

Effect of Flow Rate and Temperature on Crystallization Kinetics, Crystallinity Index, and Elastic Modulus of PEEK

AJIT KUMAR MISHRA and JEROLD M. SCHULTZ, *Materials Science Program, University of Delaware, Newark, Delaware 19716*

Synopsis

Dynamic, *in situ* wide angle X-ray scattering (WAXS) studies of the melt crystallization of injection-molded poly(ether ether ketone) (PEEK) have been carried out using an X-ray diffractometer and a position-sensitive detector. A test cell has been fabricated to fit inside the diffractometer and yet work as a complete injection molding apparatus. The rate of crystallization has been shown to increase with decreasing crystallization temperature and/or increasing flow rate in the mold. The crystallization rate decreases dramatically with increase in melt soak time at 400°C. The crystallinity index, which affects the stiffness, toughness, and fracture behavior of PEEK, has been measured under various processing conditions, by wide angle X-ray scattering, so as to optimize the process parameters: molding time, mold temperature, melt temperature, soak time at melt temperature, and flow rate. It has been shown that the crystallinity and hence the elastic modulus increase with increase in crystallization temperature and/or flow rate. Chain orientation has been shown to be absent in the bulk of the injection-molded specimens under normal molding conditions.

INTRODUCTION

PEEK is a semicrystalline polymer with a high melting point (334°C) and glass transition temperature (144°C). Both as an unfilled polymer and as a composite matrix, the material is ordinarily processed under conditions in which solidification occurs while the polymer is under considerable shear strain as it flows along the mold walls. In order to optimize processing conditions and minimize processing time, it is important to know the crystallization kinetics under the strain and flow rate existing in the operation and also to understand the effects of processing conditions on the ultimate microstructure and properties.

The kinetics of crystallization and the ultimate degree of crystallinity of PEEK solidified under quiescent conditions has been reported frequently.¹⁻⁹ There is also one report of the time for the initiation of crystallization under shear conditions.⁵ In order to rationalize processing conditions and develop processing-property relationships, one needs crystallization kinetics data under a range of shear rate and temperature conditions, and also data concerning the effect of these conditions on the crystallinity and mechanical properties of the product. This sort of information is not trivially found, for two reasons: (1) There is no simple method of measuring the degree of transformation under conditions of strain and (2) the general effect of strain is to greatly increase the rate of transformation (see Ref. 10 for a bibliography), making it difficult to record data quickly enough to follow the process.

It is the purpose of the present work to measure such crystallization kinetics and also to relate these to the elastic modulus and the degrees of crystallinity and orientation. X-ray diffraction is used to follow isothermal crystallization in a miniature injection-molding device. A position-sensitive proportional counter is used to reduce scan time.

EXPERIMENTAL

The X-ray system used was a Picker FACS-1 four-circle diffractometer (used in the $\theta-2\theta$ mode) with a Braun position sensitive detector (PSD) which enabled simultaneous recording of intensity distribution over a > 10 degree region with $60 \mu\text{m}$ (approximately 40 s) resolution. The analog pulses from the time-to-amplitude converter (TAC) are digitized in a multichannel analyzer (MCA) and counted in their respective position channels. The intensity in over 1000 channels was simultaneously obtained. A Digital VAX 11/785 computer was used to automate the data collection. Complete WAXS spectra were obtained at approximately 45-s intervals.

The test cell consisted of a mold of invar and boron nitride and a melt chamber of aluminum, as shown schematically in Figure 1. The cell was fabricated to fit inside the goniometer and yet work as a complete injection-molding apparatus. 150P Victrex PEEK supplied by ICI was melted inside the melt chamber, injected into the mold by a ram at varying injection speeds, and allowed to crystallize at various mold temperatures. The optimum melt soak time at a melt temperature of 400°C was found to be 5 min. A smaller melt soak time did not impart sufficient fluidity to the polymer to flow through the entire length of the mold and, as shown later, a larger melt soak time reduced the rate of crystallization. This melt temperature of 400°C and melt soak time of 5 min was used in every case with the sole exception specifically mentioned later.

