

Crystallization of Poly(ethylene terephthalate)/Polycarbonate Blends. II. The Effects of Fiber Reinforcement

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SYNOPSIS

The effect of fiber reinforcement on the crystallization of poly(ethylene terephthalate) (PET) in blends of PET and polycarbonate (PC) is determined using differential scanning calorimetry (DSC). Isothermal crystallization rate of PET in PET/PC blends (80% and 60% PET by weight) is depressed as a result of Kevlar 49 and glass fiber reinforcement. In contrast, the crystallization rate of the same PET (no PC present) is enhanced by the Kevlar. The degree of crystallinity and melting temperature of PET in fiber-reinforced PET/PC is also depressed relative to that of unreinforced PET/PC and fiber-reinforced PET. These results show that there is a significant interaction between the effects of fiber reinforcement and of the PC component on the crystallization of PET in PET/PC composites. The PET/PC blends studied display two glass transition temperatures, characteristic of an immiscible blend. When glass fibers are used as the reinforcing phase, the T_g of PET is depressed. Optical microscopy observations are also consistent with an immiscible blend. When Kevlar fibers lie in a crystallizable (PET) domain, crystallites are densely nucleated on the fiber surface to induce transcrystallinity. Glass fibers produce less densely nucleated surface crystals in these systems. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In Part I of this series, we reported on the crystallization of poly(ethylene terephthalate) (PET) in blends with polycarbonate (PC).¹ This study showed that blending with amorphous PC can have a significant effect on the crystallization rate and degree of crystallinity of PET. In blends with PC content greater than 60 wt %, PET crystallization rate is strongly depressed compared with that of PET. Degree of crystallinity is also depressed. Since PET/PC blends typically contain additives to suppress transesterification and oxidation, the effects of commercial PET/PC additives were also investigated. The crystallization rate of PET containing commercial transesterification inhibitor and antioxidant is significantly enhanced relative to that of PET.

In the current article, we report the effects of reinforcing fibers on the crystallization of PET in PET/PC blend composites. Our objective was to

quantify the interaction of the effects of the PC component and of fiber reinforcement on PET crystallization.

EXPERIMENTAL

The PET/PC blends used in this study, supplied in pellet form by the General Electric Company, were 60/40 PET/PC (60 wt % PET/40 wt % PC), 80/20 PET/PC, and 100% PET, as described in Part I.¹ Blends containing less than 60 wt % PET were not considered due to the need for sufficient PET fraction in the final composite for differential scanning calorimetry (DSC) analysis. Since the PET/PC blends contain a proprietary transesterification inhibitor and antioxidant (Ciba-Geigy's Irganox 1076, two parts per thousand loading), a sample of 100% PET containing these additives was prepared and is referred to as "modified PET." Samples were molded into films by placing approximately 15 g of resin pellets between two pieces of Teflon®-coated glass release fabric (supplied by Taconic Plastics) and placing the assembly on a hot press at 275°C under 200 psi pressure.

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Unidirectional fiber composites were prepared using Kevlar (duPont Kevlar 49, fiber diameter 14 μm) and glass (Owens Corning Fiberglas, fiber diameter 9 μm) fibers without fiber surface finish or sizing. Films were dried in a vacuum oven for 15 h at 100°C before molding in an aluminum mold with well dimensions 2.9 cm by 1.9 cm. Between 7 and 40 (depending on fiber type) continuous filament tows were aligned and "sandwiched" between two pieces of PET or PET/PC film. Teflon[®]-coated glass release fabric was added to the top and bottom of the sandwich, and the composites were molded under pressure (200 psi) for 10 min at 275°C. Films of PET, modified PET, and PET/PC blends were molded in the same way, so that the unreinforced systems experienced the same processing conditions as the composite systems.

The fiber weight content in the composites varied from 49% to 55%, so that the fiber surface area per gram polymer was the same in each composite. Differences in fiber diameter and density were accounted for to maintain the same interfacial contact area in the Kevlar and glass composites. To establish the effect of fiber loading for the unsized Kevlar case, additional composites were prepared with each of the four matrix materials representing low (approximately 25 wt %) and high (approximately 65 wt %) Kevlar fiber loadings.

