

Chemistry of Miscible Polycarbonate–Copolyester Blends

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Synopsis

Blends of polycarbonate and the copolyester based on 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids are known to be completely miscible. This study was concerned with various chemical events which may occur in this system, particularly during melt processing. Degradation reactions were studied by both TGA and dilute viscometry techniques, and some indications of component interaction were noted. The residual titanium catalyst from the copolyester formation was found to produce color formation by interaction with phenolic end groups in the polycarbonate and to promote interchange reactions. Both events could be suppressed by deactivation of the residual catalyst with appropriate additives. An indication of the extent of interchange reactions was obtained by following the crystallizability of the copolyester component using differential scanning calorimetry.

INTRODUCTION

In a previous article¹ it was reported that the copolyester formed from 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids is miscible with bisphenol A polycarbonate in all proportions. Since there is considerable fundamental and practical interest in miscible polymer blends, this system was chosen for a series of in-depth investigations of physical property relationships and thermodynamic behavior. The results of these studies are reported elsewhere.²⁻⁴ This system is susceptible to a variety of chemical processes, especially during high-temperature melt processing, and these issues are the subject of this paper. Like all polymers, these components are vulnerable to various thermal and oxidative degradation mechanisms. Because each component is a condensation polymer, they are also prone to molecular weight loss from hydrolysis reactions with sorbed moisture. In addition, a variety of interchange reaction mechanisms are possible. These and other chemical processes are considered here with a primary focus on the extent that these chemical events may occur during melt fabrication of these blends.

A special concern about chemistry exists in blends containing polyesters because of the residual catalyst which remains from the polymerization. Its presence may have a considerable effect on various potential reactions, and the present results demonstrate this. For some purposes, it would be desirable to eliminate the effect of residual catalyst. In most cases, it is impractical to remove the catalyst; however, it was found that the residual catalyst could be effectively deactivated by certain additives.

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MATERIALS

The polycarbonate used is a commercial product of the General Electric Co., Lexan 131-111, with $\bar{M}_n = 13.3 \times 10^3$ and $\bar{M}_w = 34.2 \times 10^3$. The copolyester used is a commercial product of Eastman Chemical Products, Inc., with the trade name Kodar A-150.

Various analyses were made to characterize the copolyester. An NMR analysis for the ratio of isophthalate to terephthalate units was made by the techniques described by Murano and Kaneishi⁵ using hexafluoroisopropanol as solvent. From these results, it was concluded that the copolyester contains 80% terephthalic and 20% isophthalic acid residues, which agrees well with an earlier estimate¹ based on melting point information.⁶ A trace metal analysis by atomic absorption showed the copolyester contained 68 ppm Ti. Titanium alkoxides are mentioned in the patent literature as effective catalysts for this system.⁷⁻⁹ Dilute solution viscometry in a 60/40 mixture of phenol/tetrachloroethane gave an intrinsic viscosity of 0.816 dl/g. Mark-Houwink parameters are apparently not known for this system; so as an estimate, values for poly(ethylene terephthalate) were used.¹⁰ This resulted in an estimate of 23,900 for the molecular weight. The manufacturer estimates \bar{M}_n at about 22,000.

It is important to note that polycarbonate does not crystallize during melt processing owing to its very slow rate of crystallization. The copolyester also crystallizes slowly and is normally wholly amorphous following the quenching associated with typical processing operations. However, unlike polycarbonate, the copolyester will crystallize at modest annealing times above its glass transition temperature.

THERMAL AND OXIDATIVE DEGRADATION

The dynamic technique of thermogravimetric analysis (TGA) can provide a useful impression of the kinetics of thermal and oxidative degradation mechanisms. It was of interest to employ this approach to gain some idea of how these blends behave in this regard relative to the pure components.

