Wide-Angle X-Ray Scattering Study of Heat-Treated Peek and Peek Composite

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Synopsis

We report the results of a study of poly(etheretherketone) (PEEK) neat resin and APC-2 carbon fiber composite samples which were processed from the melt and then subjected to a variety of thermal treatments. Wide-angle x-ray scattering was used to study the effects of quenching and annealing treatments. For both neat resin and composite, annealing resulted in perfection of the crystalline microstructure. In addition to the crystalline and amorphous scattering usually observed, disorder is frozen-in by fast cooling after heat treatment. The disordered component is detected as an additional low-angle scattering peak at 14 degrees, well separated from the crystalline reflections, and is observed in low molecular weight material synthesized in our laboratory, and in commercially available neat resin PEEK and APC-2 carbon fiber composite samples. When disordered material was subsequently heated above the glass transition, and then cooled very slowly, only the crystalline and amorphous scattering remained. Application of stress also resulted in formation of the disorder in the necked down regions of samples drawn in tension, suggesting that residual stresses may occur as a result of rapid cooling after heat treatment.

INTRODUCTION

Poly(etheretherketone) (PEEK) is a semicrystalline thermoplastic polymer being used as a composite matrix material in applications that require high temperature stability, and resistance to radiation and to solvent attack. Recent studies of PEEK have included investigation of the neat resin structure and properties,[1-7] crystallization and melting behavior,[2,5,8-15] and studies of the carbon fiber composite.[16-21] PEEK belongs to the class of polymers that can be quenched to form a completely amorphous material. Subsequent thermal treatments can then be used to introduce crystallinity into the material. Postannealing treatments are often used to improve the microstructure and increase the crystalline phase composition. Blundell and Osborn,[17] have suggested that composite PEEK can be postannealed if the crystallinity installed during the first stage of processing is too low. However, we have found that significant property changes can accompany these thermal treatments. In this paper we describe a study in which we used wide-angle x-ray scattering to investigate the effects of heat treatment on the microstructure of PEEK.

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Many workers have used wide-angle x-ray scattering (WAXS) to elucidate the structure of PEEK. The range of studies includes determination of the lattice constants,[1,3,4] correlation of crystallinity index to bulk density,[2] study of crystallite size,[10] and investigation of the effects of substrate on crystalline symmetry.[14] Effects of gamma irradiation on degree of crystallinity were studied by Yoda.[13] In that work, Yoda observed that the broad noncrystalline peak at $2\theta = 19$ degrees shifted to lower scattering angle as the temperature was increased from 100°C to 150°C. This was interpreted as being due to the thermal expansion of the amorphous chains at elevated temperatures.

In our study we have seen a similar shift of scattering intensity to lower angles in samples that are heat treated at elevated temperature and cooled quickly. Disorder is introduced into PEEK when high temperature treatments are followed by rapid cooling. The disorder is metastable and can revert to an ordered state when the material is heated above its glass transition and then cooled very slowly. The disorder may result from residual thermal stresses.

EXPERIMENTAL

The materials studied were: (1) low molecular weight PEEK synthesized in our laboratory according to the method of Attwood et al.,[22] (2) commercially available pellet-grade PEEK (from ICI, Americas, Inc.), and (3) APC-2 PEEK composite (from ICI). These materials will be referred to as LMW-PEEK, C-PEEK, and APC-2 PEEK, respectively. Relative viscosity and elemental analysis were used to establish the relative molecular weights of the LMW- and C-PEEK materials. Relative viscosity of LMW-PEEK was 1.4 (in concentrated H_2SO_4 at 25°C, 1 g/mL concentration), compared to 2.4 for C-PEEK. Elemental analysis[23] for fluorine and potassium end groups, residuals of the polymerization process, gave a chain end ratio of LMW- to C-PEEK of 4.4 : 1.

C-PEEK pellets were melt processed by heating to 400°C for 2 min in a hot press between ferrotype plates, followed by quenching to form amorphous . films. LMW-PEEK powder material was sensitive to degradation at high temperature, so this material was heated to a melt temperature of 350°C and quenched. A longer residence time of 10 min at 350°C was used. Both samples were subsequently heat treated by cold crystallization at 176°C for 24 h followed by annealing at elevated temperature for an additional 24 h. Annealing was carried out in an air flow oven in the temperature range from 230°C to 319°C. After completion of annealing, the samples were withdrawn from the oven and cooled quickly, but at an unknown rate, to room temperature.

