Boiling Water Aging of a Miscible Blend of Polycarbonate and a Copolyester

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Synopsis

Extruded films and injection molded bars of a copolyester based on 1,4-cyclohexanedimethanol condensed with a mixture of isophthalic and terephthalic acids, of a bisphenol-A based polycarbonate, PC, and of the miscible blends of these compounds were exposed to boiling water for up to 15 days. The ductility and strengths of film specimens rich in PC were found to degrade as a result of PC hydrolysis. These properties of specimens rich in copolyester were found to decline as a result of crystallization of the copolyester. Best overall performance was obtained for 50/50 blends of PC and copolyester. All amorphous materials showed a transition from ductile to brittle behavior at the same weight average molecular weight as previously observed for pure PC. This feature plus the observation that PC hydrolyzes in the blend at the same rate as it does in the pure state allows most of the superior performance of the 50/50 blends to be explained in terms of blend molecular weight.

INTRODUCTION

The choice of a polymeric material is largely dictated by the economic and property requirements of the particular end use application. This choice is often based on compromise because it is difficult to find in one material all of the properties required by the particular application. This general problem is undoubtedly the reason for the intense interest in the formation and properties of multicomponent blends and alloys of all types.¹⁻⁶

One interesting application is the use of polymeric materials to replace inorganic glass in high temperature, humid environments where clarity of the polymer, cost, and maintenance of material toughness and strength are important issues. Bisphenol A-based polycarbonate, PC, has often been specified for this application because its properties initially meet the major criteria. However, PC rapidly loses mechanical properties and clarity when continuously exposed to boiling water as a result of hydrolytic attack, and these property decreases can be related to similar decreases observed over longer periods of time at lower temperatures and humidities.⁷

This laboratory has recently examined the miscible binary blend of PC and a copolyester comprised of 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids. A series of in depth investigations of this system has been made, including thermodynamic issues,⁸ melt chemistry,⁹ mechanical behavior,¹⁰ and transport properties.¹¹ Since the copolyester was known to have good hydrolytic stability, it seemed appropriate to examine the stability of these blends in boiling water. The results of this brief study, presented below, suggest that the blends may offer distinct property improvements relative to the pure components in this application.

EXPERIMENTAL

Materials and Procedure

The PC used is a commercial product from the General Electric Company, designated Lexan 131-111. This material has a number-average molecular weight \overline{M}_n of 13.3×10^3 and a weight-average molecular weight \overline{M}_w of 34.2×10^3 and is intended for extrusion applications. The polymer shows a glass transition temperature T_g of 148°C by thermal analysis and does not crystallize when melt processed by conventional methods. The copolyester is a commercial product, Kodar A150, of Eastman Chemical Products, Inc. Approximate analyses suggest that its isophthalic/terephthalic acid proportion is 20/80 and that its \overline{M}_n is about $22 \times 10^{3.9}$ The copolyester has a T_g of 87°C and a melting temperature T_m of 265°C. This material does not crystallize when rapidly quenched to below T_g during normal molding and extrusion operations, but it will do so if cooled slowly or annealed for modest periods of time at temperatures between T_g and T_m . For this reason, it would be unsuitable for the boiling water application requiring clarity of the plastic.

Blends were prepared using identical procedures to those used for the study of mechanical properties.¹⁰ The polymer pellets were physically mixed on a weight percent basis and dried for 24 h at 70°C in a convection oven to remove moisture. This was followed by annealing for 1 h at 150°C to crystallize the copolyester. The dried mixtures were removed from the oven and immediately fed to a $\frac{3}{4}$ -in., 20:1 L/D ratio, single-screw extruder for melt mixing. Extruder temperature settings were between 290 and 300°C for all runs. Film samples for this study were obtained by attaching a slit die, with a gap setting of 0.044 in., to the extruder outlet. The film was collected and cooled with a takeup system comprised of water-cooled, polished rolls placed 2 in. from the die exit. Material for molding into bars was obtained using a $\frac{1}{8}$ -in. rod die with the extruder, a water bath, and a pelletizer. This material was redried, using the protocol above, prior to injection molding in a ram injection molding machine at temperatures ranging from 275°C for pure copolyester to 305°C for pure PC.

