Uniaxial Draw of Poly(ether ether ketone)/Poly(ether imide) Blends by Solid-State Coextrusion

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ABSTRACT: Amorphous and crystalline blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) have been drawn uniaxially by solid-state coextrusion over the whole composition range. The amorphous blends have been drawn at 125 °C which is below the T_gs of these compatible blends, and the crystalline blends have been drawn at 125 °C and also at 225 °C, which is above the single T_g. Reported are the effect of draw on T_g, PEEK crystallization, and the respective orientations of PEEK and PEI in the drawn blends. The T_gs of the miscible amorphous PEEK/PEI blends are depressed up to 6 °C by draw, but their densities are slightly increased, contrary to conventional free volume theory. The density of the crystalline PEEK drawn at 125 °C exhibits a minimum at an extrusion draw ratio (EDR) of about 2.0, whereas that of the crystalline PEEK drawn at 225 °C increases monotonically with EDR. The densities of the crystalline blends drawn at both 125 and 225 °C decrease monotonically with EDR. These observations are attributable to the interplay between the destruction of the lower-melting PEEK crystals and the increasing packing in the amorphous regions on drawing. The effect of draw on the crystallization kinetics of PEEK and in PEEK/PEI blends has been evaluated by DSC. PEEK in the drawn blends crystallizes faster on cold crystallization. On the other hand, when the samples were annealed in the melt followed by crystallization (melt crystallization), the drawn PEEK crystallizes slower than the undrawn PEEK. The orientations of PEEK and PEI in the amorphous drawn blends were studied by infrared dichroism. It is found that the orientations of both PEEK and PEI at a given draw ratio increase with increasing PEEK content in the blends.

Introduction

Poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) are both high-performance polymers with good thermal and mechanical properties. PEEK is semicrystalline with the normally observed melting temperature of 335–340 °C. The T_g of amorphous PEEK is 145 °C. PEI is a linear amorphous polymer with a high T_g of 215 °C. The blends of PEEK and PEI have been the subject of several investigations.[1–6] These two polymers were found to be miscible over the whole composition range in the melt.[1–3] Related investigations for the undrawn PEEK/PEI blends including crystallization behavior[1–6] and morphology[2–6] have been reported.

It is known that the tensile moduli of polymers can be increased by uniaxial draw. This process can create oriented and extended chains, such that the stiffness and strength of the sample along the draw direction are improved. Solid-state coextrusion is a uniaxial drawing technique developed in this laboratory, which offers advantages for producing high-modulus polymers.[7] Prior drawing studies of pure PEEK by solid-state coextrusion have been reported.[8,9]

There is an abundant literature on the uniaxial draw of homopolymers; however, such studies on polymer blends are relatively rare. There has been no prior study on the deformation behavior of PEEK/PEI blends. Since PEEK and PEI are miscible in the amorphous state and PEEK can undergo crystallization at temperatures above T_g,[1–6] it is of interest to explore the effect of uniaxial deformation on the physical properties of PEEK/PEI blends, such as T_g, PEEK crystallization, and the respective orientations of PEEK and PEI in their blends. Of interest for the draw of these blends is any change in miscibility, possible differential draw, and any crystallinity changes induced by draw starting with crystalline or amorphous PEEK.

In this paper, the uniaxial draw of PEEK/PEI blends by solid-state coextrusion is described. The amorphous blends were drawn at 125 °C which is below the T_gs of the blends, and the crystalline blends were drawn at 125 °C and also at 225 °C which is above the T_gs of the blends. The T_g trends, density, PEEK crystallization, and the orientations of PEEK and PEI in the drawn blends will be discussed.

Experimental Section

1. Sample Preparation. PEEK powder was acquired from Imperial Chemical Industries (ICI), Wilton, U.K. The molecular weights are M_n = 16 800 and M_w = 39 800. PEI was obtained from General Electric (GE, Ultem 1000). The molecular weights are M_n = 12 000 and M_w = 30 000.

Blends of PEEK and PEI were prepared by solution precipitation from dichloroacetic acid (boiling point = 194 °C). The concentration of polymers in the solvent was 4% (w/v). The mixtures were heated with stirring to 150 °C and were held at this temperature until homogeneous solutions were observed. After cooling to room temperature, the solutions were poured into a 10-fold excess volume of a methanol and water mixture (50/50 (v/v)). The precipitates were filtered, washed with a large amount of water, and then dried in a vacuum over at 95 °C to constant weight.

Fully amorphous films of PEEK and PEEK/PEI blends for solid-state coextrusion were prepared by compression molding at 400 °C under vacuum for 3 min followed by quenching in cold water. The crystalline films were obtained by annealing the initial amorphous films at 265 °C for 3.5 h.