Samples of approximately 20 mg were thoroughly dried for 14 h at 80°C in vacuo and then heated at 10°C/min in various environments at a total pressure of 100 mm Hg. This low pressure was used to minimize the effects of convective and buoyancy forces and to facilitate removal of volatile degradation products. Figure 1 shows TGA traces for various blends in air, while Figure 2 shows results

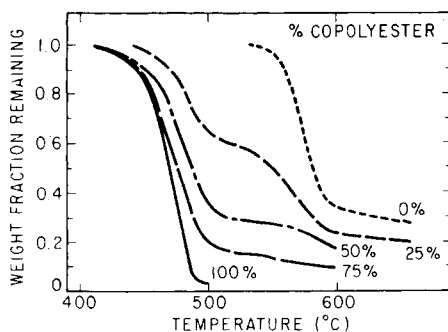


Fig. 1. Thermogravimetric analysis of blends in air.

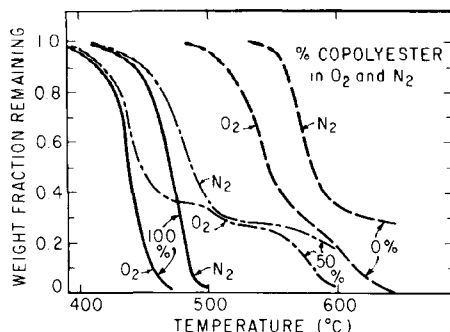


Fig. 2. Thermogravimetric analysis of blends in nitrogen and pure oxygen.

in oxygen and nitrogen. In all cases, the copolyester begins to degrade at a lower temperature than the polycarbonate, and the blends exhibit intermediate behavior. All blends show features characteristic of the pure components, but some interactions are evident. In air and nitrogen, polycarbonate forms a char^{11,12} which is insoluble; however, in pure oxygen the char is completely volatilized. Figure 3 shows the mass fraction remaining at 530°C. If the degradation processes for polycarbonate and copolyester proceeded independently, a linear relation would be expected; however, the experimental observations fall slightly below this. Apparently, addition of copolyester interferes with polycarbonate char formation. Examination of other features in Figures 1 and 2 suggests that the presence of the copolyester causes earlier decomposition of polycarbonate. Similar observations have been made for other blend systems^{13,14} and are reasonable for free radical-initiated decomposition processes. For both polymers and their blends, decomposition begins at a lower temperature in oxygen than in nitrogen, as expected.

Kinetic analyses of the early stages of decomposition in nitrogen were made using published techniques.^{15,16} The reaction order was found to be 0.96 for polycarbonate, 1.09 for the copolyester, and 0.97 for the 50% blend. Activation energies were 29, 31, and 28 kcal/mol, respectively. These are within the range expected,^{12,17,18} and the values for both parameters are essentially the same within experimental error for all materials.

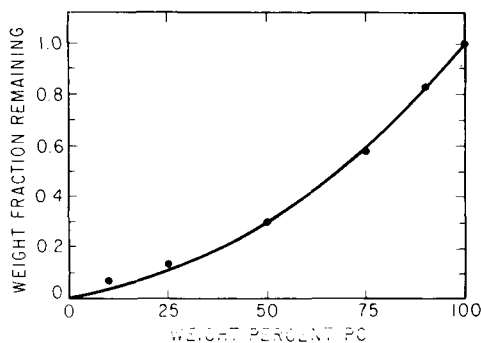


Fig. 3. Char fraction remaining at 530°C for blends in air.

MOLECULAR WEIGHT LOSS DURING MELT PROCESSING

It is quite common for most polymers to experience molecular weight degradation during processing, and one of the factors in selecting process methods and conditions is to ensure that this loss is not too serious. An essential step prior to processing condensation polymers is to remove most sorbed water by drying to avoid hydrolysis reactions. An interesting question for the present system is how the molecular weight losses at processing conditions for blends compare to those for the pure components. Changes in molecular weight were followed by monitoring the specific viscosity of solutions containing 1 g polymer per 100 ml solvent (60/40 phenol/tetrachloroethane) at 27°C.