Film test samples, $\frac{3}{6}$ in. wide by 10 in. long, were cut from the extruded film in the machine direction, and their mechanical properties were determined at room temperature using a tensile tester operated at a strain rate of 50%/min. Changes in mechanical properties with exposure to boiling water were obtained by submerging similar samples in a 4-L resin kettle equipped with a reflux condenser for up to 15 days. Samples were removed for testing every two days.

Changes in molecular weight caused by exposure to boiling water were monitored by determining the changes in specific viscosity η_{sp} of solutions prepared from 0.10 g of treated sample dissolved in 10 ml of a 60 wt % phenol/40 wt % tetrachloroethane solvent. Measurements of η_{sp} were made at 27°C using a Ostwald–Fenske capillary viscometer.

A convenient expression for molecular weight changes is formed from the ratio

$$R_t = \frac{(\eta_{sp})_t}{(\eta_{sp})_0} \tag{1}$$

where $(\eta_{sp})_t$ and $(\eta_{sp})_0$ are the specific viscosities for solutions of polymers exposed to boiling water for t days and 0 days, respectively. To the extent that the Huggins equation¹² is applicable to these solutions, the ratio of intrinsic viscosities can be easily calculated from R_t via

$$\frac{[\eta]_t}{[\eta]_0} = \frac{1 - [1 + 4K'R_t(\eta_{sp})_0]^{1/2}}{1 - [1 + 4K'(\eta_{sp})_0]^{1/2}}$$
(2)

where K' is the Huggins constant, taken to be 0.35, and $[\eta]_t$ is the intrinsic viscosity of the solution containing polymer which has been exposed for t days. The ratio of intrinsic viscosities is found by calculation to differ from R_t by a maximum of 7% for the solution concentrations employed in this study. Consequently, it is an adequate approximation to take R_t to be identical to the ratio of intrinsic viscosities. The intrinsic viscosity is related to the weight-average molecular weight \overline{M}_w of the polymer by the well-known empirical relationship

$$[\eta] = K\overline{M}^a_w \tag{3}$$

where the parameters K and a are specific to the particular polymer-solvent system considered.^{13,14} These parameters are unknown for the solutions studied here. However, parameter a is usually close to $\frac{1}{2}$ for many systems; and to within this approximation, one can estimate the change in molecular weight, from eqs. (1)-(3), as

$$\frac{M_{wt}}{\overline{M}_{w0}} = R_t^2 \tag{4}$$

Equation (4) forms the basis for integration of the observed variations in viscometric and mechanical properties with boiling water exposure, although it is recognized that this equation is only an approximation.

RESULTS

Aging of Extruded Film

Figure 1 shows the percentage decrease in specific viscosity, equivalent to $(1 - R_t)$ (100%), of solutions whose polymer components are exposed for up to 12 days in boiling water. Here it is seen that the molecular weight of pure PC, calculated from eq. (4), decreases rapidly with exposure time to about 36% of its original value at 12 days exposure. In contrast, the small percentage change in the specific viscosity of the copolyester solutions suggests that this material is relatively inert to hydrolytic attack. Its molecular weight after 12 days exposure is about 96% of the original value. These results agree, qualitatively, with those of Cooper and Williams¹⁵ who found that the hydrolysis rate constant for boiling water hydrolysis of diphenylcarbonate, a reasonable analog for PC, is 130 times greater than that for an alkylbenzoate analog for the copolyester.