Specimens for study by differential scanning calorimetry (Perkin-Elmer DSC-4) varied in weight from 4 to 20 mg, so the PET weight in each specimen was roughly 4 mg. Samples were scanned in the DSC from 25°C to 280°C at 10°C/min to determine the glass transition temperature, T_g , of each component. In isothermal crystallization experiments, samples were scanned to 280°C, held for 5 min, and then quenched at 320°C/min to the crystallization temperature of interest. Fusion data were collected after each crystallization by scanning at 10°C/min from 15°C below the crystallization temperature to 280°C. To avoid cumulative thermal history effects and degradation, a new specimen was used for each crystallization experiment. All crystallizations were repeated three times.

Model thin film composites were prepared for examination using optical microscopy. Five small pieces of film, totaling approximately 1 mg, were placed on a glass coverslip and covered with approximately 10 single filaments. The coverslip was placed on the bottom platen of a hot press at 320°C, covered with another glass coverslip, and pressed with forceps to produce a thin film. The sample was crystallized dynamically for 1 min at approximately 100°C and then quenched for examination in an optical microscope under polarized light.

RESULTS AND DISCUSSION

Morphology of Fiber-Reinforced PET/PC Blends

Optical microscopy observations of the unreinforced PET/PC blends are consistent with those of an immiscible blend of an amorphous and a crystallizable polymer. Micrographs show domains with spherulitic growth and domains in which no order is evident.¹ Figure 1 shows an unsized Kevlar fiber in the 60/40 PET/PC matrix, where it appears that the fiber lies between large crystalline and amorphous domains. The effect of the fiber on the crystalline domain in the blend closely resembles the effect of Kevlar fiber reinforcement on PET crystallization, as reported in previous studies.^{2,3} There is a transcrystalline region of densely nucleated growth emanating from the fiber surface, constrained to grow in a linear, columnar fashion. The growth farther away from the fiber surface is spherulitic, typical of PET crystallization.^{2,3} The other side of the fiber lies in an amorphous PC domain, where there is no evidence of crystallization either near the fiber surface or in the bulk.

We note that the domains in Figure 1 are unusually large. Other regions of the same thin film specimen showed smaller domains of crystalline PET and amorphous PC. We also note that strong shear forces during production of these thin films may contribute to phase separation and result in larger domain sizes than in thicker composite samples. Glass fibers in 60/40 PET/PC have an effect similar to that of Kevlar. When the fiber lies in a crystalline domain, the growth adjacent to the fiber surface appears to be more densely nucleated than in the bulk. In unordered PC domains, no interaction between the fiber and the matrix is observed. The morphological effects of these fibers are similar in the 80/20 PET/PC blend.

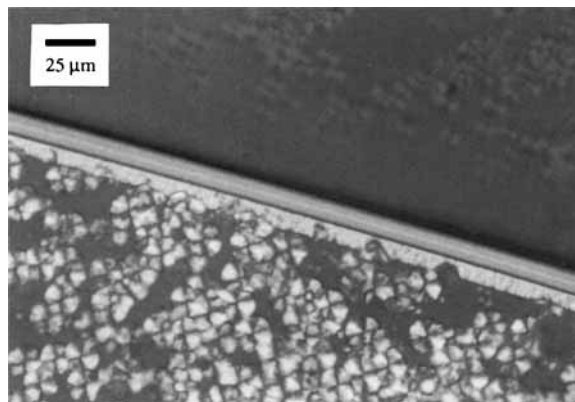


Figure 1 Optical micrograph of an unsized Kevlar fiber in 60/40 PET/PC.

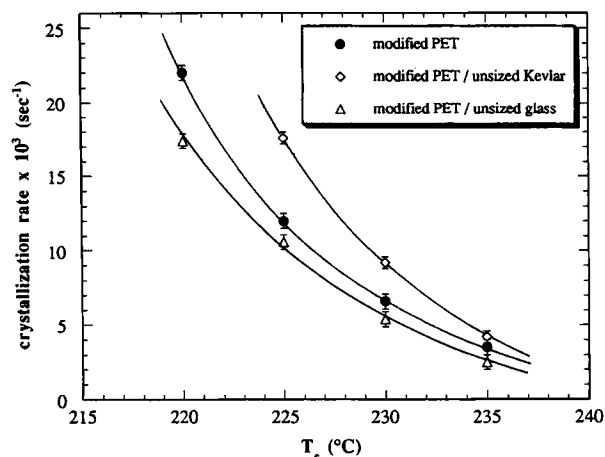


Figure 2 Crystallization rate as a function of crystallization temperature for fiber-reinforced modified PET with blend additives.