A practical picture of this issue may be had by examining the specific viscosity for each blend at various stages of a typical processing sequence.³ Figure 4 shows the observed values of specific viscosity for these mixtures prior to any melt processing, after extrusion compounding to make blended pellets, and after injection molding of the extruded pellets. Sorbed moisture levels were reduced prior to each melt processing operation by appropriate drying conditions. Details of the processing procedures are described elsewhere.³ The specific viscosity of the unprocessed materials was obtained by dissolving appropriate amounts of the two pure polymers in the solvent, and these results approximate a linear relation with blend composition. Each melt operation reduces the specific viscosity, or average molecular weight, as might be expected. However, the decrease is greater for blends than would have been expected from the decreases seen for the pure components.

These effects were further explored in a separate experiment in which polymer samples carefully dried for 14 h at 80°C in vacuo were held for various times at 280°C (typical of processing temperatures) in a glass test tube under a nitrogen atmosphere. In this experiment, the polymer-filled test tube was placed in a fluidized sand bath at 280°C for the time specified in Figure 5, after which the tube and its contents were quenched in ice water. The treated sample was then dissolved in solvent for determination of the specific viscosity. Given the dynamic nature of the experiment and the poor heat transfer characteristics of all polymers, the actual time spent by the sample at 280°C is probably somewhat less than that specified in Figure 5. However, since all specimens were treated by exactly the same procedure, the observed relative trends in Figures 5 and 6 are nevertheless valid. Figure 5 shows that the specific viscosity of treated material, normalized by the specific viscosity of untreated material, declines as treatment time is increased. By this test, the rate of decline in this ratio is greater

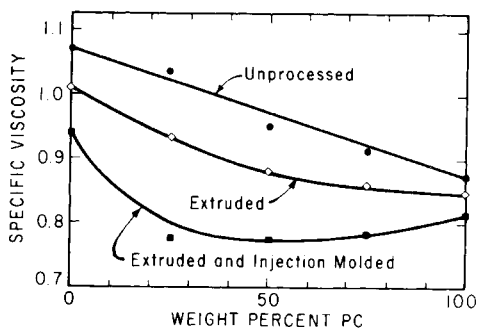


Fig. 4. Specific viscosity of blends at various stages in typical melt processing operation.

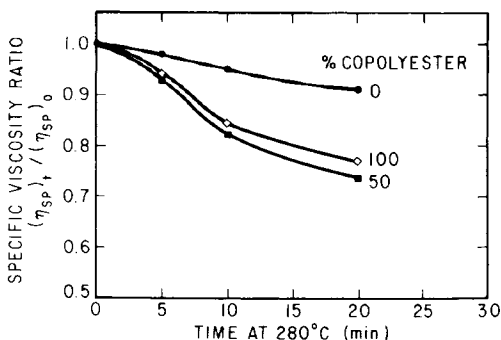


Fig. 5. Change in specific viscosity with time at 280°C for various blends.

for the copolyester than for polycarbonate. Moreover, the rate of decline in the viscosity ratio for the 50% blend is greater than that for the polyester. These results suggest a synergistic degradation akin to that seen by TGA.

In order to learn whether the residual polymerization catalyst in the copolyester might play any role in this synergism, one other set of experiments was conducted. Additional titanium catalyst in the form of tetrabutyl orthotitanate was added to the 50% blend and the previous test repeated. Similar experiments were done with blends to which arsenic trioxide, known to deactivate the titanium catalyst,¹⁹ was added. These results are shown in Figure 6. The extra titanium seems to cause a slightly larger decrease in specific viscosity, but there is no clear benefit from adding the arsenic compound. The differences noted in Figure 6 are comparable to the experimental uncertainty, and the only firm conclusion is that these additives do not have an appreciable effect on molecular weight degradation.

COLOR FORMATION

Melt-processed polycarbonate and copolyester are essentially water-white, whereas their blends experience significant discoloration. The intensity of this yellow to orange-red color is proportional to the copolyester content of the blend and is only slightly affected by processing conditions or time. This phenomenon is the result of an interaction of the residual titanium catalyst in the copolyester with free phenol groups in the polycarbonate, as the following observations demonstrate.

