Polyester–Polycarbonate Blends. III. Polyesters Based on 1,4-Cyclohexanedimethanol/Terephthalic Acid/Isophthalic Acid

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Synopsis

Melt blends of polycarbonate with Kodel, a homopolyester formed from 1,4-cyclohexanedimethanol and terephthalic acid, and with Kodar, a copolyester formed by replacing some of the terephthalic acid with isophthalic acid, were prepared and their transitional behavior were examined by thermal analysis and dynamic mechanical testing. Blends formed with either polyester were found to have a single T_g over the entire compositional range. Single composition-dependent α- and β-relaxation temperatures were also observed for blends made with either polyester at all compositions. From these data it is concluded that both Kodel and Kodar blends with polycarbonate form miscible amorphous phases. The role of ester–carbonate interchange reactions during melt mixing was experimentally examined and found to be unimportant, from which it is concluded that the observed miscible phase formation is due to physical interactions between the blend components.

INTRODUCTION

Two earlier papers in this series described the transitional behavior of blends of bisphenol A polycarbonate (PC) with the polyesters poly(butylene terephthalate) (PBT)[1] and poly(ethylene terephthalate) (PET).[2] The PBT blends were found to have multiple amorphous phases for all component proportions; however, there was some evidence of partial mixing of the PC and PBT. The PET blends were found to have complete mixing of the components in the amorphous phase for compositions rich in PET but separate amorphous phases containing mixtures of PC and PET when the overall composition was less than about 60%–70% by weight PET. These studies have been extended to include other polyesters that show complete mixing with PC in the amorphous phase for all component proportions.

This paper reports on research for two commercially important polyesters whose monomers are derived from xylenes, namely, terephthalic acid (TPA), isophthalic acid (IPA), and 1,4-cyclohexanedimethanol (CHDM). One of these is the homopolymer based on TPA and CHDM which is used in the Kodel family of fibers, while the other is a copolymer in which part of the TPA is replaced by IPA. This copolymer is commercially available for various extrusion applications under the name Kodar. Because Kodar is a copolymer, it crystallizes more slowly and to a lesser extent than the homopolymer derived from TPA and CHDM. Both polymers are made by divisions of Eastman Kodak Co. and have been described in part by a number of publications.[3-8]

Blends of either of these polymers with PC show one T_g by both differential thermal analysis and dynamic mechanical properties and thus appear to be miscible with PC. As stated earlier in this series,[1,2] there is some concern about the possibility of interchange reactions between ester and carbonate groups. This question has been addressed directly in these studies, and it is concluded that such reactions are not a significant factor for the present systems.

EXPERIMENTAL

The PC was obtained from the General Electric Co. and designated as Lexan 310. During normal melt processing it does not crystallize. Its T_g was found to be 148°C by DTA, while dynamic mechanical measurements at 110 Hz reflect this relaxation at 150°C (E'') or 158°C (tan δ), and it also has a lower temperature relaxation at −72°C (both E'' and tan δ).

The homopolyester based on TPA and CHDM will be designated here as PCDT for brevity. The glycol in this polymer is 67% trans according to published information. The copolyester used here is the commercial product designated as Kodar 150 and was supplied as amorphous pellets. Based on the location of its T_g and T_m, the diacid monomer in this copolymer is evidently composed of about 80%–87% TPA.[9] Both polymers were obtained through the courtesy of C. C. Nitschke of Eastman Chemical Products, Inc.

All of these polymers were dried in accordance with procedures recommended by the suppliers prior to melt processing. All blends were made by melt mixing in a Brabender Plasticorder at 280°C for those involving Kodar and at 310°C for those involving PCDT, which is approximately 15°C above the melting point of each polyester. One percent of the antioxidant N,N′-di-2-naphthyl-p-phenylenediamine was added to all charges containing polyesters to reduce their degradation during mixing.[4] Mixing was done at high speeds for 5 min, which was found to be a minimum but adequate time for thorough mixing. The melts were transferred to a compression mold where $1/8$-in. thick sheets were formed and then quenched into water.

