

Thermal Degradation of Poly(aryl-Ether-Ether-Ketone) (PEEK): A Differential Scanning Calorimetry Study*

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Synopsis

Differential scanning calorimetry (DSC) has been used to study the crystallization kinetics and thermal characteristics of poly(aryl-ether-ether-ketone) (PEEK) samples heated under a variety of conditions. Samples were heated in nitrogen and air at temperatures between 380 and 420°C for times up to 120 min. The results indicate that as the holding time and temperature of the melt increased, the amount of recrystallizable material decreased, especially when heated in air. Isothermal crystallization kinetics confirmed the presence of a two-stage crystal nucleation and growth process with Avrami exponents of the order of about 2.4 and 1.5 for the first and second processes, respectively. Analysis of the primary crystallization process using the Avrami equation revealed that PEEK samples heated above the melt temperature in air crystallized at a much slower rate than samples heated in nitrogen.

INTRODUCTION

The development of thermoplastic matrices for composite materials is an area in which significant advances have been made over the last few years. One of the leading polymers in this area is poly(aryl-ether-ether-ketone) (PEEK). This polymer has exceptional toughness, strength and rigidity as well as excellent chemical and radiation resistance. These properties, coupled with its indefinite shelflife, suggested ease of fabrication, repairability, and reprocessing capabilities, mean that it has potential advantages over thermoset materials.^{1,2} Because PEEK is a crystallizable polymer, the morphology and, consequently, the physical properties can be greatly influenced by the processing conditions employed during fabrication.³⁻⁶ This arises because conditions encountered during polymer processing and composite fabrication can control such key morphological features as degree of crystallinity, spherulite size, lamellae thickness, and crystallite orientation, all of which can influence the ultimate properties of the polymer or the composite it is used in.⁷⁻⁹

Because thermoplastic resins such as PEEK may be melted, quenched, and solidified several times during processing and composite fabrication, it is important to have an understanding of the effects of processing cycles and

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environment on the morphology of the final product. This effect of temperature cycling on the morphological properties of PEEK has been studied and chemical reactions have been suggested to occur when PEEK is heated above its melt temperature.¹⁰ However, repeated melting at 396°C has also been shown to cause a reduction in nuclei for crystallization, which can cause changes in the crystallization behavior. Similar changes have been noted when PEEK is exposed to air in the melt, but not in pure nitrogen.¹¹ In this study, we have used differential scanning calorimetry (DSC) to systematically study the effect of temperature, time, and environment on the glass transition temperature (T_g), crystallization, and melting of PEEK when it is held as a melt.

EXPERIMENTAL

The PEEK polymer used in this study was 0.22-mm-diameter monofilament prepared from ICI resin by Albany International. This material had an intrinsic viscosity of 0.81 dL/g when measured in 96% H₂SO₄ at 30°C and a density of 1.2945 g/cm³ measured by the floatation technique. Based on the density of the perfect crystalline material being 1.378 g/cm³ and 1.264 g/cm³ for the amorphous density, the degree of crystallinity of the original material was estimated to be 27%. This value closely agreed with the value calculated from the area under the DSC melting endotherm, assuming a value of 130 J/g for the perfect crystal.¹²

The heat exposures, thermal characterizations, and crystallization kinetics were carried out using a DuPont 910 DSC programmed with a 1090 thermal analyzer. Calibration of the temperature and heat flow scales was done using indium and zinc as standard reference materials. All experiments were performed on 7 ± 0.001 mg specimens of PEEK in open aluminum pans. Either air or nitrogen at a flow rate of 50 mL/min was used throughout all experiments.

In the thermal characterization experiments, the samples were heated in air or nitrogen at 10°C/min from room temperature to the final test temperature (380, 400, or 420°C) and held for the prescribed exposure times. Samples were then removed rapidly from the cell and quench cooled in liquid nitrogen. The DSC traces were then once more recorded using the same environment, heating at 10°C/min, and the data analyzed using the DuPont 1090 thermal analyzer DSC program.

The isothermal crystallization kinetic experiments were performed on samples heated in air or nitrogen at 10°C/min from room temperature to the final test temperature (380–400°C), and then held for the prescribed exposure times. The system was then cooled quickly to the isothermal crystallization temperature where the enthalpy of crystallization was measured as a function of time.