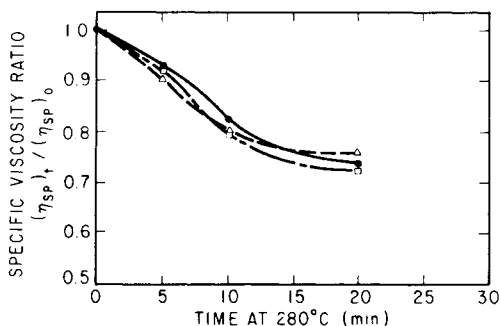
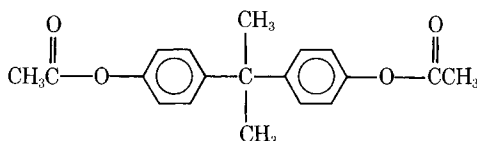


Fig. 6. Change in specific viscosity of a 50% blend containing various additives: (●) no additives; (Δ) with As_2O_3 ; (□) with $\text{Ti}(\text{OBu})_4$.

Tetrabutyl orthotitanate was mixed with polycarbonate in an extruder, and the product developed an orange-red color. During the extrusion, the specific viscosity of the polycarbonate decreased by 13% compared to a 6% decrease which occurs without this additive, see Figure 4. In order to determine the part of the polycarbonate molecule responsible for the discoloration, tetrabutyl orthotitanate was mixed in solution with various model compounds at room temperature. No color formation was noted with diphenyl carbonate; however, for phenol and bisphenol A, deep color formation similar to that seen in the blends developed. This suggests that the residual titanium catalyst interacts with free phenolic groups in the polycarbonate to give the color seen. Further confirmation of this was obtained by reacting bisphenol A with acetyl chloride to give an ester



which the titanium compound would not discolor.

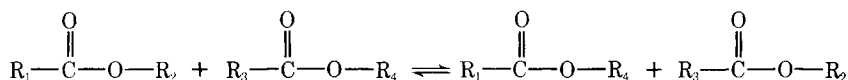
Two approaches to elimination of color formation in these blends may be envisioned. One method would be to cap all phenolic end groups on polycarbonate molecules by reactions with appropriate compounds. This route was attempted using acetyl chloride; however, degradation reactions during melt processing always created new phenolic end groups. Thus, in a practical sense, the problem was not solved.

A second method would be to deactivate or complex the residual titanium catalyst in the copolyester by an appropriate additive. Numerous materials are known to form complexes with titanium. Arsenic trioxide was selected as a candidate for this purpose since it has been shown to deactivate residual titanium catalysts in other polyesters.¹⁹ This compound has low solubility in water but is evidently quite miscible with the copolyester. It was found to be very effective for this purpose when extrusion compounded into the copolyester at the 0.1% by weight level. Subsequent blends made from the copolyester containing As_2O_3 with polycarbonate were essentially free of the color mentioned earlier, evidently because of some type of complex formed between the arsenic and titanium that precludes the interaction with phenolic groups which gives rise to color formation.

Attempts to add the As_2O_3 in the same extrusion step where the copolyester and polycarbonate were blended failed to prevent color formation. Evidently, many chromophores were formed before deactivation occurred in this one step mixing approach.

INTERCHANGE REACTIONS

Interchange reactions of the type



are well known in polyester system,²⁰⁻²⁴ and similar reactions involving polyesters and polycarbonate are recognized in the literature.^{25,26} Study of such reactions generally requires complex analytical techniques. However, examination of crystallization behavior of the copolyester component by differential scanning calorimetry (DSC) proved to be a useful approach for this system. This section examines the extent of ester-carbonate interchange reactions in the melt state for these blends and reorganization within the copolyester while in the solid state. It is shown that the residual titanium catalyst has a significant effect on the rate of such reactions, but appropriate additives deactivate this catalyst and greatly reduce the rate of these reactions.

