weight distribution[6–8], and one of these studies[8] has also considered the effect of a change in crystallinity in the polymer. In this present work we have taken samples of PEEK over a wide range of molecular weights, and have also attempted to control the crystallinity of some of them, in an attempt to investigate the dependence of the polymer properties on both these parameters, and also examine the inter-relationship between them.

This work has concentrated on three fundamental mechanical properties relating to stiffness, strength and toughness. For stiffness, the tensile modulus has been determined at very low strain, and after a loading time, in flexure, of 100 s. Strength has been measured by the yield stress under low-speed ramp conditions. For many of the samples, the yield strength had to be determined under plane strain compression conditions, although a few measurements were taken in tension, and therefore it was possible to relate compressive and tensile yield strength. Toughness has been determined by using the methods of linear elastic fracture mechanics on notched specimens in three-point bending, by the use of an instrumented falling-weight impact apparatus.

We believe that it is important to measure intrinsic material properties in this type of study. Such properties are uninfluenced by factors such as inhomogeneity and specimen geometry. Inhomogeneity may take a variety of forms, such as voiding or surface imperfections, which can easily arise after thermal treatments. Anisotropy in the plane of the sample is highly significant in fibre-reinforced systems, but in carefully injection moulded flat plaques of resin its effect can be insignificant. The injection

* To whom correspondence should be addressed

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moulded plaques of PEEK that were used in our study showed a modulus difference in the perpendicular directions of less than 5%[6,9], which we concluded as being indicative of in-plane isotropy. The most significant inhomogeneity in injection moulded polymer is likely to be through the thickness, caused by the different cooling rates between the material in contact with the mould tool, i.e. the skin, and that deep in the core of the moulding. In a material such as PEEK, with a relatively slow crystallization rate under fast cooling conditions, it is quite possible to obtain a sample which contains an amorphous skin around a crystalline core. In this case the skin is extremely thin and hence of little importance, and any effects it may have can be minimized by conducting the testing so as to include the entire cross-section of the plaque, for example, by running cracks across the plaque and not through the thickness from one skin to the other.

Specimen geometry is especially significant if one is to achieve an objective determination of the intrinsic toughness. Linear elastic fracture mechanics is used for this, but care must be taken to see that the specimen is sufficiently large so that true plane strain conditions occur at the crack tip, and that any ductility ahead of the crack is minimized. For tough materials, it is often necessary not only to use large specimens, but also to suppress the ductility (increase the yield strength) by testing at low temperatures and high speeds. Expressions and protocols exist to enable the validity of these to be ascertained[6,10].

EXPERIMENTAL

Materials

Molecular weight characterization. A number of experimental grades of PEEK were produced by standard techniques with varying molecular weights, and where each sample had a particular molecular-weight distribution. Gel permeation chromatography (g.p.c.) was used to characterize these molecular weights and their distributions by comparison with results previously obtained on samples of known molecular weight (as determined by solution light scattering). Samples for g.p.c. were prepared as amorphous films and were dissolved in a mixture of phenol and trichlorobenzene (50:50 wt/vol) with 0.1 wt/vol% topanol OC at 183°C. A Knauer high temperature g.p.c. apparatus was used with PL mixed gel (5 μm) columns at 120°C. A detailed account of the molecular weight characterization and distributions in PEEK is given by Devaux *et al.*[11].

Throughout this paper, the weight-average molecular weight, M_w, is used to characterize the materials and is referred to as, for example, 28k for a molecular weight of 28 000. Materials studied in this work were within the range $M_w = 15k–50k$, with a typical polydispersity, M_w/M_n, of between 2 and 3.

Sample form. Most of the materials were injection moulded under standard conditions into a 150 × 150 × 3 mm 'coat-hanger' gated cavity. The material with $M_w = 28k$ was injection moulded into a tool which was held at one of two temperatures, i.e. 90 and 170°C. All of the others were moulded into a mould tool held at a temperature of approximately 170°C. Some materials were moulded in the form of discs ($d = 115$ mm), or ASTM tensile bars, all with a thickness of 3 mm. The low-molecular-weight plaques received some annealing (1 h in an oven at 200°C after moulding). Some of the other mouldings (e.g. $M_w = 28k$, 31k, and 40k) received carefully controlled annealing treatments and these will be discussed in detail below.

