

# Effect of Crystallinity on Mechanical Properties of Miscible Polycarbonate-Copolyester Blends

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## Synopsis

Normally amorphous miscible blends of a copolyester and polycarbonate in the form of injection molded bars and extruded film were thermally annealed above the blend  $T_g$  to cause the copolyester component to crystallize, and the resulting mechanical properties were evaluated. The properties were found to depend in a complex way on blend composition, annealing conditions employed, the initial state of molecular orientation, and the process history.

## INTRODUCTION

Previous papers<sup>1-6</sup> have reported on the physical and chemical behavior of miscible blends of bisphenol-A polycarbonate with a copolyester formed from 1,4-cyclohexane dimethanol and a mixture of terephthalic and isophthalic acids. The latter polymer can crystallize but does so rather slowly such that it remains totally amorphous when quenched from the melt as occurs during normal processing. Crystallinity will develop when this polymer or a blend containing it is annealed for appropriate periods at temperatures intermediate to its melting point and the glass transition. This paper reports on the mechanical behavior of blends containing this copolyester and polycarbonate (PC) following such an annealing procedure. In addition to promoting copolyester crystallization, annealing also permits various relaxation processes to occur which also influence the mechanical behavior. Owing to the short duration of this annealing, chemical changes of the type mentioned previously<sup>2,5</sup> are relatively inconsequential. A companion paper<sup>7</sup> describes the effect of copolyester crystallinity on gas transport in these blends.

The main effect of copolyester crystallization under the reported circumstances is to embrittle these otherwise very ductile, glassy materials; however, crystallization under dynamic processing conditions might result in a strengthening mechanism since more favorable textures would result.

## MATERIALS AND PROCESSING PROCEDURES

All materials were the same as used previously,<sup>1-6</sup> viz., the copolyester was Kodar A-150 obtained from Eastman Chemical Products, Inc. and the polycarbonate was Lexan 131-111 obtained from the General Electric Co. Both polymers were dried at 75°C for 24 h and the copolyester precrystallized at 150°C for 1 h prior to any melt processing. Blends were prepared in a single screw extruder using similar process conditions as described earlier.<sup>3</sup> The extrudate

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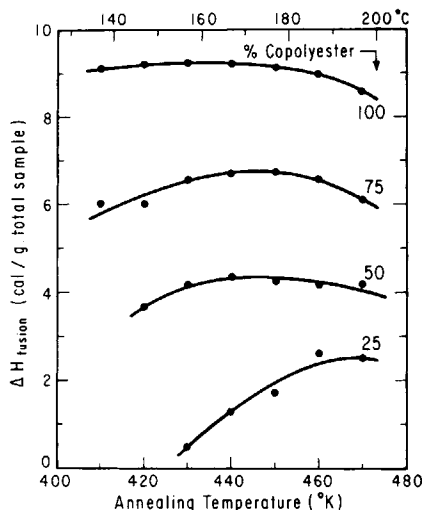


Fig. 1. Copolyester crystallization for various blends after 30 min exposure to the annealing temperature.

was chopped and injection-molded into dogbone test specimens (ASTM D-638) as before. Film specimens having a melt draw ratio of 7–10 were also prepared as before except here 0.1%  $\text{As}_2\text{O}_3$  was melt-mixed into the copolyester prior to blending with polycarbonate to deactivate residual titanium polymerization catalyst.<sup>2</sup>

The effect of processing and thermal treatment histories on molecular weight was observed by monitoring the specific viscosity of solutions containing 1 g polymer in 100 mL of 60/40 phenol/tetrachloroethane at 27°C. Specific viscosities for both pure components and their blends were found to decrease by about 5–6% after exposure to 470°K for 30 min. These results are quite similar to those described earlier,<sup>2</sup> and they suggest that molecular weight degradation is not a serious issue at the processing and annealing conditions employed in this study.

Prior to annealing, samples were dried in a vacuum oven at 75°C for 48 h to avoid hydrolysis and bubble formation. For injection-molded specimens, annealing was done in a specially constructed mold having cavities the same shape as the dogbone.<sup>3</sup> Film specimens were annealed in an air oven at constant length. The annealing period was 30 min in every case, but the temperature was varied.