The APC-2 PEEK composite samples consisted of plaques one-eighth inch thick. The plaques were heated to 400°C for two minutes, then treated as described below:

1. SC: Samples were cooled slowly in the hot press by turning the heater off. Time to reach room temperature was 17 h.
2. AC: Samples were removed from the hot press and cooled in air to room temperature in about 3 h.

3. A: Samples were cooled from 400°C to 204°C, annealed for 30 min, then quickly cooled to room temperature.
4. PA: Samples A (#3 above) were postannealed at 320°C for 1 h and cooled to room temperature.

A Siemens D-500 diffractometer with nickel filtered Cu-K_α radiation was used to obtain wide-angle x-ray scattering (WAXS) patterns in reflection mode before and after the heat treatments. A step scan interval of $2\theta = 0.1$ degree was used with a 7 s count time and diffracted beam graphite monochromater. Samples were spun to average out any orientation effects. Conditions of slit width, scan speed, and scan interval were identical for all samples.

RESULTS AND DISCUSSION

WAXS curves of treated samples are shown in Figures 1 and 2 for C-PEEK and LMW-PEEK, respectively. In Figure 1, WAXS curves of amorphous (dashed line) and treated (solid lines) C-PEEK are shown. The amorphous scattering intensity has been reported previously,[1] and consists of a large maximum at 19 degrees and a smaller relative maximum at 29 degrees. The curve is otherwise featureless, and the intensity decreases to zero rapidly in the region from 17 to 5 degrees, and above 43 degrees (not shown). The scattering from treated samples consists of four distinct crystalline reflections, reported previously[1] superimposed on the amorphous background. In addition, a large shoulder appears in the region from 5 to 17 degrees after the heat treatment. As a function of treatment temperature, the crystalline reflections become narrower as the temperature increases, indicating an improvement in crystallite size and perfection. These changes in microstructure may come about as a result of lamellar thickening, fold surface smoothing, or removal of crystal defects. As a function of treatment temperature, the shoulder at 14 degrees changes only slightly in the C-PEEK material. Little change can be seen in the relative peak height, though sharpening of the 14 degree peak was observed after heat treatment at 319°C (see curve 2 of Fig. 3).

In Figure 2, WAXS intensity for quenched (dashed line) and heat treated (solid lines) LMW-PEEK is shown. The intensity from the quenched sample is coincident with the treated sample below 17 degrees. The heat-treated samples once again show the four crystalline reflections which sharpen as the treatment temperature increases. The main feature in these curves, however, is the large intensity maximum at 14 degrees. In LMW-PEEK, the excess low-angle scattering is more pronounced than in the C-PEEK material. The position of the maximum does not vary with treatment temperature, but the absolute intensity increases dramatically so that at the highest treatment temperature the 14 degree peak intensity equals that from the (110) crystalline reflection. In addition, the 14 degree peak improves in definition (smaller full width at half maximum) as treatment temperature increases, which shows that the occurrence of this peak is related to the high temperature processing step.