Blend Reactions in the Melt State

The copolyester remains amorphous when rapidly quenched from the melt, but significant crystallinity develops during annealing at temperatures between its T_g and T_m . These conditions will not cause crystallization of the polycarbonate. Interchange reactions between the copolyester and the polycarbonate will decrease the length of the crystallizable segments in the copolyester and thereby diminish its propensity to crystallize. This fact has been used to follow the extent of such reactions occurring in these blends while in the melt state at conditions comparable to those experienced in processing.

Following a given treatment in the melt state, samples were annealed at 177°C for a period of 1 h. This temperature approximates the point where the crystallization rate is at a maximum, and essentially all of the crystallinity obtainable was developed within 1 h. After annealing, samples were heated at 10°C/min in the DSC, and the magnitude of the copolyester melting endotherm was measured. Figure 7 shows results from these experiments as a function of the time various samples were held in the melt state at 277°C. The pure copolyester shows a constant heat of fusion for up to at least 20 min in the melt with some evidence for a small decline after that. Incorporation of additional catalyst, 0.2 wt % $\text{Ti}(\text{OBu})_4$, does not change this trend. There appears to be a slight reduction in the absolute heat of fusion for samples containing this extra catalyst. The significance of this observation is unknown. The 50% blend was prepared

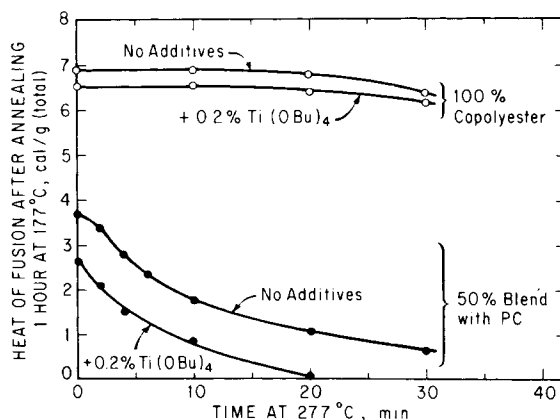


Fig. 7. Effect of interchange reactions on copolyester crystallizability.

in an extruder and, thus, has a prior period of not more than 5 min in the melt state in addition to that shown in Figure 7. Ideally, the heat of fusion for a well annealed blend should be directly proportional to the content of the crystallizable component.²⁷ The as extruded blend with no extra catalyst developed on annealing a heat of fusion per total sample mass almost exactly half of that shown by the pure copolyester. This is evidence that interchange reactions did not occur during the processing step to an extent that would interfere with the crystallizability of the copolyester. However, subsequent time in the melt caused a continued decline in the observed heat of fusion, which is evidence that interchange reactions do occur. As might be expected, incorporation of additional catalyst increases the extent of these reactions. For this case, there is evidence of substantial reaction during the processing step, and after an additional 20 min in the melt, no crystallinity is observed.

As these reactions proceed, the blend is gradually converted into a copolymer, and the speed at which this occurs depends on the amount of titanium catalyst present. Figures 8 and 9 show how the melting point and glass transition change with time in the melt for the 50% blend containing only the residual catalyst from the copolyester polymerization process. The decline in the melting point is expected for this conversion from a blend to a copolymer.²⁴ Evidently, the copolymer has a higher glass transition than does the blend. Further evidence of

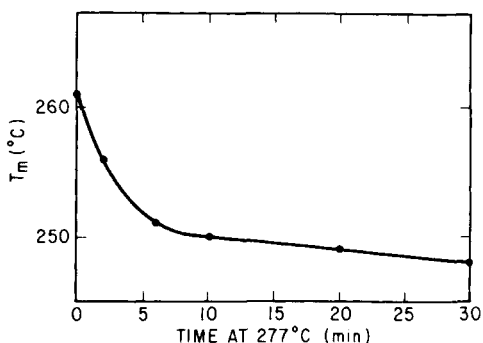


Fig. 8. Change in melting point of copolyester in 50% blend (without additives) with time in melt.

