# Thermal and Mechanical Behavior of Polycarbonate–Poly(ethylene Terephthalate) Blends

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## Synopsis

Melt blends of polycarbonate and poly(ethylene terephthalate) were formed by continuous extrusion and injection-molded into bars for mechanical testing. Thermal analysis was used to ascertain transitional behavior and the level of PET crystallinity at various points in the fabrication and testing process. The mechanical properties showed little departure from additivity except for the percent elongation at break which was substantially larger for certain blends than expected. Glass transition behavior suggests two amorphous phases for PC rich mixtures and only one mixed phase in the PET rich region. Crystallizability of the PET after the blend was held for prolonged times in the melt state suggests that interchange reactions do not occur to any great extent.

## INTRODUCTION

A previous paper from this laboratory[1] reported on the transitional behavior of melt processed blends of polycarbonate (PC) and poly(ethylene terephthalate) (PET). Blends rich in PC exhibited two glass transitions while only one $T_g$ could be found for compositions rich in PET using either differential thermal analysis or dynamic mechanical testing. These results suggest miscibility over part of the composition range for PC–PET, which is in contrast to total miscibility implied by the patent literature.[2] Nevertheless, there is still considerable practical interest in these blends as well as mixtures of polycarbonate with other polyesters.

As a result of this interest, further studies on the PC–PET system are reported here. The previous work employed simple batch melt mixing followed by compression molding into test specimens, whereas in the present work continuous extrusion was employed to make the blend and some test specimens were injection-molded using the extrudate. The latter provides a more controlled process for meaningful evaluation of product characteristics and their variation with composition. Of particular interest here are the mechanical properties of the injection-molded blends and the state of PET crystallinity at various points in the process for these blends. Also, the issue of interchange reactions between PET and PC in the blend has been reexamined in light of recent studies on related systems.[3-5]

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## MATERIALS AND PROCESSING

The bisphenol A polycarbonate used was Lexan 131-111 ($\overline{M}_n = 13{,}300$ and $\overline{M}_w = 34{,}200$) provided by the General Electric Co. The poly(ethylene terephthalate) was a bottle grade material (intrinsic viscosity = 0.74 dL/g), supplied by Celanese Plastics and Specialties Co., with the commercial designation Petpac 2113.

Pellets of PC and PET were combined in the desired weight ratio and then dried for 12–14 h in an air oven at 80°C to remove sorbed water to prevent hydrolysis during melt processing. The dried pellets were subsequently heated to 135°C to promote crystallization of the PET since this reduced plugging in the feed hopper and gave more uniform flow in the feed section of the extruder (diameter = 0.75 in., $L/D = 20$) used for melt mixing. The extrudate was quenched by passing it through an ice water bath and was chopped into pellets. Residence times in the extruder were typically 4–5 min. The blend pellets were subjected to identical drying and crystallization protocols prior to injection molding by a ram type machine to form ASTM D-638 dog-bone specimens for mechanical testing. Processing parameters for extrusion and molding were adjusted to give nearly optimum conditions for each composition.

## THERMAL ANALYSIS

Blends melt processed in the manner described above were examined by differential scanning calorimetry using a Perkin-Elmer DSC-2 equipped with a thermal analysis data station for data manipulation. All samples were run in a nitrogen atmosphere.

### Transition Behavior

As a comparison with the previous work,[1] pellets collected from the extrusion step were used to determine glass transition and melting point behavior. Glass transitions were recorded from an initial heating scan, at 10°C/min, using extruded pellets with no intermediate thermal treatment. The results are shown in Figure 1, and they are quite similar to those described previously. Blends with 60% or less of PET showed two distinct $T_g$'s while only $T_g$ could be detected for those containing 75% or more PET. This suggests that only one amorphous phase exists in these PET-rich blends. As would be expected for such materials, the location of the $T_g$ deduced by DSC could be varied over a 5–10°C range by manipulation of prior thermal history.

