Polyester–Polycarbonate Blends. II. Poly(ethylene Terephthalate)

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Synopsis

Melt blends of polycarbonate and poly(ethylene terephthalate) were prepared and examined for their transitional behavior by thermal analysis and dynamic mechanical testing. A single T_g was observed for compositions containing more than 60%–70% PET by weight while compositions below this range showed two glass transitions. From this it is concluded that PC and PET are completely miscible in the amorphous phase for PET-rich compositions, whereas PC-rich blends separate into two amorphous phases which apparently contain both components. Melting point and crystallization behavior are consistent with these conclusions and suggest that very little if any interchange reactions occur between the ester and carbonate groups during melt mixing.

INTRODUCTION

There has been considerable commercial interest in blends of various polyesters with bisphenol A polycarbonate (PC). Thus, it is of fundamental interest to study this class of blend systems since apparently some polyesters show varying degrees of partial miscibility or total miscibility with PC. The first paper in this series[1] dealt with the case in which the polyester was poly(butylene terephthalate). This paper deals with blends in which the polyester is poly(ethylene terephthalate) (PET). This blend system has been the object of numerous patents.[2-6] One of the older patents[2] presents an extensive body of data on the properties of PET–PC blends and claims significant improvements in the balance of mechanical behavior versus processing characteristics as compared to pure polycarbonate. On the basis of these results, it is stated that polycarbonate is miscible with poly(ethylene terephthalate) for all compositions. No fundamental information was given to support such a conclusion; therefore, it was of interest to investigate the validity of this claim.

PET crystallizes rather readily and, based on our previous experience[7,8] with blends containing such components, one could expect PET to crystallize from blends with PC whether the two are miscible or not. For blends with one or more crystallizable components, the question of miscibility concerns the remaining amorphous material. Generally, one may expect a system that forms a single miscible amorphous phase to show a single glass transition temperature (T_g) which varies with overall blend composition but in a way complicated by the removal of a portion of one of the components when it crystallizes, so that the composition of the amorphous phase is not equal to the overall blend composition. If the two components do not mix completely in the amorphous phase, then one may expect multiple transitions which occur at temperatures determined by the compositions of these phases. Thus, an effective means of examining the phase structure in the amorphous portions of such blends is to study the tran-

sitional behavior, but it should be recalled that this may be somewhat compli-
cated by the complex issues that confront any investigation of transitions in
semicrystalline polymers, e.g., less intense transitions because of the reduced
amorphous fraction and effects of crystallinity, morphology, and thermal history
on the nature of the amorphous phase. In this study, both dynamic mechanical
properties and thermal analysis were used to examine the transitional behavior
of PC–PET blends. It is concluded that these two components do form a mis-
cible amorphous phase at high PET contents but separate into two amorphous
phases at lower PET contents.

It is important to realize for such systems that interchange reactions involving
the ester and carbonate groups are possible in principle at the high temperatures
required for melt mixing. We see no evidence to suggest that such possibilities
actually do occur to an extent that would account for the results observed here.
Subsequent papers on other systems will deal more directly with this ques-
tion.

BLEND PREPARATION

The bisphenol A polycarbonate (PC) used here was Lexan 310 supplied by
the General Electric Co. The poly(ethylene terephthalate) (PET) was a fiber-
grade product supplied by Fiber Industries, Inc., with a viscosity-average mo-
lecular weight of 19,200.

All blends were prepared by melt mixing in a Brabender Plasticorder using
the following procedure. Pellets of the two polymers were dry blended to the
desired composition and kept in a vacuum oven at 125°C for a minimum of 2 hr
to remove moisture. A quantity of these hot pellets was transferred to the mixing
bowl of the Brabender which had been preheated to 260°C. This charge, when
melted, completely filled the mixing chamber. The mixing blades were set at
a speed of 2–4 rpm during polymer addition. After all the pellets had been
added, the lid was closed to minimize oxygen absorption by the polymer, the
speed of the mixing blades was raised to 90 rpm, and the heaters adjusted to
obtain a final blending temperature of 290°–300°C to ensure complete melting
of the crystalline PET. The high rpm was employed to reduce the mixing time
needed to approximately 8–10 min. During this time the torque stabilized, but
discoloration of the polymers had already begun. Pure PC melts were quite clear,
whereas pure PET melts were always somewhat hazy, evidently owing to addi-
tives. The melts of the blends showed translucency in proportion to the PET
content.

Prior to removing the melt from the mixing chamber, the melt was kneaded
with a spatula to remove any trapped air bubbles. Then, the molten polymer
was quickly transferred to a three-part mold made from aluminum plates, in-
ternal dimensions 3.5 in. × 4.75 in. × 1/8 in., which had been preheated to 275°C
(slightly above the melting point of PET) in a hydraulic press equipped with
heating plates. Slight pressure of about 10 psi was maintained until the polymer
melted and filled the mold. Then, a pressure of about 90 psi was applied for a
very short time. The mold was then removed from the press and quenched into
cool water to minimize thermal decomposition and oxidation. Portions of the
resulting 1/8-in. sheets were used directly for thermal analysis or to prepare thin
films for dynamic mechanical testing.

