

# Annealing Effects on the Crystallinity of Polyetheretherketone (PEEK) and Its Carbon Fiber Composite

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## Synopsis

The degree of crystallinity of polyetheretherketone (PEEK) has been measured using both the density gradient technique (DGT) and differential scanning calorimetry (DSC). The difference in results between the methods was shown to depend on crystallization taking place during the heating scan in the DSC. By freezing the sample at different stages of the DSC thermogram and measuring its crystallinity in the density gradient column, the existence of induced crystallization for PEEK was established. Though this induced crystallization is not visible in the DSC thermogram, it must be taken into account when comparing the degree of crystallinity measured by the two methods. The induced crystallization was in turn interpreted as a result of an increase in crystal perfection that is also commonly observed during the initial stages of the annealing process. Accordingly, the effect of annealing on the crystallinity was also investigated. DSC scans on annealed samples exhibited a small endothermic peak at approximately 10°C above the annealing temperature. This peak was observed in both neat PEEK and its carbon fiber-reinforced composite. Annealed PEEK shows, therefore, two melting transitions, a low one which depends on the annealing temperature and a high one which is independent of annealing temperature conditions. Collectively, the results of this study demonstrate that processing conditions and morphological features must be considered in characterizing semicrystalline-based matrix polymers for high performance composites.

## INTRODUCTION

Polyetheretherketone (PEEK) is a semicrystalline polymer that is becoming a model for thermoplastic matrix systems for high performance carbon fiber-reinforced composites. As a semicrystalline polymer, the morphology of PEEK and the resulting properties can be influenced by the processing conditions employed during the lamination and shaping operation of the composite.<sup>1-4</sup> The mechanical properties, among other factors, depend on the degree of crystallinity of the matrix polymer.<sup>5-10</sup>

It has been established that PEEK behaves in many ways like polyethyleneterephthalate (PET). PET's behavior is more well known, due to the extensive investigations that have been performed with this material. For example, it has been found that both PEEK and PET show two endothermic fusion peaks, where the lower temperature fusion peak was found to have been induced by the annealing process.<sup>11-15</sup> PEEK has a relatively high glass transition temperature and melting point, 144°C and 342°C respectively,

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which makes this polymer particularly attractive as a matrix material for high performance composite applications.<sup>15</sup>

Although progress toward the understanding of the PEEK morphology and its effect on properties has been made, there is still a need for a fundamental understanding of morphological, processing, and property characterizations. For example, it was found that even basic measurements for the degree of crystallinity of PEEK, both in its neat and composite form, sometimes gave totally different results depending on the method used.

All methods for determining the degree of crystallinity in semicrystalline polymers are based on the assumption of a two-phase system, and they all involve uncertainties in the data analysis. X-ray diffraction is regarded as the foremost method of assessing polymer crystallinity. However, the density gradient technique (DGT) will often correlate well with the former. The major drawback of the DGT is its sensitivity to voids. This problem is especially pronounced when considering composite laminates which often contain a certain amount of voids. Another technique available, which is not as sensitive to voids, is differential scanning calorimetry (DSC), in which the crystallinity is taken as the area underneath the melting peak. DSC is often used due to its ease of application; however, it is not without drawbacks, as well. The main problem concerns the definition of a proper baseline.<sup>16,17</sup> Another problem is the fact that crystallization takes place during the heating scan.<sup>13,18,19</sup> Hughes and Sheldon<sup>18</sup> found that for amorphous PET, the apparent area under the melting peak was significantly larger than the apparent area under the crystallization peak. They suggested that the crystallization peak was followed by a continuous crystallization taking place, which was undetectable in the thermogram baseline. PEEK will also show a higher value of the degree of crystallinity when measured by DSC and compared to DGT measurements. Accordingly, this work was undertaken to investigate the morphological changes which take place in PEEK during the DSC scan as they relate to annealing the polymer as a processing step. Accordingly, the thermal behavior of samples annealed at different temperatures was investigated, as well as the heating rate of dependence of the degree of crystallinity.

## EXPERIMENTAL

### Materials

The starting neat polymer was a low crystallinity PEEK film with a crystal volume fraction  $V_c = 0.018$ . The film was made from Imperial Chemical Industries (ICI) Victrex PEEK pellets 450 G. For neat PEEK studies, two additional samples were prepared, by annealing the as-received film: one at 210°C for one hour, and one at 310°C for one hour. The annealing was performed in a forced-air oven, and the samples were then allowed to cool slowly to room temperature in the oven.