For measurement of the PET melting point, extruded pellets were dried as described earlier and then rapidly heated in the DSC to 290°C. After a few seconds in the melt state, the sample was quenched to room temperature at the fastest cooling rate possible in the DSC (i.e., rate setting = 320°C/min). During subsequent heating at 20°C/min, crystallization occurred followed by melting. The peak temperature of this melting endotherm is recorded in Figure 2 for each blend. These results are substantially equivalent to those obtained earlier[1] using an analogous, but not identical, procedure. As before, the observed melting point varied considerably with thermal history.
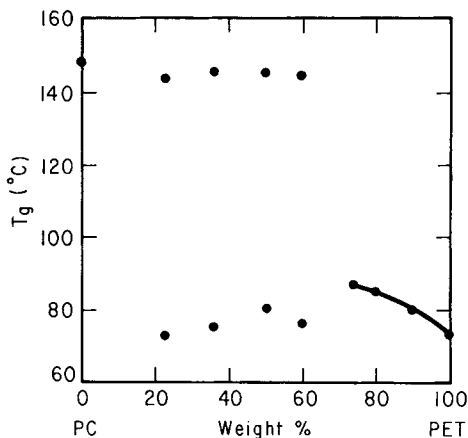
Fig. 1. Glass transition behavior for PC–PET blends.

## Interchange Reactions

Because of the functional linkages and end groups in PET and PC, various interchange reactions are possible, as recently discussed.[3-5] This type of chemical reorganization would eventually convert a simple physical blend into an essentially random copolymer consisting of residues from the two originally different types of chains. Owing to the dissimilarity of the chemical units, one expects crystallizability to diminish as such reactions progress. Consequently, as described recently,[3,4] a convenient tool for examining interchange reactions in blends is to monitor the potential for crystallization by thermal analysis, using carefully controlled procedures. The extent of such reactions will depend on the time–temperature history of the blend and the presence of any residual catalysts from the polymerization step.

In order to ascertain the extent of possible interchange reactions for PET–PC blends during melt processing type conditions, the procedure developed by Smith et al.[4] was adapted for the present system. Samples were heated in the DSC as rapidly as possible to 290°C and held there for varying times
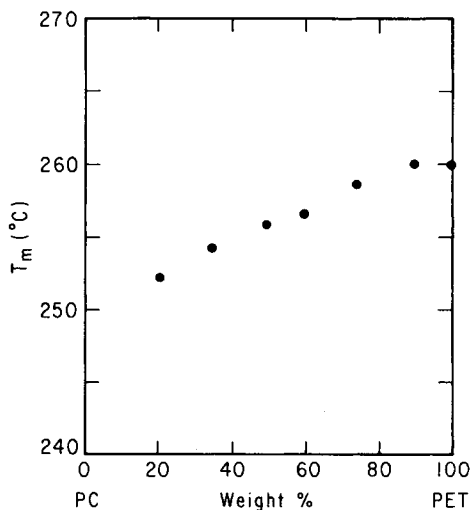


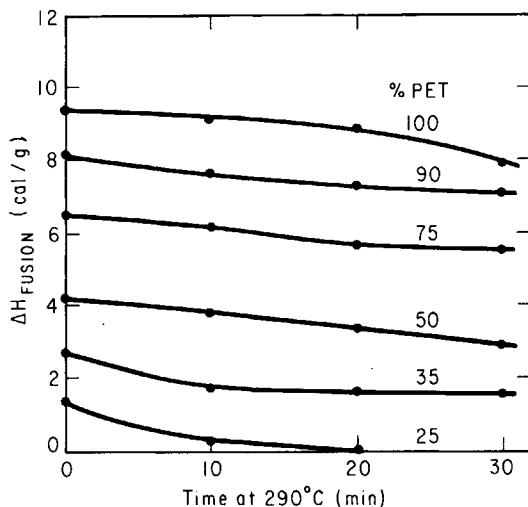Fig. 2. PET melting points. See text for thermal procedures.