Crystallization of Fiber-Reinforced Modified PET

The isothermal crystallization rate of PET, taken as the inverse of the crystallization half-time, decreases strongly with increasing crystallization temperature as a result of the reduction in undercooling from the melt. As discussed in Part I of this series,¹ there is a strong enhancement of crystallization rate in the modified PET over that of PET without blend additives, which we ascribe to the nucleating effect of the antioxidant and the transesterification inhibitor. It is important, therefore, that in characterizing the effects of fibers and the PC component on the crystallization of fiber-reinforced blends, comparisons be made with 100% PET containing the blend additives.

Figure 2 shows the crystallization rate of fiber-reinforced modified PET with blend additives. As in the case of PET,^{2,3} Kevlar fibers enhance the crystallization rate of modified PET, while glass fibers slightly depress the rate of crystallization. The depression of crystallization rate in glass fiber-reinforced modified PET is probably the result of an impingement effect. Since glass fibers have only moderate nucleating ability, these fibers would act primarily to interfere with the growth of crystals in a matrix that is already highly nucleated by the additives. In effect, the small nucleating ability of glass fibers is masked by the nucleation effect of the additives.

The degree of crystallinity of PET is determined from the experimental heat of fusion following crystallization. The heat of crystallization of 100% crystalline PET is taken to be 33 cal/g.⁴ The degree of crystallinity of neat modified PET, given as a function of crystallization temperature in Table I, is

Table I Degree of Crystallinity (%) of Molded Film and Composites of Modified PET as a Function of Crystallization Temperature

T_c	Degree of Crystallinity (%)		
	Neat	Unsized Kevlar	Water-Sized Glass
220	33 ± 1	34 ± 2	32 ± 1
225	34 ± 1	33 ± 1	31 ± 2
230	34.1 ± 0.6	34 ± 1	32 ± 1
235	34 ± 1	34 ± 1	33 ± 2

Error limits given are the standard deviation of three measurements.

found not to depend on crystallization temperature, although crystallization rate is. This has previously been observed for PET,³ and it was also previously determined that the additives present in modified PET do not significantly affect degree of crystallinity of PET.¹

The results for degree of crystallinity of fiber reinforced modified PET are also given in Table I. Fiber reinforcement, both Kevlar and glass, does not significantly affect the degree of crystallinity of PET modified with blend additives. Again, this is interesting since the fibers were shown to affect the crystallization rate. It is possible that secondary crystallization and annealing processes improve the perfection of rapidly developed crystallites.

The effect of fiber loading on the crystallization of modified PET was investigated for the unsized Kevlar composite system. The crystallization rate at two crystallization temperatures of Kevlar-reinforced modified PET is shown as a function of fiber content in Figure 3. At both crystallization temper-

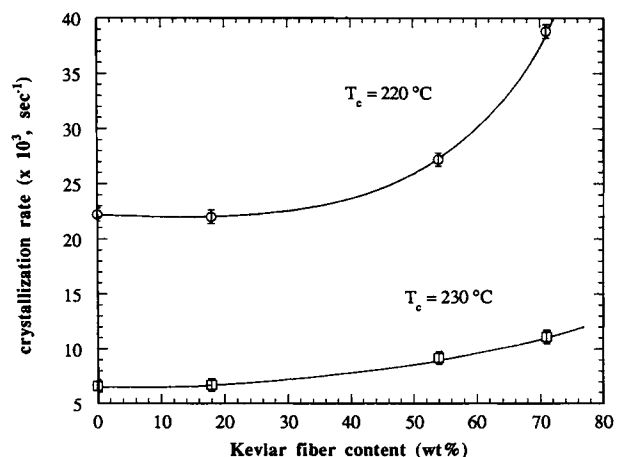


Figure 3 Crystallization rate as a function of unsized Kevlar fiber content for PET modified with blend additives.

atures, crystallization rate increases with increasing Kevlar fiber content, confirming the strong nucleating ability of Kevlar fibers.