Carbon fiber-reinforced PEEK, APC-2, supplied by ICI, was also investigated in this study, in order to compare the effect of annealing between the neat and composite samples. Although the morphology of the polymer in the composite is probably different from the neat polymer, the same thermal behavior can be expected from the two materials. For the as-received APC-2

composite prepreg sample, the weight fraction of carbon fibers was 68%, and the nominal degree of crystallinity was approximately  $V_c = 0.25$ .<sup>7</sup> A series of neat PEEK and APC-2 samples were prepared for the annealing studies by annealing the as-received sample for 30 min at various temperatures in the DSC.

### Methods

The degree of crystallinity of both composite samples was measured by differential scanning calorimetry (DSC) and density gradient technique (DGT).

The DSC thermograms were obtained using a DuPont 912 differential scanning calorimeter attached to a DuPont 9900 thermal analysis system. The experiments were carried out in an air atmosphere with specimens of approximately 10 and 20 mg, respectively, on both neat PEEK and APC-2. The scans were obtained at 20°C/min and each value of the degree of crystallinity was obtained by averaging the values from five different scans of the same sample. The degree of crystallinity was calculated from the expression:

$$X_{mc} = \frac{H_m - H_a}{H_f(1 - x_{mr})}$$

where  $X_{mc}$  = mass fraction of crystallinity

$H_m$  = heat of fusion at  $T_m$ , measured as the area under the melting peak

$H_a$  = heat of additional crystallization measured as the area under the exothermic crystallization peak

$H_f$  = theoretical heat of fusion for a pure crystalline phase

$x_{mr}$  = mass fraction of reinforcement

The mass fraction crystallinity can be converted to volume fraction crystallinity by the equation:

$$X_{vc} = \frac{X_{mc}\rho_{nc}}{\rho_c - X_{mc}(\rho_c - \rho_{nc})}$$

where  $X_{vc}$  = volume fraction crystallinity

$\rho_{nc}$  = density of the noncrystalline phase

$\rho_c$  = density of the crystalline phase

The crystal heat of fusion is known to be 130 J/g (15).

The density of neat PEEK was measured with a density gradient column prepared from aqueous solutions of calcium nitrate with a density range of 1.25 g/cm<sup>3</sup> to 1.35 g/cm<sup>3</sup>. Each DGT crystallinity value is the average value of three different measurements of the same sample. The degree of crystallinity was calculated from density measurements using the following expression:<sup>1,7</sup>

$$X_{vc} = \frac{\rho_b - \rho_r x_{vr} - \rho_{nc}(1 - x_{vr})}{(1 - x_{vr})(\rho_c - \rho_{nc})}$$

where  $\rho_b$  = measured bulk density of the composite  
 $\rho_r$  = density of the reinforcing phase  
 $x_{vr}$  = volume fraction of the reinforcing phase

The density of the noncrystalline and crystalline phase is known to be 1.2626 g/cm<sup>3</sup> and the crystal density 1.4006 g/cm<sup>3</sup> (15).

## RESULTS AND DISCUSSION

### Induced Crystallization

The degree of crystallinity was measured on the three neat PEEK samples using both the DSC and DGT. Table I shows the results measured using the two methods. Comparing samples 1 and 2, the difference in the values is larger at a lower degree of crystallinity. The PEEK sample annealed at 310°C gave identical crystallinity values as measured by the DSC and the DGT. This indicated that additional crystallization had taken place during the DSC scan, even though it was not possible to detect this in the DSC thermogram. The DSC thermograms of the three samples are shown in Figure 1. This behavior has been shown to occur for other polymers which can crystallize by heating them above their glass transition temperature.<sup>13,18,20</sup> It has been suggested

TABLE I  
The Degree of Crystallinity of Neat PEEK Obtained by DSC and DGT

Sample	$X_{vc}$ (DGT). % ±	$X_{vc}$ (DSC) % ±
1	1.8 ± 0.12	11.1 ± 0.22
2	22.0 ± 0.18	28.2 ± 0.61
3	32.6 ± 0.16	32.2 ± 0.23