A few samples of PEEK film, produced either by extrusion or pressing, and with a nominal thickness of 0.25 mm, were also used in this study.

Post-moulding treatment. Some of the plaques of certain materials, i.e. those with $M_w = 28k$, 31k or 40k, were subjected to further thermal treatment in order to vary the crystallinity. For this purpose, a matched metal tool was used, with a rectangular cavity that would take approximately one third of the moulded plaque. This tool fitted between the plates of a hot press which was equipped with a programmable heater. Two distinct types of thermal treatment were carried out, namely annealing (i.e. heating below the melting point) and remelting (with subsequent cooling and recrystallization).

In the annealing treatment, the plaque was held at a given temperature for a set time under low pressure; it was then air cooled for 6 min, followed by rapid water cooling. Melting of the plaque was carried out at 350°C for 7 min under low pressure (so as to maintain the approximate plaque thickness). The programmable cooling controls on the press were then used to cool the assembly at a given rate (0.33, 1, or 3°C min^{-1}).

Characterization

Crystallinity determination. A density gradient column was used for determination of the densities of the mouldings and films, both before and after annealing and recrystallization. Calcium nitrate solution was used as it is known to give a stable column over the required range of densities ($> 1300\ kg\ m^{-3}$). Each density value was taken as the mean of those obtained from several small pellets, cut through the mouldings so as to incorporate both skin and core regions, and hence give an average density for the sample. In addition, specimens were cut from different regions of an annealed plaque in order to check on the uniformity of the heat treatment. These measured densities were found to be essentially identical, thus confirming a uniform heat treatment for the annealed samples.

Density was converted to crystallinity by assuming a linear relationship between the densities quoted by Blundell and Osborn[2] for amorphous and 100% crystalline PEEK, namely 1263 and 1401 $kg\ m^{-3}$, respectively.

Modulus. Measurements of the modulus were made on strips (width = 5 mm) cut from the plaques. These were tested in a 3-point bending mode through the thickness, over a range of 60 mm. An isochronous technique was used and the deflection for a given applied load was measured after a period of 100 s[12]. Each specimen was tested several times, and each time the load was increased, so as to improve the accuracy of the method. The maximum strain of the skin did not exceed 0.25%, thus ensuring that the specimens could recover from any previous loading history before retesting was carried out.

Yield strength. This is conventionally measured in tension by using specimens with a 'gentle' waist such that the stress concentration factor is only fractionally greater

than unity. Unfortunately, it was found that specimens cut from some of the moulded plaques broke prior to any yielding and hence this method was unreliable. A few specimens of film (thickness $\approx 250\,\mu m$) were tested using this tensile method and gave satisfactory yielding when using a test speed of $5\,mm\,min^{-1}$.

Therefore, for the other samples plane strain compression[13] was used to determine yield strength by employing a cross-head speed of $0.5\,mm\,min^{-1}$. Several widths of compression die (3–10 mm) were used and the results were extrapolated to an infinite die width. The variation in the measured yield stress as a function of the die width was small. It is recognized that the yield stress as measured in plane strain compression is greater than that which would be measured in tension, and therefore the limited results that were available on film samples were used to provide an approximate conversion factor. Plasticity theory suggests a ratio of 1.3 between compressive yield strength and tensile yield strength, but as will be discussed later, we observed a value of 1.4.

Fracture toughness. The concepts of the European Structural Integrity Society (ESIS) protocol for linear elastic fracture mechanics (LEFM) applied to plastics[10] were used to determine the fracture toughness. Testing was performed in a 3-point bending configuration on an instrumented falling-weight impact apparatus at a rate of $1\,m\,s^{-1}$. Unless otherwise stated, the temperature of testing was −40°C. Low temperatures were achieved by immersing the specimens in a mixture of dry ice and methanol and only removing them immediately prior to testing, thereby allowing minimal time for warming-up. Where quantity of material permitted, a variety of notch depths between 0.2 and 0.6 of the depth dimension were chosen and the results were averaged. Where samples were more restricted in quantity a smaller range of depths was used.