When interpreting x-ray scattering from semicrystalline polymers, it is usual to consider the bulk material as consisting of two phases, the amorphous
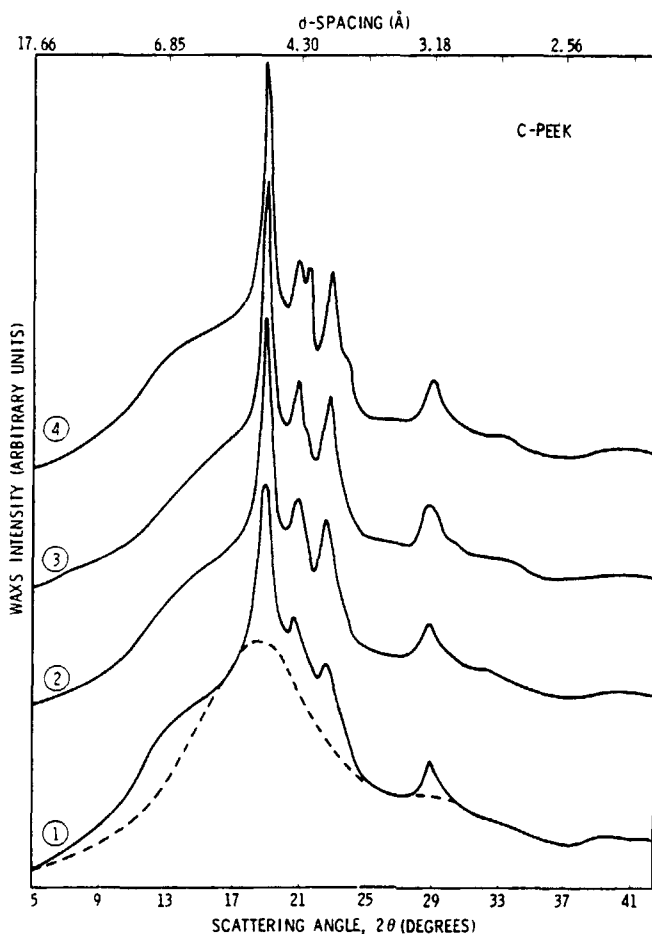
Fig. 1. WAXS intensity vs. scattering angle for heat-treated (solid) and quenched (dashed) C-PEEK films: (1) cold crystallized at 176°C, 24 h; (2)–(4) as in (1) then annealed 24 h at 230°C (2), 266°C (3), or 302°C (4).

and crystalline regions. This has been the assumption whenever PEEK x-ray scattering data have been presented. Whenever additional reflections occur in WAXS profiles, new phases of the material may be suspected. In fact, broad low-angle reflections have been seen in other heat-treated polymers, most recently in poly(di-n-alkylsilanes),[24,25] where the low-angle scattering occurs along with the crystalline reflections. Using in situ high temperature WAXS, Lovinger and Davis were able to show that this reflection represented a metastable disordered phase.[24] The disordered component could be frozen-in if the cooling rate through the ordering transition was rapid. The situation in PEEK is different since the metastable component appears to have its origin in the amorphous material and not in a new crystalline structure, judging from preliminary results of high temperature WAXS.

In the higher molecular weight C-PEEK (Fig. 1) the disordered component appears only in the heat-treated semicrystalline samples. The quenched
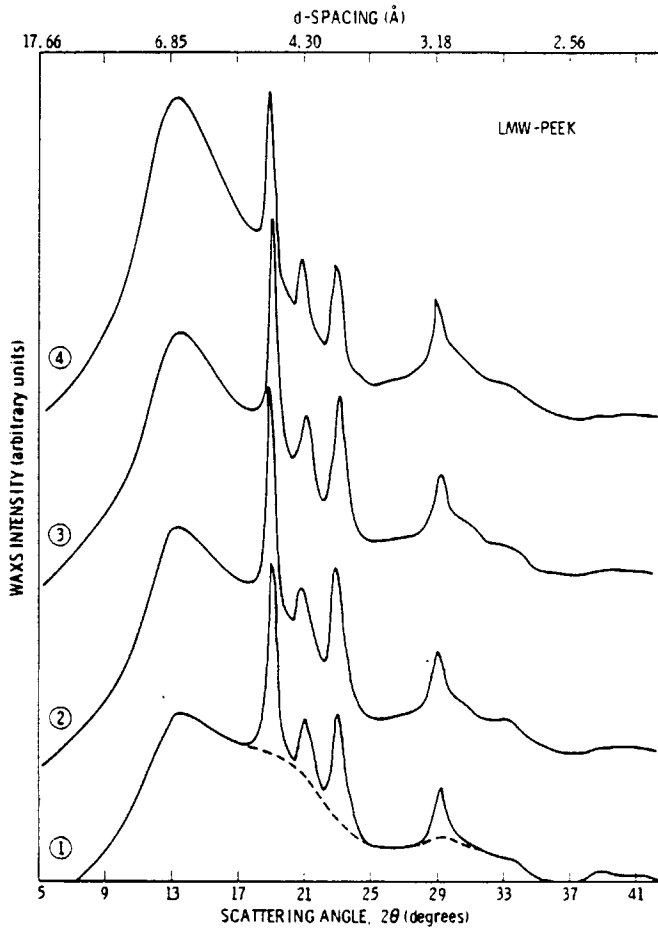
Fig. 2.   WAXS intensity vs. scattering angle for heat-treated (solid) and quenched (dashed) LMW-PEEK films. Curves (1)–(4) as in Fig. 1.