## CRYSTALLIZATION BEHAVIOR

Thermal analysis was performed using a Perkin-Elmer DSC-2, computer-assisted by a Model 3500 Thermal Analysis Data Station, at a scanning rate of 10°C/min. Heats of fusion were determined by computer-aided integration of melting endotherms. If crystallization was incomplete for an annealed sample and it further crystallized during the scan, the area of the crystallization exotherm was subtracted from the area of the melting endotherm to determine the sample's

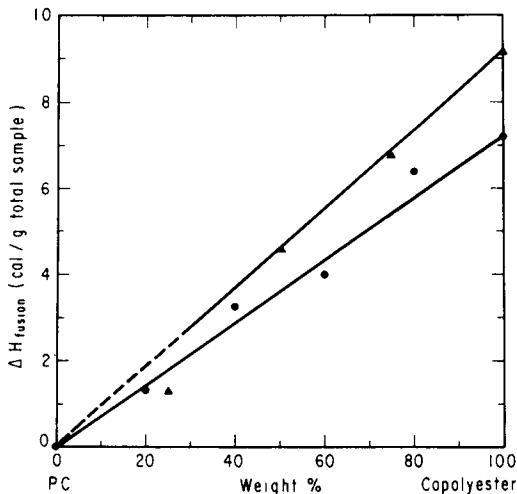


Fig. 2. Comparison of copolyester crystallization in annealed bars (▲) and film (●). Annealed at 440 K for 30 min.

original heat of fusion. No crystallinity was detected for any polycarbonate specimen.

For injection-molded materials, the heat of fusion is shown in Figure 1 for each blend composition as a function of annealing temperature. Since the annealing time was fixed at 30 min, the heat of fusion trends reflect the rate of crystallization. Except for the blend containing 25% copolyester, a maximum crystallinity level is reached in the 430–450°K range. Crystallization from the 25% blend is probably more diffusion-controlled than for the other compositions more rich in copolyester. Barnum<sup>5</sup> has estimated the heat of fusion for a completely crystalline polyester to be 29.8 cal/g; hence, the copolyester develops a maximum crystallinity of 31%.

The film samples were annealed at a single temperature of 440°K for 30 min, and these results are compared in Figure 2 with those for injection-molded bars annealed at the same conditions. The molded materials generally develop higher levels of crystallinity than do the film which is probably the result of the combined effects of higher molecular orientation and lower molecular weights for the former on crystallization rates. Except for the 25% copolyester blend made by molding, the heat of fusion is very nearly proportional to the copolyester content of the blend.

For the protocol described above, the level of crystallinity achieved is relatively insensitive to the annealing temperature except for the 25% copolyester blend. However, we may anticipate that the crystalline texture will vary with the temperature of crystallization in all cases, and this will influence mechanical property behavior.

### MECHANICAL PROPERTIES OF INJECTION-MOLDED BLENDS

All mechanical testing of dogbone specimens was done with a floor model Instron. For modulus determination, an extensometer with a 1-in. gauge length

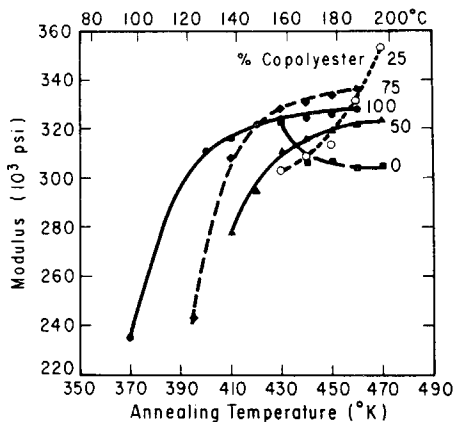


Fig. 3. Effects of annealing and blend composition on moduli of molded bars.

was employed using a crosshead speed of 0.1 in./min. Yield or failure behavior was tested at a crosshead speed of 2 in./min with the grips set 4.25 in. apart, and this dimension was used as the gauge length in estimating elongations at break. The majority of the annealed tensile bars were sufficiently brittle that no yielding occurred; hence, for consistency only ultimate strengths are reported here.