Testing was carried out so as to grow the crack either through the plaque thickness, or across the plaque. Conventionally, the depth in the direction of crack growth is known as W and the thickness as B. In the first case, therefore, $W<B$ and in the second, $W>B$. The criteria for a valid LEFM analysis state that both of the following should apply:

$$\frac{W}{W_{min}} > 1 \tag{1}$$

and

$$\frac{B}{B_{min}} > 1 \tag{2}$$

where

$$W_{min} = 5\left(\frac{K_c}{\sigma_y}\right)^2$$

and

$$B_{min} = 2.5\left(\frac{K_c}{\sigma_y}\right)^2$$

K_c is the critical stress intensity factor and σ_y is the yield stress under the same test conditions[6,10]. It can therefore be seen that it is advantageous to test specimens in which $W>B$. The validity criteria were calculated for all of the fracture tests by using values of σ_y that had been corrected from those measured in plane strain compression, with the conversion to tension applied from the factor calculated above. The effects of temperature and test rate were determined by using the curves obtained by Jones *et al.*[6]. The fracture mechanics data almost always satisfied these size criteria, with the only exceptions to this relating to the two highest-molecular-weight samples with plaque thicknesses of 3 mm. The vast majority of data correspond to valid plane strain geometry independent properties.

RESULTS AND DISCUSSION

Crystallinity

The measured crystallinities for all of the samples are shown in *Figure 1* as a plot of the percentage crystallinity *versus* M_w. Four distinct sets of samples are shown on the figure. Generally, the lowest crystallinities are observed in those materials which were injection moulded with no further heat treatment. Higher crystallinities can be seen in the set of mouldings which had received a 'gentle' post-moulding annealing treatment. An upper limit to the crystallinity that is achievable by annealing mouldings of several different molecular weights is given by the specimens annealed for 1 h at 330°C, labelled as 'maximum annealing' in *Figure 1*. A still higher crystallinity was attained by a very slow cooling from the melt. All four sets of data show a decrease in crystallinity with an increasing M_w. It would therefore appear that the nature of the crystallization process influences the general level of crystallinity, with slow cooling capable of giving the highest levels, but that for any given treatment the crystallinity achieved will be influenced by the length of the polymer chain, as identified by its molecular weight (M_w).

Three of the materials (i.e. those with $M_w = 28k$, 31k, and 40k) were subjected to a comprehensive study of the effects of annealing on crystallinity. One sample of polymer, namely that with $M_w = 28k$, was moulded at different mould tool temperatures (90 and 170°C), after which the resulting crystallinities were found to be 23.5 and 28.8%, respectively. Plaques moulded at 90°C had a clear brown glassy surface, whereas those moulded at 170°C were a pale grey in colour. The brown layer was clearly amorphous PEEK which had been quenched by the relatively cold metal surface of the tool, but it proved

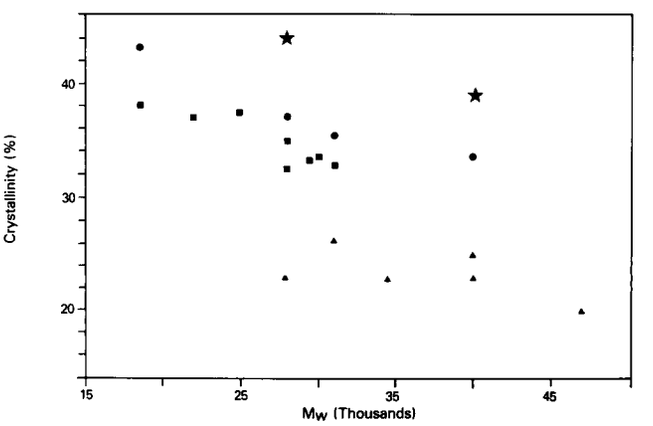

Figure 1 The crystallinity of samples of PEEK after different moulding treatments, as a function of the weight-average molecular weight: (▲) 'as-moulded'; (■) 'gentle' annealing; (●) maximum annealing and; (★) remelted and slow cooled