Isotactic polypropylene (PP) rods were used as coextrudates for the uniaxial draw of PEEK/PEI blend films by solid-state coextrusion at 125 °C, and Nylon 6 rods were used for the draw at 225 °C. The PEEK films were cut and inserted as a ribbon within the PP or Nylon split billet and then press fitted into

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the $^3/_8$-in.-diameter barrel of an Instron capillary rheometer. The billet assemblies were then extruded through a conical brass die of 20° entrance angle. The extrusion draw ratio (EDR) was determined from the displacement of lateral ink marks placed initially on the ribbon surface before (l_0) and measured after extrusion (l_t), viz., EDR = l_t/l_0.

2. Thermal Analysis. The glass transition and PEEK crystallization in drawn PEEK/PEI blends were studied by a Perkin-Elmer DSC-7. The DSC scans were all at a heating or cooling rate of 20 °C/min. The DSC thermograms were normalized to 1 mg of the sample.

3. Density Measurement. The densities of the uniaxially drawn PEEK/PEI blends were measured by a density gradient column at 23 °C. A calcium nitrate aqueous solution was used to establish the density gradient ranging from 1.2400 to 1.4000 g/cm^3. The sensitivity of the column was about 0.0001 g/cm^3.

4. Infrared Dichroism. The relative orientations of PEEK and PEI in the drawn blends were determined by infrared dichroism. The infrared dichroic ratios were measured by an IBM IR/32 Fourier transform infrared spectrometer with a resolution of 2 cm^{-1} after computer-averaging 256 scans. The polarization of the incident beam was realized by a Perkin-Elmer gold wire-grid polarizer. The infrared dichroic ratio was calculated as $D = A_{par}/A_{per}$, with A_{par} and A_{per} being the optical densities at the absorption maximum.[10]

Results and Discussion

1. Uniaxial Draw of Amorphous PEEK/PEI Blends. Drawing experiments on amorphous PEEK by solid-state coextrusion at 154 °C have been reported.[8,9] Because this temperature is above the T_g of PEEK, PEEK crystallized during drawing. In the present study, amorphous PEEK and PEEK/PEI blends were drawn at 125 °C, which is below the T_g (cold drawing). Since there is no thermally-induced crystallization in cold drawing, the structural change of amorphous PEEK/PEI blends is induced solely by drawing.

The effect of draw on the T_gs of amorphous PEEK/PEI blends has been studied. Figure 1 shows the T_g regions of amorphous drawn PEEK and the 50/50 blend. The exotherms observed in the DSC traces are due to the cold crystallization of PEEK. It can be seen that the T_gs of both PEEK and the blend are depressed by drawing. The T_gs of amorphous PEEK and 50/50 blends are decreased by about 6 °C as the EDR reached 2.8, as seen in parts a and b of Figure 1. Figure 2 displays the T_g vs EDR plot. The T_g depression by drawing is seen to occur over the whole composition range. It is also noted that, in contrast to T_g, the heat capacity increment at the glass transition (ΔC_p) is increased by drawing, as can be seen in Figure 1. The increase in ΔC_p may be expected from the Simha–Boyer rule, which suggested the product $T_g \Delta C_p$ is a constant.[11]

It has been established that tensile stretching may lower the T_g of a polymer.[12-17] The decrease in T_g with increasing tensile stress has been ascribed to the increase in free volume with increasing applied stress.[13,17] The increase in free volume upon tensile stretching is visualized by the experimental observation that tensile stretching is normally a dilation process (the Poisson's ratio of a glassy polymer is normally less than $^1/_2$, and hence the volume is increased by elongation).[13-15] The theoretical treatment by Chow has provided a quantitative prediction for the tensile stress dependence of T_g.[17]

To test if the volume of amorphous PEEK/PEI blends was increased by drawing (so that the conventional free volume theory can explain the observed T_g depression by drawing), the densities of the drawn samples were measured. Figure 3 is the plot of the measured density vs EDR for the drawn amorphous PEEK/PEI blends. Over the whole composition range, the density increases with increasing EDR, which is not expected from the conventional free volume concept.