amorphous material shows no disorder. However, in the LMW-PEEK (Fig. 2) disorder is apparent in both quenched and heat-treated samples. Since the quenched LMW-PEEK received only the melt processing followed by quenching, rapid quenching freezes in the disorder in LMW-PEEK. Absence of the disorder in quenched C-PEEK and its presence in quenched LMW-PEEK is a point that requires further investigation, but may be a result of the lower melt temperature used with the LMW-PEEK material. Nguyen and Ishida have recently shown[12] that the arrangement of the diphenyl ether segments in the amorphous material may vary with the melt temperature, and persist in the material at room temperature. We are currently conducting experiments to examine whether the Fourier transform infrared spectra of samples used in the current study are affected by the annealing and quenching treatments.

We heated several C-PEEK and LMW-PEEK samples above their respective glass transition temperatures and then very slowly cooled them to room temperature. The results are shown in Figure 3. Solid lines refer to the

d - SPACING (Å)

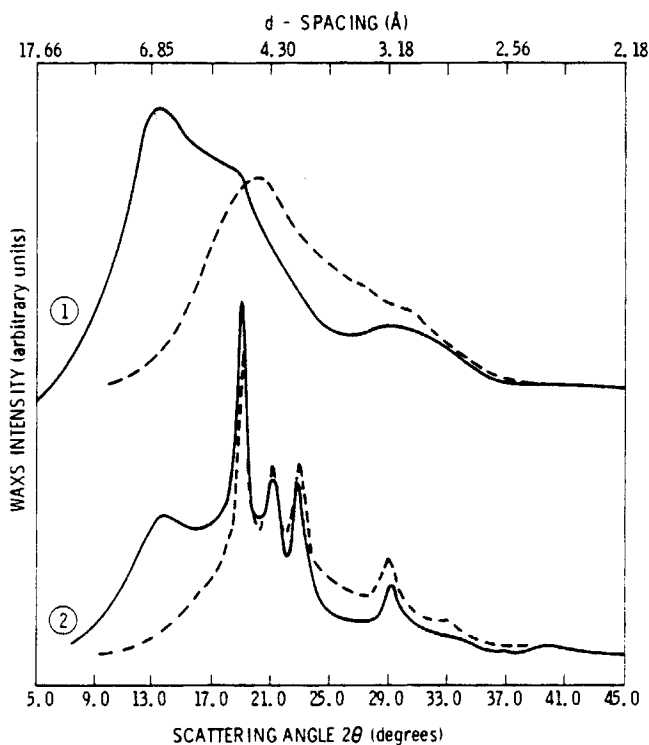17.66   6.85   4.30   3.18   2.56   2.18

Fig. 3. WAXS intensity vs. scattering angle for heat-treated films after fast cooling from the treatment temperature (solid), and after heating above the glass transition and slowly cooling: (1) quenched LMW-PEEK; (2) C-PEEK cold crystallized at 176°C, 24 h and annealed at 319°C, 24 h.

disordered state of the samples immediately after quenching, while the dashed lines show the effect of heating above T_g and slowly cooling. The two samples shown in Figure 3 are quenched LMW-PEEK (curve 1) and C-PEEK annealed at 319°C (curve 2). Different samples were used for this test, and no attempt was made to keep the scattering volume the same. Therefore, comparisons can be made only between the peak positions and curvature in the before- and after-treatment cases. The large scattering peak at 14 degrees is removed, that is, the intensity is redistributed, when samples are cooled slowly from a temperature above the glass transition. Brief heating above T_g would serve to relieve residual thermal stresses that may remain after quenching.