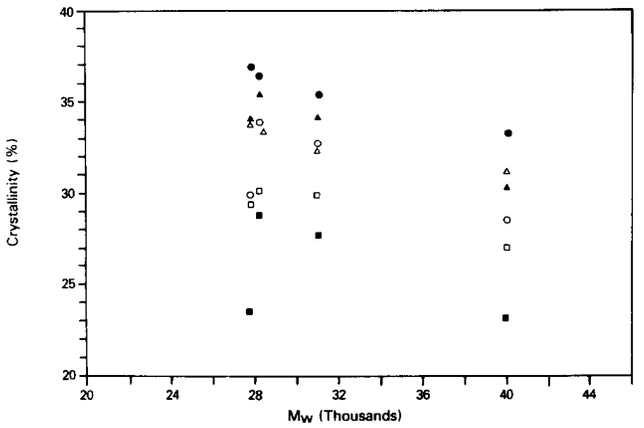

Figure 2 The crystallinity of samples of PEEK with different weight-average molecular weights after annealing at different temperatures for more than 60 min: (■) no annealing; (□) 250; (○) 300; (△) 310; (▲) 325 and; (●) 330°C

impossible to remove this layer for specific analysis. The two other materials (M_w=31k and 40k) were injected into the mould tool at 170°C, and exhibited lower crystallinities, with values of 27.7 and 23.2% for the 31k and 40k polymer, respectively. Neither showed any sign of a quenched skin layer.

Annealing was carried out on all four sets of mouldings, at different temperatures (up to 330°C) and for different times. Short times at a given temperature led to small increases in crystallinity, but for annealing times longer than approximately 50 min the resulting crystallinities were independent of time. These latter values therefore appeared to be the maximum achievable for that particular material at a given temperature. It should be noted that the resulting crystallinities achieved by annealing two plaques of different initial crystallinities (but having the same M_w) were effectively the same, giving increased weight to this argument. *Figure 2* shows the crystallinities achieved after annealing each material for more than 60 min over a range of temperatures. Even at a temperature of 250°C, which is 85°C below the melting temperature, it is possible to observe substantial increases in crystallinity. As already discussed, there is a trend which achieves a lower crystallinity with increasing molecular weight of the material, for similar heat treatments. However, it is possible to select the annealing temperatures of materials with different molecular weights in order to achieve a common crystallinity. Therefore it should be possible to investigate the separate influences of crystallinity and molecular weight on the material properties.

Remelting of polymer with subsequent cooling from the melt shows again that the achievable crystallinities are molecular-weight dependent (as shown in *Figure 1*). The lowest cooling rate (0.33°C min^{-1}), when applied to the polymer with M_w=40k, produced a higher crystallinity than those achieved when using the higher rates (1 and 3°C min^{-1}). In the case of the 28k material, the effect of rate seemed less marked, with a 42% crystallinity being achieved. Despite the careful application of pressure in the hot press, these materials were still found to contain some bubbles. An X-ray shadowing technique permitted the bubble-free regions to be identified, in order to ensure freedom from such defects in any crucial part of a test specimen.

Stiffness

Variation in the tensile modulus (determined from 3-point flexure at 100 s) with crystallinity for PEEK materials with different M_ws is shown in *Figure 3*. This includes data for polymers of all three molecular weights (28k, 31k and 40k) and all three heat treatments (i.e. as moulded, annealed, and after cooling slowly from the melt). Although the technique used is inherently very accurate[12], there is considerable scatter in the results, but a general trend towards an increase in modulus with increasing crystallinity can be observed. It is rather more difficult to distinguish if there is any effect of the molecular weight.

There are several reasons why the scatter in the results is so great. Specimens were in the form of strips cut from the plaques and were tested in flexure through the thickness of the plaque. This method weights the effect of each layer of material by the cube of its distance from the mid-plane, and hence any surface inhomogeneities, such as poorly crystallized skin layers, will considerably influence the results. In addition, the voiding in slow cooled samples may also give rise to some scatter in the modulus measurement.

Yield strength

Plots of the yield strength of various PEEK samples (measured in plane strain compression) *versus* the crystallinity are given in *Figure 4*, which shows data obtained from materials with three different molecular weights, i.e. 28k, 31k and 40k. A very clear pattern of the yield strength increasing linearly with crystallinity can be seen, and there is no sign of any effect of the molecular weight. In contrast to the modulus measurements, the scatter is small, which is probably the result of compressing the entire thickness of the plaque and also the necessity of averaging the results by testing several pieces of material with different die widths.