Of particular interest is the rather nonlinear behavior of solution viscosity changes with blend composition (Fig. 1), where it appears that even small amounts of copolyester addition greatly reduce the percentage viscosity decrease relative to that of pure PC. Some reasonable approximations can be made which strongly suggest that this compositional variation is what would result if the blend



Fig. 1. Viscosity decrease of solutions made from polymers exposed to boiling water. Solvent 60% phenol/40% TCE; concentration 1 g/dL.

components were to hydrolyze at the same rates in the blend as they would when independently exposed to the same hydrolysis conditions. Provided the molecular weight distribution is unaltered by the hydrolysis process, an assumption which is quite good for PC,⁷ one can write for each pure component i

$$\frac{(M_{wi})_t}{(\overline{M}_{wi})_0} = f_i(t) = R_{it}^2$$
(5)

in which $f_i(t)$ contains all of the kinetic information and varies from 1 toward zero as degradation proceeds. In the context of Figure 1, $f_i(t)$ can be a rather complicated expression, however, it need not be specified analytically since it can be evaluated from the observed variation in viscosity ratio for each pure component. Provided each component *i* hydrolyzes in the blend at the same rate as it does in the pure state, eq. (5) also describes the molecular weight variation of each component in the blend; and if the blend also follows eq. (4), one can write an expression for the viscosity ratio of the blend, R_{bt} , with the help of the definition of \overline{M}_w :

$$R_{bt} = (\phi_{01}R_{1t}^2 + \phi_{02}R_{2t}^2)^{1/2} \tag{6}$$

where

$$\phi_{01} = 1 - \phi_{02} = \frac{\omega_1(\overline{M}_{w1})_0}{\omega_1(\overline{M}_{w1})_0 + (1 - \omega_1)(\overline{M}_{w2})_0}$$
(7)

for a binary mixture of components 1 and 2, and ω_1 is the mass fraction of component 1 in the blend.

From the work of Smith,⁹ the initial molecular weights of extruded pure components are $(\overline{M}_{w1})_0 = 32.3 \times 10^3$ for PC and $(\overline{M}_{w2})_0 = 40 \times 10^3$ for the CPE. Both materials are degraded slightly by the thermal history associated with extrusion, and the molecular weights of their blends are also commensurately lower and follow the above relationships with specific viscosity. Table I shows a comparison of the observed percentage viscosity decrease with that predicted from eq. (6) using these initial molecular weights. Equation (6) seems to do a very good job of predicting the viscosity decrease of the blends after 12 days of exposure, and it does a similarly good job at other hydrolysis times as well. The

Wt % PC in blend	Viscosity decrease, $(1 - R_t)$ (100%)			
	Observed	Calc. from eq. (6)		
100	41	41		
75	25	26		
50	16	15		
25	9.5	7.0		
0	2.0	2.0		

TABLE I Compositional Variation in Solution Viscosity Decrease for Materials Exposed to Boiling Water for 12 Days

success of eq. (6) inclines one to conclude that the blend components do hydrolyze at the same rates in the blend as in their respective pure states and that the compositional nonlinearities observed in Figure 1 are primarily the result of the usual viscosity dependence on molecular weight.

The rate of hydrolysis of any polymer, information embodied in $f_i(t)$, should depend on the concentration of the water reactant, the concentration of hydrolyzable species, and the reaction temperature. One should therefore expect, in this particular case, that the hydrolysis rate of PC in the blend should be less than in the pure state because of the lower concentration of hydrolyzable species. The reason that this expectation is not borne out or that the above analysis is apparently correct can be seen in Figure 2 where it is shown that the concentration of water sorbed by the blend increases as its PC content decreases. These effects apparently nearly compensate, kinetically, so that the assumption in the foregoing analysis that $f_i(t)$ is the same in the blend as in the pure state appears correct.

Figure 3 shows T_g measurements made on samples which were aged in boiling water and then dried in a vacuum oven prior to heating at 10°C/min in a differential scanning calorimeter. Samples that have PC concentrations high enough to set the blend T_g above 100°C do not crystallize in boiling water, and the T_g values for these blends are seen to decrease as the hydrolysis time increases. Blends which contain high levels of copolyester and have T_g values below 100°C show an increase in T_g with boiling water exposure as a result of the crystallization of copolyester from the blend.¹⁶ These materials rapidly develop crystalline opacity on exposure to boiling water, whereas blends containing 50% PC or more remain transparent for up to 15 days.