Fig. 3.   Heat of fusion after crystallization at 167°C for 30 min as a function of time at 290°C.

up to 30 min—this temperature is typical for melt processing operations. Following this melt reaction period, the sample was quenched at a rate setting of 320°C/min to an annealing temperature of 167°C and held there for 30 min. These conditions should allow complete development of any potential crystallinity without any further reaction possible. After annealing, the sample was cooled to room temperature, and, after equilibration, a thermal scan up to 290°C was made at 10°C/min. Since complete crystallization occurred during annealing, no exotherm was noted on this scan. Figure 3 shows the heat of fusion measured by this procedure for each blend composition as a function of the simulated processing time at 290°C. There is a slow decline in heat of fusion with time at each composition, but there is no precipitous loss in crystallizability like that noted by Smith et al.[4] for the PC–copolyester system they examined. In the present case, samples held in the melt for 20 min or longer had an amber to dark brown color after removal from the DSC. Thus, thermal degradation may account for some of the loss in heat of fusion at these longer times, which are considerably in excess of the residence period in any practical processing procedure.

The data in Figure 3 are replotted in Figure 4 as the heat of fusion vs. the composition of the blend for two fixed periods of time at 290°C. In the absence of any physical or chemical interaction between PET and PC, one would expect the results to follow the dashed line shown. In every case, the blends fall slightly below this ideal limit with the departure being larger the longer the time at 290°C. The corresponding curve for 30 min was not constructed because of the significant decline in the heat of fusion for pure PET which obviously is not the result of copolymer formation by interchange reaction.

It is interesting to note that blends rich in PC seem to experience a larger reduction in the heat of fusion than those rich in PET. We might have expected the extent of interchange reactions to have been exactly the opposite of this based on the conclusions about amorphous phase behavior
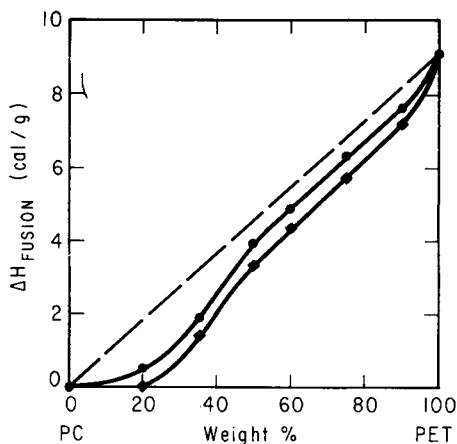
Fig. 4.   Replot of data from Fig. 3 as a function of blend composition: (●) 10 min; (◆) 20 min.

derived from the glass transition observations noted above. We would expect PET-rich blends to form a homogeneous melt which would maximize the opportunity for reaction between PC and PET linkages or end groups. On the other hand, PC rich blends are not expected to form a single phase melt; hence, encounters between PC and PET would be less frequent since they would be restricted to the interface between phases or the result of limited solubility of one component in the other. In any case, we may conclude that while there is some evidence for interchange reactions their extent is quite limited here as compared to that noted previously[4,5] for PC with other aromatic polyesters. This conclusion may not be true for all commercial PETs as they could have different types and amounts of residual polymerization catalysts which might promote greater amounts of reaction.

## Crystallinity after Processing

The extent of PET crystallinity for blend samples after extrusion and after injection molding were assessed by thermal analysis. Since PET crystallization was quite limited in every case, further crystallization occurred
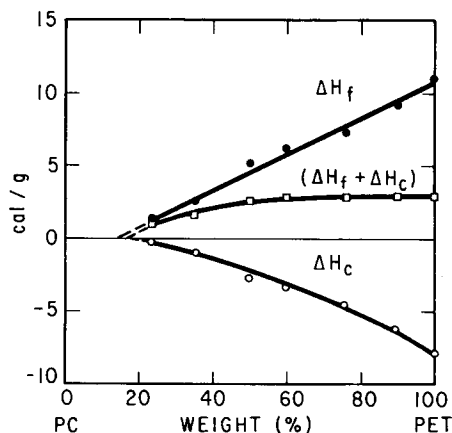