### Modulus

The change in modulus with the temperature of annealing is shown in Figure 3. For blends rich in copolyester, there is a dramatic increase in modulus as these blends are annealed just above their  $T_g$  owing to the strong influence of annealing temperature on the level of crystallinity developed—results in this region were not included in Figure 1 since crystallinity was not detected at the lowest temperatures shown here. For blends containing 50% or more copolyester, the modulus appears to approach an asymptotic limit at high annealing temperatures. Because polycarbonate does not crystallize but does relax its molecular orientation under these conditions, its modulus decreases with annealing temperature. The 25% copolyester blend is anomalous in that its modulus continues to rise rapidly even at the highest temperature of annealing apparently owing to its continued development of crystallinity at these conditions. However, the fact that the modulus of this blend exceeds that for other blends is evidently related to its crystalline texture since the crystallinity of its copolyester fraction never exceeds the maximum attained at other compositions.

The room temperature moduli of the two pure component polymers have been examined over a wide range of annealing conditions to better understand the competing processes affecting blend modulus. For polycarbonate there is a substantial reduction in modulus, from 350,000 to 325,000 psi, on annealing for 30 min just below  $T_g$ . As demonstrated earlier,<sup>3</sup> this is the result of relaxation of molecular orientation induced during injection molding and similar annealing of an isotropic specimen would result in an increase in modulus caused by volume relaxation. A further step loss in modulus, from 325,000 to 315,000 psi, occurs when the material is annealed just above  $T_g$ , but further reductions do not occur

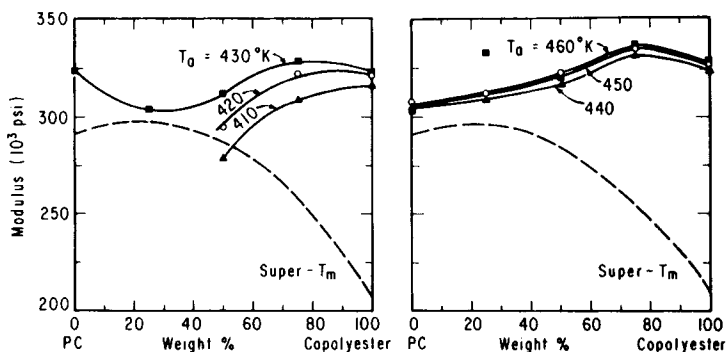


Fig. 4. Effect of annealing conditions on the moduli of PC/copolyester molded bars.

until the annealing temperature exceeds  $510^\circ\text{K}$ . Beyond this annealing temperature, a slow decline in modulus with increasing annealing temperature is observed to a modulus of 292,000 when annealed at  $550^\circ\text{K}$  for only 4 min. In contrast to this behavior, the copolyester modulus declines from 245,000 to just 235,000 on annealing just above its  $T_g$  due to relaxation. Then its modulus increases dramatically to about 315,000 psi when it is annealed at about  $30^\circ\text{C}$  above its  $T_g$  for 30 min. Annealing for 30 min at temperatures to about  $200^\circ\text{C}$  causes its modulus to continue to rise with the annealing temperature used to a plateau of about 325,000 psi.

The results from Figure 3 are replotted vs. blend composition in Figure 4 and compared with the behavior of totally amorphous blends annealed above the copolyester  $T_m$  to relax most of the molecular orientation induced by molding—dashed line.<sup>3</sup> The plot on the right is for annealing temperatures which are above the  $T_g$  for all compositions, whereas, on the left, the annealing temperatures are below the  $T_g$  for some PC-rich compositions. The shapes of these

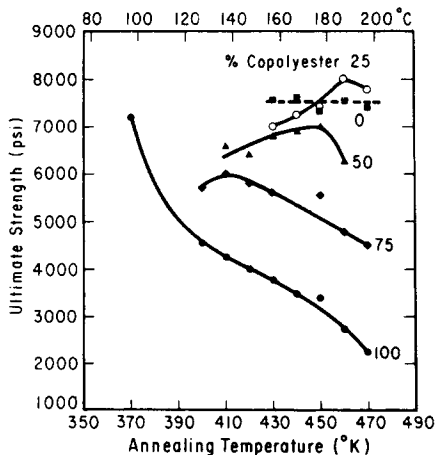


Fig. 5. Effect of annealing conditions on the ultimate strengths of PC/copolyester molded bars.