Fig. 2. Water sorption at 100°C of blends.



Fig. 3. Glass transition temperatures of films exposed to boiling water.

The decrease in amorphous blend T_g with hydrolysis time is primarily the result of hydrolytic degradation of the PC component molecular weight, as can be demonstrated by application of two well-known relationships. The first describes the T_g dependence on the number-average molecular weight \overline{M}_n via

$$T_g = T_{g^{\infty}} - \frac{K''}{\overline{M}_n} \tag{8}$$

where $T_{g^{\infty}}$ is the T_g corresponding to infinite molecular weight and K'' is an empiricial parameter in the range $0.3-1.5 \times 10^5$ for a wide variety of amorphous materials.¹⁷ Equation (8) can be rearranged and combined with eq. (4), together with the assumption that the molecular weight distribution is not altered by hydrolysis, to yield for pure PC, component 1,

$$(T_{g1})_t = (T_{g1})_0 - \frac{K''}{(\overline{M}_{n1})_0} \frac{1 - R_{1t}^2}{R_{1t}^2}$$
(9)

where $(T_{g1})_0$ and $(T_{g1})_t$ are the T_g values observed initially and after t days exposure, respectively. As shown in Figure 4, a good straight-line correlation is obtained for PC using the data from Figures 1 and 3. The slope of this line, to-



Fig. 4. Variation of T_g of polycarbonate with changes in its molecular weight as determined by the specific viscosity ratio of PC solutions.

Doning water								
	Glass transition temperature, °C							
Blend composition,	0 days ^a		6 days		12 days			
wt % PC	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.		
100	148	148	145	146	140	140		
75	130	131	127	129	123	125		
50	114	115	112	114	108	111		
25	98	100		_		_		
0	87	87	-		—	—		

TABLE II Comparison of Predicted and Observed Glass Transition Temperatures for Blends Exposed to Boiling Water

^a Exposure time.

gether with $(\overline{M}_n)_0 = 12.4 \times 10^3$ calculated for extruded PC, yields $K'' = 0.52 \times 10^5$, a value which is well within the expected range. In principle, a similar analysis could be obtained for component 2; however, the copolyester does crystallize at 100°C, which complicates the thermal analysis and its molecular weight does not change substantially with exposure time so that no molecular weight dependence is expected. The second relationship is the usual expression for calculating the compositional dependence of the T_g for amorphous miscible binary blends⁴:

$$\frac{1}{(T_{gb})_t} = \frac{\omega_1}{(T_{g1})_t} + \frac{1 - \omega_1}{(T_{g2})_t}$$
(10)

where $(T_{gb})_t$ is the blend glass transition temperature after t days of exposure to boiling water; and for this particular system, $(T_{g2})_t$ is set equal to $(T_{g2})_0$, the initial T_g for amorphous copolyester. Table II shows a comparison of the blend T_g values calculated from eqs. (9) and (10) with those observed in Figure 3. Agreement is quite good, although the prediction of T_g for treated blends is consistently high by 2 to 3°C. The reason for this may lie in the assumption that $(T_{g2})_t = (T_{g2})_0$, since Figure 1 does suggest that there should be a slight depression in T_g for amorphous copolyester. On the whole, however, one must conclude that the decrease in blend T_g with hydrolysis time is quite well explained by the hydrolysis of the PC fraction alone.

Figure 5 shows the reduction in tensile ductility of the blends and pure components resulting from exposure to boiling water. Both pure PC and pure copolyester are seen to show marked losses in ductility after just a few days of exposure, whereas the 50/50 blends of these materials remain quite ductile for up to 15 days in boiling water. Crystallization of the copolyester from copolyester-rich systems on exposure to boiling water is primarily responsible for the loss of ductility in these materials. In contrast, PC and PC-rich blends do not crystallize for up to 15 days of exposure, as judged by film clarity, although one could reasonably expect continued hydrolysis of the PC component to eventually lower the T_gs values of the blends to values below 100°C at which time copolyester crystallization would occur, see Table II.