Fig. 5.   Heats of fusion, $\Delta H_f$, and crystallization, $\Delta H_c$, after extrusion.
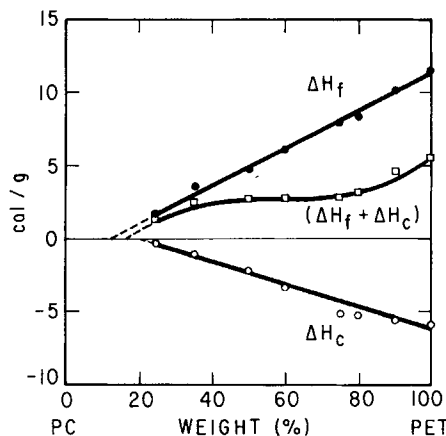
Fig. 6.   Heats of fusion, $\Delta H_f$, and crystallization, $\Delta H_c$, after injection molding.

upon heating in the DSC. The energy change associated with fusion, $\Delta H_f$, at the PET melting point was assigned a positive sign while the exothermic energy associated with crystallization during heating in the DSC, $\Delta H_c$, was given a negative sign. The results for extruded and injection molded materials are given in Figures 5 and 6, respectively. The algebraic sum ($\Delta H_f$ + $\Delta H_c$), also plotted, is indicative of the level of crystallinity which existed in the materials directly after processing and prior to heating in the DSC. These could be converted into fractional crystallinities by dividing by the heat of fusion for completely crystalline PET; however, this has not been done here owing to uncertainties in the value that should be used for this quantity.[6] Based on a typical value, the maximum crystallinity for as extruded PET is about 15%. Injection-molded PET has about twice this level, apparently owing to the greater stresses experienced during molding as compared to extrusion. Values for $\Delta H_f$ and $\Delta H_c$ are virtually identical after extrusion as after molding except for pure PET and the blend containing 90% PET. Both quantities appear to be zero for blends containing about 20% PET or less. These blends fail to develop significant crystallinity even after annealing for 30 min at 167°C as noted earlier.

The crystallinity of the as molded specimens no doubt influences the mechanical behavior of these materials.

## MECHANICAL PROPERTIES

The injection-molded dog-bone specimens were mechanically tested on an Instron using the following procedures. An extensiometer with a 1-in. gauge was used while determining the modulus at a crosshead speed of 0.1 in./min. Yield and failure properties were measured at a crosshead speed of 2 in./min with strains computed from crosshead movement and an effective gauge length.

The moduli and yield strengths are shown in Figure 7. The values are quite similar for each property across the composition range. The trends indicated are complex and may not be significant owing to the small size of the variations. In any case, interpretation would be difficult. The ultimate stress at failure (see Fig. 8) shows a large change reflecting the varying nature of the stress–strain diagram after yielding with blend composition.
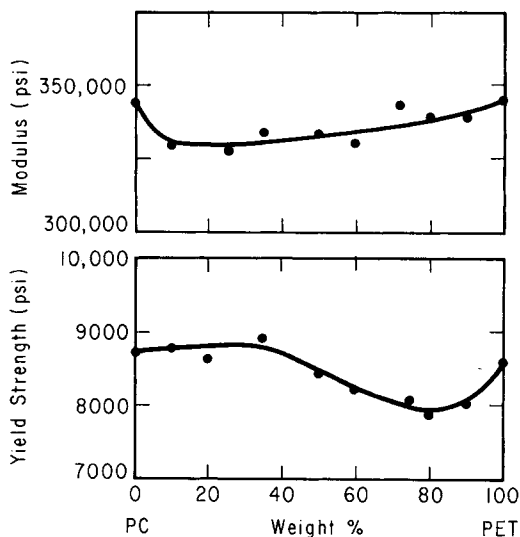
Fig. 7. Modulus and yield strength for injection molded blends.

Compared to their yield stresses, PET broke at a lower stress while PC broke at a higher value.