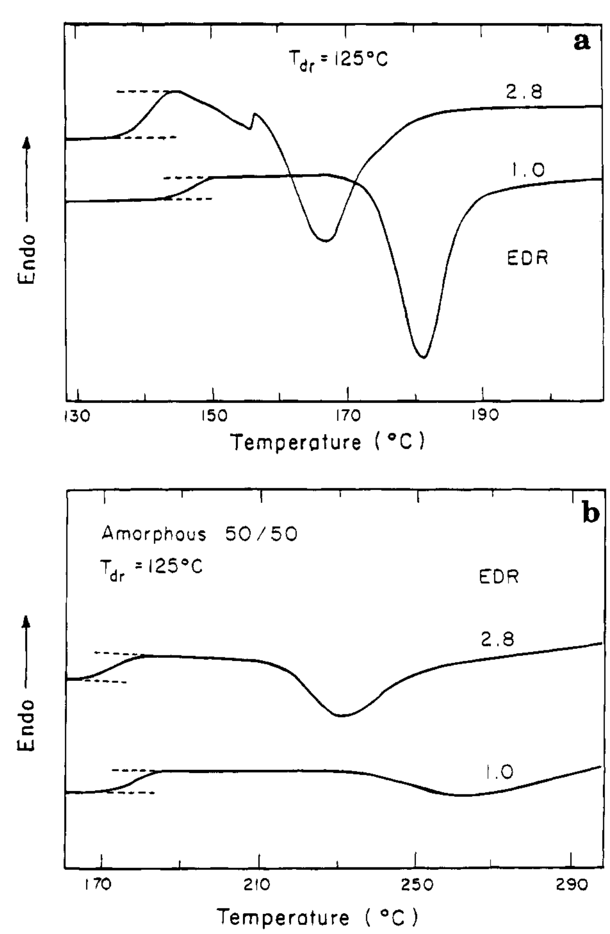

Figure 1. DSC scans of (a) amorphous PEEK and (b) an amorphous PEEK/PEI 75/25 blend drawn at 125 °C.

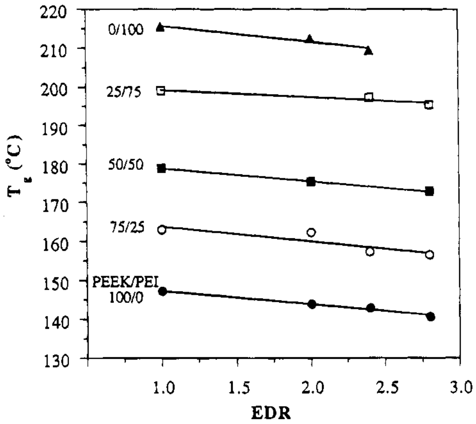

Figure 2. Variation of T_g with EDR of amorphous PEEK/PEI blends drawn at 125 °C.

During the drawing of the blends, crystallization of PEEK may be induced. Such crystallization will shift the concentration of the amorphous phase, and consequently a shift in T_g is expected. However, if such a process takes place in PEEK/PEI blends on drawing, the blend T_g should be increased rather than be decreased by drawing, since the concentration of PEI in the amorphous phase is increased upon PEEK crystallization. Therefore, the observed T_g depression cannot be explained by the possible occurrence of strain-induced crystallization of PEEK in the blends. The X-ray scattering studies on the structural change accompanying volume change in polystyrene have been reported

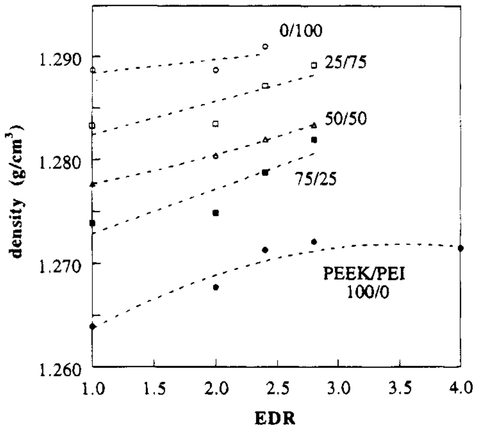

Figure 3. Variation of density with EDR of amorphous PEEK/PEI blends drawn at 125 °C.

by Song and Roe.[18] The results suggested that the specific volume alone is not sufficient to characterize the glassy state. The local segmental packing or the free volume distribution is another parameter that should be considered. Therefore, it is likely that cold drawing of PEEK/PEI blends has altered the segmental packing, the chain conformation, and the distribution of free volume to such an extent that it induced the depression in T_g is spite of the increased density.

In this study, the maximum draw ratio obtained for PEEK film is 4, and this was achieved by two-stage solid-state coextrusion. This draw ratio could not be achieved for the blends. For pure PEI, the maximum draw ratio was only 2.4, and a further increase in the drawing temperature to 230 °C did not increase the drawability of PEI. Strain-induced crystallization is observed for amorphous PEEK. Figure 4a displays the DSC scans of PEEK drawn from the amorphous state at 125 °C. It can be seen that the cold crystallization exotherm on heating is not observed for PEEK at EDR = 4.0, consistent with the crystallization of PEEK having been induced by drawing. Figure 4b shows the plot of the fractional crystallinity determined from the enthalpy of melting vs EDR of PEEK drawn from the amorphous state at 125 °C. The crystallinity increases with increasing EDR, confirming that the crystallization of PEEK has been induced by drawing.