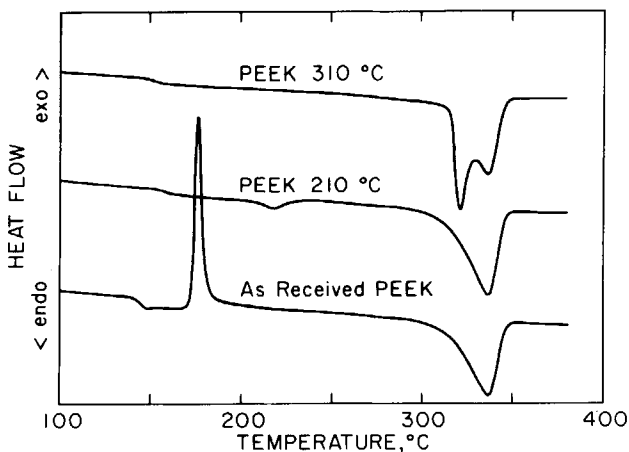


Fig. 1. DSC heating scans at 20°C/min for as-received PEEK, PEEK annealed at 210°C for 1 hour, and PEEK annealed at 310°C for 1 hour.

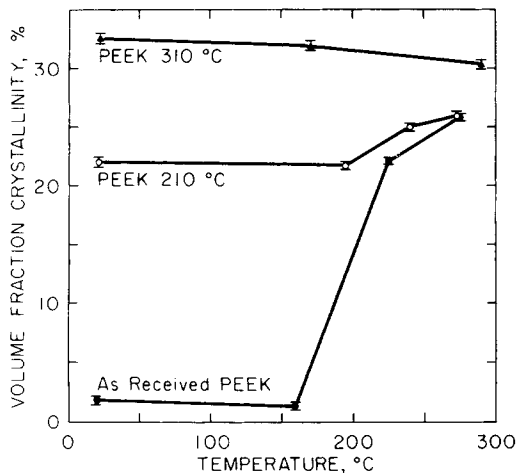


Fig. 2. Volume fraction crystallinity measured by the density gradient technique as a function of temperature, to which the sample was first heated in the DSC at a rate of  $20^{\circ}\text{C}/\text{min}$  and then quenched.

that during the heating between the glass transition and the melting point, partial melting and recrystallization take place which result in a higher degree of perfection in the crystalline regions.<sup>11,12,20,21</sup> Optical microscopy on PET has revealed that the changes occurred within the original spherulites.<sup>20,22</sup>

In order to verify that the degree of crystallinity increases during a heated scan, the following experimental testing procedure was performed. Each sample was heated in the DSC to a predetermined temperature, followed by quenching, and subsequent measurement of the degree of crystallinity in the density gradient column. Figure 2 shows the results of such measurements on the three PEEK samples. The volume fraction crystallinity measured by DGT is plotted as a function of the temperature to which the sample had been heated during the DSC scan. Focusing on the as-received sample of Figure 2, it appears that the crystallinity remains constant up to the recrystallization transition, which is seen as an exothermic peak in the DSC thermogram. The recrystallization transition, as measured by the DSC from the area under the exothermic peak, was found to be 18.8% by volume. Since the as-received sample was 1.8% by volume crystallinity originally, the overall degree of crystallinity after the DSC scan was calculated as the sum of these two processes, viz. 20.2%. Comparing this to 22.2% which is calculated from DGT data, the two methods can be seen to yield comparable values. The peak area of the recrystallization is difficult to define (i.e., define an appropriate baseline). This may be attributed to a change in the heat capacity during the transition, and to a long tail of the crystallization transition. For the samples heated to just before the melting initiation, the degree of crystallinity increases further by 4%. This additional crystallization is not visible in the DSC thermogram, and can therefore be referred to as the induced crystallization.

The PEEK film annealed at  $210^{\circ}\text{C}$  showed similar behavior. No induced crystallization was observed before the annealing temperature, which shows that the amount of material that could be affected by slow heating has already crystallized during the annealing. This is in agreement with

Zachmann et al., who found that the increase in perfection occurs within the first few minutes of the annealing process.<sup>11, 12, 21</sup> Heating above the annealing temperature caused further induced crystallization to occur. For this sample, induced crystallization of 4% took place up to a temperature just before the melting initiation. It is important to note that the quantitative determination of the induced crystallization has only been done when no other transitions were present in the DSC thermogram. The induced crystallization probably takes place continuously between the glass transition or the annealing temperature (for annealed materials), and the melting temperature.

For the sample annealed at 310°C, no induced crystallization was observed, which was expected from the results of the sample annealed at 210°C. Instead, the degree of crystallinity has slightly decreased, possibly due to the melting of low molecular weight crystals. Similarly for PET, Zachmann and Stuart<sup>11, 12</sup> have found that on heating "well-crystallized" samples, only partial melting occurred without recrystallization.