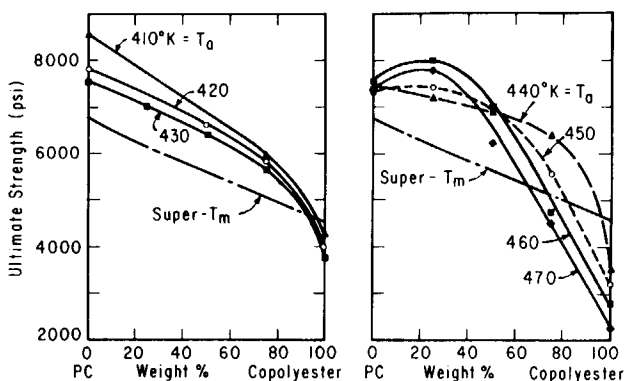


Fig. 6. Ultimate strengths of annealed bars.

curves are complex owing to the combination of processes mentioned above which occur simultaneously.

### Ultimate Strength

Figure 5 shows the ultimate strength of the various blends as the annealing temperature is changed. There is a marked decline for those compositions rich in copolyester owing to embrittlement caused by several factors. Crystallization under stress-free conditions generally leads to the type of embrittlement shown and this effect is usually more severe the higher the crystallization temperature owing to the coarser texture developed at these conditions. Further, molecular weight degradation of the copolyester during processing may be an additional contributing factor. In the range shown, there is little effect of annealing temperatures on the ultimate strength of PC. As seen for modulus, the 25% copolyester composition behaves somewhat anomalously.

The effect of annealing temperature on the room temperature ultimate strengths of both pure components has been examined for a wide range of temperatures. The ultimate strength of polycarbonate declines from an unannealed value of 8700 psi to a value of 6900 psi after annealing for 30 min at 270°C. Again, a step decrease, from 8700 psi to 7500 psi, is seen when annealing is done just above  $T_g$  for 30 min. For annealing temperatures between  $T_g$  and 270°C the ultimate strengths are observed to fall linearly with increasing annealing temperature. These responses are primarily the result of relaxation of the molded in molecular orientation. The ultimate strength of the copolyester falls linearly with increasing annealing temperature from 6500 psi for the as-molded material to 2100 psi after annealing for 30 min at 200°C. This response is due to both relaxation of orientation and crystallization. The contribution to decrease in ultimate strength by relaxation of orientation can be seen by annealing above  $T_m$ , followed by rapid cooling to prevent crystallization. We find that the ultimate strength after this treatment is about 4500 psi.

The trends with blend composition are displayed in Figure 6 with comparison to amorphous blends annealed above the copolyester  $T_m$  to relax most of the molecular orientation. Compared to the latter, these annealing conditions result in higher strengths for PC since none of them allow as much relaxation.

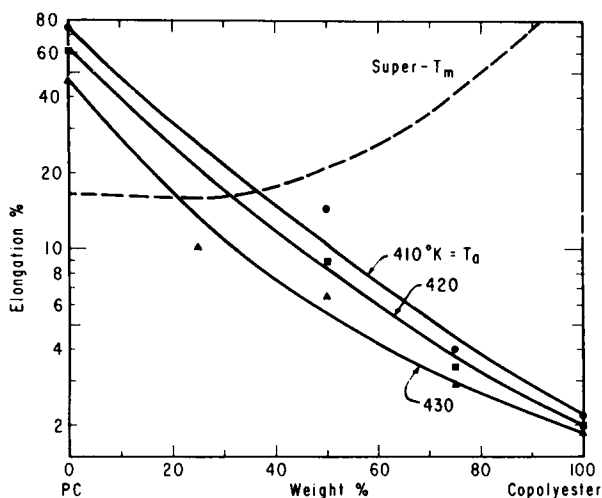


Fig. 7. Effect of annealing conditions on the ultimate elongation at break of molded bars.