The degree of crystallinity of modified PET is shown as a function of fiber content in Figure 4, indicating that there is no effect of Kevlar fiber loading on degree of crystallinity over the entire fiber loading range. Although the crystallization rate of high Kevlar fiber content composites is very high compared with neat modified PET, secondary crystallization processes in this matrix appear to be rapid enough to provide the same ultimate crystallinity levels.

Crystallization of Fiber Reinforced PET/PC Blends

Crystallization Rate

The crystallization rate of composites of 80/20 PET/PC is shown as a function of crystallization temperature in Figure 5. Crystallization rate in blend composites again decreases strongly with increasing crystallization temperature due to the reduction in undercooling from the melt at higher crystallization temperatures. In 80/20 PET/PC, unsized Kevlar fibers significantly depress the rate of PET crystallization, in direct contrast to the enhancement of crystallization rate observed as a result of Kevlar fiber reinforcement in 100% modified PET. The depression in crystallization rate in glass fiber-reinforced 80/20 PET/PC is even greater than that of the Kevlar composite.

The depression in crystallization rate of 80/20 PET/PC composites due to Kevlar is particularly interesting. It appears that the presence of the

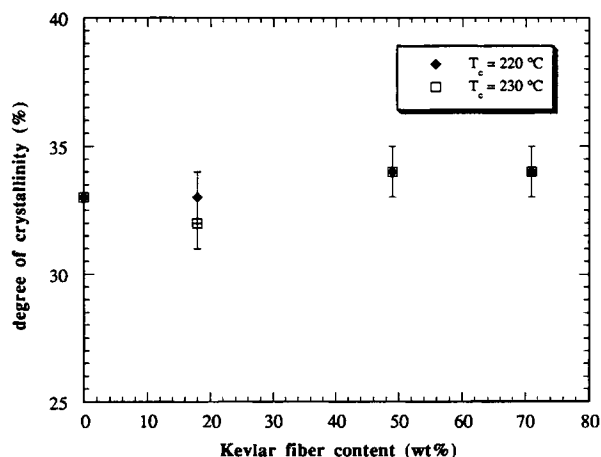


Figure 4 Degree of crystallinity as a function of unsized Kevlar fiber content for PET modified with blend additives.

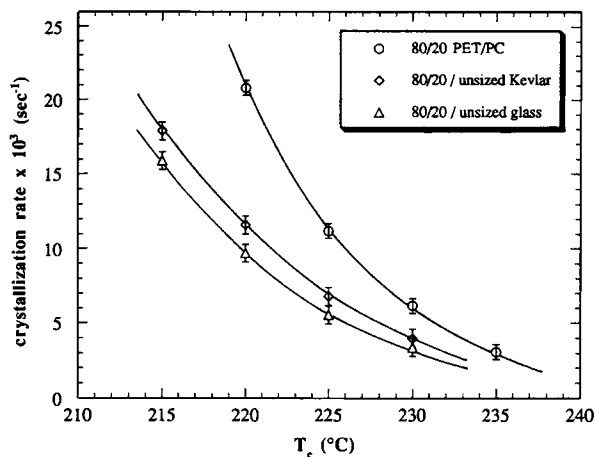


Figure 5 PET crystallization rate as a function of crystallization temperature for 80/20 PET/PC composites.

amorphous PC phase reduces or even eliminates the rate-enhancing effect that Kevlar fibers normally have on PET crystallization. We have shown that the crystallization rate of PET is unaffected by the amorphous PC domains and that Kevlar fibers enhance the crystallization rate of modified PET. Yet when the three phases are combined, we observe a significant depression in PET crystallization rate. As a mechanism, we suggest that during composite melt processing PC wets the Kevlar fibers preferentially or to a greater extent than does PET. If this were the case, the nucleating ability of the Kevlar fibers would be reduced or even eliminated because of reduction in the effective contact between the fiber surface and PET. While the nucleation on the fiber surface would be reduced, the interference with spherulite growth during crystallization posed by reinforcing fibers would not be eliminated. It would appear that, in Kevlar-reinforced 80/20 PET/PC, the interference effect overcomes any remaining nucleating ability of Kevlar fibers, and the result is a depression in the crystallization rate of PET.

Alternatively, it is possible that there is a cumulative constraining effect on PET crystallization of the amorphous PC domains and the fibers. Perhaps when these two phases both constrain the crystallizable domains, the result is a depression of crystallization rate. However, this explanation does not seem as likely as the preferential wetting effect, since we have shown that crystallization rate of Kevlar fiber-reinforced modified PET increases with increasing fiber loading, even for fiber loadings greater than 50 wt %.