Thin films were prepared according to the following standardized procedure.

A 1–g sample was cut from one of the $\frac{1}{8}$-in.-thick sheets and dried in a vacuum oven for 15 hr at 120°C. Two aluminum plates were preheated in the press to 280°C. Then, the sample was removed from the vacuum oven and immediately inserted between the aluminum plates with four metal shims 0.005 in. thick placed along the four sides to control thickness. Only the weight of the top aluminum plate was applied to the sample until it had melted and started to flow, and then a pressure of 90 psi was applied to form a film of uniform thickness. The plates (at 280°C) were then immersed into liquid nitrogen to give a clear and bubble-free film with good flexural mechanical properties. However, slowly cooling the mold in the press to room temperature produced an annealed film that was opaque and brittle.

DYNAMIC MECHANICAL BEHAVIOR

Dynamic mechanical properties of samples cut from the thin films described above were determined using a Rheovibron at a frequency of 110 Hz. In some cases, the magnitude of the mechanical damping peak exceeded the maximum range of the tan δ meter (1.73 at 70 db). Therefore, the range of the tan δ meter was extended to higher values by drawing an additional logarithmic scale (analogous to the other scales on the tan δ meter) that could be used at 60 db.

Polycarbonate

The dynamic mechanical properties of melt-processed PC were found to be largely independent of the thermal treatment and history of the polymer in contrast to PET as described later. Figure 1 summarizes the dynamic mechanical behavior of 100% PC. Only two mechanical transitions are seen, viz., the β-transition at low temperature and the α-transition at high temperature. The β-transition, which is associated with the in-chain motion of the carbonate group, appears at −75°C in both the loss modulus (E'') and the mechanical damping (tan δ) curves. The α-transition, T_g, occurs at 145° and 150°C in the E'' and tan δ curves, respectively. The locations and mechanisms of these relaxations in PC have been described extensively in the literature.[9–15]

Poly(ethylene Terephthalate)

PET is more complex than PC due to its crystalline character, which depends strongly on previous history. Consequently, the dynamic mechanical properties of PET depend greatly on thermal treatment and history. A comparison between the mechanical properties of the α-transition of a quenched (first heat) and annealed (second heat) sample of PET is illustrated in Figure 2. After the first heat of the quenched sample was completed, the same sample was annealed under slight tension by keeping it in the Rheovibron furnace as it was slowly cooled from 200°C to start the second heat run (annealed, and therefore higher crystallinity) at room temperature. The peculiar nature of the first heat results is simply attributed to PET crystallization in the Rheovibron as the amorphous PET is heated above the T_g region. Because of this phenomenon and the confounding effects it produces, it is clearly not practical to examine quenched samples even though for blends this would be of interest since the transition behavior in the absence of PET crystallinity is an important issue. The tech-
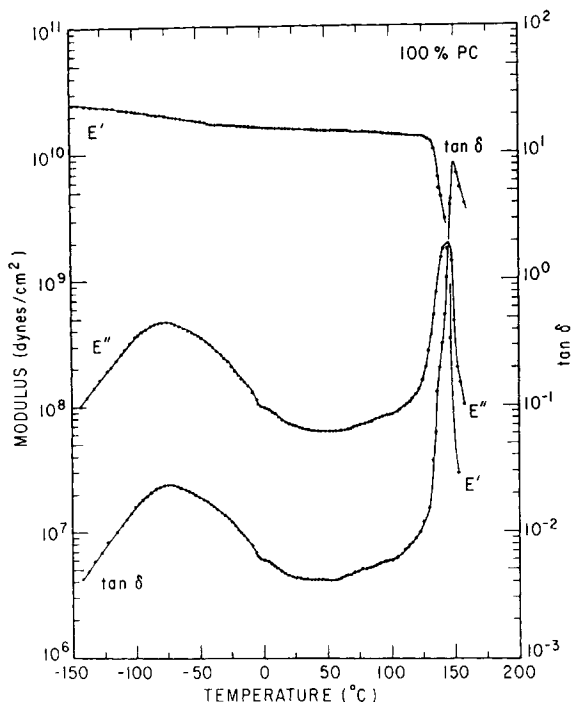
Fig. 1. Dynamic mechanical behavior at 110 Hz for PC slowly cooled from 270°C to room temperature.

nique of thermal analysis appears to be more appropriate for such measurements as described later. To avoid the problem of crystallization during testing, most of the dynamic mechanical data shown here for PET containing specimens were obtained on samples which were heat treated to produce a stable PET crystalline phase. This was done in some cases by slowly cooling the specimen in the mold or by a more prolonged annealing at about 150°C for several hours. Figure 3 shows Rheovibron results for a thoroughly annealed PET sample over a broader temperature range which reveals the well-known α- and β-relaxations for this semicrystalline polymer plus a much smaller peak near 37°C whose origin is unknown.

