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The effect of annealing on the short and long term behavior of PEEK

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SUMMARY

Short and long-term tensile tests have been done on injection-moulded poly-ether-ether-ketone (PEEK) in order to assess the effect of annealing on its mechanical behavior. In addition to the behavior reported before, namely increases in yield and drawing stress, the annealed specimens exhibit a distinct work hardening behavior in the beginning of the drawing phase at temperatures between 80°C and 160°C. Subsequent creep tests show that the annealing treatment also influences greatly the long-term static properties of PEEK with creep rates after annealing being considerably below those recorded on the standard injection-

DSC thermograms of the samples annealed for more than 20 minutes exhibit similar curves as those reported before, two endothermic peaks: a major peak at 340°C and a minor one at 260°C which is10 K higher than the annealing temperature.

The experimental results support that a type of secondary crystallites grow in the material by the annealing treatment. The existance of those secondary crystallites enhances the mechanical properties of PEEK.

INTRODUCTION

As a result of their improved manufacturing efficiency for finished components, their recyclability and their superior physical properties (1), high performance thermoplastics are being considered as candidate materials for the replacement of more conventional engineering materials.One such thermoplastic, poly(ether-ether-ketone) (PEEK), is currently being used as the matrix system in carbon fiber composites for aerospace applications. Its outstanding properties (2), such as high chemical resistance, good high temperature mechanical properties (toughness and abrasion resistance),low flamability, and excellent resistance to nuclear radiation, offer great potential for widespread application. Composite components based on this polymer offer further advantages such as very high interlaminar fracture toughness (3) and good impact properties (4). A complete understanding of the behavior of these advanced composites can only be achieved through a thorough understanding of the thermoplastic matrix itself. Indeed, much work is currently being undertaken in this area (5-11). Since PEEK is a semi-crystalline material, it is possible to alter its morphology by annealing at temperatures below its melting point (12-16). Work by Lee *et al* (7) on a thin PEEK film has shown that annealing can greatly enhance the short-term mechanical properties.Very little work has, however, been undertaken in order to assess the creep properties of PEEK and the effect of annealing on its long-term properties. This is clearly an important consideration if this material is going to have widespread application in engineering components.

In this paper, the effect of annealing on both the short and long term tensile behavior of injection-moulded PEEK is studied.In order to span a large range of operational conditions, tests have been undertaken at four temperatures between 23 and 160°C.

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EXPERIMENTAL DETAILS

Materials and Samples

Type 450G pellet-form PEEK was injection-moulded at 400°C to form dog-bone specimens with gauge dimensions 3 x 6 x 40 mm^3. As a result of the limitations of the injection-moulding machine the mould was heated to only 120°C instead of the manufacturer's recommended value of 200°C.

After manufacture, many of the specimens were annealed in an air-circulating oven heated to 250°C. Four annealing times were examined, these being: 7, 20, 90 minutes and 26 hours. After the heat treatment, the specimens were removed from the oven and allowed to cool naturally to room temperature.

Experimental Procedure

The effect of annealing on the crystal structure of PEEK was examined using a differential scanning calorimeter(Perkin-Elmer DSC-4 System). Samples weighed approximately 5 mg with the size of half of the cross section in the gauge length and were analyzed at a scanning rate of 20 K per minute.

The short-term mechanical properties of the annealed and the un-annealed specimens were determined by undertaking tests on a Zwick 1484 universal testing machine at a cross-head speed of 5 mm/min. The tests were carried out at four temperatures, these being: 23, 80, 120, and 160°C. The variation of strain during each test was measured by a mechanical extensometer. At least 4 specimens were tested at each temperature.

For convenience, the creep programme was divided into two parts. Creep tests of short duration (less than two hours) were undertaken on the test machine outlined above. Here, again, the strain history was measured using the mechanical extensometer. The long-term creep tests were done in constant temperature creep ovens in which the load was applied via a system of levers and dead-weight loads. The variation of strain with time was measured using a travelling microscope with an accuracy of ± 0.07 mm. Five to six data points were taken during the first hour of testing and then one point every day. At least 2 specimens were tested in each condition.

RESULTS AND DISCUSSION

Morphology

An examination of the cross section of PEEK specimens immediately after injection moulding revealed a surface layer much darker in color than the core material, as shown in Fig. 1. Subsequent DSC scans of the surface layer and the core showed that the former exhibited a distinct exothermic peak at 170°C whereas the latter did not. It is believed that this thin surface layer represents a zone of amorphous PEEK. This was almost certainly formed in the rapid cooling of the molten PEEK occurring at the surface of the mould.