As crystallization occurred, X-rays were passed through the specimen. The collection time used was 30 s. The WAXS spectra at successive points of time enabled accurate determination of the time taken for crystallization to commence and to be complete. The polymer was held at the crystallization temperature for 60 min in each case before being allowed to cool to room

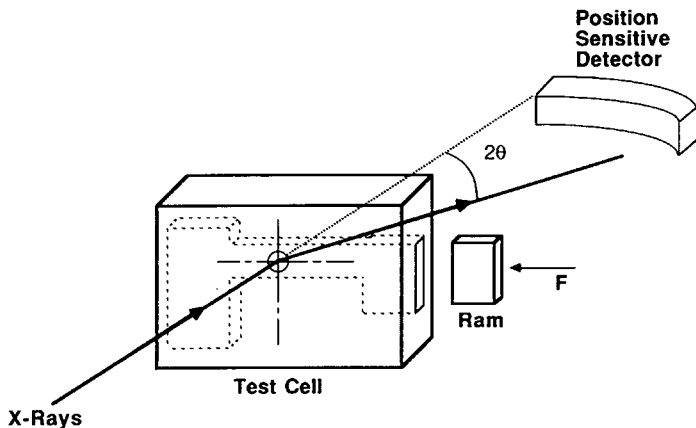


Fig. 1. Experimental setup (schematic).

temperature, even though the WAXS spectra ceased to change long before that, as shown later. This was done to be absolutely certain that crystallization was complete at the crystallization temperature and that no further spherulitic growth occurred while the specimen was being cooled.

RESULTS

Figure 2 shows a set of WAXS spectra obtained as crystallization occurred in the mold. Figure 2(a) is the spectrum obtained beginning 10 s after the melt

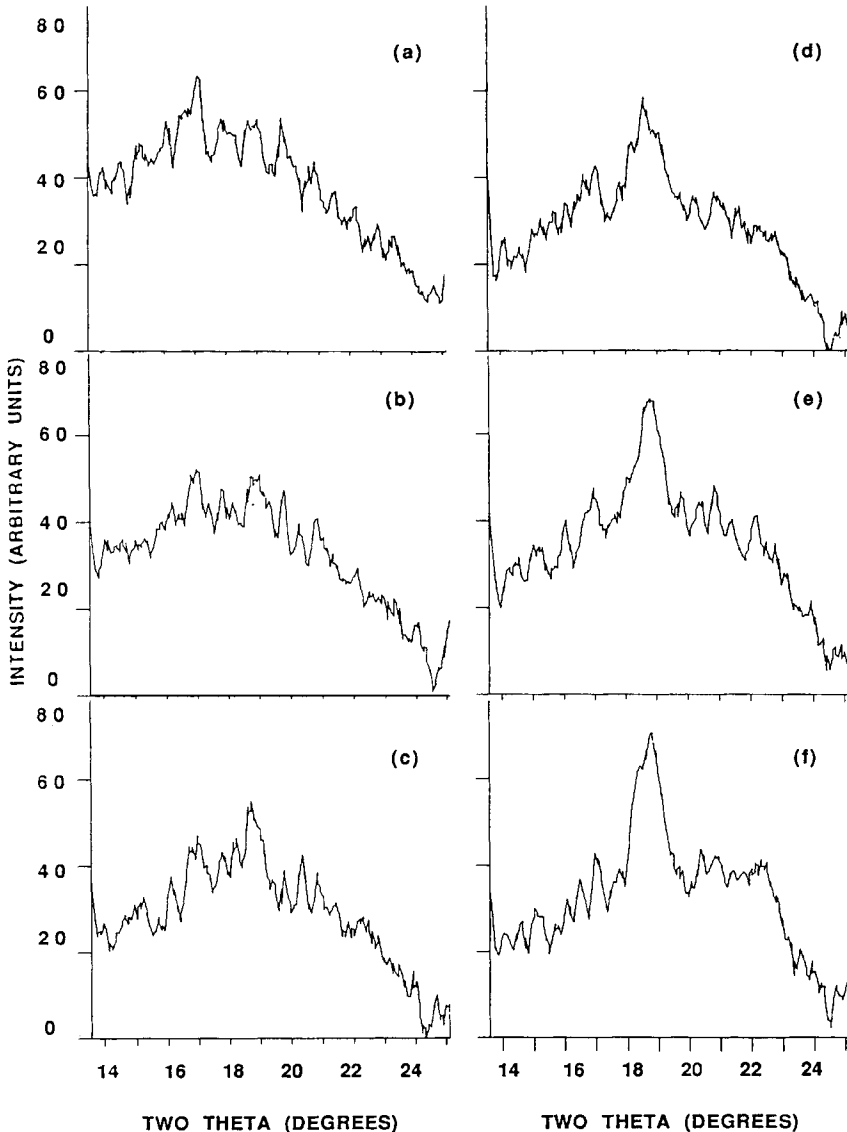


Fig. 2. *In situ* WAXS spectra of injection-molded PEEK. Mold temperature = 325°C and flow rate = 1.5 m/min (melt temperature = 400°C and soak time = 5 min in this as well as every succeeding figure): (a) 10 s after injection into the mold; (b) after 55 s; (c) after 1 min 45 s; (d) after 2 min 30 s; (e) after 3 min 30 s; (f) after 7 min 45 s. Note that crystallization begins after 1 min 45 s and is complete after 3.5 min. Collection time is 30 s in each case.