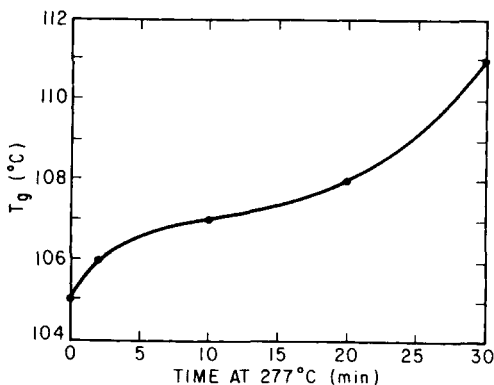
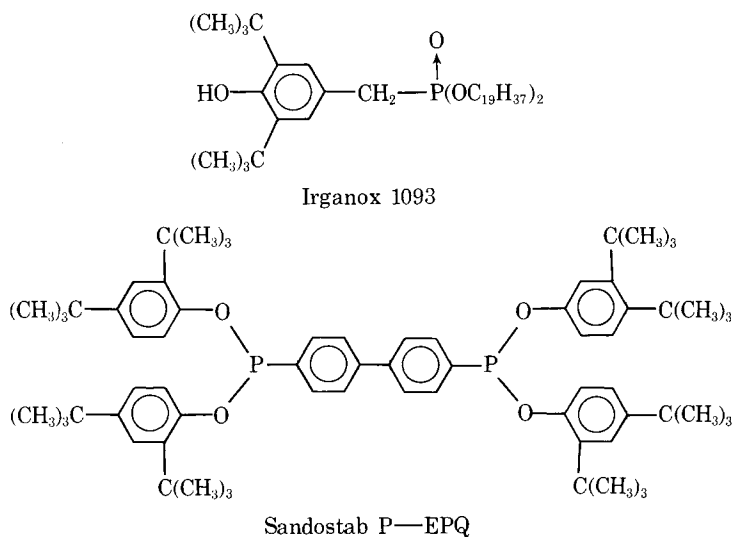


Fig. 9. Change in glass transition temperature of 50% blend (without additives) with time in melt.

these reactions may be seen by examining solubility characteristics of the blend.²⁶ Polycarbonate is soluble in chloroform, whereas the copolyester is not, owing to its crystallinity.

Figure 10 shows the fraction of the 50% blend which could be extracted by chloroform. Prior to any melt history after processing, exactly 50% of the blend could be extracted. NMR analysis showed the soluble component to be polycarbonate. The soluble fraction increased with further time in the melt since the noncrystallizable copolymer is soluble. The increase in soluble fraction parallels very closely the decline in the heat of fusion, as might be expected.

Since the extent of interchange reactions between the polycarbonate and the copolyester appear to be greatly affected by the concentration of titanium catalyst, it was hypothesized that deactivation of the residual catalyst through appropriate additives should greatly help to suppress interchange reactions. As stated earlier, arsenic compounds are known to deactivate titanium, and there is evidence that certain phosphorous compounds have a similar effect. In addition to As_2O_3 , two commercially available phosphorous stabilizers for polymers were examined for this purpose:



The effectiveness of this approach was evaluated as follows: Each of the com-

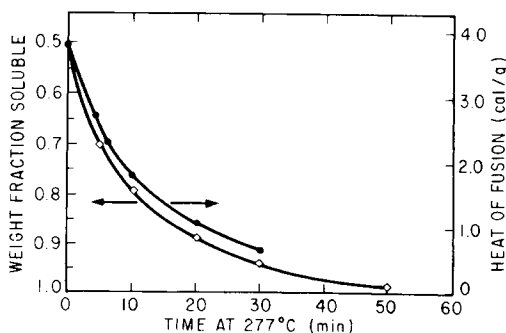


Fig. 10. Correlation of solubility and heat of fusion for a 50% blend held in the melt state for various times.