RESULTS AND DISCUSSION

Thermal Characterization

Figure 1 shows the DSC traces for a series of quenched samples subjected to different heat treatments. It will be noted that all samples show the char-

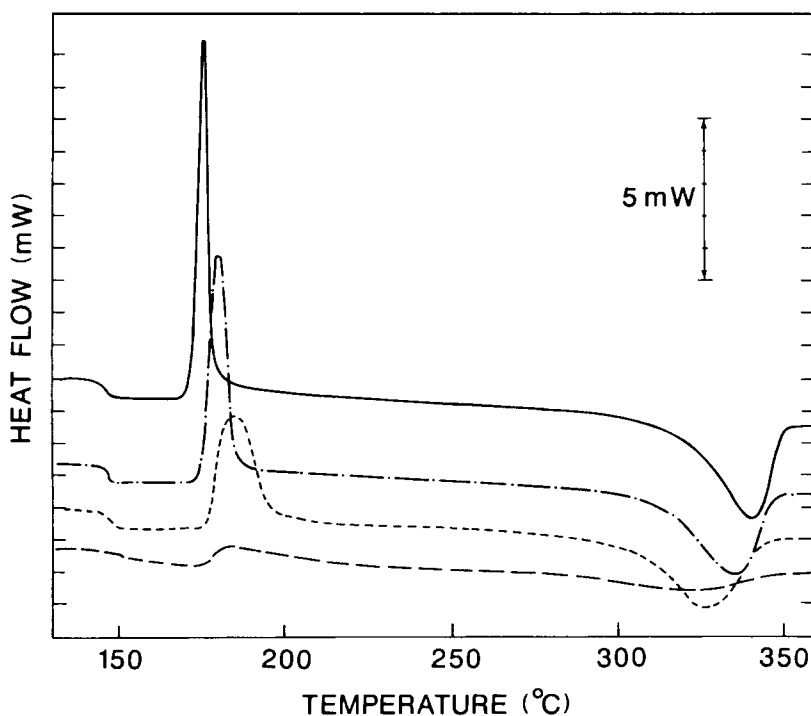


Fig. 1. DSC traces of liquid N_2 quenched PEEK samples after heating to 400°C and being held for: (—) 5 min in N_2 ; (-·-·) 120 min in N_2 ; (---) 30 min in air; (- - -) 120 min in air.

acteristics of amorphous PEEK.^{4,12} There is a T_g step at about 145°C , followed by an exothermic peak at about 175°C associated with the crystallization, and an endothermic peak at about 340°C associated with the melting of crystalline PEEK.

Examination of these representative traces indicates that changes are taking place in the morphology of PEEK. The effects of exposure temperature, exposure time, and environment on the T_g , crystallization, and melting of quenched samples are summarized in Figures 2, 3, and 4, respectively.

Three temperature values were computed for the glass transition temperature: onset temperature, midpoint temperature, and end-point temperature. These values were computed using the DuPont DSC program and correspond to the points of intersection of the tangent drawn from the point of greatest slope and the extrapolated base lines. For the sake of simplicity, only two temperatures are reported in Figure 2, the onset temperature and the midpoint temperature. Changes in the end-point temperature were found to closely reflect those of the midpoint temperature and generally were found to relate to a broadening of the glass transition. The data shown in Figure 2 suggest that heat treatment in nitrogen is having a negligible effect on the measured T_g values except for a possible very slight shift in the midpoint temperature when high temperatures are employed for long time periods. When samples are heated in air, however, noticeable changes in the measured T_g values are noted with the largest changes being noted at the higher temperatures and longer exposure times.