All blends were transparent in the melt state. Transparency in the solid state depended on the level of polyester crystallinity that developed, and this varied with thermal history of the blend.

Differential thermal analysis was performed in the following standardized manner.[9] Dried samples were melted in the DTA pan, quenched into liquid nitrogen, and then transferred to the sample chamber which had been precooled to −140°C. A first heat was made at 10°C/min, and after the sample was melted, it was cooled at 10°C/min to −100°C. Second heats were made by immediately reheating at 10°C/min. Then, the sample was annealed for 4 hr at 200°C prior to reheating in the DTA again at 10°C/min.

Dynamic mechanical measurements were made using a Rheovibron at 110 Hz with samples prepared as follows. Thoroughly dried blends were melted and pressed into 5-mil films from which specimens were cut to proper size. They were then annealed at 200°C for 4 hr to avoid crystallization during heating in the Rheovibron.[2]

RESULTS FOR PC–KODAR BLENDS

Differential Thermal Analysis

Melt-processed Kodar showed a T_g of 86°C by DTA, whereas unprocessed pellets exhibited a value 2°–3°C higher. The reported T_g is 87°C.[10] A crystallization exotherm was noted at 150°C (T_c). The melting point was observed in the range of 270°–277°C, depending on thermal history. Quenched samples gave values near 277°C, while annealed samples gave values near 270°C. For some annealing conditions, a second melting peak near 255°C was observed. The 4-hr annealing time was selected because it gave a single melting peak. The reported[10] T_m for unspecified conditions and techniques is 265°C. Similar variations in melting behavior dependent on thermal history are well known for other polymers.

Figure 1 illustrates the various thermal events for quenched Kodar, PC, and a 50/50 blend of the two. The glass transition locations are marked by arrows. The blend shows a single T_g at a temperature intermediate between the glass transitions of PC and Kodar. All blend compositions showed a similar behavior. Figure 2 shows the dependence of the observed T_g on composition for blends quenched from the melt. First and second heats gave substantially the same values. Such a response for T_g is evidence that PC and Kodar are completely miscible in the amorphous phase.

For unannealed blends, a crystallization exotherm was observed upon heating above the T_g. Figure 3 shows how the temperature at which the maximum in this peak, T_c, is raised by dilution of Kodar with PC. A similar effect was noted for the PET–PC system in the miscible range, and evidently this increase in T_c results from the kinetic hindrance of Kodar crystallization caused by the presence of soluble PC. Samples containing 100% or 90% PC did not crystallize under these conditions. The exotherm for the 50% PC blend was rather broad in comparison to that for other blends; consequently, its T_c is shown in Figure 3
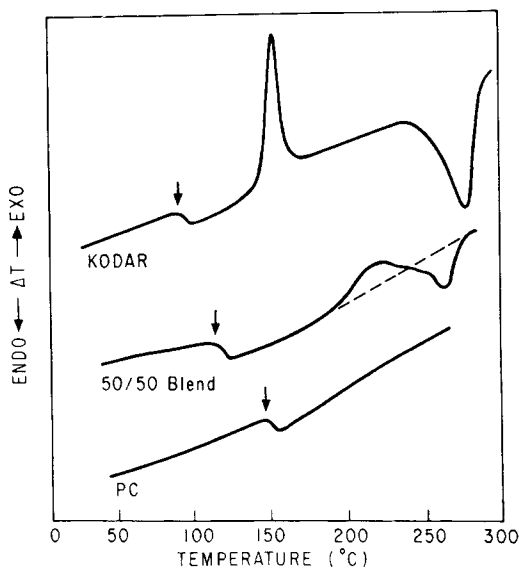