The loss of ductility for the amorphous materials is primarily due to the loss of PC molecular weight by hydrolysis. This is demonstrated in Figure 6, where the fraction of initial ductility remaining after exposure, from Figure 5, is plotted against the material weight-average molecular weight calculated from eqs. (4), (6), and (7) and the observations in Figure 1. The solid line in Figure 6 shows



Fig. 5. Ultimate elongation of film as a function of exposure time to boiling water.

the same trend for pure PC taken from the works of Gardner and Martin⁷ and Long and Sokol.¹⁸ These investigators observed that the ductility of pure PC decreases rapidly as its molecular weight is decreased through either hydrolysis⁷ or deliberate choice of lower-molecular-weight grades.¹⁸ For purposes of the comparison shown in Figure 6, the "apparent weight-average molecular weight" \overline{M}_{wa} , obtained by these investigators from gel permeation chromatography measurements calibrated with polystyrene standards, were corrected via \overline{M}_w = $C\overline{M}_{wa}$. The factor C was obtained from the \overline{M}_{wa} data of Gardner and Martin for Lexan 141 and $\overline{M}_w = 26 \times 10^3$ for this material, kindly provided by Mr. R. B. Allen of the General Electric Company, Pittsfield, MA.



Fig. 6. Fractional retention of film ductility vs. weight-average molecular weight: (\diamond) 100% PC (Long and Sokol); (\circ) 100% PC (Gardener and Martin); (\bullet) 100% PC (this work); (Δ) 75% PC (this work); (\Box) 50% PC (this work).



Fig. 7. Yield strength of film as function of exposure to boiling water.

The comparison shown in Figure 6 is remarkably good when one considers all of the estimates and different techniques used in this study and the others, and it strongly suggests that the ductility dependence on molecular weight is the same for the blends as for pure PC. That is, the ductility of these amorphous materials can be expected to fall rapidly when their molecular weights on a weight-average basis fall below 25×10^3 regardless of blend composition. On this basis, the retention of ductility of the 50/50 blend, Figure 5, is related to its higher initial weight-average molecular weight relative to blends containing higher amounts of PC and to its smaller change in molecular weight as hydrolysis proceeds because of its reduced PC content. Figure 6 suggests that the 50/50 blend will probably embrittle shortly after 16 days of exposure to boiling water. However, the use of a somewhat higher-molecular-weight grade of copolyester should extend the ductile life of this blend by simply increasing its initial molecular weight. That is, if the \overline{M}_w of the copolyester were initially 50×10^3 , Figure 6 would suggest that a 50/50 blend would not embrittle even though the PC component were completely hydrolyzed. What would happen, of course, is that copolyester crystallization, leading to opacity and embrittlement by this mechanism, would eventually occur when the blend T_g were reduced to 100°C by the hydrolysis of the PC fraction.

Figure 7 shows the yield strengths observed for films exposed to boiling water. The crystallization of the copolyester from materials containing 75% or more copolyester is responsible for the observed increases in yield strength in these materials. The initial enhancement of yield strength with exposure observed for the amorphous materials is probably caused by sub- T_g annealing effects which increase local ordering of the molecules.⁷ This phenomenon also occurs for films at all compositions when annealed in a dry oven environment at T_g -15° C,¹⁰ and the magnitudes of maximum yield strength observed in Figure 7 are nearly identical to those observed when the blends are oven annealed at T_g -15° C for 150 h. Interestingly, the ductility of oven-annealed specimens also decreases with local ordering, and one could expect that some of the loss of ductility observed in Figure 6 is due to this phenomenon as well as to the decline in PC molecular weight. This possibility could explain why the ductilities of the blends in Figure 6 lie below the portion of the line from the work by Long and Sokol which did not involve thermal annealing.

The maxima in yield strengths of amorphous blends in Figure 7 are somewhat more difficult to explain. One expects that the strength of glassy materials



Fig. 8. Microcavity development in injection-molded bars of PC.

should decline with decreasing molecular weight,¹⁹ and maxima resulting from the countervailing material responses to thermal annealing and molecular weight degradation could be expected. However, the locations of the observed maxima do not fall into a consistent pattern corresponding to any of the variables examined in this study, and no firm conclusions regarding the reasons for their presence can be reached at this time.