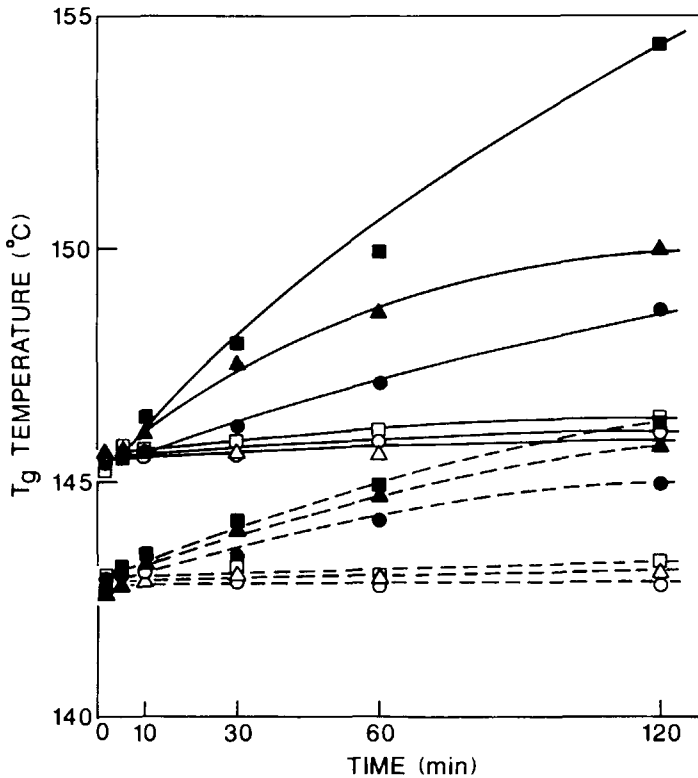


Fig. 2. Changes in onset (---) and midpoint (—) of the glass transition temperatures as a function of exposure time: (○, ●) 380°C data; (△, ▲) 400°C data; (□, ■) 420°C data. Open symbols in N₂, closed symbols in air.

The effect of exposure on the measured crystallization exotherm, as a function of temperature and hold time, are presented in Figure 3. The peak crystallization temperature was noted to increase with increased exposure time and increased temperature for experiments performed both in air and nitrogen. However, in all cases, the temperature increases were always substantially larger in air than in nitrogen. Despite shifts in the peak temperatures, the heats of crystallization of samples heated in nitrogen remained relatively constant under the test temperatures and times employed in this study. However, Figure 3 clearly indicates that at temperatures above 380°C in air, the heats of recrystallization decrease dramatically, indicating that the amount of crystallizable material is decreasing as a result of increased exposure time and temperature.

While the measured heat of recrystallization gives some indication of the amount of amorphous material capable of undergoing recrystallization, the endothermic peak associated with the melting of PEEK indicates the amount of crystalline material. Examination of the DSC scans in Figure 1 clearly show that the enthalpy of fusion is dependent upon such variables as environment, hold time, and hold temperature. The extent of these changes on the melting temperature and heat of fusion are summarized in Figure 4. These data parallel those observed for the recrystallization except that the melting point temperatures decrease, while those for recrystallization increased. For exam-

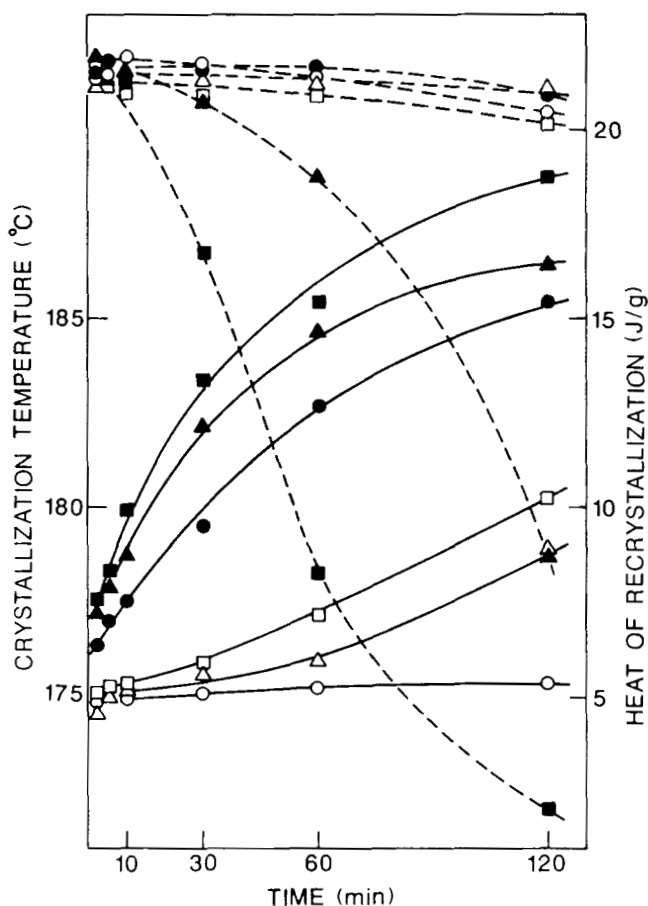


Fig. 3. Changes in recrystallization temperature maximum (—) and heat of recrystallization (---) as a function of exposure time: (○, ●) 380°C data; (△, ▲) 400°C data; (□, ■) 420°C data. Open symbols in N_2 , closed symbols in air.