The transitions in PET have been thoroughly discussed in the literature,[1,16-21] and the glass transition temperature, which corresponds to the α-peak, has been shown to increase significantly as the level of crystallinity increases.[17,21] This same trend may be seen in Figure 2 by comparing the location of the first peak in the quenched or amorphous specimen, 82°C on the E'' curve, with that for the second heat or annealed specimen, 95°C on the E'' curve. It has also been reported, however, that beyond a certain level of crystallinity the α-transition shifts toward lower temperatures once again.[17,21] The exact relationship between T_g and the level of crystallinity is therefore somewhat difficult to interpret.

The lower-temperature β-transition, shown in Figure 3 to occur at −35°C, is believed to be the result of a combination of motions of limited portions of the chain.[9]
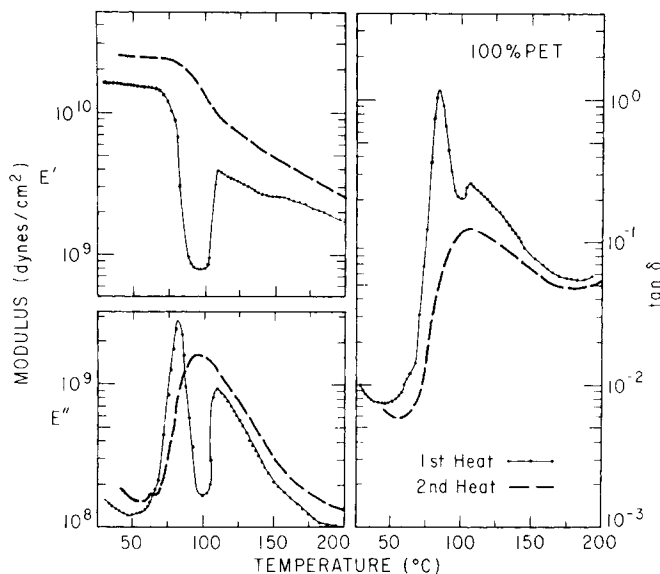
Fig. 2. Dynamic mechanical behavior at 110 Hz for PET. Sample was quenched from melt into liquid nitrogen prior to first heat and then cooled slowly from 200°C to room temperature prior to second heat.

PC–PET Blends

PC–PET blends show two types of patterns with respect to behavior in the α-transition range of the two pure components. Figures 4 and 5 show that blends containing 50% PET or more by weight have a single α-peak whose location depends on blend composition. This may be taken as evidence for a single amorphous phase comprised of a miscible mixture of PC and PET. However, Figures 6 to 8 show that blends containing 50% PET or less have two peaks in the α-range. At high PC levels these peaks are well developed and distinct whereas at the 50% level the lower peak appears as a shoulder on the higher-temperature peak. This might be taken as evidence for two amorphous phases differing in composition, i.e., this systems appears to have a miscibility gap.