Fig. 1. Typical thermal events for quenched Kodar, PC, and their 50/50 blend.
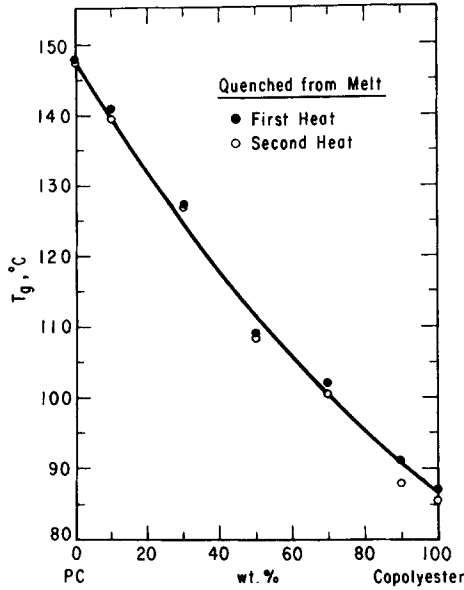
Fig. 2. Effect of overall blend composition on the glass transition temperature as observed by DTA for Kodar/PC blends. Quenched from melt: (●) first heat; (○) second heat.
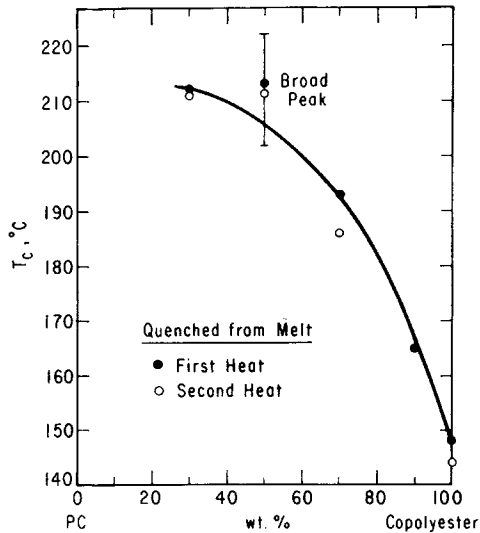

Fig. 3. Crystallization temperatures observed on heating unannealed Kodar/PC blends. Quenched from melt: (●) first heat; (○) second heat.

as a range. The difference in T_c on first and second heats is seen to be rather minimal. Annealed samples did not show any crystallization exotherm.

Figure 4 shows the area under the melting endotherm for the various samples quenched from the melt, with again little difference appearing between first and second heats. The blends contain less crystallinity than expected by simple dilution of Kodar by PC, which most likely reflects the kinetic hindrance of PC on Kodar crystallization for the present fixed thermal history.

Figure 5 shows the area under the crystallization exotherm for these blends,
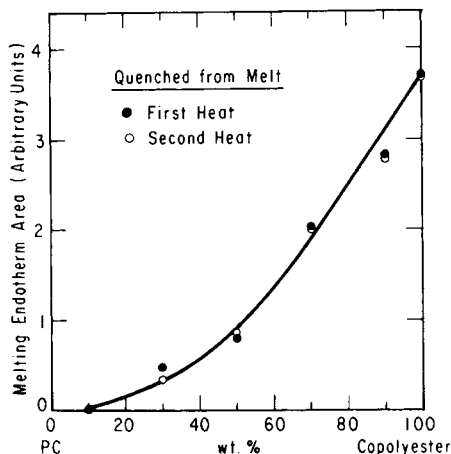
Fig. 4. Areas of melting endotherms for quenched Kodar/PC blends. Quenched from melt: (●) first heat; (○) second heat.
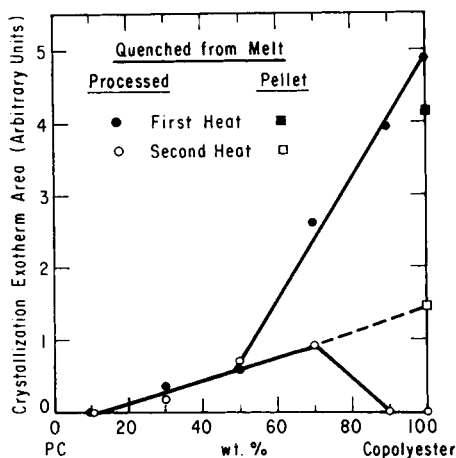