ple, in a nitrogen environment, the reduction in the melting temperature is only slight as a result of heat exposure up to 420°C for even 2 h, and the measured heats of fusion remain relatively constant around 30 J/g. Thus, in a nitrogen atmosphere, the amount of crystallizable material remains relatively constant with increasing temperatures up to 420°C and hold times of up to 120 min. In air, however, the measured melting temperature and the heat of fusion decrease substantially as the exposure temperature is increased from 380 to 400 to 420°C and the hold time is increased. This information confirms that observed with the recrystallization peak, namely, that the crystallizable material is decreasing as a result of higher hold temperatures and hold times in an air environment. These observations confirm previous information noted in the crystallization behavior of PEEK when exposed to air at the melt.¹¹

Crystallization Kinetics

While the above study provided information on the morphological makeup of PEEK samples exposed to temperatures above the melt for different time periods, a study of the crystallization behavior was also undertaken. The

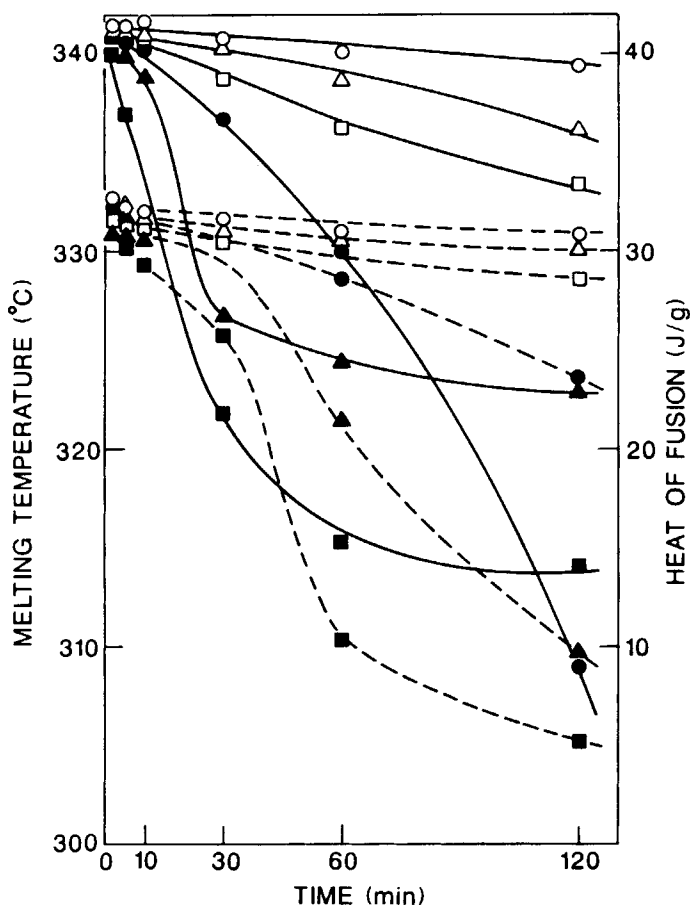


Fig. 4. Changes in melting point temperature (—) and heat of fusion (---) as a function of exposure time (○, ●) 380°C data; (△, ▲) 400°C data; (□, ■) 420°C data. Open symbols in N_2 , closed symbols in air.

isothermal crystallization kinetics were obtained from the analysis of the heat flow curve as a function of time according to the procedure utilized by Cebe and Hong.⁴ The development of the relative crystallinity as a function of time was analyzed using the Avrami equation¹³:

$$(1 - X_t) = \exp(-kt^n)$$

where X_t is the weight fraction of crystallized material at time t , k is the rate constant, and n is the Avrami exponent. The plots of $\log\{\ln[1/(1 - X_t)]\}$ against $\log(t)$ were then constructed, and n was determined from the slope and k from the intercept. When the Avrami plots were made from these data, the crystallization kinetics of the PEEK samples (see Fig. 5) were found to follow a dual mechanism, as noted by Velisaris and Seferis⁵ and observed in the data of Cebe and Hong.⁴