2. Density Changes of Drawn Crystalline PEEK/PEI Blends. The density changes on drawing of the crystalline PEEK/PEI blends have been investigated. Figure 5 displays the density vs EDR plot of crystalline PEEK drawn at two temperatures. It is seen that, for the higher drawing temperature (T_{dr}) of 225 °C, the density stays approximately constant in the region of EDR < 2.8, and the density increases monotonically with increasing EDR for EDR > 2.8. On the other hand, for T_{dr} = 125 °C, the density vs EDR shows a minimum at an EDR of 2.0 or lower. Such a density minimum has also been reported by Lee and Porter for PEEK drawn from the amorphous state at 154 °C.[8] In their study, the minimum was observed at EDR = 3.0. This may be due to the occurrence of thermally-induced crystallization, and such an effect also contributed to the change in density on drawing, which consequently shifted the minimum to higher EDR. Density minima have also been observed for solid-state extruded poly(ethylene terephthalate) at an EDR of 3[19] and for HDPE at an EDR of 5−10.[20]

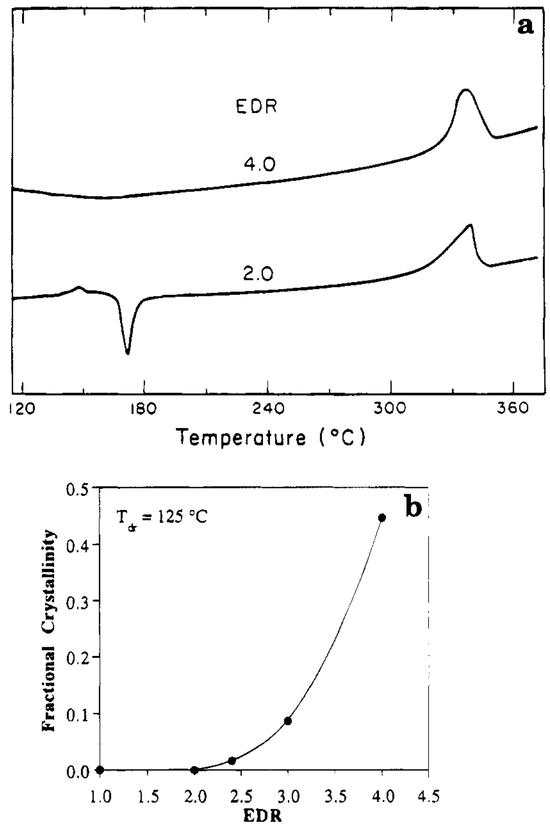

Figure 4. (a) DSC scans of amorphous PEEK drawn at 125 °C. (b) Fractional crystallinity determined from the enthalpy of melting vs EDR of amorphous PEEK drawn at 125 °C.

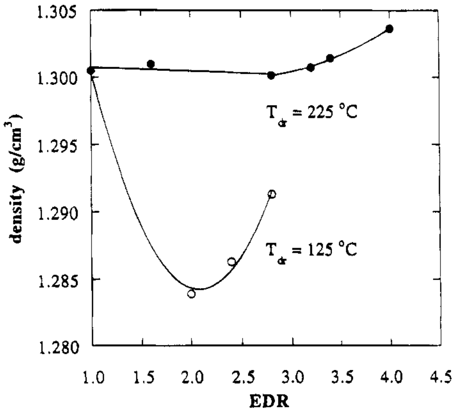

Figure 5. Densities of crystalline PEEK drawn at 225 and 125 °C.

The density changes of the crystalline PEEK/PEI 75/25 blend on drawing are shown in Figure 6. In contrast to PEEK, the densities decrease monotonically with increasing EDR for both draw temperatures. It is also noted in Figures 5 and 6 that the densities of the samples drawn at 225 °C are higher than those of the samples drawn at 125 °C.

The decrease in density with EDR in some semicrystalline polymers has been suggested to result from the partial distortion and subsequent destruction of the original crystals on transformation into a fibril structure.[21] During this process some oriented interfibrillar voids are created. At high EDR, the chains in the amorphous regions are extended to pack more closely and extended-chain crystals are formed. This transformation increases the density, and the combination of these two opposing effects may generate a minimum in the density vs EDR plot, as observed for PEEK. For the blends, the decrystallization by drawing dominated over the densification in the amorphous regions, and

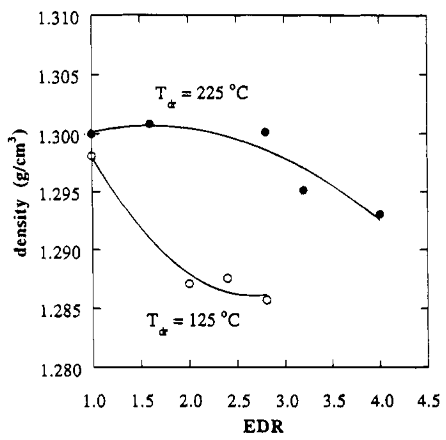

Figure 6. Densities of a crystalline PEEK/PEI 75/25 blend drawn at 225 and 125 °C.

hence the density decreased monotonically with increasing EDR. This would also imply that the densification in the amorphous regions on drawing is more difficult in the blends.