Some film samples were also tested, but in tension in this case, and these showed good yielding behaviour. It was observed that the results measured in plane stain compression were approximately 40% above those measured in tension and therefore the compressive yield strength data of *Figure 4* can be divided by 1.4 in order to present them as tensile yield strength data. *Figure 5* shows the tensile yield strength of PEEK as a function

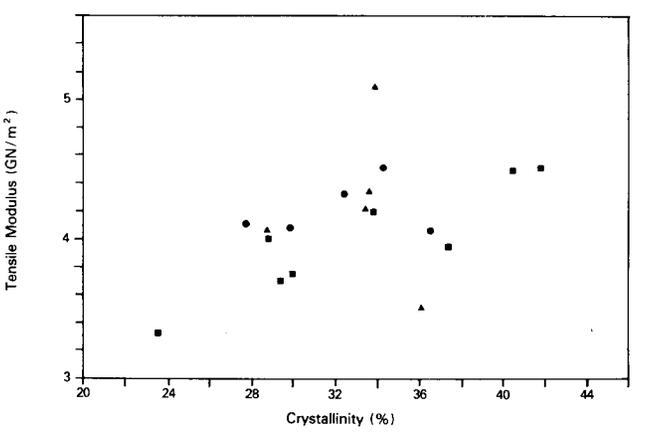

Figure 3 The tensile modulus as a function of the crystallinity, shown for PEEK samples of various molecular weights: (■) 28k; (●) 31k and; (▲) 40k: modulus was determined from 3-point flexure after 100 s at 23°C

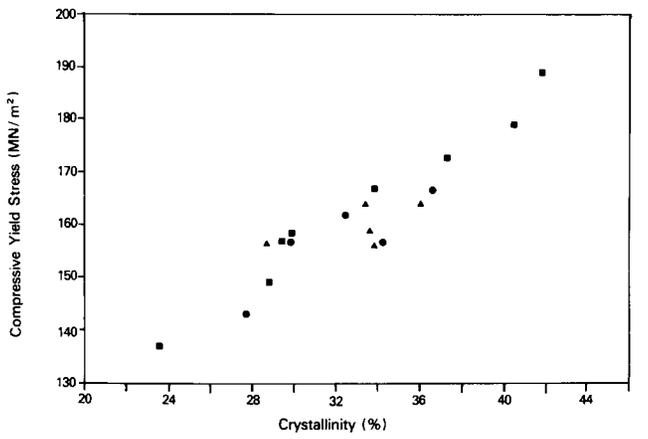

Figure 4 The compressive yield stress as a function of the crystallinity, shown for PEEK samples of various molecular weights: (■) 28k; (●) 31k and; (▲) 40k: compression measured under plane strain conditions at 23°C

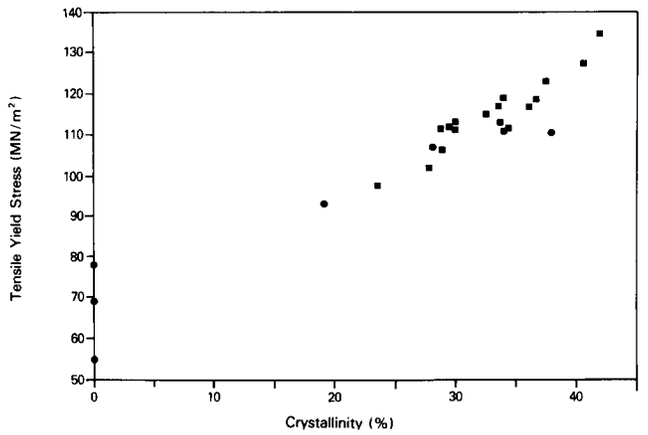

Figure 5 The tensile yield stress of PEEK as a function of the crystallinity: (●) data obtained for film samples in tension and; (■) data derived from the compressive yield strength results shown in *Figure 4*

of the crystallinity with results obtained by using the tensile data measured for film specimens and also for the derived data on the moulded samples. The assignment of 'zero', i.e. 0% crystallinity, to a film specimen was done on the basis of its optical clarity. As this is clearly not a measure of crystallinity it might account for the scatter in the data at '0%' crystallinity.

This 'master curve' of the tensile yield strength of PEEK, i.e. *Figure 5*, was used to ascribe values for the determination of the validity of the fracture mechanics results (see below).