was injected into the mold. Only the amorphous hump is seen and, evidently, crystallization has not yet commenced. Figure 2(b) which shows the spectrum after 55 s is identical to 2(a). Figure 2(c), the spectrum after 1 min 45 s, shows the first sign of crystallinity, as the (110) peak, which is the most intense diffraction peak in PEEK, becomes discernible at 18.7° . Figure 2(d) shows that the (110) peak has grown considerably with further crystallization. In Figure 2(e), the spectrum after 3.5 min, the (110) peak has become even larger and two smaller peaks have appeared at 20.7 and 22.5° , corresponding to the (113) and (200) planes, respectively. After 7 min 45 s [Fig. 2(f)], the size of the peaks has not changed any further, indicating that crystallization was complete after 3.5 min. The onset and completion of crystallization under each set of processing conditions were determined in this manner.

Figures 3 and 4 show the time taken for crystallization to commence and the time for crystallization to be complete as a function of the mold temperature at various flow rates. Both times increase with increasing mold temperature. As the mold temperature approaches the crystalline melting point, the time required increases steeply. For instance, at a flow rate of 600 mm/min, the time for crystallization to be complete increases from 2 min at 315°C to 20 min at 332°C . The flow rate mentioned here is the rate of motion of the polymer through the mold, which determines the shear rate experienced by the polymer. It is not possible to rigorously determine the shear rate, since the expression for viscosity of 150P PEEK at 400°C as a function of shear rate is not available. However, one can obtain the nominal shear rate for a Newtonian fluid flowing between two parallel plates from the formula¹¹:

$$\dot{\gamma}_B = 6U/B$$

where $\dot{\gamma}_B$ = nominal shear rate, U = fluid flow velocity, and B = distance between plates (2 mm in this experiment). Hence the nominal shear rate (in

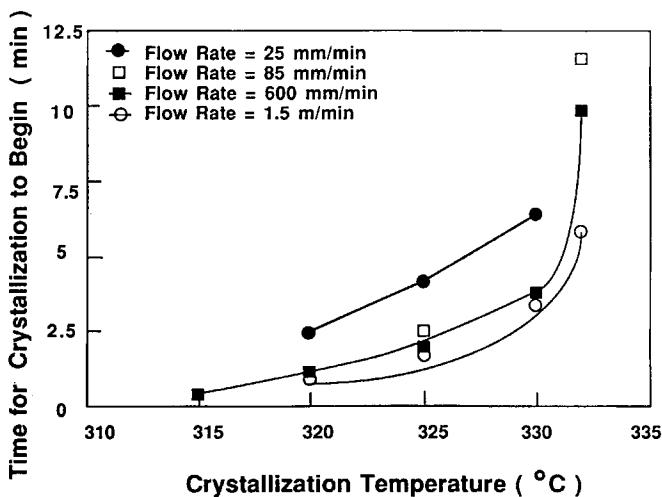


Fig. 3. Time for crystallization to commence as a function of crystallization temperature and flow rate. The nominal shear rate (in s^{-1}) for a Newtonian fluid can be obtained by dividing the corresponding flow rate (mm/min) by a factor of 20.

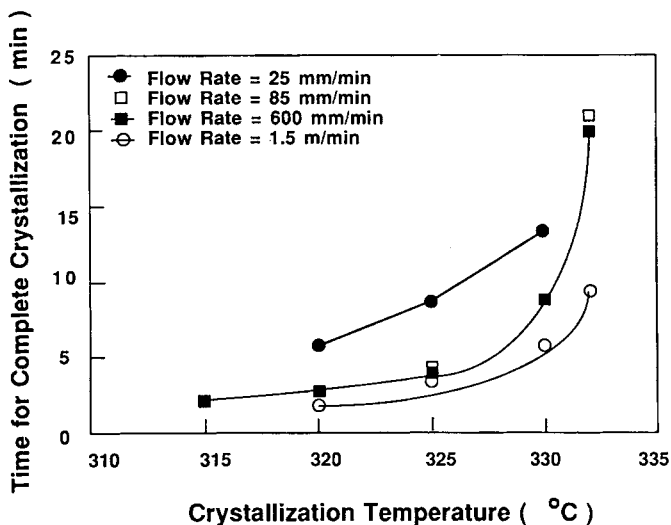


Fig. 4. Time for complete crystallization as a function of crystallization temperature and flow rate. Crystallization is complete when the diffraction peaks stop growing.

s^{-1}) can be obtained in each case by dividing the corresponding flow rate (in mm/min) by a factor of 20.