The upper part of Figure 9 shows the temperature location of the observed peaks seen in Figures 4–8 as a function of overall composition. Both peak locations are recorded for blends rich in PC. For blends containing 20%, 30%, and 40% PET the lower peak occurs at approximately the same temperature, 104°C on the E'' curve, which is higher than that seen for pure PET, suggesting that this phase may contain both PC and PET. The lower peak degenerates into a shoulder for blends containing 50% PET. Consequently, a precise peak location cannot be assigned; however, it appears that if a peak could be resolved, that it would occur at a slightly higher temperature than 104°C. This peak appears at 82°C in the 10% PET blend (see also Fig. 8) which is even below that for pure, crystalline PET. The full curves in Figure 8 were obtained on a quenched sample in which the PET was not crystalline. This sample was slowly cooled to room temperature and annealed as shown. Then, it was heated a second time (see dashed tan δ curve) which gave a peak at the same location. Subsequent thermal analysis on this sample showed no PET crystallinity. Evidently, the low-temperature location of this peak in the 10% PET blend results from the effect of crystallinity on T_g to be expected for PET-rich phases as discussed earlier.
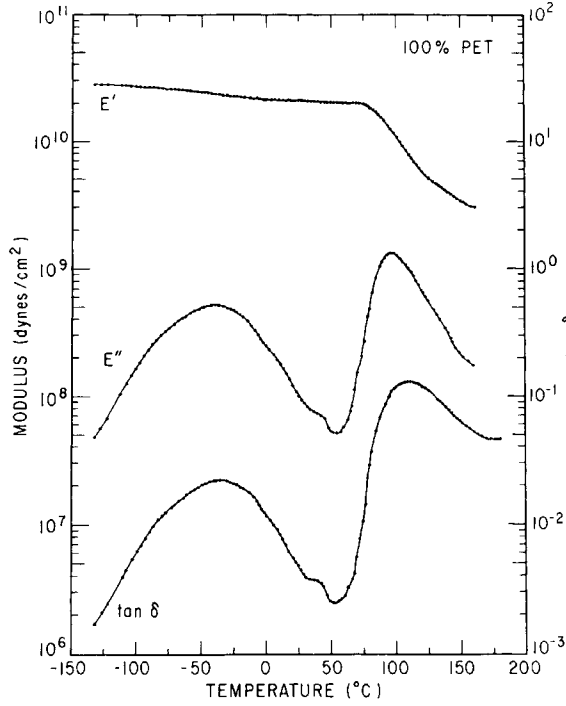
Fig. 3. Results for annealed PET to show low-temperature damping peak.
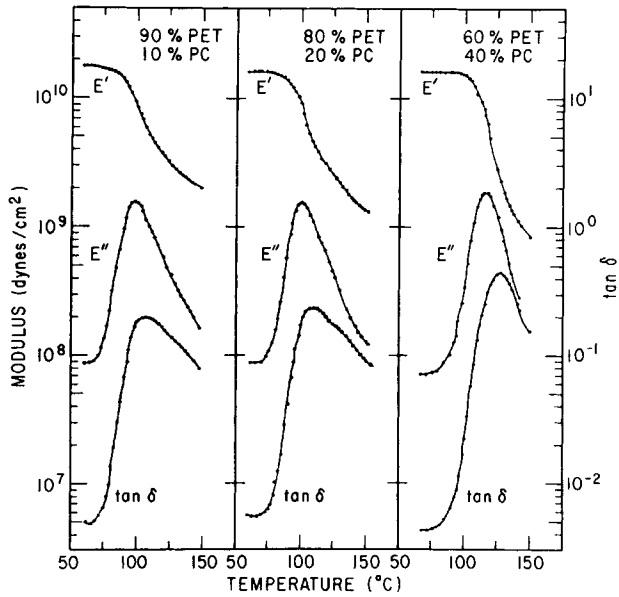

Fig. 4. Dynamic mechanical behavior in the glass transition region for PET-rich blends. All samples were thermally conditioned to develop crystallinity.

All of the blends showed a single β-peak (see Figs. 5, 7, and 8) whose temperature location varied with blend composition in the manner shown in the bottom portion of Figure 9.
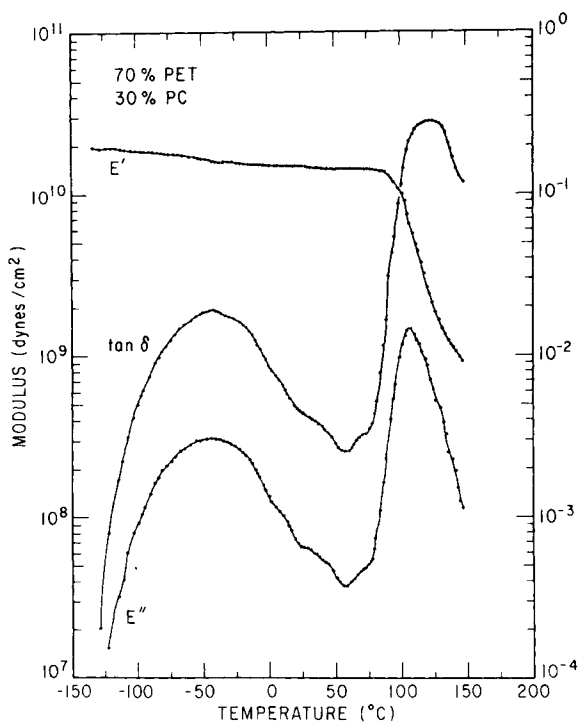
Fig. 5. Results for an annealed 70% PET blend to show low-temperature damping peak.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

Because the glass transition temperature (T_g), the crystallization temperature (T_c), and the crystalline melting point (T_m) may depend greatly on thermal history, all results reported in this section were determined (using an R. L. Stone DTA) on samples that were identically treated thermally to provide a valid comparison. Each sample was subjected to three heating cycles at a heating rate of 10°C/min. However, PC–PET blends containing more than 50% PET were subjected to one additional heating cycle. Each of the four heating parts of the cycles (referred to here as first, second, third, and fourth heats) had a different thermal history. Prior to the first heat, each sample was annealed for 55 hr at 170°C. At the end of the first heat and prior to the second heat, the sample was removed from the heating chamber of the DTA and quickly quenched into liquid nitrogen from a melt temperature of 285°C. At the end of the second heat and prior to the third heat, the sample was quenched in a similar manner and then annealed for 2 hr at 180°C. At the end of the third heat, the sample was quenched into liquid nitrogen from 285°C, and then the fourth heat was started. So, the odd-numbered heats (① and ③ in the figures) correspond to annealed samples and the even numbered heats (② and ④), to quenched samples.