The destruction of PEEK crystals upon drawing is supported by the DSC study. The DSC traces of the drawn crystalline PEEK (Figure 7a) and 75/25 blend (Figure 7b) show that the lower melting endotherms observed at ca. 273 °C for the undrawn samples are not observed for the drawn samples. This indicates the lower-melting PEEK crystals were disrupted by drawing. The degree of crystallinity determined from the enthalpy of melting is plotted against the EDR in Figure 8. It can be seen that the DSC crystallinity decreases with increasing EDR for all compositions investigated.

Assuming an ideal crystalline and amorphous two-phase model, the density of the amorphous phase can be calculated from the overall density and the DSC crystallinity. A density of 1.415 g/cm^3 was adopted for 100% crystalline PEEK.[22] The calculated density of the amorphous phase is plotted against EDR in Figure 9. The absolute values of the calculated densities may be subject to some error, since there are still controversies over the density of 100% crystalline PEEK (reported between 1.378 and 1.415 g/cm^3).[23,24] Nevertheless, the relative change in the density with EDR is the primary interest here. Figure 9 shows that, for both PEEK and its blends, the densities of the amorphous phase exhibit a minimum somewhere near EDR = 2. This indicates that the density of the amorphous region was decreased in the early stage of draw, probably due to the destruction of the lower-melting PEEK crystals. As the EDR was further increased, the orientations of the chains in the amorphous regions induced closer packing and hence the density was increased.

For pure PEEK drawn at 225 °C, the density maximum is not clearly observed (Figure 5). Since 225 °C is 80 °C above the T_g of PEEK, after the destruction of the lower-melting PEEK crystals by drawing, the recrystallization in the amorphous regions can occur. Such an effect would increase the density of the sample, and hence no minimum is observed for T_{dr} = 225 °C. For PEEK rods drawn at 310 °C, the density has been found to increase monotonically with EDR.[8]

3. Crystallization Behavior. It is known that the crystallization rate of polymers can be promoted by orientation. Molecular orientation decreases the entropy and hence increases the degree of supercooling at a given crystallization temperature, so that the crystallization rate is increased.[25,26] Figure 1 shows that the cold crystallization exotherms of amorphous drawn PEEK/PEI blends shift to lower temperatures upon drawing. Figure 10 displays the peak temperature of the cold crystallization exotherm (T_c) vs EDR plot. For

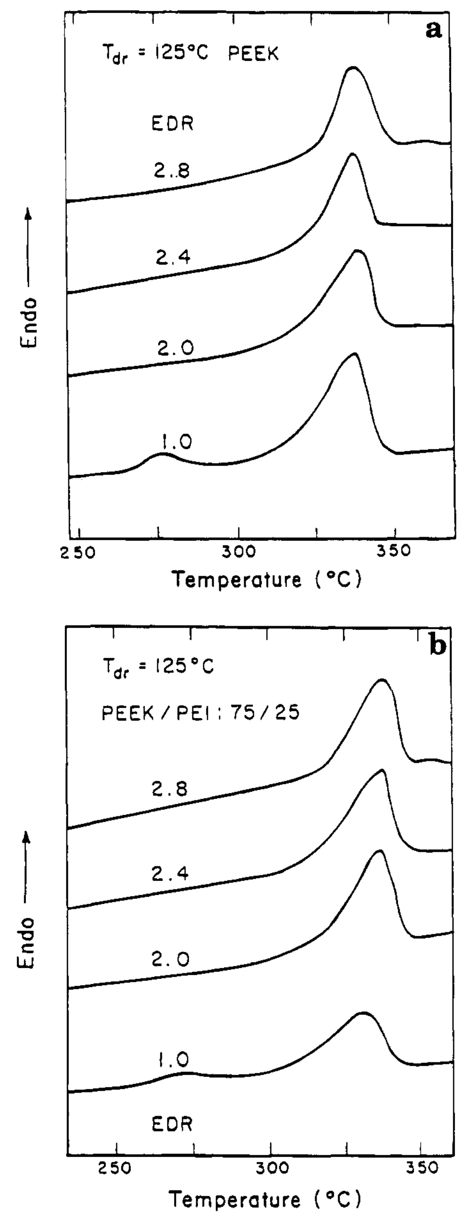

Figure 7. DSC scans of (a) crystalline PEEK and (b) a crystalline PEEK/PEI 75/25 blend drawn at 125 °C.