Fig. 5. Areas of crystallization exotherms obtained for differing thermal histories for Kodar/PC blends. Quenched from melt: (●) first heat, processed; (■) first heat, pellet; (○) second heat, processed; (□) second heat, pellet.

and the response is more complex than the melting behavior because of a strong dependence on previous thermal history. Crystallization behavior is quite similar for quenched and cyclic heating in blends containing up to 50% Kodar. Beyond this point, the samples begin to develop some crystallinity on cooling in the DTA, and consequently the crystallization exotherms in the second heat are smaller than in the first heat. Beyond 70% Kodar, full crystallinity is developed on cooling in the DTA, so there is no crystallization exotherm at all in the second heat. It is interesting that there is a large difference in the crystallization behavior of Kodar which has been melt processed compared to the as-received pellets. The exact cause of this is unknown. Despite the complexities shown in Figure 5, the melting endotherm areas shown in Figure 4 were independent of heating or processing history. It is curious that the crystallization exotherm areas in Figure 5 are about 20% larger than the melting endotherm areas in Figure 4. It is not known whether this unexpected finding is the result of baseline construction, instrumental factors, or other causes.

Because of the strong influence of prior thermal history on the T_m for Kodar, the melting point behavior for the blends was somewhat erratic. However, their melting points were slightly depressed by PC addition as would be expected for a miscible blend system. To illustrate this trend, a 50% Kodar blend had a melting point about 12°C below that of pure Kodar when both samples were subjected to the same thermal history.

Dynamic Mechanical Behavior

Figure 6 shows the Rheovibron results obtained for samples prepared in the manner outlined earlier. The pure Kodar copolyester, shown at the extreme left, exhibits an α relaxation, which peaks at 113°C on the tan δ curve and at 103°C on the E'' curve, that corresponds to the glass transition. There is a β relaxation at -36°C (tan δ) or -43°C (E'') similar to that for other polyesters. Lexan 310 also has prominent α and β relaxations as shown and described earlier.[1,2] All of the PC–Kodar blends show a single α transition, although slight shoulders seem to be evident for 30% and 50% Kodar blends. The temperature location of these peaks varies rather uniformly with blend composition, as shown in Figure 7. It is interesting to note that the curvature is opposite to that seen for T_g measured by DTA and shown in Figure 2. No definitive reasons for this difference can be given. The behavior of the α relaxation for these blends sup-
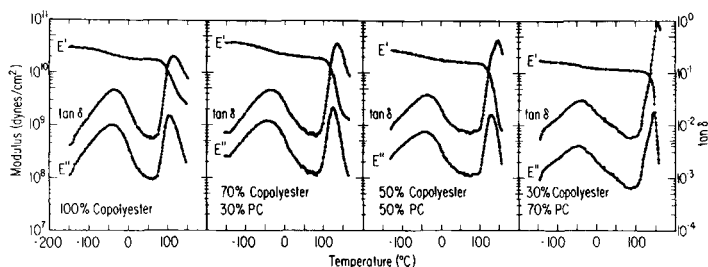

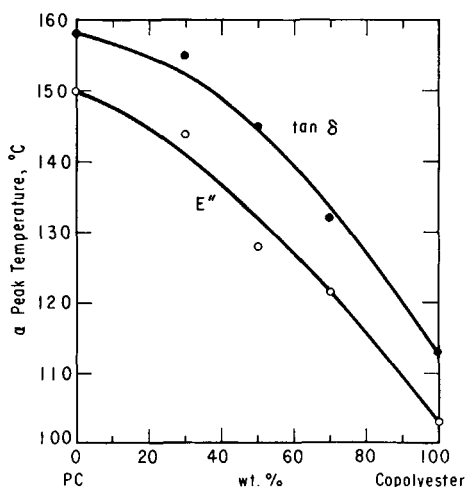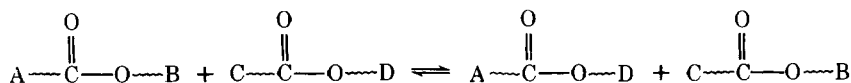Fig. 6. Dynamic mechanical behavior at 110 Hz of pure Kodar and its blends with polycarbonate.