Figure 5 shows the effect of flow rate more clearly. When the rate of motion of the ram which injects the melt into the mold is increased (i.e., the flow rate of the melt in the mold and, hence, the shear strain rate experienced by the melt, are increased), the crystallization rate increases significantly. At a crystallization temperature of 320°C, the time for crystallization to be complete decreases from 5 min 40 s at a flow rate of 25 mm/min to 1 min 45 s at a flow rate of 1.5 m/min.

On increasing the soak time of the melt at 400°C from 5 to 30 min, the crystallization rate decreases significantly. At a mold temperature of 280°C, a flow rate of 25 mm/min and a melt soak time of 30 min at 400°C, the first sign of crystallinity was observed only after 15 min in the mold and it took almost 3 h for crystallization to be complete. In contrast, after a melt soak time of 5 min at 400°C, at the same flow rate and mold temperature, crystallization was complete before the 30 s required to collect one set of data. Even at the much higher mold temperature of 320°C and the same flow rate of 25 mm/min, it took only 5 min 40 s for crystallization to be complete. A similar effect has been reported previously for PEEK.^{12,13}

After crystallization was complete, a final WAXS spectrum was obtained using a much larger collection time of 5 min to improve the signal-to-noise ratio. This spectrum was used to determine the crystallinity of the specimen. An experimentally obtained amorphous hump with a suitable scaling factor was subtracted from each spectrum to obtain the crystalline peaks. The area under the peaks and the area under the hump were both determined using the trapezoidal rule. The ratio of the area under the intensity peaks to the total area under the curve (peaks plus amorphous hump) is a measure of the crystallinity.

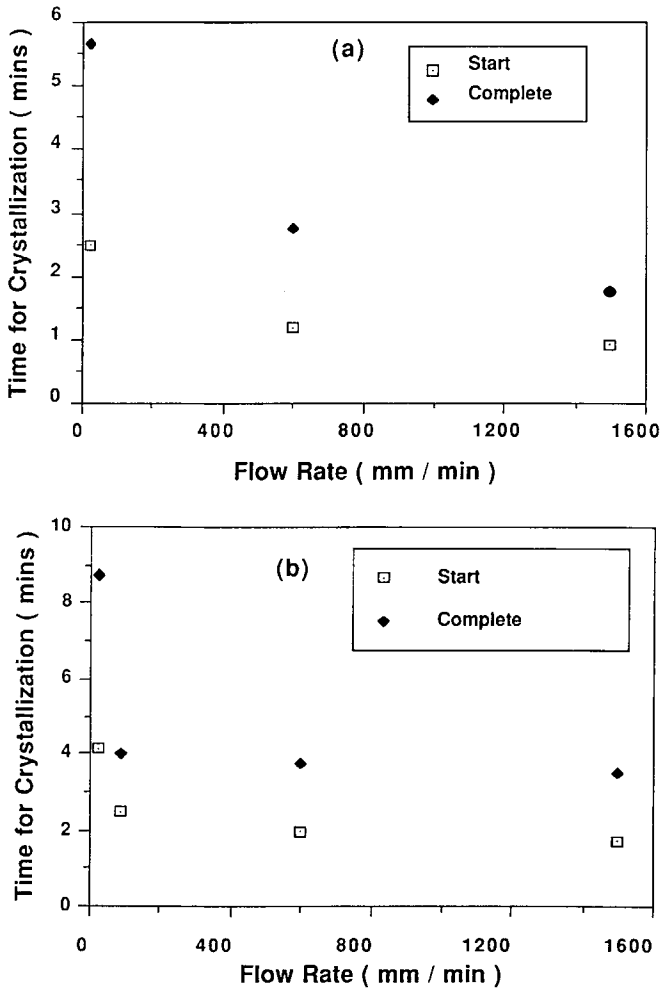


Fig. 5. Crystallization kinetics as a function of flow rate at a particular temperature. Crystallization temperature is 320°C in (a), 325°C in (b), 330°C in (c), and 332°C in (d).