The DSC scans of the PEEK specimens annealed at 250°C for different periods of time shows that all specimens annealed longer than 20 minutes have a secondary peak at about 10 K higher than the annealing temperature. In the subsequent discussions this peak will be termed 'the low temperature peak'. The large endothermic peak at 340°C will be termed 'the high temperature peak'. This phenomenon has been reported by several groups before (5-8,11). The explanation for these two peaks has been contraversial in the past few years. Some suggested that the two peaks came from the same crystal structure which melt and recrystallized during the thermal scan (8). The other idea (5-6,11) suggested that the two endothermic peaks represented different components of the structural morphology. The high temperature peak is caused by the melting of the major lamellae formed during crystallization from the melt, Cebe (5) suggested that the high temperature peak could also include the crystals which had formed during the scan. The low temperature peak is caused by the disintegration of crystals assumed to be just stable at annealing temperature. As will be shown later, the results obtained here tend to support this idea.

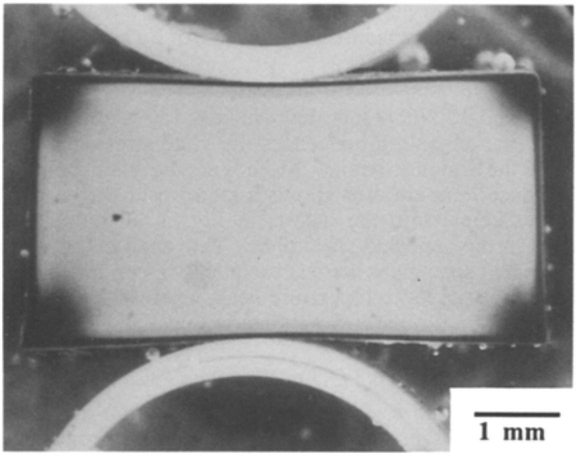

Fig. 1 Optical micrograph of the cross section of an injection-molded PEEK specimen.

Enthalpy of fusion

The enthalpy of fusion determined from the endothermic peaks in the DSC scan are plotted in Fig. 2. The information corresponding to the un-annealed samples was obtained from the core material with the amorphous layer being removed; this point is plotted at t = 0. The trends apparent in this figure show that while the enthalpy of fusion associated with the low temperature peak grows slightly with annealing time, the enthalpy of fusion related to the high temperature peak does not change significantly with the heat treatment.

Stress-strain behavior

The stress-strain curves of annealed and un-annealed PEEK at 23°C are characterized by a yield stress at approximately 100 MPa, a yield strain of about 2% and a drawing stress of 77 MPa. During the test, all of the bulk specimens necked in the gauge section. The draw ratio determined from the resulting cross section of the neck after testing was 2 for un-annealed specimens and 1.85 for 26-hour-annealed ones.

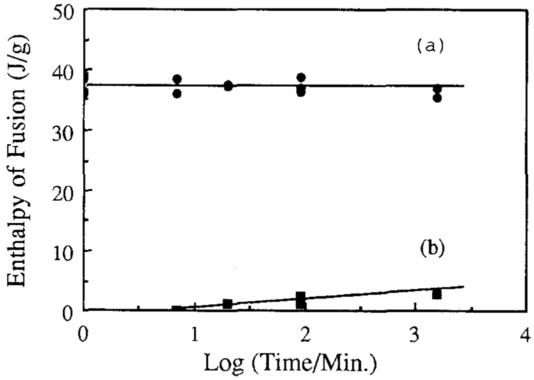

Fig. 2 The variation of enthalpy of fusion of the high temperature peak (a) and the low temperature peak (b) in the DSC scans as a function of the annealing time.

However, the neck grew to the whole gauge length in the un-annealed specimens and only to about one half of it in the specimens annealed for 26 hours. A similar behavior was noted earlier by Lee *et al* (7) for thin films.

An additional effect of annealing treatment on tensile behavior was shown by our specimens tested at 80 and 120°C. Only the results at 120°C are presented in Fig. 3. The figure confirms again that annealing influences the yield stress, the drawing stress during neck propagation and the fracture strain. Moreover, the yield behavior of the annealed specimens tested at these temperatures shows a significant difference immediately after yielding. As becomes clear from the inserts in Fig. 3, an increasing amount of work hardening is observed in the annealed specimens. Thin sections of the necked and the un-necked regions of annealed specimens were subsequently examined by DSC. The DSC scan of the former does not have the low temperature peak, whereas the latter does. This suggests that the crystals corresponding to the low temperature peak have been destroyed during the drawing process.