The crystallization rate of 60/40 PET/PC composites is shown in Figure 6 as a function of crystallization temperature. Again, as in the case of the 80/20 composites, fiber reinforcement results in a

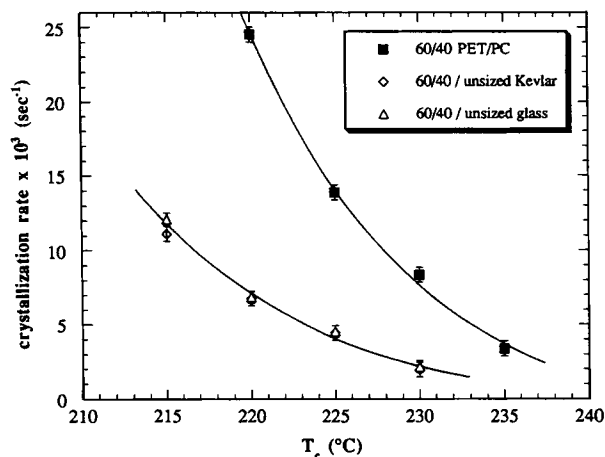


Figure 6 PET crystallization rate as a function of crystallization temperature for composites of 60/40 PET/PC.

significant depression in crystallization rate for all crystallization temperatures. The crystallization rate of unsized Kevlar and water-sized glass composites of 60/40 PET/PC is approximately equal, and the extent of the depression caused by the fibers is greater than in the 80/20 case. This is consistent with our suggestion that the fibers are preferentially wet by PC during melt processing and that the coated fibers interfere with crystal growth by impingement. With more PC present in the 60/40 blend, a greater proportion of fibers may be coated by PC, reducing their ability to nucleate crystallization, which would account for the greater depression in crystallization rate in the 60/40 composites than in the 80/20 systems.

Degree of Crystallinity

Degree of crystallinity of modified PET, 80/20 PET/PC, and 60/40 PET/PC composites, averaged over the crystallization temperature range studied, is given in Table II. While fiber reinforcement does not have a significant effect on degree of crystallinity of modified PET and the amorphous PC phase does

not significantly affect degree of crystallinity for the PC compositions of 40 wt % and less,¹ the degree of crystallinity of fiber-reinforced PET/PC blends is depressed. Both glass and Kevlar fibers result in a depression of degree of crystallinity in both 80/20 and 60/40 PET/PC, relative to that of the unreinforced blends and to the composites of modified PET. While these results suggest an interaction between the effects of fiber reinforcement and the effects of the PC component in the blends, the reason for the depression is not obvious. The depression of crystallinity in the blend composite would not seem to be the result of excessive "dilution" of the PET phase, because on a volume fraction basis, the fraction of PET is greater in Kevlar-reinforced 80/20 PET/PC than in the 70 wt % Kevlar modified PET composite, which exhibited no depression in crystallinity. However, it is possible that the interaction of fiber and blending effects results in PET domains in the composite which are more highly constrained than in the PET composites. Perhaps the combined effects of geometrical constraint of growth, provided by the fibers and PC domains, and the absence of nucleation on the surface of the fibers result in reduced crystallinity.

Another possible explanation for the depression in crystallinity in the blend composites is transesterification reactions. Perhaps transesterification and other degradation reactions during composite melt processing are enhanced by the presence of reinforcing fibers. Transesterification would be expected to reduce degree of crystallinity by removing material available for crystallization.

Fiber Content Effects

The effect of Kevlar fiber loading on the crystallization rate of 80/20 PET/PC composites at 220 and 230°C is shown in Figure 7. For both crystallization temperatures, crystallization rate decreases with increasing fiber content. These results are consistent with the proposed mechanism that the PC

Table II Degree of Crystallinity (%) of Fiber-Reinforced Modified PET and of Fiber-Reinforced PET/PC Blends

Fiber Reinforcement	Degree of Crystallinity		
	Modified PET	80/20 PET/PC	60/40 PET/PC
Neat	34 ± 1	32 ± 1	33 ± 1
Unsize Kevlar	34 ± 1	28 ± 1	29 ± 1
Water-Sized Glass	32 ± 2	26 ± 2	27 ± 2

Results are the average of three measurements at four crystallization temperatures. Error limits given are the standard deviation of 12 measurements.