Polycarbonate

DTA results for melt-processed PC indicate a glass transition temperature of 150°C in agreement with that reported by others.[9] Upon excessive annealing, it appears that amorphous PC developed slight crystallinity (sample was still clear after annealing) as indicated in the first heat by the broad and small fusion
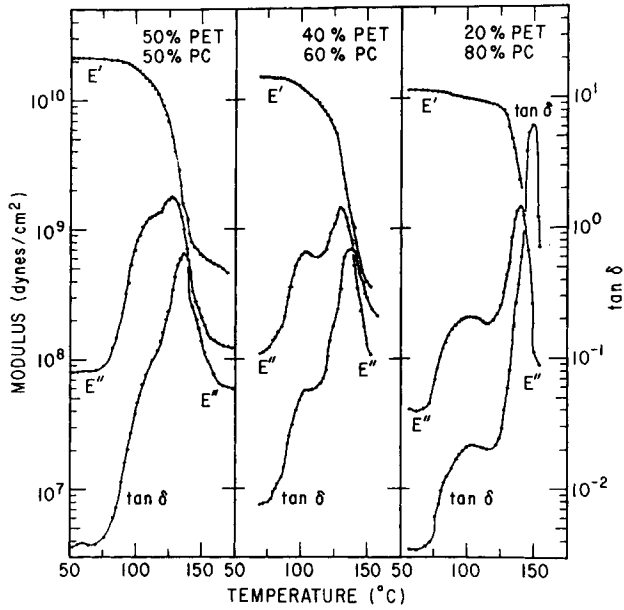
Fig. 6. Dynamic mechanical behavior in the glass transition region for PC-rich blends. All samples were thermally conditioned to develop crystallinity.
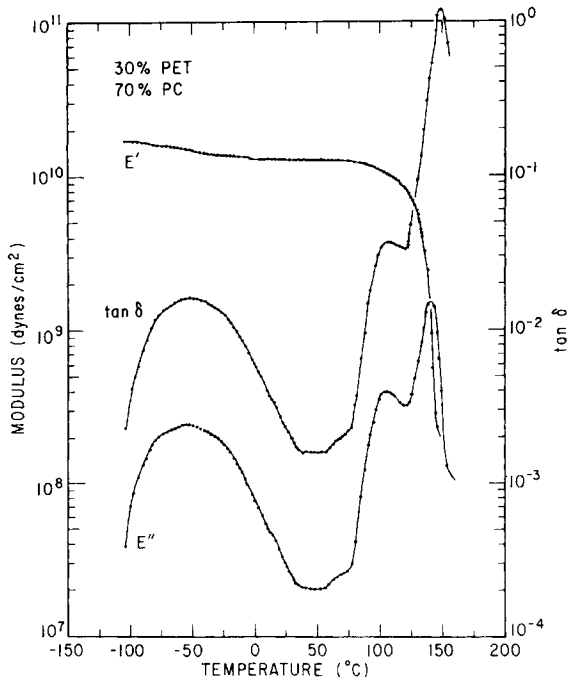

Fig. 7. Results for an annealed 30% PET blend to show low-temperature damping peak.

endotherm at 213°C, which is 14°C lower than the reported T_m.[9,22] However, this endotherm did not appear on the second heat prior to which the sample had been heated to 285°C and quenched into liquid nitrogen. It has been reported that besides annealing, amorphous PC can be converted into the partially crys-
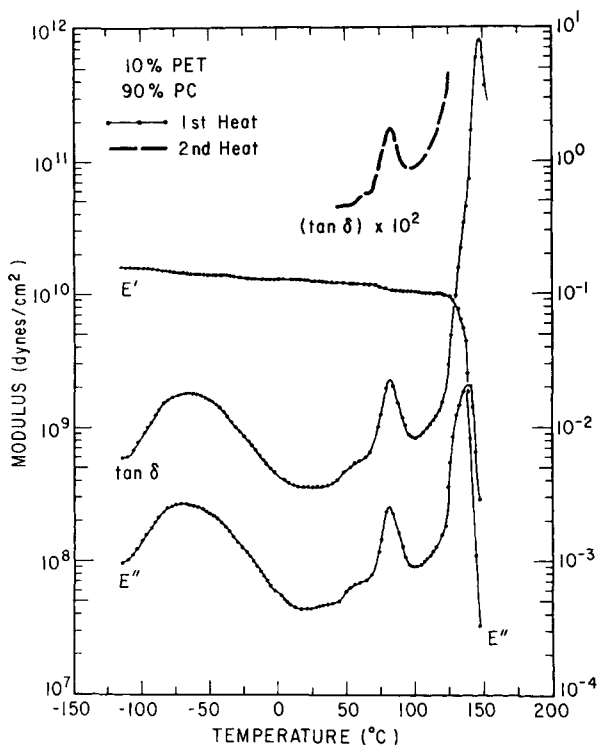
Fig. 8. Dynamic mechanical behavior for a 10% PET which shows the unusually low T_g for the PET-rich phase. Sample was quenched from the melt into liquid nitrogen prior to the first heat and then annealed for 11 hr at 160°C prior to the second heat.