The most unusual feature was the percent elongation at failure, which is shown in Figure 9. The blends failed at higher strains than did the pure components, and, in fact, blends containing between 60% and 80% PET did not fail within the available crosshead travel—corresponding to a strain of about 200%. The nature of the stress–strain diagram for compositions in this region are contrasted in Figure 10 with that of pure PET. It is perhaps significant that the elongation at break appears to go through a maximum very near the border between miscibility and immiscibility. All specimens on the left branch of the curve in Figure 9 had two glass transitions while those on the right branch all had a single glass transition.
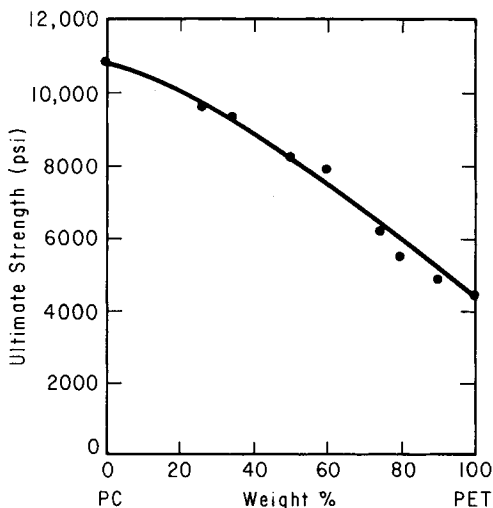

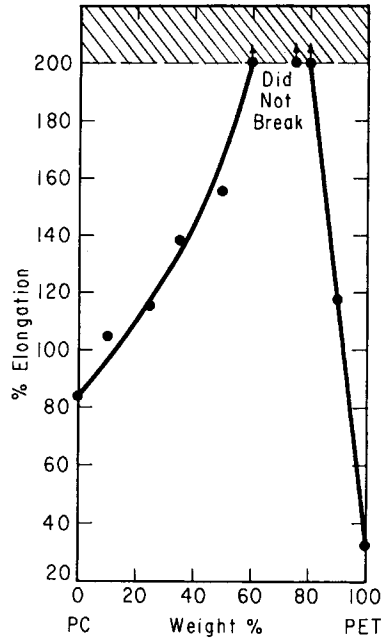
Fig. 8. Ultimate strength for injection molded blends.

Fig. 9. Elongation at break for injection molded blends. Maximum available crosshead equivalent to 200% elongation.

Figure 11 shows a photograph of typical dog bone specimens after extension in the Instron. The samples containing 0%, 25%, 50%, and 100% PET broke in the middle of the gauge section (sample halves are refitted together for photo) after necking. The 60% and 80% PET bars did not fail in the available crosshead travel. The relative lengths of these tested specimens gives a direct visual reflection of the quantitative data shown in Figure 9. There was a progressive whitening of the specimens in the necked region as the PET content increased. This is especially apparent in the bars which did not fail. This is believed to be due to stress-induced crystallization during extension. Material excised from the necked region of each composition was examined by DSC to assess changes in crystallinity during mechanical
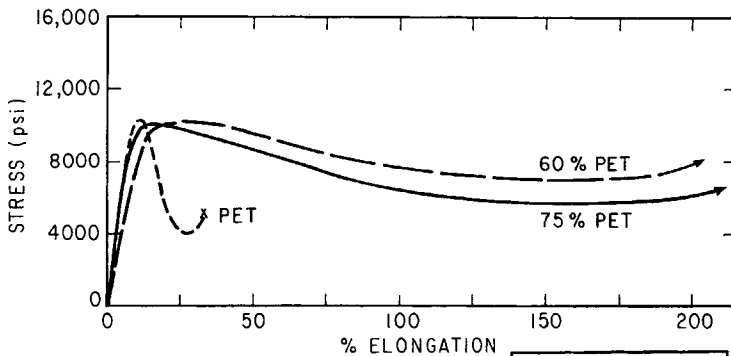


Fig. 10. Typical stress-strain diagrams illustrating high ductility of 60 and 75% PET blends.