Toughness

Three distinct, but inter-related, experiments have been carried out in order to elucidate the effects of molecular weight and crystallinity on the toughness of PEEK. The methods of linear elastic fracture mechanics (LEFM) were used throughout, with toughness being characterized by the K_c and G_c values[10]. In this analysis K_c is the critical value of the stress field intensity factor, while G_c is the critical value of the strain energy release rate, where both of these are determined in a crack-opening mode (i.e. mode I). (For simplicity, these terms are referred to as the fracture mechanics strength, K_c, and the fracture toughness, G_c, but such terminology is not rigorous.)

The effect of the test temperature on the toughness of 'as-received' moulded samples of PEEK with different molecular weights (M_w = 28k, 31k, and 40k) is shown in *Figure 6*. (All testing was performed at a speed of 1 m s^{-1}.) It is concluded that there is only a minimal effect of the test temperature on the values of K_c. All tests were valid when considering the geometry criteria for W and B, as discussed above. However, the close similarity of the crystallinity of one of the 28k samples and the 40k samples at a level of 23% crystallinity, plus the clear separation of their toughness values suggests that there is an effect of molecular weight on the toughness. Higher molecular weights give increased values of K_c. The scatter in the values for the 28k material with two different crystallinities suggests that at best any effect of crystallinity is small.

The effect of crystallinity can be seen more clearly in the results obtained for the 28k and 40k PEEK samples at the extremes of their available crystallinity ranges, as shown in *Table 1*. There is a highly significant statistical difference between the values of K_c and G_c at levels of 23 and ≈40% crystallinity in both of these systems; the more highly crystalline samples have lower toughness values. As before, the effect of molecular weight can be seen for samples that have approximately the same crystallinity.

Therefore, there are two reinforcing effects determining the toughness of semicrystalline PEEK. An increase in molecular weight gives rise to an intrinsic increase in the toughness. In addition, material of higher molecular weight is likely to be of lower crystallinity (unless processed under exceptional conditions), and lower crystallinity also results in increased toughness, since cracks can propagate more readily in the crystallites.

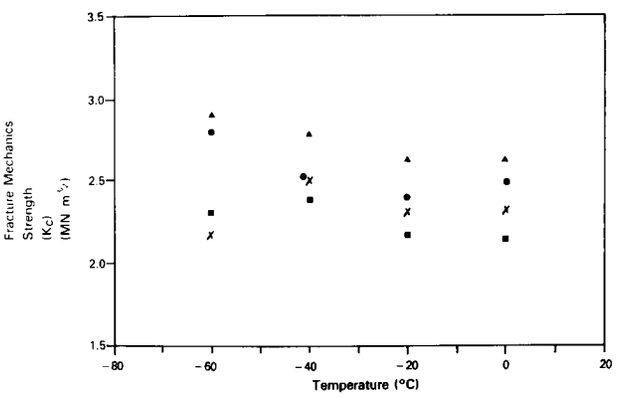

Figure 6 The fracture mechanics strength (K_c) of PEEK samples of different molecular weights as a function of the test temperature: (■) 28k, mould at 90°C; (×) 28k, mould at 170°C; (●) 31k and; (▲) 40k

Table 1 Fracture mechanics data obtained for PEEK samples with different molecular weights and crystallinities

M_w	Crystallinity (%)	K_c ($MNm^{-3/2}$)[a]	G_c (kJm^{-2})[a]	W/W_{min}	B/B_{min}
28k	23	2.30 (0.03)	2.78 (0.10)	8	6
	44	1.82 (0.12)	1.36 (0.12)	21	14
40k	23	2.65 (0.06)	3.60 (0.16)	6	4
	39	2.29 (0.14)	2.76 (0.24)	12	8

[a] Fracture data obtained at 23°C using a test speed of 1 m s^{-1}, with standard deviations shown in parenthesis

These effects can be seen in the data which have been obtained at $-40°C$ (at a test speed of $1\ m\ s^{-1}$) and which are presented in *Figures 7* and *8*. When K_c is plotted as a function of M_w (see *Figure 7*), there is a clear increase in the toughness with increasing molecular weight, and a similar, but greater, effect is also observed for G_c (see *Figure 8*). The specimens used in these cases were prepared so that the cracks propagated through the moulding thickness (which is quite small), and consequently the validity condition on W is violated at the highest toughness values (which coincides with low crystallinity and hence a low yield stress). The effect of this is to depress the measured value of K_c by a small amount. In these plots, the crystallinity of the specimens has been disregarded. This may help to explain the low values for the toughness which have been recorded in 'as-moulded' and slowly cooled samples. The K_c data have therefore been replotted as a function of the crystallinity (*Figure 9*), but now disregarding the molecular weight, and again a broad general trend can be seen, with, this time, the moulded and slow cooled samples following more closely this general trend. It should be noted that these latter samples were all tested such that the crack propagated across the plaque, which should be most representative of the entire material.