talline form by solvents or by stretching.[22–25] The magnitude of the glass transition was larger in the second heat than in the first one. This may be attributed to the smaller amount of amorphous material in the sample during the first heat.

Poly(ethylene Terephthalate)

PET is more complex than PC due to its crystallinity, which in turn greatly depends on the thermal history of the polymer. It is well established that the location of the glass transition as well as its magnitude are a function of the amorphous fraction of the polymer.[26] Therefore, annealed runs, namely, first and third heats, gave a very broad and shallow glass transition compared to the sharp and steep ones exhibited by the quenched samples (second and fourth heats). Figure 10 indicates each glass transition temperature by its respective heat cycle, while in the quenched section of Figure 10 the average value of the second and fourth heat is plotted.

Thermograms of well-annealed PET, first and third heats, show T_g's of 90° and 82°C, respectively. These values are both higher than the reported value of 81°C,[10] and their difference is probably related to the different annealing times used. The quenched pure PET samples show a strong glass transition at 78°C, which is higher than the reported values of 67° and 75°C.[26] Crystallization exotherms appear in the second and fourth heats at 140° and 136°C, respectively; these are shown in Figure 11 by their respective heat cycles. The first heat in-
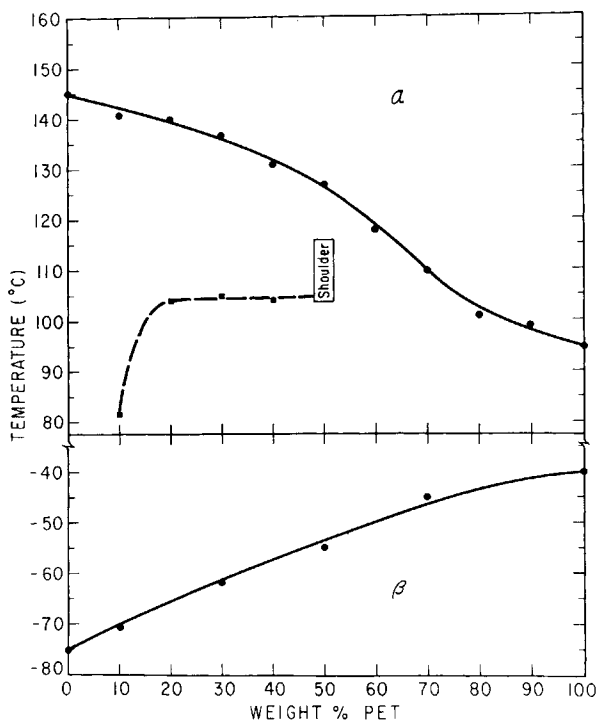
Fig. 9. Effect of overall blend composition on the temperature at which E'' curves show a maximum. Top part applies to α-region which shows either one or two peaks depending on composition. Lower part applies to β-region which appeared to give only one peak.

dicates a higher melting point of 271°C as compared to 267, 265, and 264°C for the second, third, and fourth heats, respectively. The above melting points are in good agreement with the reported range for commercial PET.[9] The higher crystalline melting point of the first heat may indicate that a more perfect crystal has been formed upon annealing. A second melting endotherm was observed at 229°C in the first heat and at 195°C in the third heat, indicating that additional irregular crystal structures may have been formed upon annealing.[25,26] Also, it is observed that with longer annealing this second endotherm approaches the main melting peak.[26]