In the case of PEEK heated at 400°C for 10 min in nitrogen, the crystallization kinetics have an Avrami exponent of 2.4 up to about 70% completion of

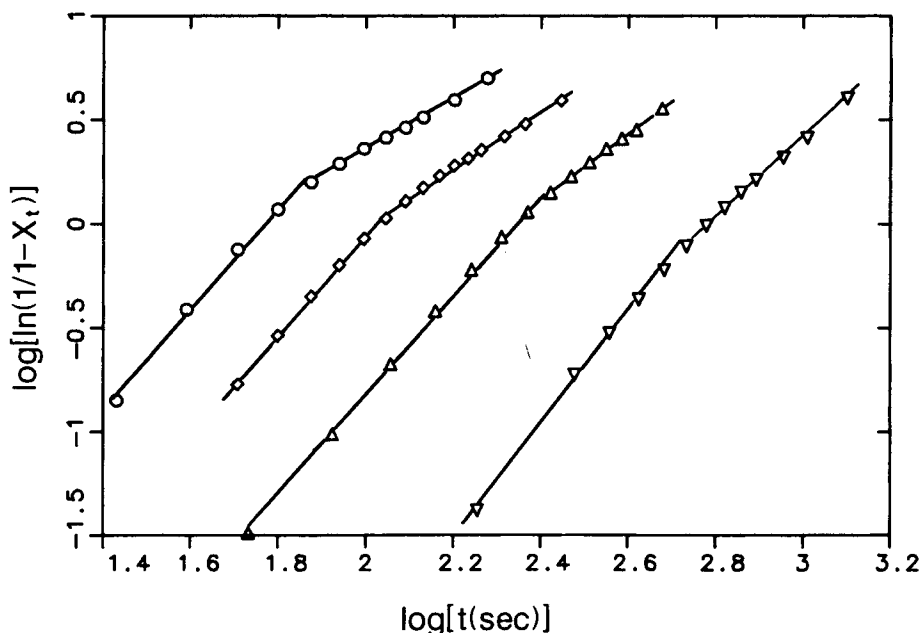


Fig. 5. Avrami crystallization plots for the isothermal crystallization of PEEK samples heated at 400°C for 10 min in N₂ and crystallized at 304°C (○), 309°C (◇), 314°C (Δ), and 319°C (▽).

the crystallization process and an Avrami exponent of 1.5 for the remainder of the crystallization process. These data confirm that reported in the literature,⁵ in which the crystallization kinetics of PEEK heated above the melt in nitrogen and then allowed to cool to an isothermal crystallization temperature involves two competing nucleating and growth processes. The Avrami exponents determined for several different heat-treated samples are summarized in Table I. In this table are listed the Avrami exponents for the first mechanism (n_1) up to about 70% relative crystallinity and the exponent for the second mechanism (n_2). These values suggest that the first process might correspond

TABLE I
Avrami Exponents for Isothermal Crystallization of Heat-Treated PEEK Samples

| Heat treatment | Avrami exponent | Approximate crystallization temperature (°C) | | | | | |
|---------------------------------------|-----------------|--|------|------|------|------|------|
| | | 294 | 299 | 304 | 309 | 314 | 319 |
| 380°C for 2 min in N ₂ | n_1 | | | 2.74 | 2.46 | 3.36 | 3.88 |
| | n_2 | | | 1.34 | 1.24 | 1.47 | 2.21 |
| 380°C for 10 min in N ₂ | n_1 | | | 2.21 | 2.61 | 2.92 | 3.49 |
| | n_2 | | | 1.22 | 1.40 | 1.48 | 2.36 |
| 400°C for 10 min in N ₂ | n_1 | | | 2.45 | 2.42 | 2.43 | 2.38 |
| | n_2 | | | 1.32 | 1.41 | 1.59 | 1.85 |
| 380°C for 10 min in air | n_1 | | 2.44 | 2.00 | 2.51 | 2.72 | |
| | n_2 | | | 1.85 | 1.14 | 1.33 | 1.78 |
| 400°C for 10 min in air | n_1 | 1.46 | 1.74 | 1.84 | 1.80 | | |
| | n_2 | — | 1.10 | 1.65 | — | | |