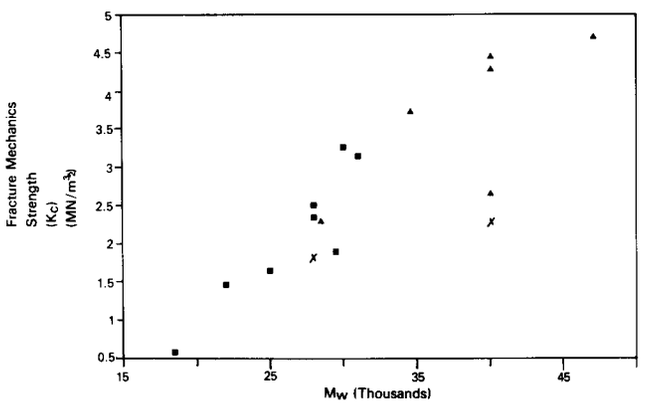

Figure 7 The fracture mechanics strength (K_c) as a function of molecular weight, shown for PEEK samples over a range of crystallinities: (▲) 'as-moulded'; (■) annealed at 200°C and; (×) remelted and slow cooled: measurements made at $-40°C$ at a rate of $1\ m\ s^{-1}$

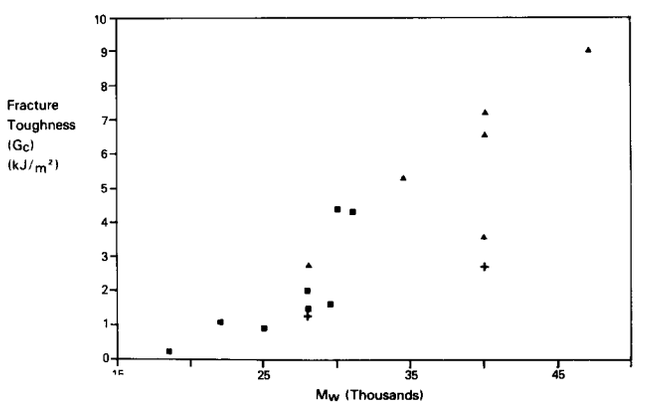

Figure 8 The fracture toughness (G_c) as a function of molecular weight, shown for PEEK samples over a range of crystallinities: (▲) 'as-moulded'; (■) annealed at 200°C and; (+) remelted and slow cooled: measurements made at $-40°C$ at a rate of $1\ m\ s^{-1}$

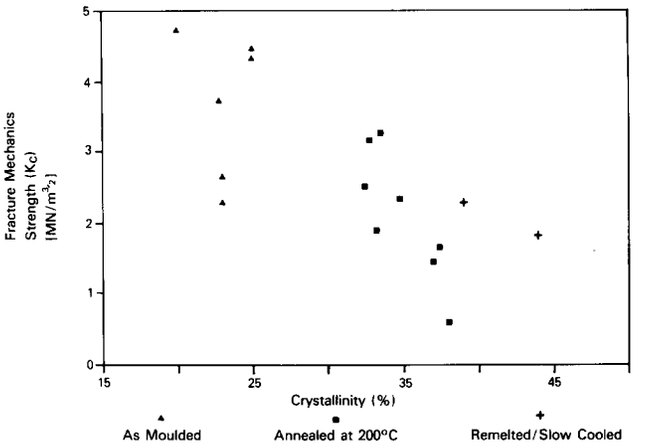

Figure 9 The fracture mechanics strength (K_c) of PEEK as a function of the crystallinity, over a range of molecular weights: (▲) 'as-moulded'; (■) annealed at 200°C and; (+) remelted and slow cooled: measurements made at $-40°C$ at a rate of $1\ m\ s^{-1}$

Implications for material toughness

The previous sections have articulated the influence that molecular weight and crystallinity have on the properties of the polymer, such as tensile modulus yield strength and fracture mechanics toughness. However, it would be useful to know what influences these parameters have on the overall behaviour of, for example, the toughness of a component fabricated from PEEK? How do the materials' properties combine in a practical sense? Although the general consequences of this are beyond the scope of this paper, there is one particular feature, however, that can be discussed here.