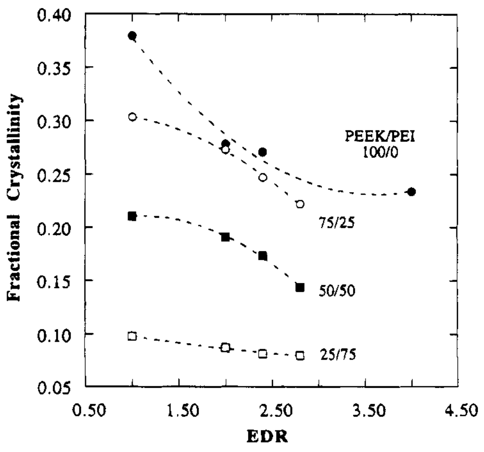

Figure 8. Fractional crystallinity measured by DSC vs EDR of crystalline PEEK/PEI blends drawn at 125 °C.

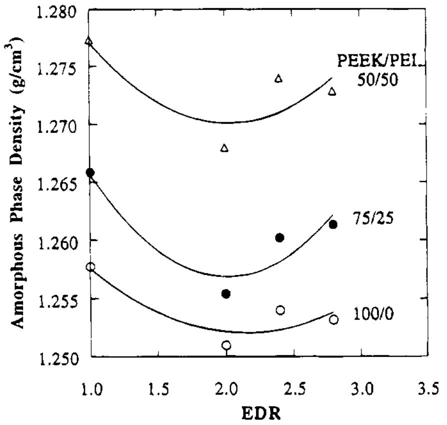

Figure 9. Density of the amorphous phase calculated from the two-phase model for crystalline PEEK/PEI blends drawn at 125 °C.

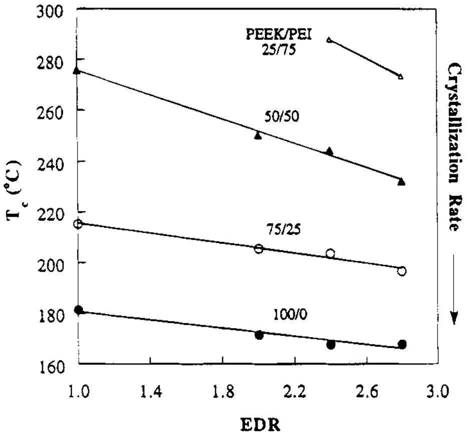

Figure 10. Peak temperature of cold crystallization exotherm vs EDR of amorphous PEEK/PEI blends drawn at 125 °C.

all compositions investigated, T_c decreases with increasing EDR, indicating the cold crystallization is promoted by drawing.

The crystallization following melt annealing (melt crystallization) of the drawn blends is also of interest. A previous study on the melt crystallization of drawn PEEK has shown some interesting results.[9] In the previous investigation, the drawn PEEK was annealed at 370 °C for 5 min followed by a DSC cooling scan. The results showed that the drawn PEEK actually crystallized slower than the undrawn PEEK after melt annealing. It was proposed that the drawn PEEK chains had to relax first before crystallization. In the present study, similar but more thorough melt annealing experiments were carried out for both drawn PEEK and PEEK/PEI blends.

Figure 11 displays the DSC cooling scans of amorphous drawn PEEK after annealing at 370 °C for 5 min. The crystallization exotherms of the drawn PEEK are located at lower temperatures, confirming the melt crystallization in the drawn PEEK is slower than that in the undrawn PEEK. Figure 12 is a plot of the exothermic peak temperature vs EDR. It can be seen that the melt crystallization of the drawn crystalline PEEK is faster than the drawn amorphous PEEK. This may be due to the ample presence of unmelted residual crystals that serve as the nuclei for the subsequent crystallization.[27]

The same melt annealing experiment has also been found for the drawn PEEK/PEI 75/25 blend. Figure 13 displays the DSC cooling scans of this blend. It can be

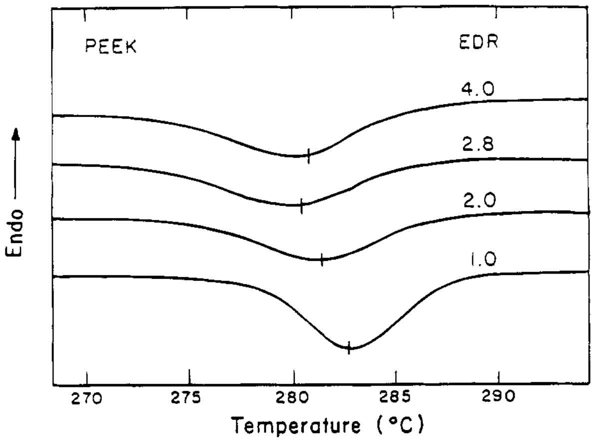

Figure 11. DSC cooling curves of amorphous drawn PEEK after annealing at 370 °C for 5 min. Cooling rate was 20 °C/min.