This is not a rigorous determination of the degree of crystallinity, as would be obtained by Ruland's method.¹⁴ The figures given here should be considered to be relative values which show the trend of the variation in crystallinity with variation in mold temperature and flow rate. However, a similar method has been used in the past by several authors.^{1,15}

Figure 6 shows two typical final spectra used to determine the crystallinity. The larger collection time used here (as compared to the spectra used for determination of the kinetics) makes it easier to determine the area under the diffraction peaks. Figure 6(a) shows a very high level of crystallinity, as evidenced by the large peaks and the small amorphous hump. Figure 6(b) shows a smaller crystallinity index, associated with the lower flow rate used in this case.

On plotting the crystallinity index as a function of crystallization temperature at various strain rates, it is seen from Figure 7 that the crystallinity increases with increase in crystallization temperature and/or flow rate.

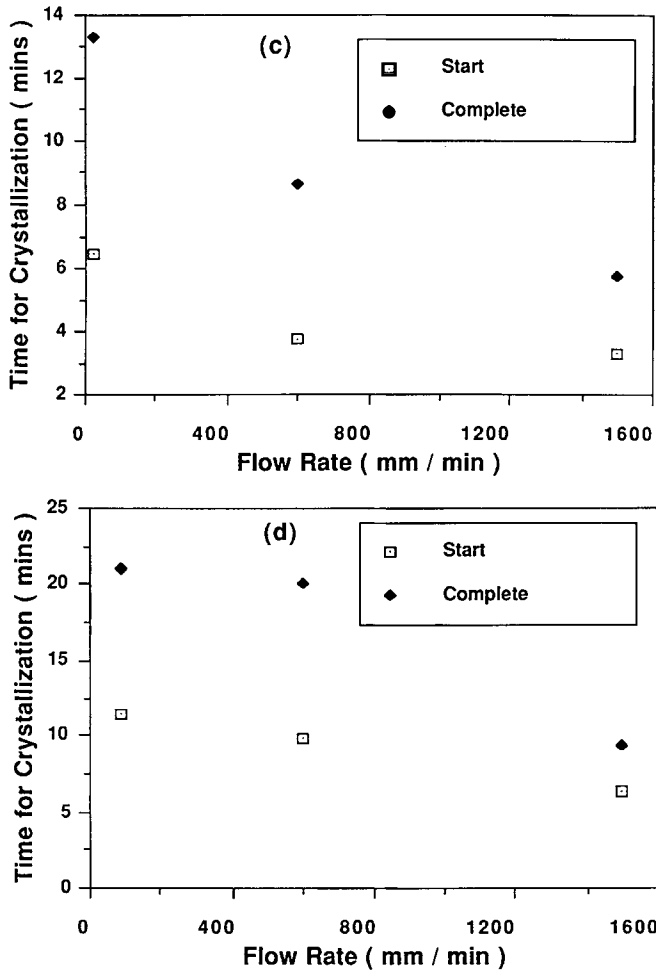


Fig. 5. (Continued from the previous page.)

A density gradient column was used to verify the trend of change in crystallinity with the process parameters. Figure 8 shows that the density increases with increasing crystallization temperature and/or flow rate. This supports the trend in the crystallinity indices obtained from the WAXS studies. The density values are, however, slightly lower than expected in each case, possibly due to the presence of some microporosity.

The elastic modulus of each specimen was determined by the three-point bend test in an Instron testing machine, using the formula given below¹⁶:

$$E = PL^3/4bh^3y$$

where E = modulus of elasticity in bending, P = applied load, y = deflection at center of specimen, h = thickness of specimen, b = width of specimen, and L = span length between support rollers.

Even though the specimens were rather small, the direction of change of modulus with the process parameters was obvious, as shown in Figure 9. The elastic modulus increases with increase in crystallization temperature and/or