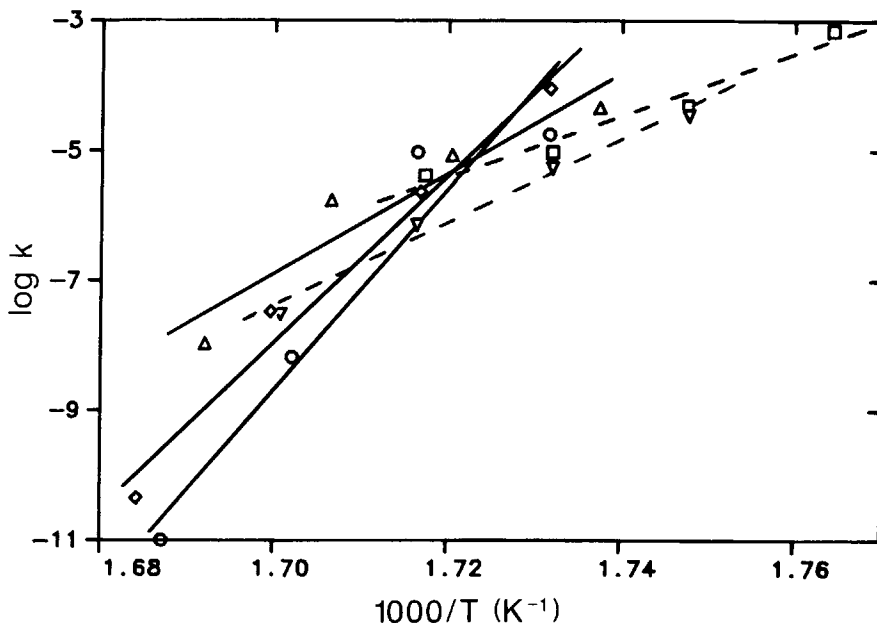


Fig. 6. Arrhenius plots for the Avrami parameter k deduced from the isothermal crystallization data for the primary crystallization process after the following heat treatments: (○) 380°C for 2 min in N_2 ; (◇) 380°C for 10 min in N_2 ; (△) 400°C for 10 min in N_2 ; (▽) 380°C for 10 min in air; (□) 400°C for 10 min in air.

to a spherulitic, diffusion-controlled growth with thermal nucleation, while the second process might correspond to rod-shaped, diffusion-controlled growth with thermal nucleation as suggested by Velisaris and Seferis.⁵

Although there appears to be some slight variation in the Avrami exponents with crystallization temperature and heat treatment of the samples, the actual magnitude of the changes are not large. This would suggest that the nucleation mechanism and crystal growth geometries are similar for all samples. Although the Avrami exponents n_1 and n_2 were very similar for the various heat-treated samples, the actual kinetic rate constants for the primary crystallization process (up to 70%) did show differences. The Arrhenius plots of $\log(k)$ against reciprocal temperature for the various PEEK samples are given in Figure 6. These plots gave the activation energies listed in Table II for the primary crystallization process. These values can be compared with

TABLE II
Arrhenius Parameters for the Primary Crystallization Process

| Heat treatment | $\log A$ (s^{-1}) | Activation energy ($MJ mol^{-1}$) |
|---------------------------|-----------------------|--|
| 380°C for 2 min in N_2 | -260 | 2.83 |
| 380°C for 10 min in N_2 | -228 | 2.48 |
| 400°C for 10 min in N_2 | -138 | 1.47 |
| 380°C for 10 min in air | -117 | 1.23 |
| 400°C for 10 min in air | -85 | 0.89 |