In some cases, the scattering peak at 14 degrees was reduced but not eliminated, depending upon the rate of cooling from the treatment temperature. Rate of cooling appears to be a very important factor in creation of the disorder, even at treatment temperatures that might be considered low (a little above the glass transition temperature). In Figure 4 we show the WAXS curves from two samples heat treated in a Mettler hot stage at 180°C for 1 h. From previous experiments[8,9] we know that PEEK cold crystallizes rapidly at this temperature, forming very imperfect crystals. WAXS scan in Figure 4 (solid curve) shows the scattering from a sample which was withdrawn from the heating stage and quenched between cold metal plates. A second sample
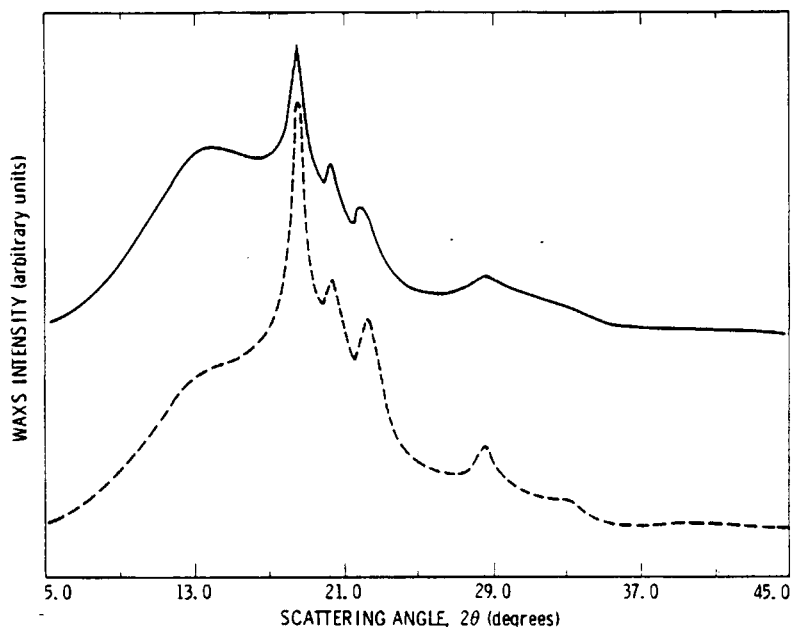
Fig. 4.   WAXS intensity vs. scattering angle for C-PEEK film cold crystallized 1 h at 180°C, then quenched (solid) or slowly cooled (dashed) to room temperature.

(dashed curve) was allowed to cool for two hours in the heating stage by shutting off the heating element. The intensity at 14 degrees is much larger in the quenched sample compared to the sample that was more slowly cooled. These two samples received the same high temperature treatment at 180°C and differ only in the cooling rate. There are, nonetheless, significant differences in the WAXS profiles as a result of the cooling rate.

Using the quenched amorphous scan as a reference, we can estimate the amount of scattered intensity contributing to the amorphous (A), disordered (D), and crystalline (C) scattering. This will provide some insight into the effects of slow cooling versus quenching. Beneath the total intensity curves (Fig. 4), a scaled amorphous curve is drawn whose profile is that shown in Figure 1. When the amorphous intensity is subtracted from the total intensity, two portions remain that can be associated with the crystalline region (scattering above 17 degrees) and the disordered region (scattering below 17 degrees), respectively. For the quenched sample (Fig. 4, solid curve), the relative proportions are: A (51%), D (31%), and C (18%). In the slowly cooled sample (dashed curve), the proportions are: A (69%), D (16%), and C (15%). Area measurements from WAXS are always subject to large errors, so the difference in proportion of crystalline (C) material is probably not significant. However, the main effect of slow cooling is the large increase in proportion of amorphous (A) material and the corresponding decrease in the proportion of disordered (D) material. From this we conclude that slow cooling allows a type of relaxation to occur such that the disordered component becomes more densely packed, and contributes to the usual amorphous scattering background which peaks at 19 degrees. The shift from a disordered peak at 14
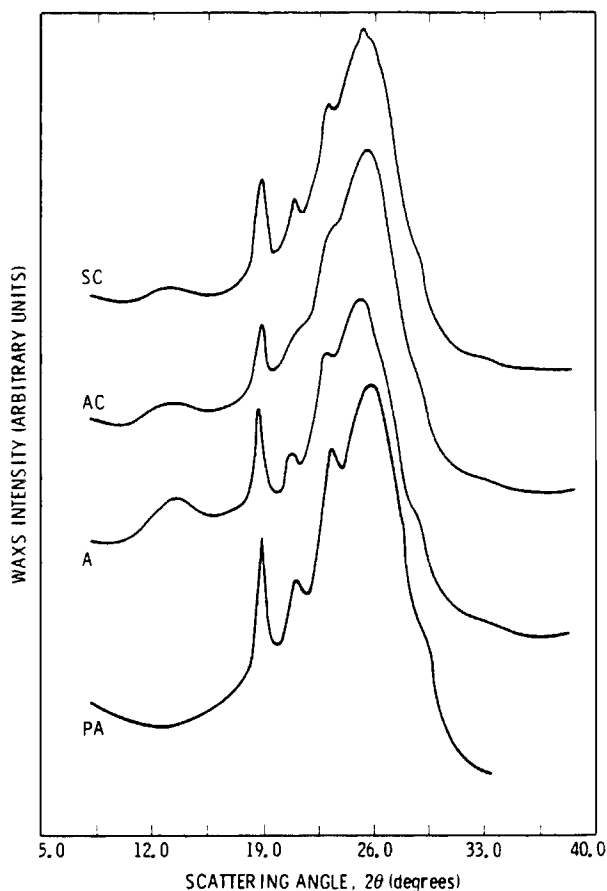
Fig. 5.   WAXS intensity vs. scattering angle for heat treated APC-2 composite PEEK. See text for description of the heat treatments.