Strengths for the pure copolyester drop below this isotropic, amorphous limit in every case owing to the embrittling factors mentioned earlier. Most blends lie above the super- $T_m$  line, and in some cases a maximum in strength versus composition occurs because of the anomalous behavior of the 25% copolyester material noted earlier.

### Elongation at Break

The elongation at break for the molded tensile bars annealed at various temperatures are shown in Figures 7 and 8 versus blend composition. The dashed lines shown for comparison correspond to the behavior of molded bars annealed above the copolyester  $T_m$  to relax orientation and subsequently quenched to yield

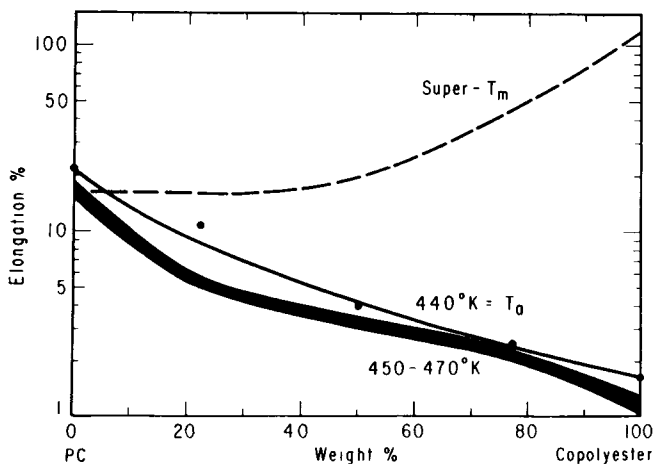


Fig. 8. Ultimate elongation at break of bars annealed at higher temperatures.

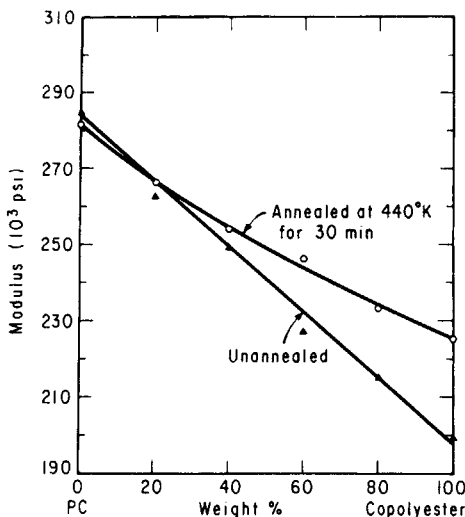


Fig. 9. Effect of annealing on the moduli of PC/copolyester film specimens.

fully amorphous materials.<sup>3</sup> To understand the response shown here, it is important to recall that the ductility, as indicated by the elongation at break, for these materials is greatly enhanced by molecular orientation<sup>3</sup>—all as-molded materials had elongations at break higher than those given by the dashed lines. The low annealing temperatures employed in Figure 7 are quite close to the  $T_g$  of polycarbonate, but in the short annealing time used, 30 min, complete relaxation of orientation could not occur so the elongation remains rather high compared to the super- $T_m$  annealed case. However, for the higher annealing temperatures shown in Figure 8 relaxation could occur in 30 min so that the elongation at break for polycarbonate goes to the limit of the super- $T_m$  relaxed specimens. For all other compositions, crystallization occurs and the elongation at break drops below the super- $T_m$  line in every case. The decline in ductility is initially greater the higher the annealing temperature, but this trend plateaus at the highest values used with the results in the range of 450–470°K being indistinguishable within the experimental scatter—see the band in Figure 8.

Compositions rich in the copolyester are severely embrittled by the annealing procedures described here. Since the copolyester experiences molecular weight degradation on processing,<sup>3</sup> one might wonder what role this factor plays in the embrittlement observed. Specific viscosity measurements following the most severe crystallization conditions used, 470°K for 30 min, for the various blends fell between the values for molded specimens and the molded specimens after super- $T_m$  annealing. Thus, these conditions do not degrade the copolyester any more than the latter mentioned process, and following this treatment the amorphous copolyester has an elongation at break greater than 100%.<sup>3</sup> Consequently, the embrittlement observed here must be primarily due to crystallization and not degradation.