From the above results, it may be concluded that when PEEK is scanned in a DSC it may be assumed that low temperature-formed crystalline regions increase in perfection as a result of partial melting and recrystallization during the scan, which leads to an overall increase in the degree of crystallinity. Heating an as-received low crystallinity PEEK sample in the DSC to a specific temperature above the recrystallization temperature, and subsequently cooling the sample immediately and then running the sample again, causes a small endothermic peak just above this specific temperature. Thus it is possible to conclude that the structural changes taking place in PEEK during a thermal scan may be viewed as similar to those in PET.

It may also be expected that the PEEK-based composite, APC-2, would also exhibit this behavior. It was observed that heating the composite material to a certain temperature followed by an immediate cool down, and subsequent rerun will cause a small endothermic peak to appear, just as with neat PEEK. However, due to high void content of the as-received prepreg PEEK APC-2 material, no reliable quantitative degree of crystallinity could be obtained using density measurements. In this case, other techniques such as X-ray diffraction or Fourier transform infrared spectroscopy must be used where the void content can be accounted for explicitly in crystallinity measurements and calculations.<sup>6</sup>

### Effect of Annealing

It is well known that annealing above the glass transition will cause structural changes to occur, such as an increase in the perfection and the growth of crystalline regions.<sup>23, 24</sup> The increase in perfection occurs during the first few minutes of the annealing, while the growth of the crystalline regions occurs at a longer duration of the annealing process. It was shown above that the perfection process was fast enough to change the crystallinity of the polymer during the DSC scan. However, the exact physical changes behind these phenomena are not easily explained. For example, it was seen in Figure 2 that annealing will cause an extra small endothermic peak to appear in a thermal scan just above the annealing temperature. Two melting transitions have been reported earlier on several other materials<sup>13, 25, 26</sup> and specifi-

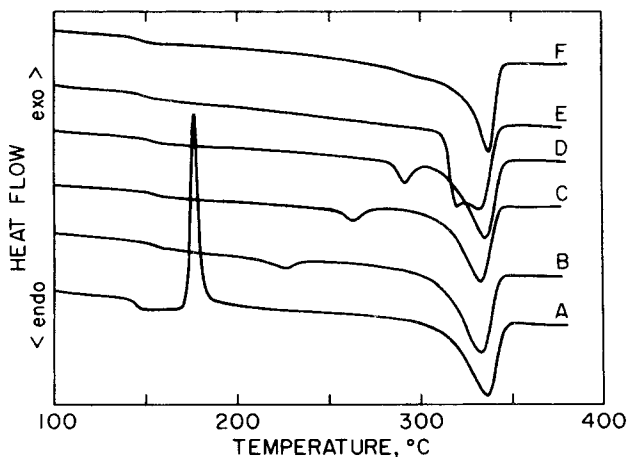


Fig. 3. DSC scans performed at 20°C/min of neat PEEK annealed at different temperatures: (A) as-received, (B) 210°C/30 min, (C) 250°C/30 min, (D) 280°C/30 min, (E) 310°C/30 min, (F) 350°C/30 min.

cally on PEEK by Blundell and Osborn.<sup>15</sup> The transition can be moved to higher temperatures simply by annealing the sample at higher temperatures. Figure 3 shows the thermogram of neat PEEK annealed at several different temperatures, each for 30 min. The higher the annealing temperature, the higher the melting peak temperature. In addition, the area under this peak was observed to increase with increasing annealing temperatures. The higher melting peak temperature remained constant over the range of annealing temperatures examined. At low temperatures the peak area of the low melting peak was rather small, approximately 5% of the higher melting peak for a sample annealed at 210°C. But for higher annealing temperatures, the area increased at the expense of the higher melting peak area. The low peak temperature was also shown to depend on the annealing time. An as-received sample annealed at 210°C for 30 minutes exhibited a peak temperature of 225°C, while a sample annealed at the same temperature for 12 hours showed a peak temperature of 233°C. This observation is consistent with earlier work where annealing at a given temperature will produce a higher crystal population of an intermediate perfection. The increase in perfection which occurs during the heat treatment is also followed by additional crystal growth which occurs at longer annealing times.<sup>11,12,20</sup> When an annealed sample is reheated, the heat of fusions from this population may be observed as an additional melting transition.