degrees to a more ordered component centered at 19 degrees corresponds to the slight increase in density that we observe in the ordered material. When samples containing the disordered peak were heated above T_g and slowly cooled, in all cases the density increased by about 0.3%.[23]

Creation of disorder after thermal treatment is not limited to neat resin PEEK. Very similar disorder is introduced by certain heat treatments of composite PEEK. WAXS intensity from APC-2 composite samples is shown in Figure 5. The crystalline reflections are superimposed upon the much stronger carbon peak at 26 degrees. In the upper three curves, the peak at 14 degrees is seen very clearly, whereas in the lowest curve, sample PA, there is no evidence of this feature. The upturn in the scattering below 12 degrees in the PA sample is part of the background scatter. As a function of treatment, the AC and A treatments resulted in least perfect crystals, as judged by the broad poorly defined crystalline reflections. Qualitatively, the PA treatment produces the most perfect crystals. No attempt has been made to correct the data for the differences in sample volume detected, so all intensities are in arbitrary units. Nonetheless, we can say that the scattering peak at 14 degrees

appears to have the greatest relative intensity in the A sample, and least relative intensity in the SC sample.

The composite samples shown in Figure 5 indicate a similar pattern of disorder for SC, AC, and A treatments. Only the PA treatment resulted in a nearly ordered material, judging by the absence of the disorder at 14 degrees. Both samples AC and A were cooled relatively quickly after their heat treatment, so the disorder is frozen-in in much the same way as in the quickly cooled neat resin materials. For composite SC, slowly cooled overnight in the hot press, the rate of cooling was sufficiently rapid to result in creation of the disorder. We tentatively attribute the disorder in SC, and its absence in PA, as being due to different, and uncontrolled, rates of cooling of the surface of the composite plaques. Degree of crystallinity is not thought to be as important a factor in the creation of the disorder since all composite samples had nearly the same degree of crystallinity (37–39%).[26]