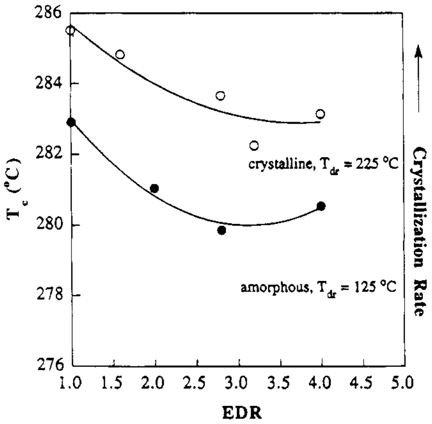

Figure 12. Peak temperature of the crystallization exotherm during cooling vs EDR of crystalline and amorphous drawn PEEK.

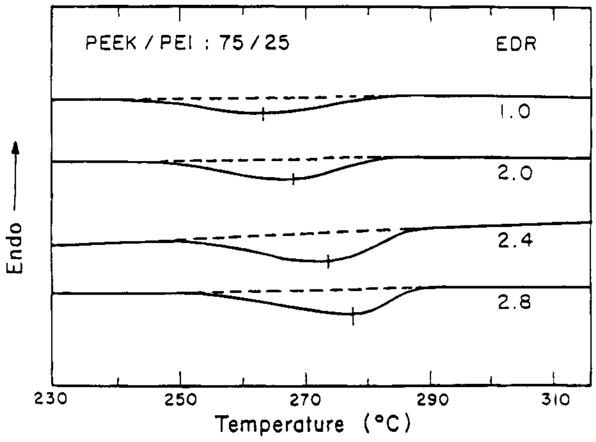

Figure 13. DSC cooling curves of an amorphous drawn PEEK/PEI 75/25 blend after annealing at 370 °C for 5 min. The cooling rate was 20 °C/min.

seen that the crystallization exotherm actually moves to higher temperature with increasing EDR. Figure 14 is the plot of the exothermic peak temperature vs EDR for the drawn 75/25 blends. Like PEEK itself, the crystalline drawn blend crystallizes faster than the amorphous drawn blend. However, the melt crystallization rate in the blend is increased by drawing, in contrast to that found for PEEK.

According to the previous study,[9] the reduction in the melt crystallization rate of PEEK by drawing is due to the necessity of molecular relaxation before the occur-

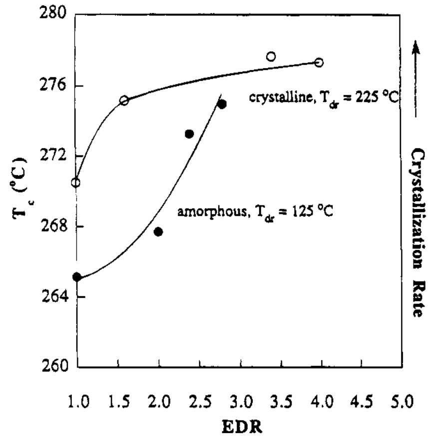

Figure 14. Peak temperature of the crystallization exotherm during cooling vs EDR of crystalline and an amorphous drawn PEEK/PEI 75/25 blend.

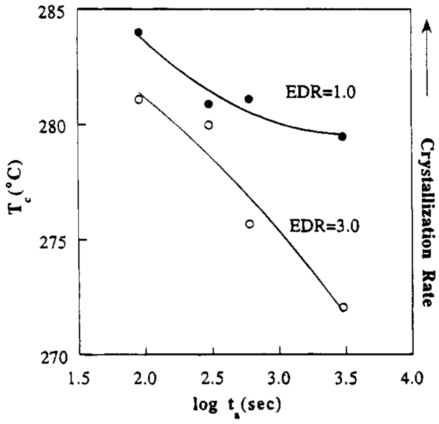

Figure 15. Peak temperature of the crystallization exotherm during cooling vs the annealing time at 370 °C of undrawn and drawn PEEK.

rence of crystallization. But this model seems to post a question, "why did this not occur in the cold crystallization?", because all the drawn samples crystallized faster in the cold crystallization. An experiment was carried out by annealing the amorphous drawn PEEK in the melt for various annealing times. If the annealing time is longer, then PEEK chains should relax more, and hence the subsequent crystallization should be faster according to the proposed model. Figure 15 displays the plot of the cooling exothermic peak temperature vs annealing time. It can be seen that the crystallization rate is indeed reduced by increasing the melt annealing time, which is unexpected based on the proposed relaxation model. This suggests that the previous relaxation model is not sufficient to describe the melt crystallization of drawn PEEK, and the melt crystallization in drawn PEEK appears to be more complicated.