Fig. 7. Effect of overall blend composition on the α-transition temperature as determined by the maxima in E'' and tan-δ curves for the Kodar/PC system.

ports the notion that there is substantially complete miscibility of PC and Kodar in the amorphous phase of these annealed blends.

These blends also show a single β peak whose location depends on composition, as shown in Figure 8.

The Role of Interchange Reactions

Interchange reactions between ester linkages in polyesters are well known[11,12]:

$$ A{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}B \ + \ C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}D \ \rightleftharpoons \ A{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}D \ + \ C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}B $$

These are especially likely to occur at the high temperatures required for melt processing and when catalysts for polymerization are still present and active. In principle, a similar reaction is possible involving an ester linkage,

$$ {-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O\,, $$
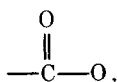
and a carbonate linkage,

$$ {-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}\,, $$
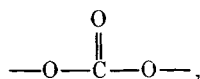
although there appears to be very little published on this possibility. Thus, the question arises as to whether such reactions may occur in polyester–polycarbonate blends. For simple contact reasons, it is very unlikely that any appreciable reaction could occur between the polyester and the polycarbonate unless the two were miscible.

If interchange reactions did occur during processing or mixing, this would affect the *chemical* nature of the final product. In the limit of a very high degree of interchange reaction, the product would be a "random" copolymer. Such a
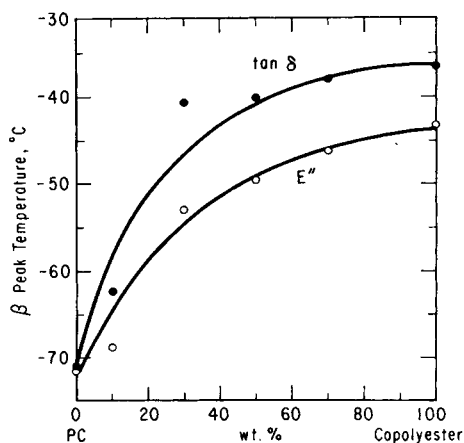

Fig. 8. Effect of blend composition on the β-transition temperature of PC/Kodar blends.

structure would also have a single T_g, and one must ask whether this is the reason for the response seen in the previous sections. However, such random copolymers would have a severely depressed melting point[12] and probably would not crystallize at all for compositions near equal proportions of the two components. We do not see this at all in the present system. Of course, the short processing times used here would not be expected to result in a complete "scrambling" in any case. An interesting experiment would be to follow the characteristics of a blend as a function of mixing time to see if any trends can be observed suggestive of interchange reactions and to carry this to longer than normal mixing times.

For this purpose, a 50/50 composition of polycarbonate and Kodar was selected. The melt mixing chamber was set at 280°C and dry-blended pellets of the two polymers were introduced. The temperature dropped immediately but recovered to 280°C in 2–3 min. At about 5 min, the melt was clear and the first sample was taken. Others were taken at various times out to 30 min (much longer than any practical processing times). These samples were examined by DTA. Figure 9 shows that the location of the T_g is independent of reaction time out to 30 min. The blend has a melting point T_m somewhat lower than that of the Kodar, and Figure 9 shows its value also is independent of processing time. The blend also shows a crystallization exotherm at a higher temperature than Kodar does, and it too is independent of processing time (see Fig. 9).