All of the specimens tested at 160°C, i.e. above the glass transition temperature (T_g) of PEEK (143°C), were drawn uniformly in the gauge section and no local necking was observed. The stress-strain curves are presented in Fig. 4. It should be noted that the well defined yield stress, which appears in all curves tested below T_g, has largely disappeared at 160°C; however, the work-hardening which occurred after the yield in Fig.3 still exists. Another work hardening behavior, occurring after the plateau of drawing, is apparent in all specimens. The strain for the onset of this work hardening increases with annealing time, a trend also noted by Lee *et al* (7) for thin PEEK films tested at room temperature.

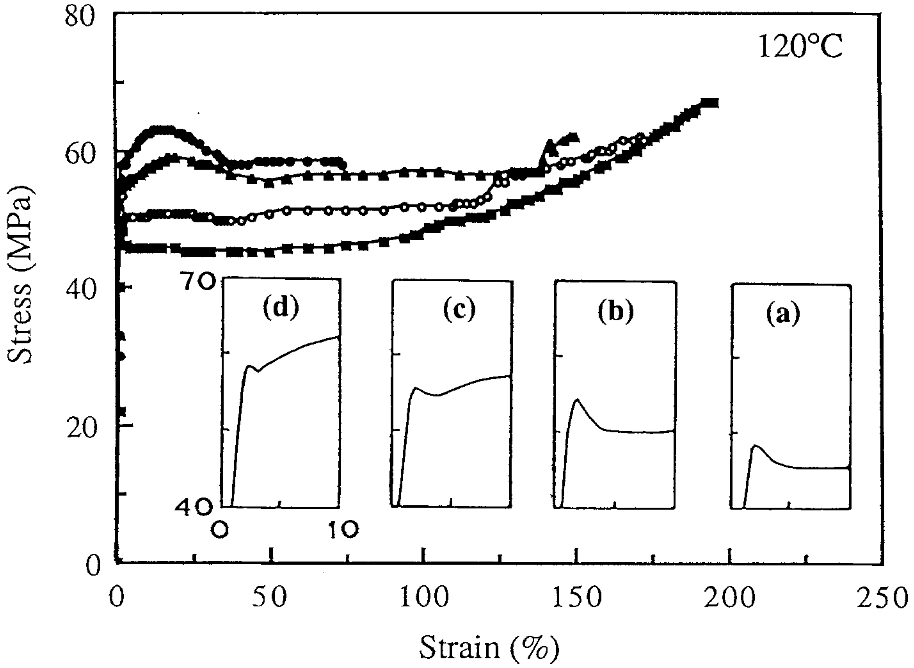

Fig. 3 Stress-strain curves for the annealed and un-annealed PEEK at 120°C; (■) un-annealed, (o) 7 minutes, (▲) 20 minutes and (●) 26 hours. For clarity, the data for the specimens annealed for 90 minutes have been omitted. The curves (a)-(d), are magnified ones to show the work hardening behavior agter yield; (a) un-annealed, (b) 7 minutes, (c) 20 minutes and (d) 26 hours.