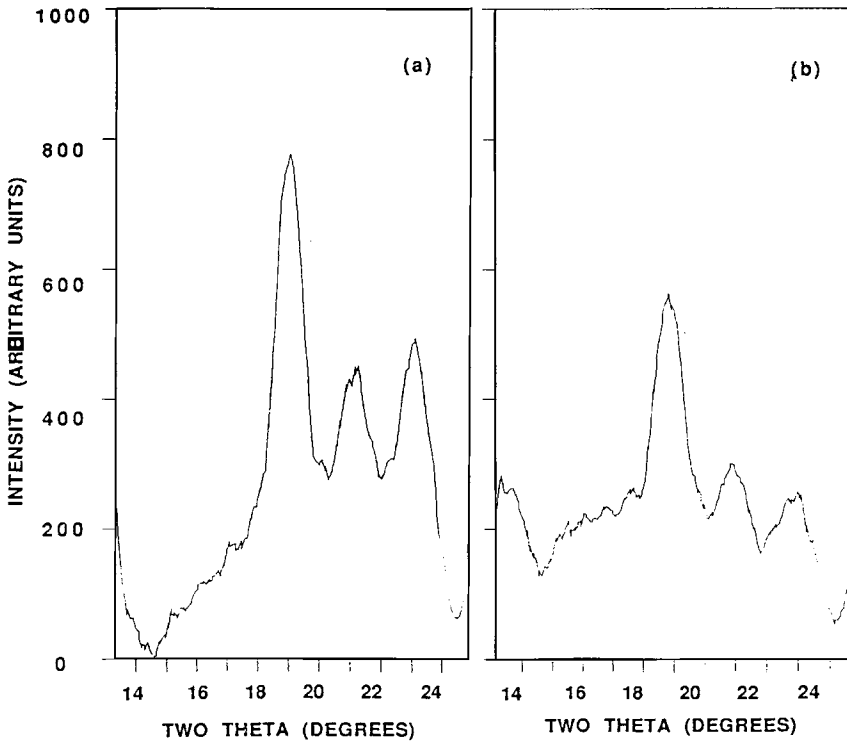


Fig. 6. Final WAXS spectra after crystallization is complete. Collection time used is 5 min. Mold temperature is 330°C in both cases. Flow rate is 1.5 m/min in (a) and 85 mm/min in (b).

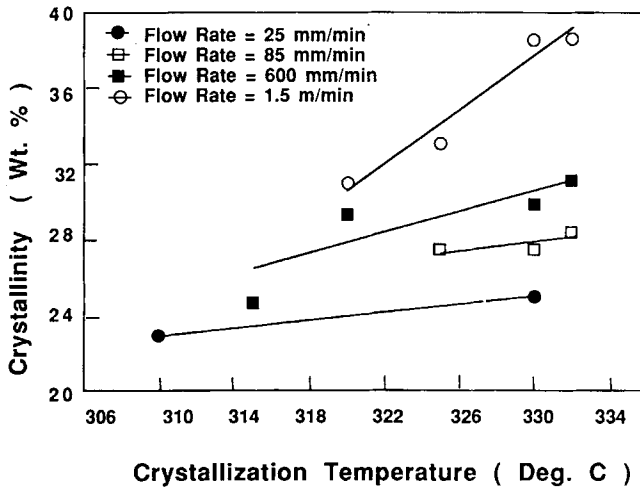


Fig. 7. Crystallinity of PEEK, as determined by WAXS, as a function of crystallization temperature and flow rate. Note that the crystallinity seems to be leveling out at about 38%.

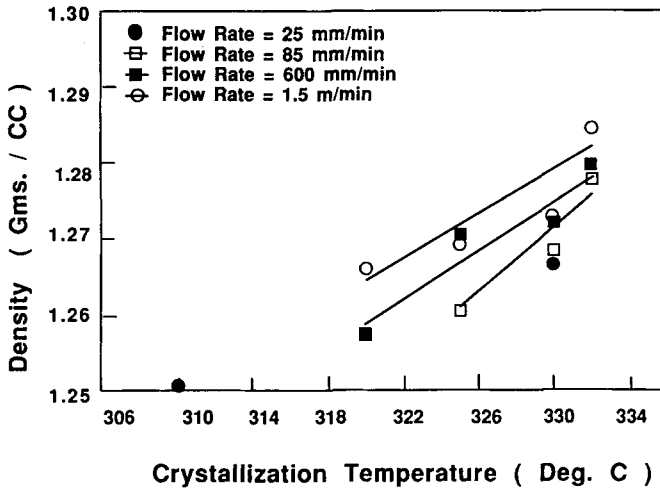


Fig. 8. Density of PEEK as determined by the density gradient column method.

flow rate. For instance at a flow rate of 25 mm/min, the modulus increases from 3.74 GPa when the crystallization temperature is 320°C to 4.08 GPa when it is 330°C. Similarly, at the crystallization temperature of 320°C, the modulus increases from 3.74 GPa at a flow rate of 25 mm/min to 3.93 GPa at a flow rate of 1.5 m/min.