### MECHANICAL PROPERTIES OF EXTRUDED FILM

All film specimens were mechanically tested using a table model Instron. Most specimens were  $\frac{3}{8}$  in. wide with a 10-in. gauge length. The modulus was ob-



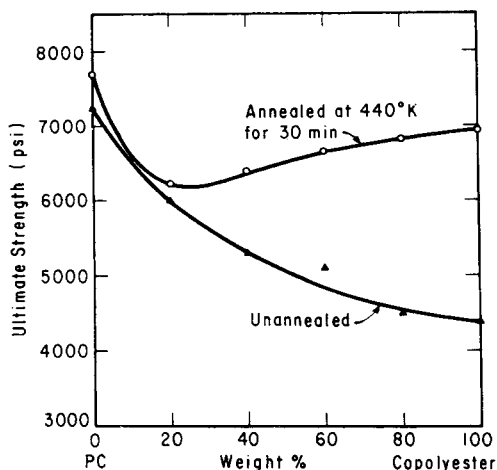


Fig. 10. Effect of annealing on the ultimate strengths of PC/copolyester film specimens.

tained, without using an extensometer, at a crosshead speed of 0.5 in./min. Yield or failure behavior was tested at a speed of 5 in./min. For comparison, a few specimens having a gauge length of 1 in. were tested. In every case, the films were stressed in the machine direction only.

The film samples were annealed at only one condition, 440°K for 30 min, which results in less crystallinity development than for molded bars under corresponding circumstances as shown in Figure 2. The mechanical properties obtained using film with a 10-in. gauge length are shown in Figures 9–11 for unannealed and annealed specimens. Data for the former agree well with previous results at this draw ratio.<sup>3</sup> The response to annealing film specimens is in marked contrast to that observed for molded bars described above. The modulus of the pure copolyester film is not increased as much by annealing as the same treatment causes for the molded bars. Annealing markedly *increases* the ultimate strength of the copolyester film and film rich in this component. The elongation at break of the copolyester in film form is not decreased as much on

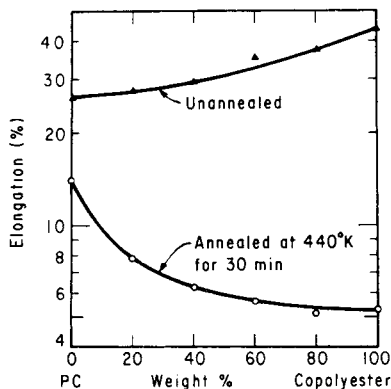


Fig. 11. Effect of annealing on ultimate elongations of PC/copolyester film specimens (10-in. gauge length).

annealing as observed for molded bars. The better retention of mechanical properties of the copolyester-rich blends on annealing is partly related to the lower level of crystallinity developed by the film; however, it is believed that at least part of this response is owing to a different crystalline texture developed, resulting from the differences in sample histories.

The elongation at break data in Figure 11 are substantially lower than previous data.<sup>3</sup> The reason for this can be entirely related to end effects during tensile testing. The data in Figure 11 were obtained using a 10-in. gauge length whereas the previous data were obtained using a 1-in. gauge length. We have repeated the measurements in Figure 11 using a 1-in. gauge and have obtained nearly identical results with those reported previously. Clearly, end effects during testing are very important.

### SUMMARY

This study indicates that the crystallization of the copolyester component from the blend by annealing at various temperatures between the blend  $T_g$  and the copolyester  $T_m$  generally leads to a loss in blend ductility. The effect of annealing on the ductilities, strengths, and moduli of molded bars cannot, however, be simply related to the crystallization of the copolyester component because of the competing influences of relaxation of molded-in orientation and some molecular weight degradation which also occur when the bars are annealed. The effect of annealing on the mechanical properties of molded bars is consequently a quite complex function of these various phenomena and their dependence on blend composition. The variation in film mechanical properties with annealing are more consistent with the simple expectation based on crystallization of the copolyester because the film materials have less initial molecular orientation than bars, less crystallization, and a probably different crystal texture at the same annealing conditions than is developed in the bars, and are thermally degraded less than bars because of the milder process history used in their formation.

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