PEEK chains have been shown to adopt the planar zigzag conformation in the crystalline state.[28] Such a conformation should be created by drawing of PEEK, because the crystallization of PEEK can be induced by drawing. Consequently, it is expected that the chain packing during crystallization can be facilitated by orientation. In the melt annealing, the relaxation of the oriented PEEK chains may not be complete and hence the rate of the subsequent crystallization should still be increased, rather than be decreased as observed experimentally. This study presents an interesting aspect for the future study of the crystallization in oriented polymers.

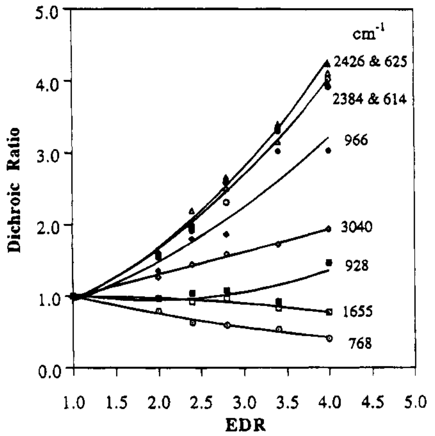

Figure 16. Dichroic ratios of various infrared bands of amorphous drawn PEEK vs EDR.

4. Orientations of PEEK and PEI in Drawn PEEK/PEI Blends.

The respective orientations of the polymers in a drawn blend are an interesting subject. Due to the effect of miscibility, the orientation of a polymer at a given draw ratio can be affected by blending.[29-32] Several studies on the orientations in polymer blends have been reported.[29-32] It is also of interest to see the respective orientations of PEEK and PEI in their blends. Infrared dichroism can be used for such an investigation.

Figure 16 displays the variations of the measured dichroic ratios with EDR for pure amorphous PEEK drawn at 125 °C. The dichroic ratio, D, increases with EDR for the bands of $D > 1$ and decreases with increasing EDR for the bands of $D < 1$, indicating an increase of PEEK orientation with draw ratio.

Since the angles between the transition moments and the chain axis have not been determined for the various bands of PEEK and PEI, the absolute orientations of these two polymers cannot be determined at this stage. However, it is still valuable to consider the relative orientations of these two polymers in the blends, and this can be evaluated directly from the dichroic ratios. To examine the orientation of PEEK in the blends, the overtone band at 2426 cm^{-1} was used, since it overlaps weakly with the bands of PEI. For the orientation of PEI in the blends, the aliphatic C−H stretching at 2965 cm^{-1} overlaps only weakly with the bands of PEEK, and hence it can be used for evaluating PEI orientation in the blends. Due to relatively weak absorptions, the absorbances of these two bands are below unity, so Beer's law is applicable.

Figure 17 displays the composition variations of PEEK and PEI orientations in amorphous drawn blends at fixed draw ratios. It can be seen that the orientations of both polymers are increased by increasing the PEEK content in the blends. In other words, the orientation of PEEK is decreased by blending with PEI, but that of PEI is increased by blending. In PS/PPO blends, it has been found that the orientations of both polymers were decreased by increasing PPO content in the blends.[30]

It has been shown that drawing of PEEK tends to pack the chains to form crystals. On blending with PEI, the miscibility between these two polymers hinders strain-induced crystallization of PEEK, since such crystallization cannot occur without phase separation between these two polymers. Therefore, it is expected that the conformations of PEEK chains in the drawn blends are not as extended as in the pure state at a

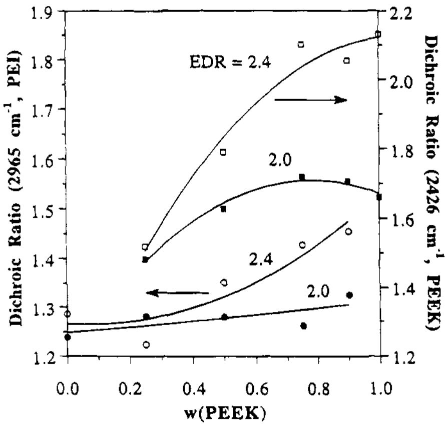

Figure 17. Composition variations of the respective orientations of PEEK and PEI in amorphous drawn PEEK/PEI blends.

given draw ratio. As a consequence, the orientation of PEEK chains is decreased by blending.

Conclusions

The uniaxial draw of amorphous and crystalline PEEK/PEI blends has been studied. The T_gs of the amorphous drawn PEEK/PEI blends are depressed by draw, whereas the densities of these samples are increased. This demonstrates that a higher density sample can have a lower T_g. The densities of the drawn crystalline PEEK and blends exhibit different types of variation with EDR. This has been attributed to the interplay between the destruction of PEEK crystals and the densification in the amorphous zones on drawing. The orientation study by infrared dichroism indicates the orientations of both PEEK and PEI are increased by increasing the PEEK concentration in the blends.

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