0    20    40    60    80    100
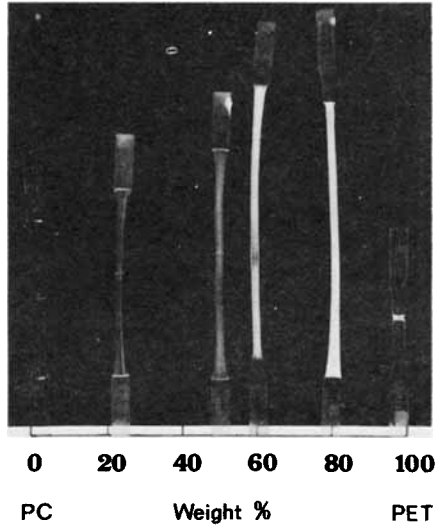
PC            Weight %            PET

Fig. 11.   Photographs of dog bone specimens after testing.

testing. Crystallization exotherms did not appear on heating in the DSC
except for the sample containing 25% which showed a very small one. The
heats of fusion for these elongated specimens are shown by the upper curve
in Figure 12. The lower curve then is the net heat of fusion, $\Delta H_f + \Delta H_c$,
for the as-molded bars—data reproduced from Figure 6 for comparison.
Clearly, there is a very large increase in the level of crystallinity as a result
of the drawing process which occurs during mechanical testing. These data
suggest that the lack of PET crystallinity at very low PET contents in
specimens after processing is owing to physical reasons since the $\Delta H_f$ after
testing extrapolates to the origin. In fact, $\Delta H_f$ after testing seems to be a
linear function of blend composition, i.e., a constant fraction of PET present
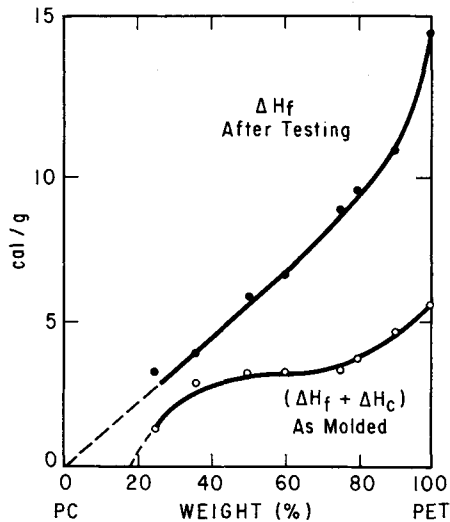


Fig. 12.   PET heat of fusion for material taken from necked region of samples after me-
chanical testing (upper curve). Lower curve reproduces net heat of fusion from Fig. 6 prior to
testing for comparison.

in crystalline, except for a rapid upswing as pure PET is reached. Crystallization during testing is no doubt a significant factor in the yield and ultimate mechanical properties of these materials.

As part of our earlier work with PET–PC blends, a preliminary assessment of mechanical properties was made using thin sheets compression-molded from batch mixed blends. These results[7] show a remarkable similarity to the trends exhibited by the current data including the maximum in percent elongation at failure shown in Figures 9 and 11. The previous results were more variable, of course, owing to the less controlled conditions of processing and testing, and the absolute values for properties in the two studies reflect differences in molecular orientation resulting from compression vs. injection molding.

## SUMMARY

The results reported here support the previously published conclusion that PET–PC blends rich in PC exhibit two glass transitions indicating the presence of two amorphous phases. In contrast, only one $T_g$ is apparent for certain PET-rich blends, suggesting a single, mixed amorphous phase. Based on observations of crystallization behavior, it is concluded that the extent of interchange reactions between PC and PET during practical processing conditions is not very great and does not lead to a randomized copolymer as reported for blends of some other condensation polymers.

The mechanical properties of PET–PC are quite good and do not show any significant negative departures from additivity typical of many phase-separated blends. In fact, there is an interesting increase in the elongation at break on blending whose origin remains unclear. These good properties are no doubt a reflection of the favorable interactions between PC and PET at the molecular level,[8,9] which make this system on the edge of complete miscibility. These mechanical properties plus the inherent chemical resistance PET brings to blends with PC justifies current interest in this system.

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