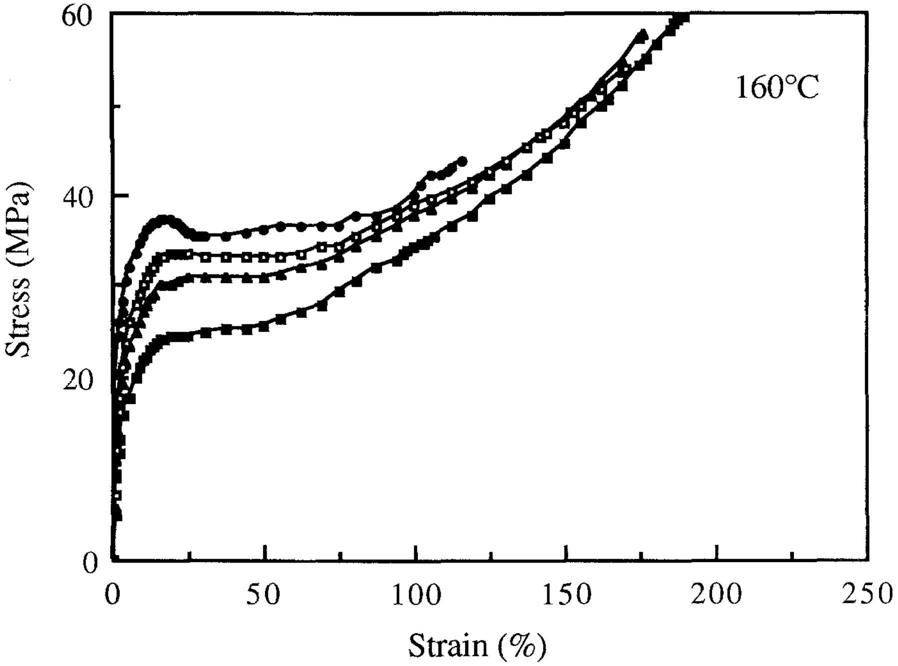

Fig. 4 Stress-strain curves for the annealed and un-annealed PEEK at 160°C; (■) un-annealed, (▲) 20 minutes, (□) 90 minutes and (●) 26 hours. For clarity, the data for the specimens annealed for 90 minutes have been omitted.

Initial Modulus

Initial moduli of the stress-strain curves were measured by imposing a strain of less than 1% before the tensile test. In this region the deformation behavior is still considered to be in the linear anelastic range (21). The results show that, at a test temperature below T_g, the annealing treatment does not affect the values of the modulus, but a significant effect occurred at 160°C. Fig. 5 presents the moduli as functions of annealing time and test temperature (23°C and 160°C).

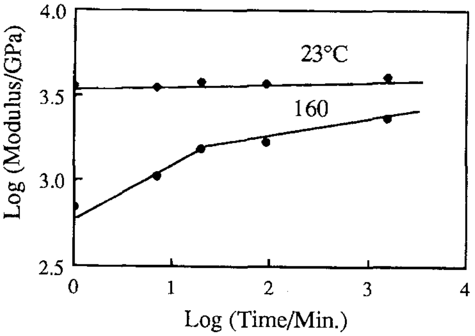

Fig. 5 The variation of initial modulus with annealing time for PEEK specimens tested at 23 and 160°C.

Creep

In addition to the tensile tests reported above, a series of creep tests were undertaken at the same four temperatures in order to study the effect of annealing on the long-term behavior of PEEK.

At room temperature, 23°C, two different load levels were used: 70% (70 MPa) and 80% (80 MPa) of the maximum tensile strength of 26-hour-annealed specimens. The former is below the drawing stress of the un-annealed material, which is 77 MPa, whereas the latter is above. Specimens with three different annealing histories were tested and the corresponding results are shown in Figs. 6 and 7.

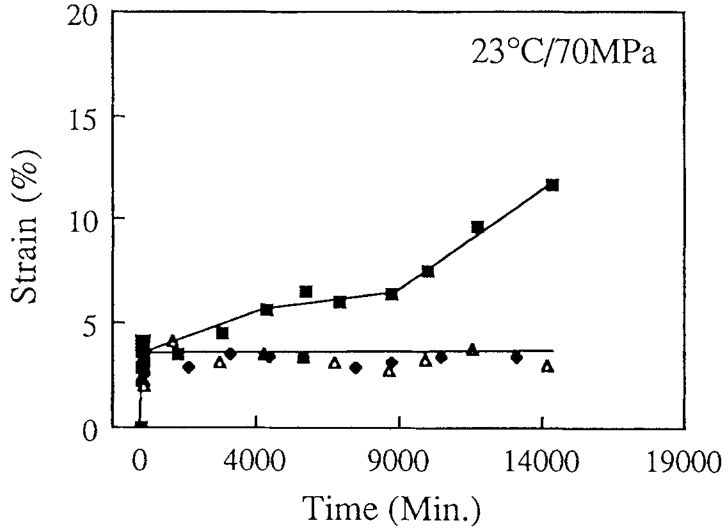

Fig. 6 Delayed yielding of un-annealed samples in creep at 23°C; annealing times: (■) un-annealed, (●) 20 minutes and (▲) 26 hours.

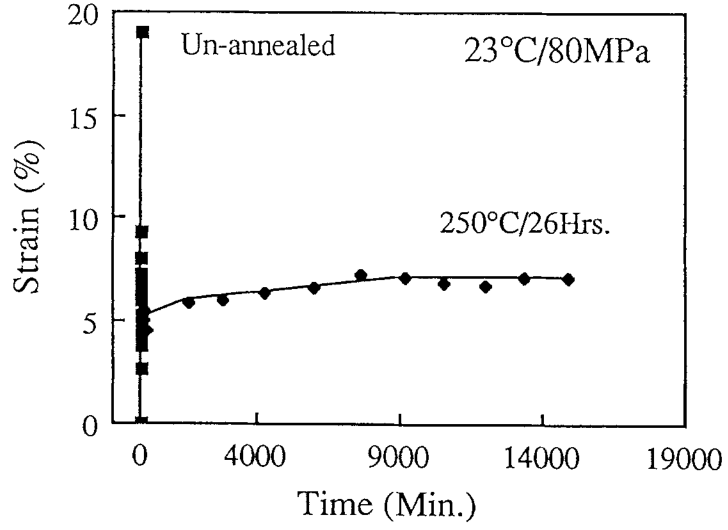

Fig. 7 Instantaneous yielding of un-annealed samples at 23°C. The load is 80% of the maximum strength of the 26-hour-annealed specimens.