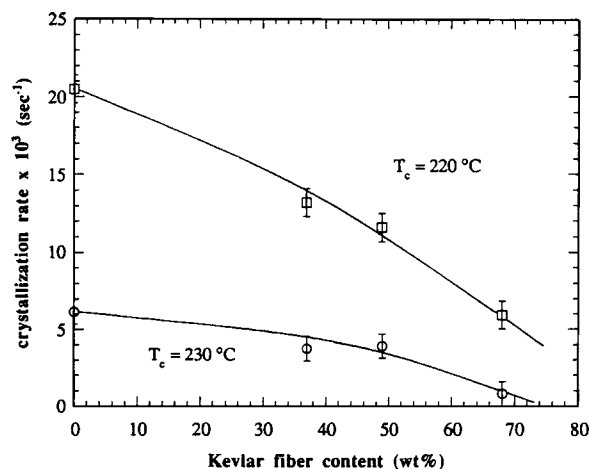


Figure 7 PET crystallization rate as a function of un-sized Kevlar fiber content for 80/20 PET/PC at two crystallization temperatures.

phase interferes with the nucleating ability of the Kevlar fibers by preferential wetting. The Kevlar fibers would then be expected to act simply to interfere with crystallization by impingement, giving rise to the decrease in crystallization rate with increasing fiber content shown in Figure 7.

Figure 8 shows the degree of crystallinity in Kevlar-reinforced 80/20 PET/PC as a function of fiber loading. For both crystallization temperatures, degree of crystallinity in fiber-reinforced PET/PC is depressed relative to that in the neat 80/20 PET/PC. Fiber content appears to have a stronger effect on crystallinity of samples crystallized at 230°C than 220°C. While all 80/20 PET/PC composites show a depression of crystallinity over the neat sample, the level of fiber loading does not seem to have a strong effect, except for the 70% fiber content sample crystallized at 230°C. This significant depression may be the result of incomplete crystallization resulting from the slow crystallization rate of this system.

The effect of fiber content on the crystallization rate of 60/40 PET/PC is shown in Figure 9. Crystallization rate decreases strongly with increasing fiber loading. In fact, at the highest fiber content considered, 67 wt % Kevlar, crystallization rate was so depressed that the crystallization exotherm could not be separated from the DSC machine response in cooling to T_c and from the noise in the DSC signal. Crystallization rate in fiber-reinforced 60/40 PET/PC appears to be even more dependent on fiber loading than 80/20 PET/PC, which probably reflects the greater fraction of PC available to interact with fibers in the 60/40 composites.

Degree of crystallinity in composites of 60/40 PET/PC is also significantly affected by fiber con-

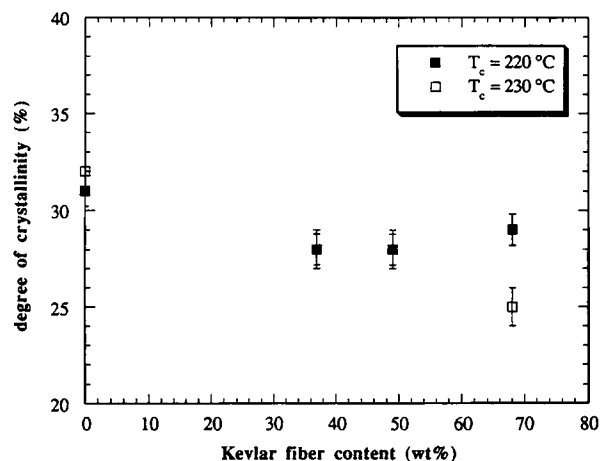


Figure 8 PET degree of crystallinity as a function of un-sized Kevlar fiber content for 80/20 PET/PC at two crystallization temperatures.

tent, as shown in Figure 10. For both crystallization temperatures, degree of crystallinity decreases strongly with increasing Kevlar fiber content. Degree of crystallinity for the 67 wt % Kevlar composites was determined by the usual fusion method after the samples were allowed to crystallize for 1 h. A very long crystallization time was allowed to insure that crystallization was complete. The excellent agreement between the measurements at two different crystallization temperatures indicates that crystallization was indeed complete in both cases. The depression in degree of crystallinity is therefore not due to incomplete crystallization, but rather to an interaction between the effects of fiber reinforcement and the PC component in the blend.