PC–PET Blends

Glass Transition Behavior

With respect to glass transition behavior, the DTA results show a similar pattern of behavior for blends as observed by dynamic mechanical behavior. Figure 10 summarizes these results for both the annealed and quenched samples. Blends containing 90%, 80%, and 70% PET exhibited a single T_g although this appeared somewhat broad for the latter when annealed. The DTA results clearly show dual transitions for the 50% PET blend, whereas this composition appeared to show only a single peak by dynamic mechanical testing. It is not certain whether this difference is due to the different thermal histories of the two samples or to differences in sensitivity of the two techniques. For compositions containing less PET, the two glass transitions observed depend on overall blend
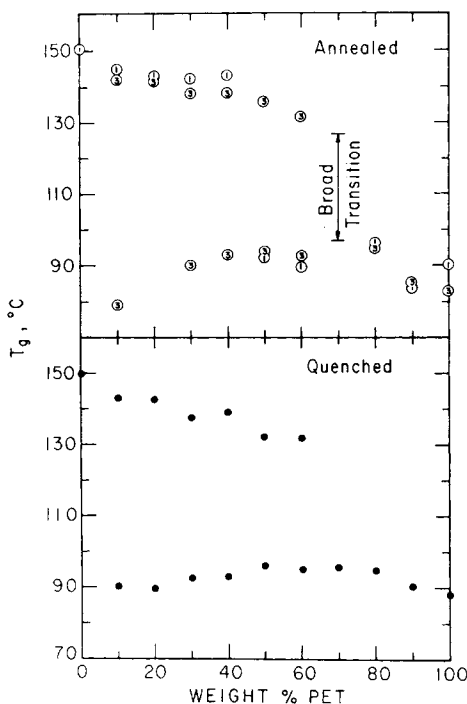
Fig. 10. Effect of overall blend composition on the glass transition temperature observed by DTA on annealed (top part) and quenched (lower part) samples.   Numbers refer to heat number—see Figure 13 for key.
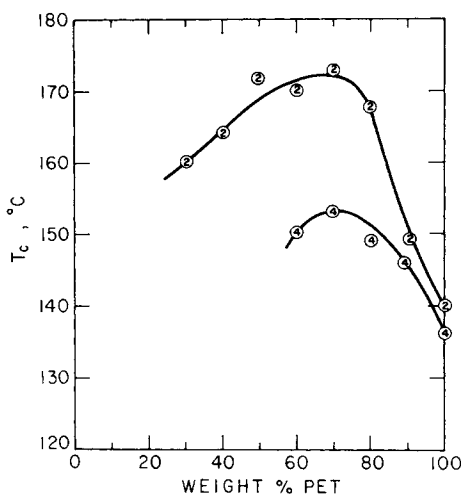

Fig. 11. Crystallization temperatures observed on heating quenched samples.   Numbers refer to heat number defined in Figure 13.

composition in a manner quite similar to that shown in the upper part of Figure 9 for the dynamic mechanical analysis.   The quenched samples exhibit about the same pattern of behavior as the annealed ones, except that the glass transitions were stronger due to the increased amorphous material.   The quenched 70% PET sample gave a sharp lower glass transition temperature compared to the broad transition in the annealed heats.

The T_g behavior observed by DTA support the notion of a single amorphous phase for blends quite rich in PET, whereas there is evidence for two amorphous phases in blends containing roughly 70% PET or less. Presumably, one phase is relatively rich in PET and does not change composition much as the overall composition of the two components is varied while the other phase is relatively richer in PC and seems to incorporate more PET as the overall blend content of PET is increased. The transition behavior observed by dynamic mechanical properties for blends with somewhat different thermal histories qualitatively agree with the DTA trends and conclusions.

Crystallization and Melting Behavior

Samples which were quenched presumably crystallized very little if at all on cooling and showed an exothermic crystallization peak on subsequent heats. Figure 11 shows the temperature at which these exotherms peaked, T_c, as a function of overall blend composition for the second and fourth heats. In both cases, T_c initially increases as PC is added to PET as one would expect for kinetic and thermodynamic reasons if the PC were miscible with the PET. However, T_c reaches a maximum at about 70% PET and then decreases as more PC is added. Interestingly, this maximum occurs in the same composition region which divides the one- and two-phase behavior for the amorphous portions of these blends. Evidently, further addition of PC beyond the 30% level diminishes the overall hindrance this component has on PET crystallization processes indicated by T_c. Closer inspection of Figure 10 shows that the lower T_c actually tends toward lower values as PC is added beyond the 30% level. One interpretation would be that this corresponds to an enrichment of this phase in PET with further PC addition in the region of the miscibility gap. This would explain the trend in T_c in this region; however, it is difficult to reationalize this response in terms of any consideration of an equilibrium phase diagram. As shown in Figure 11, the fourth-heat T_c values are all lower than observed on the second heat. This is quite possibly the result of the accumulated crystallization history which has left vestiges of order or nuclei available for more rapid crystallization in this later heating cycle compared to the earlier one.

No crystallization exotherms were observed on the second heat for the 10% and 20% PET blends. The 20% blend showed a small endotherm which evidently reflects melting of PET crystals formed during quenching. No endotherm at all was seen for the 10% blend. Apparently, it could not crystallize fast enough on either cooling or heating. No fourth heats were run for blends containing less than 60% PET. Figure 12 shows the magnitudes of the melting endotherms (in arbitrary units) observed on heating the quenched samples. All blends showed less PET crystallinity than would have been expected if PET present in the blend had crystallized to the same degree it does in the pure state (dotted line). Annealed blends showed slightly more crystallinity than the quenched one when the PET content was 40% or less and about the same levels at higher PET contents. These crystallinity observations for annealed blends are slightly obscured by the presence of additional melting endotherms other than the main one, as discussed later. The endotherm areas shown in Figure 12 are not representative of crystallinity present on passing through the T_g region since most of this crystallinity developed during heating as mentioned earlier.