These results are strong evidence that interchange reactions are not of any major consequence within the processing time scale that one would normally use in making blends. The slight melting point depression seen in Figure 9 is entirely within the range to be expected from physical depression by a diluent.[13,14] All other responses are in accord with simple miscibility as opposed to any chemical explanations for the single T_g. Thus, there is strong evidence that interchange
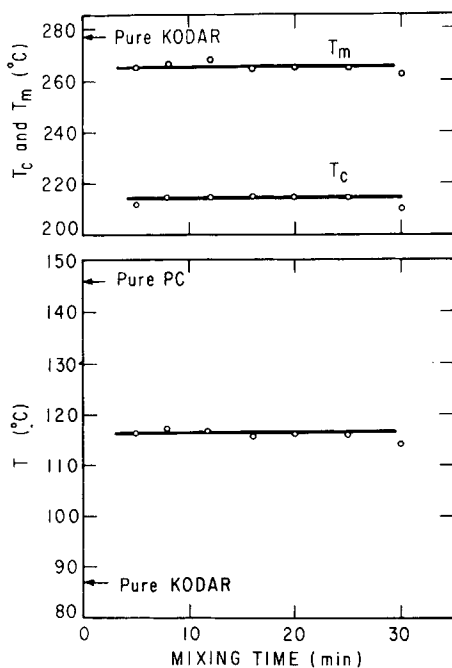

Fig. 9. Effect of processing time at 280°C on the transition properties of a 50% Kodar blend.

reactions are of no major consequence here, at least within normal processing conditions. One might suggest the slight reduction in T_g, T_m, and T_c for the blend in Figure 9 at 30 min marks the onset of such possibilities.

RESULTS FOR PC–PCDT BLENDS

Differential Thermal Analysis

The transition behavior of pure PCDT was found to be strongly dependent on thermal history. Quenched samples exhibited a T_g of 91°C and a T_c of 138°C, which is quite close to values reported by others.[4] Samples that had been cyclically heated and cooled at 10°C/min gave a weak T_g at 102°C with no crystallization exotherm. Annealed samples exhibited a T_g at 112°C. The T_g of numerous polymers[15–17] are similarly affected by the level of crystallinity. The main T_m of PCDT was found to be 294°–295°C, with smaller endotherms whose magnitude and location depended on prior history.

All blends of PC with PCDT showed one T_g by DTA irrespective of thermal history. Figure 10 shows how this T_g depends on blend composition. The difference in T_g between quenched and annealed blends, apparently arising from variations in the level of crystallinity, is directly related to the content of PCDT as Figure 10 shows. This observation of a single, composition-dependent T_g is strong evidence that the PC–PCDT system forms a miscible amorphous phase.

The location of the crystallization exotherm T_c for quenched blends increased as the PCDT was diluted with PC, as shown in Figure 11. This is comparable to the response observed for the PC–Kodar system.

The magnitude of the crystallization exotherms and the melting endotherms for quenched samples are shown in Figures 12 and 13, respectively. Interestingly,
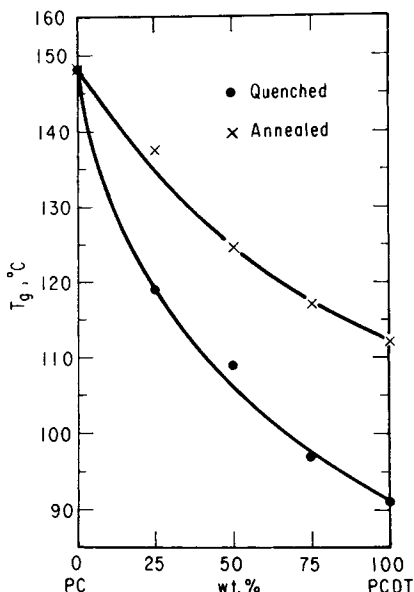