In general terms, a component will be ductile in service provided that its dimensions are comparable with a plastic zone size for the material being used. Although the determination of the plastic zone size can be approached by a number of routes, it has already been shown to be related to a specific function of the materials' properties, $(K_c/\sigma_y)^2$, which is sometimes known as the ductility factor[14]. The results shown in *Figure 5* for the yield strength in tension *versus* crystallinity, together with those given in *Figure 9*, namely K_c *versus* crystallinity, enable the influence of this ductility factor to be determined.

The effect is illustrated in *Figure 10*, where it can be seen that a change in the crystallinity from 20 to 40% can give rise to a decrease in the ductility factor by a factor of approximately fourteen. The combined effects of fracture strength and yield strength on the toughness can be seen to be considerable.

The continuous curve shown in *Figure 10* is based on the K_c data of *Figure 9*, so that a mixture of molecular weights for the samples has to be accommodated. In fact, the number of different samples that would have to be tested is far in excess of the number available, if proper separation of the influence of molecular weight and crystallinity on the ductility factor is to be comprehensively examined. Nevertheless, it should be recognized that in a given component a certain range of crystallinities is to be expected, which results from the crystallization capabilities of the particular molecular weight that is used (see *Figure 1*). We can, however, speculate over the separate effect of molecular weight on the ductility factor, and this is represented by the dashed curves in *Figure 10*.

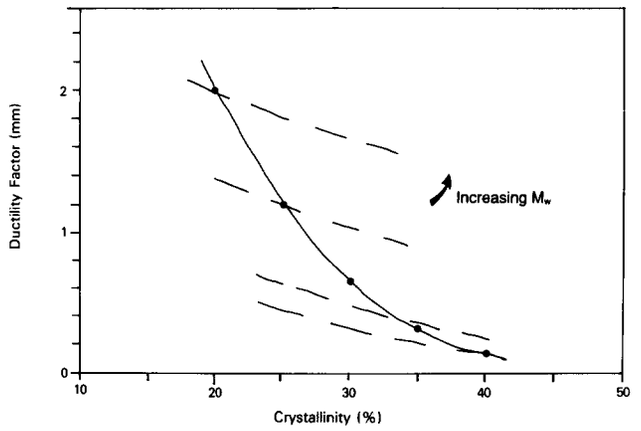

Figure 10 The ductility factor of PEEK as a function of crystallinity: the continuous curve represents the mean molecular weight data obtained from *Figure 9*, while the dashed curves postulate the separate effects of specific molecular weights

A practical demonstration of the effect of both molecular weight and crystallinity on toughness can be seen in a sample of PEEK with $M_w = 18$k, which was annealed to achieve 43% crystallinity. This sample was so brittle that preparation of carefully notched specimens was impossible, and hence measurements of K_c and G_c could not be attempted. In contrast, a sample of PEEK in which $M_w = 47$k, at 20% crystallinity, had a true K_c probably in excess of 5 MN m$^{-3/2}$.

CONCLUSIONS

The crystallinity of PEEK may be readily changed by using a variety of thermal treatments. Amorphous PEEK can only be produced in very thin sections by rapid cooling, and even apparently clear film may include a low level of crystallinity. The highest crystallinities may be obtained by very slow cooling from the melt. Intermediate crystallinities are achievable by moulding into cavities held at different temperatures and by annealing at different temperatures for times greater than 1 h. For any specific heat treatment the resultant crystallinity depends both on the molecular weight and the molecular weight distribution in the material.

The modulus and the yield strength of PEEK both increases with increasing crystallinity, as would be expected since the ordered crystallites confer stiffness on the material, as well as binding the molecules and hence making yielding more difficult. There would appear to be no effect of molecular weight on either of these properties.

The fracture toughness of PEEK, however, has been shown to depend both on the molecular weight and the crystallinity of the material. A high molecular weight confers a high toughness. Low crystallinity also confers high toughness on the material, with the crystallites proving to be the least fracture resistant elements in the system. Since high-molecular-weight PEEK is also likely to be of low crystallinity, the overall effect on the toughness is therefore augmented.

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