The results presented above show that thermal treatment involving rapid cooling may result in disorder in neat resin or composite PEEK. Heat treatment is not the only way in which the disorder may be installed. Externally applied stress may also result in formation of a disordered component in drawn neat resin PEEK. A low-angle scattering peak at 14 degrees was seen in samples of C-PEEK which had been drawn in tension at temperatures below the glass transition temperature.[27] WAXS intensity from the necked down regions of two drawn samples is shown in Figure 6. Curve 1 is from a semicrystalline C-PEEK film cold crystallized at 180°C for 1 h, then drawn at
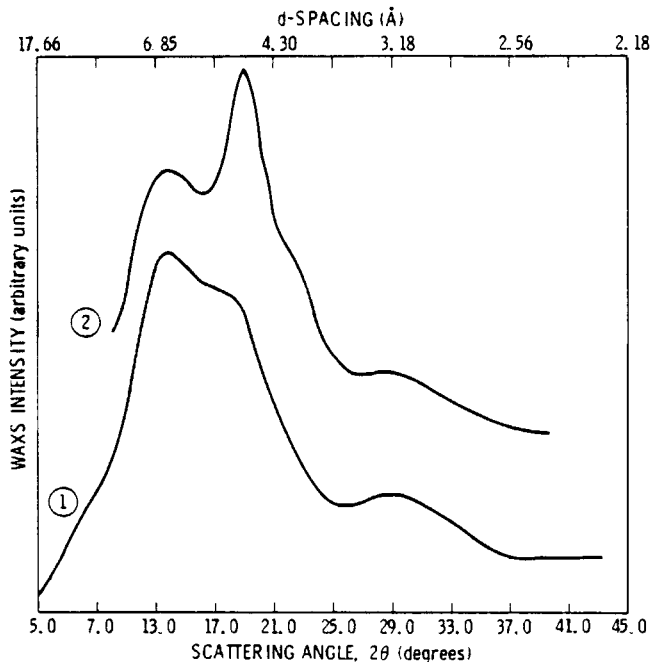

Fig. 6. WAXS intensity vs. scattering angle from the neck region of C-PEEK films drawn in tension: (1) film cold crystallized at 180°C, 1 h, then drawn at 25°C to 80% strain; (2) film quenched, then drawn at 125°C to 500% strain.

25°C to a strain of 80%. WAXS from the undrawn film[27] consists of four relatively broad crystalline reflections, and the shoulder at 14 degrees which was similar to that in the treated samples of Figure 1. After drawing, the neck region shows no distinct crystalline reflections. This sample was spun to average out orientation effects, but even when the sample was examined in equitorial or meridional scans, the crystalline reflections present in the undrawn material were absent in the neck region. The shoulder at 14 degrees is much more prominent in the neck, and its intensity exceeds that of the peak at 19 degrees.

Curve 2 in Figure 6 is from the neck region of a drawn amorphous film of C-PEEK. Prior to drawing, the WAXS intensity was exactly as shown in Figure 1 by the dashed line. After drawing at 125°C to a strain of 500%, the WAXS pattern shows a strong reflection at 19 degrees followed by several weaker bumps. The peak at 14 degrees is evident once more though its intensity is smaller relative to the 19 degree peak. In the quenched drawn C-PEEK, drawing results in two weak shoulders on the high angle side of the maximum. These shoulders are very indistinct, making their exact d-spacing difficult to assign, but they are approximately located at 21 and 23 degrees, which correspond to the positions of the (111)/(102), and (200) reflections in the semicrystalline undrawn material, and may reflect a partially crystalline nature in the neck region of the drawn sample. This may be the result of the very large strain that occurred in forming the neck in the quenched PEEK film.

Results shown in Figure 6 on the drawn C-PEEK samples suggest that disorder may be created by the effects of applied stress. Tensile drawing below T_g caused the neck regions in both quenched and heat-treated samples to display a very strong peak at 14 degrees, compared to the rather weak shoulder that was introduced after heat treatment alone.

CONCLUSIONS

We have shown that an additional reflection at 14 degrees shows up in the WAXS patterns of thermally treated neat resin and composite PEEK. This peak is due to a disordered component in the material. That the disorder is related to the high temperature processing can be determined by the sharpening of the reflection in both LMW-PEEK and C-PEEK after high temperature treatments. The disorder is metastable, being quenched into the material during the fast cooling treatments applied to the thin film neat resin samples. Similar disorder is seen in composite PEEK after several thermal treatments. However, we are not able to explain satisfactorily the absence of the disordered peak in the PA composite sample, although we suspect that cooling rate at the surface of the plaques may be an important factor which we were not able to control fully. Crystal perfection may also be a significant factor especially if the disorder occurs near the crystal-amorphous interface.

The existence of the disorder peak in the neck regions of stressed samples, and its relationship to the disorder introduced by thermal treatment, suggest that residual stresses may occur when neat resin and composite PEEK are subjected to rapid cooling. High temperature in situ WAXS experiments will be necessary to understand the molecular origin of the disorder.

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