Chain orientation in the specimens was monitored using the Debye rings obtained by the monochromatic pinhole technique in a Warhus camera. Figure 10 shows the Debye rings of the specimen molded at the highest flow rate of 1.5 m/min used in this experiment. It can be seen that there is no discernible chain orientation in the bulk of the specimen. Thus chain orientation can be ensured only by using much higher strain rates and a cooling system which ensures that the specimen is quenched from the melt tempera-

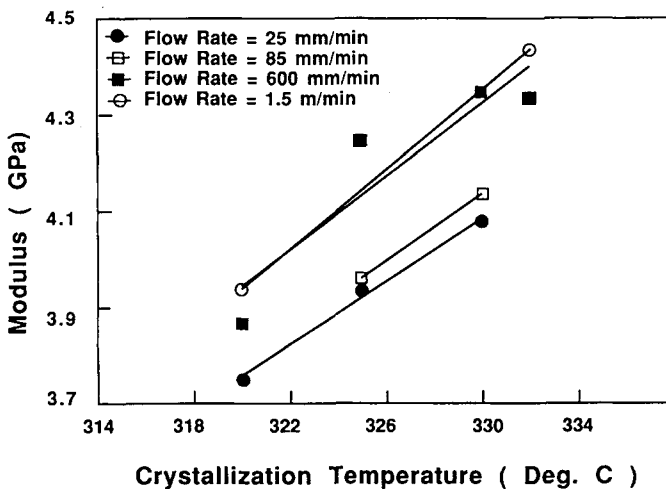


Fig. 9. Elastic modulus of PEEK (from three-point bend test) as a function of crystallization temperature and flow rate.

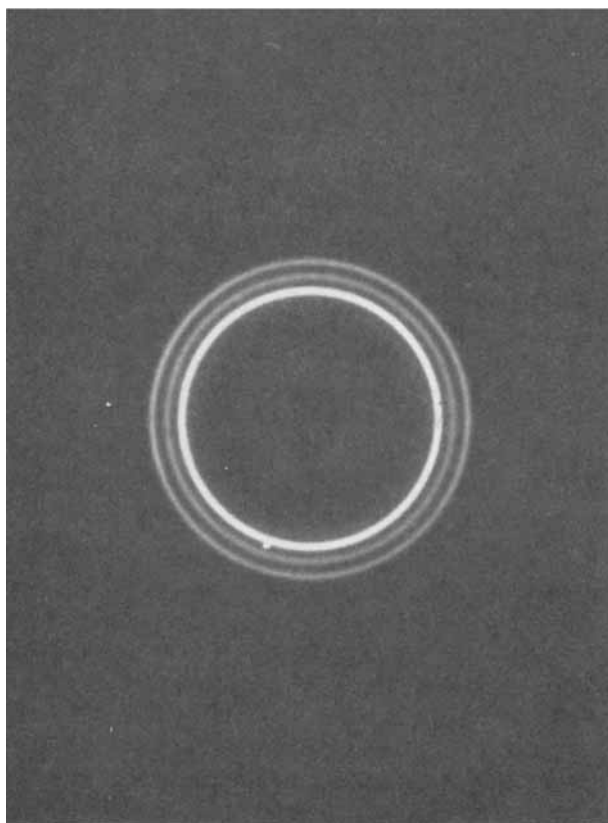


Fig. 10. Debye rings of PEEK injection-molded at a mold temperature of 325°C and a flow rate of 1.5 m/min. The rings are continuous, i.e., there is no chain orientation in the bulk of the specimen.

ture to the mold temperature in a much shorter time than the approximately 1 s that it takes in the present case.

Isothermal thermogravimetric analysis (TGA) of PEEK was carried out in air to investigate the effect of melt soak time. The specimen was held at 230°C for 24 h to ensure complete moisture removal. It was subsequently heated rapidly to 334°C and then, over a 10-min period to 400°C (the same amount of time taken in the *in situ* WAXS experiments), and held at 400°C, in air, for 60 min. A weight loss of approximately 0.5% was observed after 30 min and 1% after 60 min.

DISCUSSION

When the crystallization temperature is increased, the undercooling, which is the driving force of crystallization, decreases. Thus the rate of crystallization decreases. Increasing the flow rate causes an increase in shear strain rate which produces molecular extension, thereby decreasing the entropy in the noncrystalline state and increasing the driving force for crystallization. This effect of molecular extension is well known in polymer systems (see Ref. 10 for a bibliography of strain and strain rate effects in polymer crystallization). An

effect of shear rate on the time for the onset of crystallization in PEEK has been reported previously by Chien et al.⁵ They were, however, unable to detect beyond the onset.