Figure 13 shows the variation of the PET melting point for the various heats
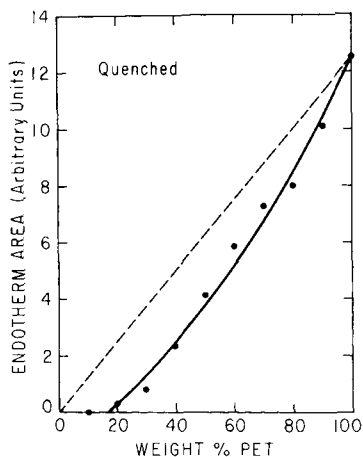
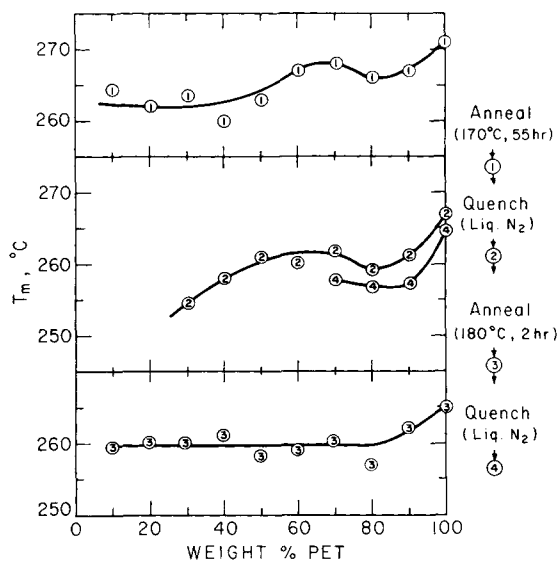Fig. 12. Area of melting endotherm for quenched samples.

Fig. 13. Melting point for PET observed in blends on the various heats indicated.

with composition. Before interpreting these results, it is worth remembering that T_m may be highly dependent on thermal history, crystalline morphology, as well as mixing of miscible components in the amorphous phase. With this in mind, we offer the following observations and tentative interpretations. There is a general trend in all cases for T_m to decrease from the particular value observed for pure PET in a given heat as PC is added until about 80% PET where it becomes constant thereafter or varies in some complex way. This decrease is of the order of 5°–8°C. We feel that this depression is mainly the result of lowering the chemical potential of PET by addition of PC which leads to a classical equilibrium T_m depression.[8] This is supported by evidence for PC–PET miscibility in the amorphous phase as described earlier. However, further addition of PC fails to produce a significant and consistent T_m depression because two amorphous phases exist beyond this PC content. This seems to be the most useful conclusion to be gleaned from these results; however, the fol-

lowing observations are interesting. Comparison of the heats of annealed samples (first and third) reveals the first heat to give a somewhat higher T_m than the third. This suggests more perfect crystals were formed during the much more prolonged annealing prior to the first heat compared to the third. For the quenched samples, the second heat consistently had a higher T_m than did the fourth heat. These effects are not pertinent to any issue about blending since they also apply equally to pure PET. Heats one and three for annealed blends showed some additional minor endotherm peaks. These were located at 197° and 205°C for 40%, 50%, and 60% PET samples and at 207° and 232°C for the 70% PET blend. These did not reappear on subsequent reheats of these samples which were quenched after melting. We do not attempt to offer any explanation for the apparent maxima in T_m that occurs in the 60%–70% PET region for heats one and two.

SUMMARY

Based on both thermal analysis and dynamic mechanical studies, we conclude that blends of PC and PET that contain at least more than 70% PET by weight form a single amorphous phase, whereas at lower PET levels two amorphous phases exist. There is evidence that these two phases contain both components. It is not possible to establish any form of thermodynamic phase diagram from this information or whether the miscibility gap for PC-rich blends is the result of an upper or lower critical solution temperature,[27] although the general nature of the phase behavior would seem to make the latter unlikely since no cloud point was observed in the melt[27] for the miscible side of the composition range.

The presence of the PC greatly alters the crystallization behavior of the PET but does not completely prevent its development.

If a large degree of interchange reaction did occur, one would expect a dramatic lowering of the melting point of the crystalline phase owing to the copolymerization effect. However, the small melting point depression seen here, 5°–8°C, is well within the range one might expect from simple mixing effects[8,28] and depends on composition in a manner consistent with this interpretation. We feel that this is strong evidence against such reactions in this system.

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