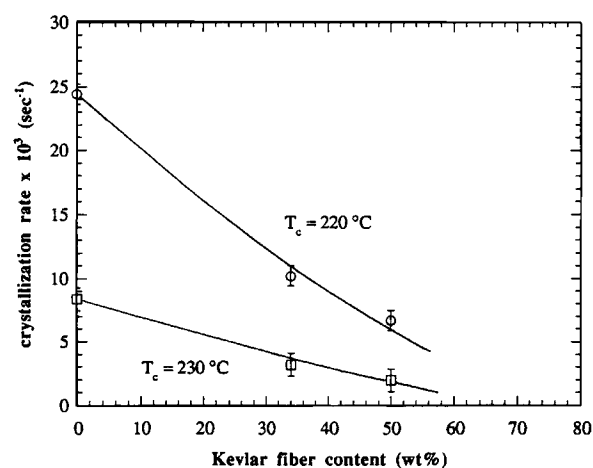


Figure 9 PET crystallization rate as a function of un-sized Kevlar fiber content for 60/40 PET/PC at two crystallization temperatures.

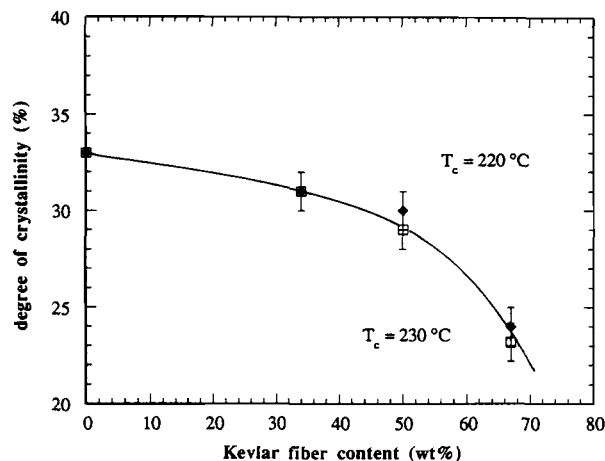


Figure 10 PET degree of crystallinity as a function of unsized Kevlar fiber content for 60/40 PET/PC at two crystallization temperatures.

Glass Transition Temperature of Fiber-Reinforced PET/PC

In Part I we have shown that these PET/PC blends display two glass transition temperatures (T_g 's) for PET and PC, characteristic of an immiscible blend.¹ In the fiber-reinforced PET/PC blends (high PET content) considered here, the PC fraction is small and the T_g of PC is therefore very weak and difficult to observe. Thus, only the T_g of PET will be considered.

The glass transition temperature data are summarized in Table III. Unsized Kevlar reinforcement results in a slight increase in the T_g of modified PET. An increase in T_g of unsized Kevlar/PET composites has been reported previously and was attributed to a friction effect at the fiber surface.³ The blend additives would not be expected to affect a phenomenon of this kind. A depression in T_g resulting from glass fiber reinforcement is observed in modified PET composites. Again, such a depression has been observed previously in PET/glass fiber composites.³ The observed T_g depression due to glass fiber may

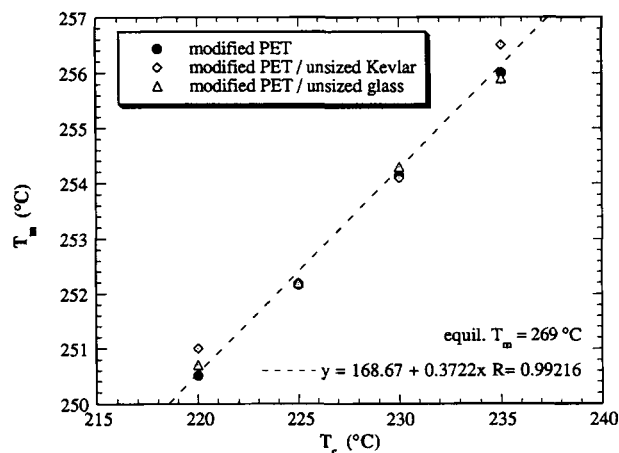


Figure 11 Hoffman and Weeks plot of melting temperature as a function of crystallization temperature for composites of modified PET with blend additives.

be the result either of plasticization by water or polymer degradation or other reaction.