The effect of melt soak time and temperature has been reported several times.^{5,7,12-14} While Velisaris and Seferis¹³ report that PEEK degrades under prolonged exposure to air at 375°C, Cogswell¹⁷ and Ma et al.¹⁸ state that the polymer is little affected by prolonged treatment at 400°C. It is likely that the effect of melt soak time is to remove persistent crystal nuclei. Such persistent nuclei are common in polymer systems and are removed only by using long melt treatment or high melt temperatures. This effect has been used to control the fineness of the spherulitic microstructure in polypropylene^{19,20} and is reported for PEEK.^{7,14}

The isothermal TGA data indicate the possibility of a small amount of degradation as well on prolonged melt treatment. Ma et al.¹⁸ do not observe this small effect, possibly because it is obfuscated by the much greater degradation occurring at higher temperatures in their continuous heating experiment.

The effect of flow rate on the crystallinity is surprising. In general, one finds an inverse relationship between the rate of crystallization and the crystallinity. However, in the present investigation, increasing the flow rate was seen to increase both the rate of crystallization and the crystallinity. While this result is clear cut, there is not yet sufficient supplementary information to be certain about its interpretation. However, one possible explanation is that the increase in crystallinity could be due to greater secondary crystallization, i.e., formation of new crystallites between those formed at the primary stage. Secondary crystallization has been observed in polyethylenes.²¹ The long tail of the DSC curve of Lee and Porter⁷ during isothermal crystallization at 306°C indicates the possibility of secondary crystallization in PEEK as well. At the higher flow rates in our experiments, the half-time of crystallization is lower. Thus, the holding time of 60 min is a greater multiple of the half-time and, hence, the duration of secondary crystallization is greater, thus increasing the crystallinity. However, this is merely a postulate at this time and needs to be verified.

The increase in elastic modulus observed with increasing temperature and/or flow rate is a direct result of the increase in crystallinity. Similar trends in PEEK have been observed previously.²²

Finally, it is somewhat surprising to have found a marked effect of flow rate on the kinetics when there is no measurable macroscopic orientation. A possible explanation for this is as follows: The melt strain caused the development of short, fibrillar strain-induced nuclei, thereby reducing the time for nucleation. The nuclei are, however, far enough apart that any effect of initial orientation is submerged in spherulitic development.

This work was supported by the U.S. Army Research Office under Grant DAAG29-85-K-0042.

References

1. D. J. Blundell and B. N. Osborn, *Polymer*, **24**, 953 (1983).
2. D. J. Blundell and B. N. Osborn, *SAMPE Q.*, **17**, 1 (1985).
3. D. J. Kemmish and J. N. Hay, *Polymer*, **26**, 905 (1985).

4. P. Cebe and S.-D. Hong, *Polymer*, **27**, 1183 (1986).
5. M. C. Chien, R. A. Weiss, and A. L. Miller, *SPE/ANTEC*, '86, 449 (1986).
6. J. P. Jog and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **32**, 3317 (1986).
7. Y. Lee and R. S. Porter, *Polym. Eng. Sci.*, **26**, 633 (1986).
8. W. J. Sichina and P. S. Gill, *31st Int. SAMPE Symp.*, 1104 (1986).
9. C. N. Velisaris and J. C. Seferis, *Polym. Eng. Sci.*, **26**, 1574 (1986).
10. W. A. Tiller and J. M. Schultz, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 143 (1984).
11. S. Middleman, *Fundamentals of Polymer Processing*, McGraw-Hill, New York, 88 (1977).
12. W. J. Sichina and P. S. Gill, *SPE / ANTEC '85*, 293 (1985).
13. C. N. Velisaris and J. C. Seferis, *SPE/ANTEC*, '85, 401 (1985).
14. S. Kumar, D. P. Anderson, and W. W. Adams, *Polymer*, **27**, 329 (1986).
15. J. N. Hay, D. J. Kemmish, J. I. Langford, and A. I. M. Rae, *Polym. Commun.*, **25**, 175 (1984).
16. *Ann. Book ASTM Stand.*, **03.01**, 823 (1985).
17. F. N. Cogswell, *Int. Polym. Process.*, **1**(4), 157 (1987).
18. C.-C. Ma, J.-T. Hu, W.-L. Liu, H.-C. Hsia, B.-Y. Shieh, and R.-S. Lui, *31st Int. SAMPE Symp.*, 420 (1985).
19. J. H. Reinshagen and R. W. Dunlap, *J. Appl. Polym. Sci.*, **17**, 3619 (1975).
20. B. V. Ceres and J. M. Schultz, *J. Appl. Polym. Sci.*, **29**, 4183 (1984).
21. J. M. Schultz, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2291 (1976).
22. J. C. Seferis, *Polym. Compos.*, **7**, 158 (1986).

Received July 28, 1988

Accepted August 1, 1988