Fig. 10. Effect of thermal history on the glass transition temperature of Kodel and its blends with PC: (×) annealed; (●) quenched.
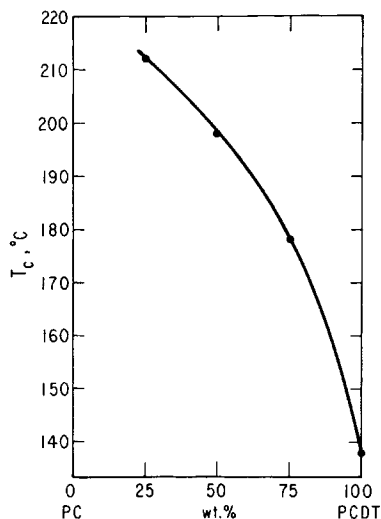
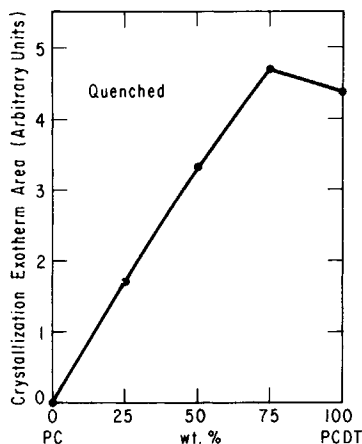Fig. 11. Crystallization exotherm peak temperatures observed for quenched Kodel/PC blends.

Fig. 12. Crystallization exotherm areas obtained on reheating quenched Kodel/PC blends in the DTA at 10°C/min.

blends containing 25% PC develop more crystallinity during heating in the DTA than does pure PCDT. Evidently, the presence of PC affects the kinetics of PCDT crystallization to a certain degree. Responses for other thermal histories were not examined. Curiously, the areas of the melting endotherms in Figure 13 are slightly smaller than the exotherm areas in Figure 12, as was also observed for the PC–Kodar system.

Dynamic Mechanical Behavior

Figure 14 shows the Rheovibron results obtained for PC–PCDT samples prepared in the way described earlier. Pure, crystalline PCDT exhibits two peaks in the temperature range of interest similar to those of Kodar. The α peak, corresponding to the glass transition, occurs at 113° and 129°C on both the E'' and tan δ curves.

Each of the blends has a single α peak and a single β peak. The temperature
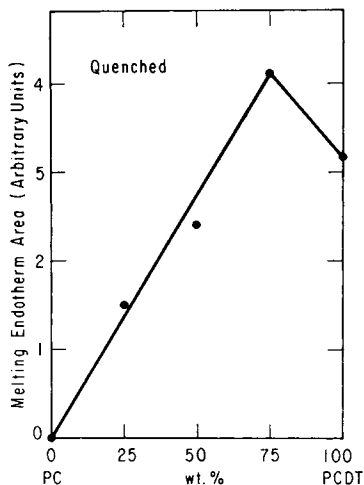
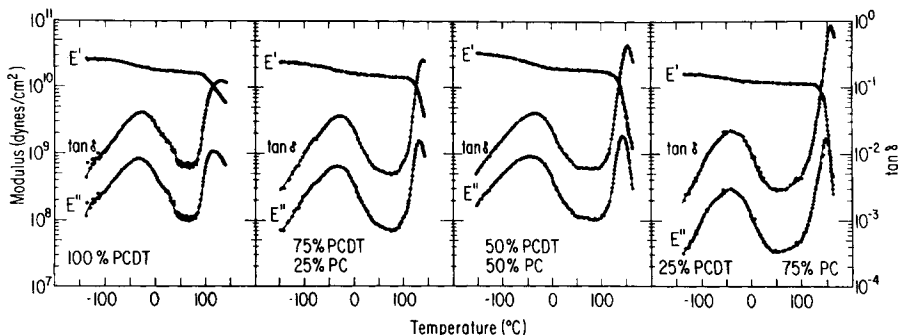Fig. 13. Melting endotherm areas obtained on heating quenched Kodel/PC blends in the DTA at 10 °C/min.