pounds mentioned above was incorporated into the copolyester at the 0.1 wt % level during extrusion. A subsequent extrusion step was used to generate a blend containing equal parts polycarbonate and the additive containing copolyester. A DSC analysis like that in Figure 7 was used to obtain the results shown in Figure 11. Compared to the control, which contained none of these additives, each of these compounds was dramatically effective at preserving the ability of the copolyester to crystallize. As_2O_3 appears to show a small advantage over the others during the first 20 min; but after that, some loss of crystallinity is seen. The latter may be the result of As_2O_3 loss by volatilization. In any case, 20 min is much longer than the time needed for processing. It is concluded that these compounds are effective for suppressing interchange reactions and the attendant loss in copolyester crystallinity. Presumably, this occurs by deactivation of the residual titanium catalyst. The blends containing As_2O_3 were the most color free; and, based on this, it would appear to be the best choice of additives among those examined.

Solid-State Rearrangements in the Copolyester

Annealing of the pure copolyester at high temperatures below its melting point produces evidence of chemical rearrangements analogous to that described by Lenz and co-workers.²⁸⁻³¹ Lenz has shown that certain copolymers capable of undergoing reversible reorganization reactions can be converted from a random to a block structure when one of the repeating units can be incorporated into the existing crystalline phase and the other cannot. This assumes that the reorganization reactions occur at an observable rate and that units in the amorphous phase are more susceptible to reaction than those in the crystalline phase. Copolymers which have experienced crystallization-induced rearrangements exhibit altered crystallinity and melting behavior.

The present copolyester would appear to be a candidate for such possibilities. Ester-interchange reactions catalyzed by residual titanium ought to provide the chemical mechanism needed. The polymer contains mixtures of both isophthalic/terephthalic acid and *cis/trans*-1,4-cyclohexanedimethanol residues either of which ought to provide the combination of crystallizable/noncrystallizable repeat units this phenomenon requires. Figures 12-14 show evidence for such behavior. The heat of fusion increases as either the time or temperature of annealing is increased. The time dependence may involve the kinetics of both

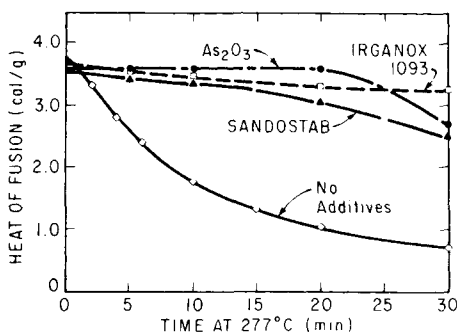


Fig. 11. Effect of various additives on the crystallizability of copolyester from a 50% blend held in the melt for various times.

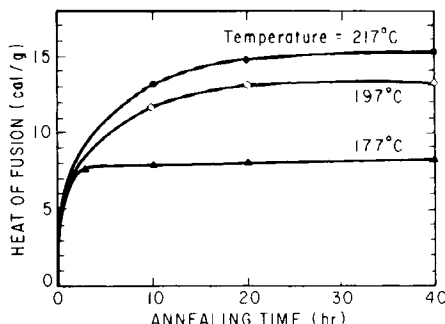


Fig. 12. Effect of thermal treatments on the heat of fusion of pure copolyester.

crystallization and reaction. The dramatically increased asymptotic levels which the heat of fusion attains for higher temperature of annealing is suggestive of chemical rearrangements. Figure 13 shows that the observed melting point increases with annealing. In addition, the melting point becomes sharper, as seen in Figure 14. All of these effects are consistent with chemical reorganization to produce more refined crystals composed of units with higher points. However, purely physical effects could result in trends qualitatively similar to each of those shown here.