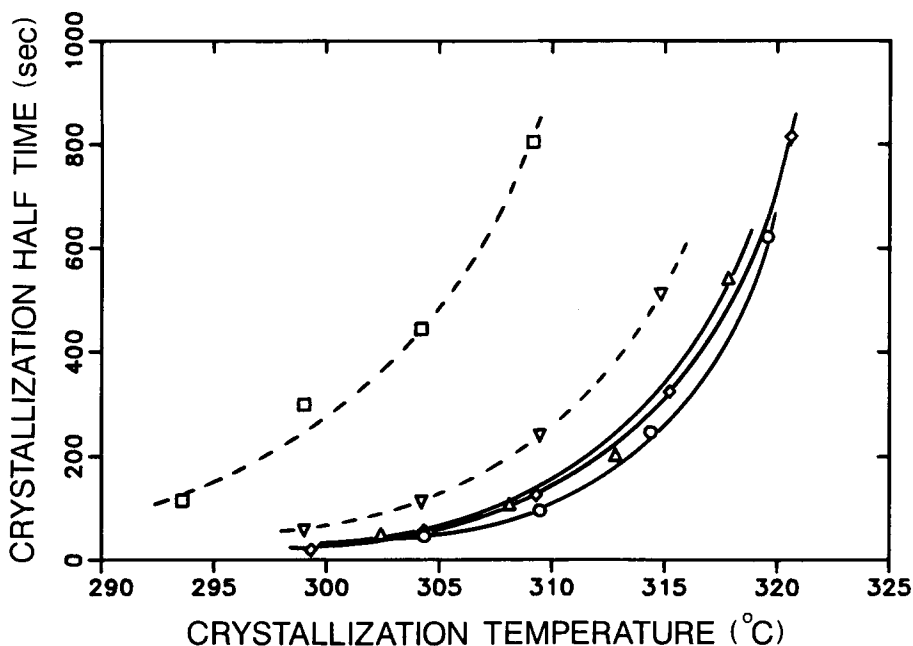


Fig. 7. Variation of crystallization half-time with crystallization temperature after the following heat treatments: (○) 380°C for 2 min in N₂; (◇) 380°C for 10 min in N₂; (Δ) 400°C for 10 min in N₂; (▽) 380°C for 10 min in air; (□) 400°C for 10 min in air.

those reported by Cebe and Hong⁴ and Kemmish and Hay¹⁴ of 0.22 and 1.35 MJ/mol, respectively. Interestingly, it would appear that heat treatment is clearly influencing the measured activation energies, with lower values being noted from samples heated for longer periods at higher temperatures. There also appear to be significant differences in rates of crystallization due to the presence of air. These differences become clearly evident when the crystallization half-time ($t_{1/2}$) is plotted as a function of crystallization temperature (Fig. 7). This crystallization half-life is defined as the time at which the extent of crystallization is 50% complete and is determined from the measured kinetic parameters, i.e.,

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{1/n}$$

Figure 7 clearly indicates that for a given crystallization temperature, the crystallization half-times of the air-treated samples are substantially higher than the corresponding heat treatments in nitrogen. It would therefore appear that oxidative exposure of PEEK above the melt for times as low as 10 min is sufficient to retard the crystallization process. This retardation is especially pronounced when melt process temperatures of 400°C and above are employed. The crystallization of PEEK is known to depend on the hold time in the melt,^{15,16} with less bulk nucleation being the result of longer melt annealing times. Although the origin of the nucleating sites is uncertain,¹⁵ it would appear that thermal exposure in air appears to be responsible for a reduction

in the number of these sites. Thermal oxidative crosslinking reactions may be responsible for this reduction in nucleation since PEEK is known to crosslink if aged at high enough temperatures (ca. 400–450°C) for sufficiently long periods of time.¹⁷ Based upon the data presented in our study, it would therefore appear that these crosslinking reactions are affecting the nucleating sites remaining after holding at the melt. These changes are then capable of affecting the rate of crystallization and degree of crystallization and consequently the related physical properties.

CONCLUSIONS

This study has shown that PEEK is sensitive to processing conditions, i.e., melt temperature, melt time, and environment. Changes in these conditions can influence the morphological values for the T_g , the crystallization and melting processes as measured by DSC. The kinetics of the crystallization processes are also changed with different environments with oxidative reactions appearing to be the precursor of crosslinking reactions. Data presented in this study indicate that the longer the time and the higher the temperature that PEEK is held in the melt, the greater is the reduction in the recrystallizable material in the final product and the longer will be the annealing time. Based upon previous studies which have demonstrated the importance of morphology in the physical properties of resultant materials,⁷⁻⁹ it follows that careful control of the processing conditions is required in PEEK fabrication. To minimize these thermal effects, PEEK should be processed in a nonoxidative atmosphere, preferably at temperatures below 400°C. Reheating of PEEK composites (e.g., for repair, or adjustment of a layup) may result in morphological changes unless these processing conditions are carefully controlled.

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