Table III shows that the same T_g effects observed in fiber-reinforced modified PET occur in fiber-reinforced PET/PC blends. Both 80/20 PET/PC and 60/40 PET/PC show an increase in T_g as a result of unsized Kevlar fiber reinforcement and a depression of T_g as a result of glass fiber reinforcement.

Melting Behavior of Fiber-Reinforced PET/PC

Melting temperature as a function of crystallization temperature is shown for composites of modified PET in Figure 11. Fiber reinforcement does not have a significant effect on the melting temperature of modified PET. In fact, when the equilibrium melting temperature, T_m^o , is determined by the method of Hoffman and Weeks,⁵ all composites have $T_m^o = 269^\circ\text{C}$. This is within the error estimate of T_m^o for modified PET (270°C). However, it is important to note that the equilibrium melting temperature of

Table III Glass Transition Temperature ($^\circ\text{C}$) of PET in Fiber-Reinforced Modified PET and Fiber-Reinforced PET/PC Blends

Fiber Reinforcement	T_g ($^\circ\text{C}$)		
	Modified PET	80/20 PET/PC	60/40 PET/PC
Neat	75 ± 1	77 ± 1	76 ± 1
Unsized Kevlar	78 ± 1	78 ± 2	78 ± 1
Water-Sized Glass	72 ± 1	74 ± 1	73 ± 2

Results are the average of three measurements.

Table IV Equilibrium Melting Temperature ($^{\circ}\text{C}$) of PET in Fiber-Reinforced Modified PET and Fiber-Reinforced PET/PC Blends Determined by the Method of Hoffman and Weeks

Fiber Reinforcement	T_m° ($^{\circ}\text{C}$)		
	Modified PET	80/20 PET/PC	60/40 PET/PC
Neat	270 ± 3	270 ± 2	269 ± 2
Unsize Kevlar	269 ± 4	261 ± 4	262 ± 5
Water-Sized Glass	269 ± 3	262 ± 5	263 ± 5

modified PET is depressed in comparison to PET without the blend additives.¹

While both fiber reinforcement and blend additives have a significant effect on PET crystallization rate, only the additives have a significant effect on melting temperature. This suggests that the uniformly distributed additives throughout the PET phase act as impurities to cause defects within crystals, thereby depressing T_m° . The primary effect of fiber reinforcement, on the other hand, is on crystallization rate. Rapid crystallization, as in the case of Kevlar-reinforced composites, would produce less perfect crystals, but such imperfections in the crystal phase would be removed in secondary crystallization and annealing processes during the fusion scan. This would tend to reduce differences in melting behavior in the composites as compared with the unreinforced matrix.

The equilibrium melting temperature for fiber-reinforced blend systems is given in Table IV. In contrast with modified PET, there is a significant depression in T_m° of the fiber-reinforced blends relative to that of the unreinforced blends. This depression in T_m° correlates with the depression in degree of crystallinity of fiber-reinforced PET/PC and reflects a less perfect crystal phase.

CONCLUSIONS

Unsize Kevlar fibers enhance the crystallization rate of PET modified with blend additives, while water-sized glass fibers depress the rate of crystallization. However, in PET/PC blends (80/20 PET/PC and 60/40 PET/PC), both Kevlar and glass fibers depress the rate of crystallization. These results indicate that there is an interaction between the amorphous PC phase and the fiber reinforcement, and we have suggested that the wettability of fibers by PC is greater than that by PET. The amorphous PC phase would then reduce or eliminate the nucleating ability of the fibers, and the fibers would

act primarily to interfere with crystal growth by impingement.

The degree of crystallinity and melting temperature of fiber-reinforced PET/PC blends are depressed relative to the unreinforced blends. However, fiber reinforcement does not result in a depression of these properties in modified PET. These results again point to an interaction of fiber and PC component effects. In fiber-reinforced blends, crystallization appears to be suppressed or altered as a result of this interaction. This study of crystallization in PET/PC fiber composites has shown that independently quantifying the effects of fiber reinforcement on PET crystallization and the effects of blending with PC is insufficient. By considering crystallization in fiber-reinforced PET/PC relative to unreinforced PET/PC and relative to fiber-reinforced PET, the interaction of fiber and PC component effects is better understood.

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