The previous section has shown that certain additives effectively deactivate the residual titanium which catalyzes these reactions; thus, this should provide a useful approach for determining whether these changes in melting behavior are, in fact, chemical in origin. Arsenic pentoxide was used as the additive since

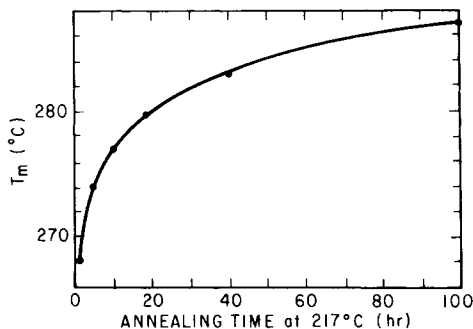


Fig. 13. Effect of annealing on melting point of pure copolyester.

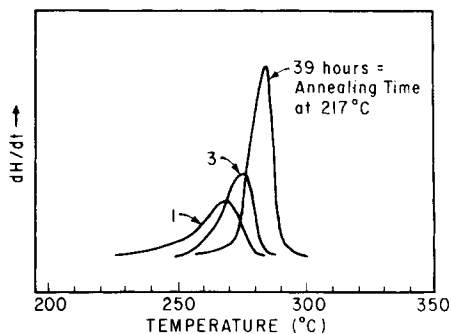


Fig. 14. Effect of thermal treatments on the shape of the pure copolyester melting endotherm.

it is less volatile than the trioxide but has a similar deactivating effect. Samples of copolyester containing 0.1 wt % arsenic pentoxide and without this additive were annealed at 217° for 57 h; the results in Table I were obtained. The sample without the arsenic compound developed a substantially higher heat of fusion and melting point than the one with this additive which should greatly suppress rearrangement reactions. Thus, it is concluded that the changes noted here during annealing are the consequence of crystallization-induced rearrangements of the copolyester in the manner demonstrated for other systems by Lenz.

SUMMARY

This report has examined a number of chemical reactions that can occur in miscible blends of polycarbonate and the copolyester based on 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids. Some of these reactions are accelerated by the presence of the residual titanium polymerization catalyst which remains in the copolyester. This catalyst can be deactivated, presumably by complexation, by various additives, with arsenic oxides being particularly effective. Evidence was shown for crystallization-induced rearrangements in the copolyester via ester-interchange reactions. These lead to supercrystallinity when the copolyester is annealed for long times just below the melting point. On the other hand, ester-carbonate interchange reactions occur in the melt state for blends and reduce the crystallizability of the copolyester compound, since a random copolymer is formed. Interchange reactions are greatly suppressed by deactivating the residual titanium catalyst.

Molecular weight loss during processing and thermal or oxidative degradation at high temperature occur in blends to a greater extent than expected from additive behavior of the pure components. It is not clear what effect residual catalyst has on these processes, if any.

Color formation occurs in blends because of interaction of the residual titanium catalyst in the copolyester with free phenolic and groups in the polycarbonate. Deactivation of the titanium catalyst by appropriate addition of arsenic trioxide eliminates this chromophore formation.

Previous studies³ have examined the mechanical properties of these blends in some detail. A comparison of the properties of blends with and without deactivation of the titanium catalyst shows no significant effect resulting from the minimal interchange reactions which occur during normal processing.

The observation in this work that suppression of interchange reactions by deactivation of the residual titanium catalyst does not alter the miscibility of the melt suggests that extensive interchange reactions are not essential for miscible behavior. Ample evidence presently exists for this system⁴ as well as

TABLE I
Effect of Arsenic Deactivation of Residual Catalyst on Melting Behavior of Annealed Copolyester

	T_m , °C	ΔH_f , cal/g
Without As ₂ O ₅	284	15.2
With As ₂ O ₅	269	9.08

for many others where such reactions are not an issue³² to suggest that miscible phase behavior results from physical interactions between unlike blend components which lead to small exothermic heats of mixing. The presence of interchange and other chemical reactions between blend components is, in part, the result of the ample opportunity for reaction which exists between the intimately mixed polymers in the miscible blend.

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