Fig. 14. Rheovibron test results at 110 Hz for annealed Kodel and its blends with PC.

location of the α peak is shown in Figure 15 and is seen to vary in a manner similar to that for the PC–Kodar system. Note that the curvature in Figure 15 is opposite of that in Figure 10. Figure 16 shows the temperature location of the β peak for the PC–PCDT system.

The dynamic mechanical behavior shown here further supports the idea that this system forms a miscible amorphous phase.

SUMMARY

Blends of PC with either Kodel or its copolyester with isophthalic acid, Kodar, show the presence of a single amorphous phase throughout the entire composition range. This phase has the properties expected of a thermodynamically miscible solution, and the blends are consequently judged to be miscible.

The mechanism of miscibility in these systems is unknown, but it is believed to be related to physical interactions between the polyester and the polycarbonate chains rather than to chemical reactions occurring during melt processing. No evidence of chemical reactions, such as the ester–carbonate interchange reaction, could be found when Kodar–PC blends were processed for excessively long times at 230°C. While this experiment was not repeated for Kodel–PC blends, the
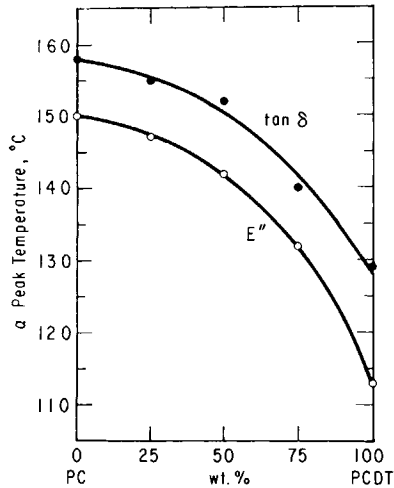
Fig. 15. Effect of overall blend composition on α-transition temperature of annealed Kodel/PC samples.
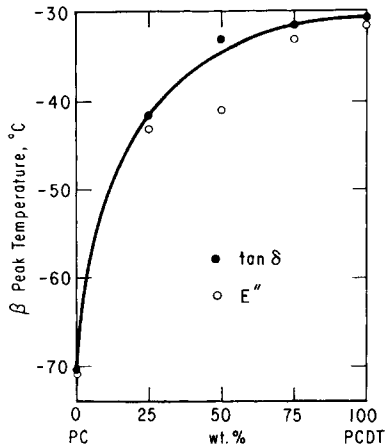

Fig. 16. Variation of the β-transition temperature with overall composition of Kodel/PC blends.

chemical similarities of Kodel and Kodar and the observed similarities in the blend properties resulting from their respective mixing with PC would suggest that the chemical interchange reaction is not a factor in the Kodel–PC system as well.

The similarity in the properties of blends made with either Kodel or Kodar further suggests that the factor responsible for miscibility in these systems is not greatly affected by the steric changes in the polyester resulting from the replacement of some of the terephthalic acid by isophthalic acid. This replacement does affect the rate and extent of crystallization and also the extent to which thermal history or the degree of crystallization affects the location of the glass transition temperature of the polyester, however. The net result of isophthalic acid addition is to cause the transition behavior of Kodar and its blends with PC to be somewhat less complicated by thermal history variables than that of Kodel and its blends.

Blends of PC with either polyester show a monotonic decrease in their glass transition temperatures as the polyester content increases. The temperature location of the α-relaxation peak varies with composition in a similar way to the glass transition temperature for both blend systems. It is interesting to note that while the overall trends with composition are the same, the T_g curve is concave upward when plotted versus polyester content, whereas the α-temperature curves are concave downward for both polyester blend systems. The reason for this behavior is presently unknown. The low-temperature β-relaxation peaks are observed to shift toward higher temperatures with increasing polyester content for both blend systems. To the extent that sub-T_g toughness depends on the relative location of the β peak to testing temperature, the polyester–PC blends should prove more tough than the pure polyesters. At any rate, the smooth variation of the β peak with blend composition can be taken as further evidence of the presence of a single amorphous, miscible phase.

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