The noncrystal region may also be affected by annealing.<sup>23,24,27</sup> Depending upon the detailed macromolecular structure of the polymer, the mobility of the molecules adjacent to crystals may be assumed to be restricted. Thus, as an initial approximation, the glass transition can be used as an indicator of the interaction between the noncrystal and crystal regions.<sup>23</sup> Figure 4 shows the glass transition temperature as determined from the DSC scans as a function of the volume fraction crystallinity for the three PEEK samples investigated in Figure 1. The glass transition temperature is higher for the sample with 22.0% crystallinity than the sample with 32.6%. This could

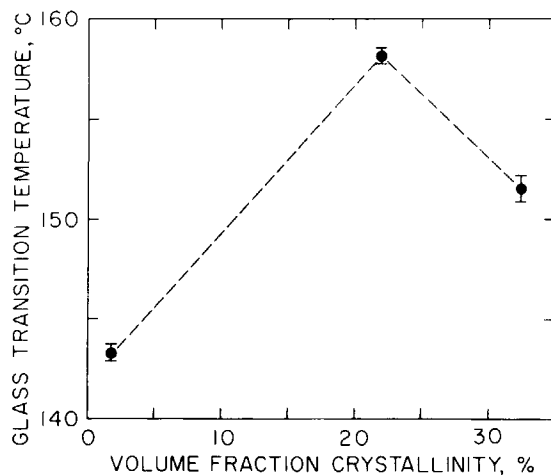


Fig. 4. Glass transition temperature of neat PEEK as measured by the DSC as a function of the degree of crystallinity measured by the DGT.

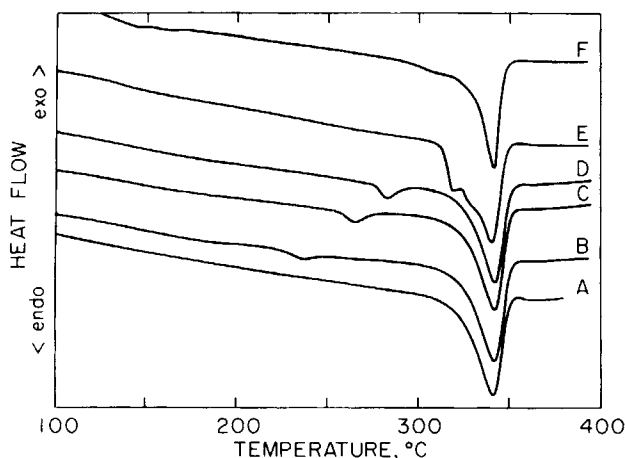


Fig. 5. DSC scans performed at 20°C/min of carbon fiber-reinforced PEEK composite (APC-2) annealed at different temperatures: (A) as-received, (B) 220°C/30 min, (C) 250°C/30 min, (D) 270°C/30 min, (E) 310°C/30 min, (F) 350°C/30 min.

indicate that at higher annealing temperature, the relaxation phenomena of noncrystalline regions influence the restriction caused by increases in the size and perfection of the crystal regions. Longer annealing time may also allow stresses to relax.

Finally, Figure 5 shows the effect of annealing temperatures on the thermal behavior of APC-2. Two endothermic peaks also appear here, showing that annealing causes structural changes similar or equal to those in neat PEEK. This further supports the assumption put forth earlier, that the heat of fusion measurements on the composite includes the induced crystallization phenomenon.



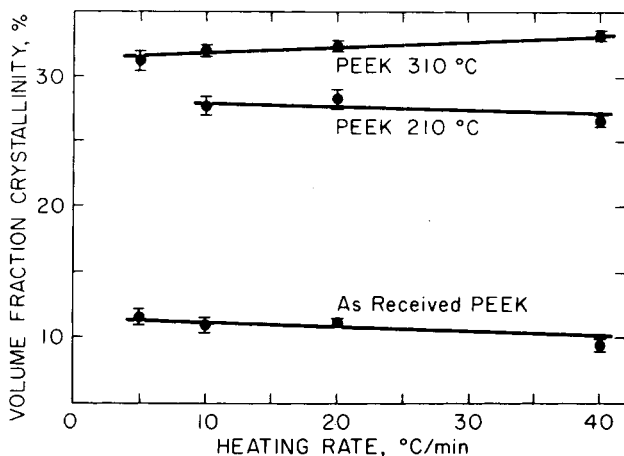


Fig. 6. Volume fraction crystallinity of neat PEEK, measured by the DSC, as a function of the heating rate.