These results show firstly that in creep un-annealed specimens yield, although the load in Fig. 6 is below the drawing stress of the un-annealed specimens; secondly yield strains were much higher than those of the annealed ones. One of the two un-annealed specimens tested started necking after being loaded for about 6 days(21600 minutes). The other one, of which the data are shown in Fig. 6, yielded shear deformation bands visible on the surface of the gauge section.

A load of 80 MPa was used to see if yield could be provoked at this load level. The results showed that after applying the load, the un-annealed specimens started necking in less than two hours, but the 26-hour-annealed specimens still had a limited deformation even at the end of the test period of 240 hours (Fig. 7).

As discussed previously, the maximum tensile strength of PEEK decreases with increasing temperature. To study the effect of annealing on the creep behavior at higher temperatures, the un-annealed and the 26-hour-annealed specimens were tested with a load of 80% of the maximum tensile strength of the 26-hour-annealed specimens at that temperature. At 120°C and 160°C, the instantaneous extension of the un-annealed specimens upon applying the load was 18mm, corresponding to 60% of strain, which was probably because the load was above the yield stress of un-annealed specimens. At 80°C,the un-annealed specimens started necking in 3 minutes. However,the 26-hour-annealed specimens showed small and limited deformation, less than 10% of strain, at both 80°C and 120°C during the test period, 10 days, and they gradually crept to a strain above 60% in one day at 160°C. The results of 160°C are plotted in Fig. 8. Some creep tests at 160°C with a load of 55% of the drawing stress of the 26-hour-annealed specimens (corresponding to 90% of that of the un-annealed specimens) were also carried out;the results showed that the 26-hour-annealed specimen approached a stable strain of less than 10% by the end of 10 days, while the un-annealed specimen started to creep to a strain greater than 50% in one hour.

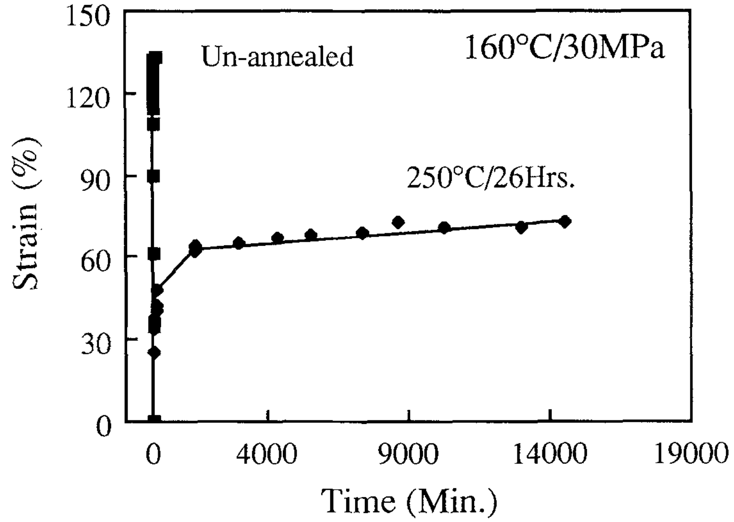

Fig. 8 Instantaneous yielding of un-annealed samples at 160°C. The load is 80% of the maximum strength of the 26-hour-annealed specimens.

Results

The results presented here support that annealing enhances the growth of secondary crystals which have a lower melting point. Their crystal structure may not be as perfect as that of the major lamellae. However, the network of the crystal structure becomes tighter because of those secondary crystals, which improves the short and long term mechanical behavior.

CONCLUSIONS

The results show that annealing can enhance significantly both the short and the long-term mechanical properties of PEEK. This enhancement probably results from the reorganization of the molecular chains between the major lamellae. This in turn increases the resistance to deformation and may lead to increases of up to 50% in the drawing stress. It should be noted that the structure of the specimens examined here is very fine, with spherulite sizes of 3μm measured by optical microscopy, while it has been reported (22) that spherulites with sizes above 10μm exist commonly in the matrix of the carbon fiber/PEEK composites.

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