### Effect of Heating Rate

The effect of the heating rate during the DSC scan on the overall degree of crystallinity was also examined for the three PEEK samples. This was done to provide an indication of how fast the induced crystallization occurs, which will be useful in future modelling studies. Figure 6 demonstrates the degree of crystallinity as a function of heating rate. The crystallinity remains fairly constant over the chosen range of heating rate. This indicates that the induced crystallization that takes place during the DSC scan occurs rapidly, as has been observed in previous studies.<sup>11,12</sup> Thus, from these results, it may be concluded that the induced crystallization may be a consequence of the changes in crystal perfection that occurs within the first few minutes of the annealing process.

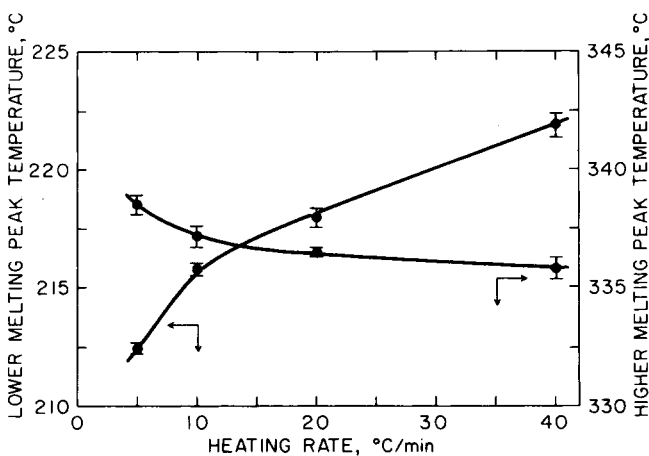


Fig. 7. Melting peak temperature of the two fusion transitions as a function of the DSC scan heating rate.

It is of interest to note the heating rate dependence of the two melting peaks. Figure 7 shows the melting peak temperatures of the two peaks, as a function of the heating rate for the sample annealed at 210°C. The higher melting peak indicates a typical heating rate dependency of a semicrystalline polymer that undergoes reorganization during the DSC scan, while the lower melting peak shows a superheating behavior.<sup>28,29</sup> Fakirov et al.,<sup>29</sup> in studying the melting behavior of PET, proposed that the superheating effect was due to the two competitive processes of melting and recrystallization. The heating rate dependence of the two peaks of the PEEK sample annealed at 310°C is the same as that for a PEEK sample annealed at 210°C, although the exact positions of the peaks are difficult to discern, due to overlapping. It was also possible to show the same heating rate dependence of the two peaks of carbon-reinforced PEEK composite, which indicates that the process observed with the neat PEEK matrix also takes place in the composite.

### CONCLUSIONS

The degree of crystallinity of PEEK measured using differential scanning calorimetry was compared with density gradient technique measurements. It was found that the difference between the methods was larger at a low degree of crystallinity with the DSC giving a higher value. The observed difference was shown to be due to induced crystallization taking place during the heating of the sample during the DSC experiment. Although this induced crystallization cannot be explicitly detected in the DSC thermogram, it results in a higher calculated overall degree of crystallinity by the DSC method. Thus these DSC scans may not be a direct reflection of the state of the PEEK polymer at room temperature. This was shown by freezing the PEEK samples at different stages of the DSC thermogram and measuring its degree of crystallinity by DGT. For a PEEK sample annealed at 210°C and scanned using the DSC, the induced crystallinity was of the order of 4%, up to a temperature just before the melting initiation. The induced crystallization was observed solely at the temperatures above the annealing temperature of the sample. This may be attributed to changes in perfection of the crystalline regions, which may occur during the initial stage of an annealing treatment. However, by accounting for the induced crystallization taking place during the heating scan, the crystallinity measured by DSC can become an acceptable method for quantitative measurements of crystallinity in both neat and composite samples.

Annealing of both neat PEEK and carbon fiber-reinforced PEEK composite demonstrated the emergence of an additional melting peak just above the annealing temperature. This additional peak was observed to increase in area as the annealing temperature at a given time approached the melting point. Furthermore, changes in the glass transition temperature of samples with different degrees of crystallinity indicated that the noncrystalline regions were also affected by the annealing process.

The heating rate dependence of the degree of crystallinity further supports the hypothesis that the induced crystallization may be viewed as a result of the increase in crystal perfections that occur within the first few minutes

of the annealing process. These effects of annealing observed on neat PEEK were also observed on the APC-2 composite.

Collectively, the results of this work have demonstrated that both processing histories and morphological features must be considered when comparing and utilizing different characterization techniques for semicrystalline-based matrix polymers for high performance composites.

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