Aging of Molded Bars

In contrast to PC film which remains totally transparent for up to 15 days of exposure to boiling water, PC injection-molded bars develop visible internal microcavities after exposure for just a few days. These microcavities appear first along the injection stream lines; but as exposure time increases, the microcavities increase in number and to some extent in size until the bars become totally opaque and very brittle, (Fig. 8). Since microcavities do not develop in the film specimens, one might tentatively conclude that their development depends on the presence of molecular orientation induced during injection molding as well as hydrolysis. This tentative conclusion seems to be verified by the lack of microcavity production in dry oven-annealed bars¹⁰ and by the lack of microcavity development in bars containing 25% copolyester after 10 days of exposure to boiling water (Fig. 9). Addition of copolyester lowers the blend melt viscosity, lowers the blend T_g , and reduces the concentration of hydrolyzable material, all of which could contribute to the lack of microcavity development.



Fig. 9. Appearance of injection-molded bars after 10 days exposure to boiling water.

The opacity of the injection-molded bars from 50/50 blend material (Fig. 9) also contrasts with the optical clarity observed when films of this material are exposed to boiling water. In this instance the copolyester has crystallized from the material molded into bars. The reason for this is related to the additional molecular weight degradation and subsequent lowering of the blend T_g caused by the extra thermal history associated with the molding step. The initial T_g of 50/50 blend material after molding is only 106°C, compared to 114°C for the same blend after extrusion. This initially lower value is reduced further by hydrolysis during boiling water exposure until the blend T_g approaches 100°C, at which point crystallization can occur. Smith⁹ points out that the molecular weight loss during thermal processing occurs in this blend system to a greater extent than expected by additive approximations. This phenomenon is probably responsible for the observed lowering of molded bar T_g prior to hydrolysis.

SUMMARY AND CONCLUSIONS

This study has considered the potential use of polycarbonate/copolyester blends for applications requiring stable mechanical properties and optical clarity in hot, humid environments. In boiling water, extruded films from blends containing approximately 50% copolyester are found to maintain these properties for extended periods relative to the pure components. The incorporation of 50% PC in the blend raises the blend T_g to above 100°C and so prevents loss of duc-

tility and clarity by crystallization of the copolyester fraction. Relative to pure PC, the incorporation of 50% copolyester, a hydrolytically more stable polymer, serves to increase the blend \overline{M}_w , initially, and to reduce the decrease in \overline{M}_w caused by hydrolysis of the PC.

This blend system is interesting in a general sense because it seems to show a critical molecular weight required for ductile behavior which is nearly identical to that for pure PC. This, plus the observation that PC appears to hydrolyze in the blend at the same rate as it does in the pure state, allows one to estimate the loss of blend properties in the humid aging environment by considering the lowering of blend T_g , which could lead to crystallization of the copolyester, or the lowering of \overline{M}_w , which could lead to loss of ductility in amorphous systems, by simply knowing the initial properties of the blend components, their fractions in the blend, and the molecular weight loss of pure PC at the hydrolysis conditions of interest.

For example, Gardner and Martin⁷ find that the apparent weight-average molecular weight of Lexan 141 falls to 25×10^3 after 78 weeks of exposure to 100% RH at 65°C, at which time the material elongation at break is under 5%. If a 50/50 blend with copolyester were tested under comparable conditions, the true weight-average molecular weight of the blend at 78 weeks should be about 27.5 \times 10³; the blend elongation at break, from Figures 5 and 6, should be about 90%; and the blend T_g , from eqs. (8) and (10), should be about 114°C, which precludes crystallization of the copolyester fraction. The blend could therefore be expected to retain most of its initial ductility and clarity at these exposure conditions. While no experimental evidence is available to verify this prediction, the superior performance of this blend system in boiling water suggests that it may also prove superior to pure PC in those applications requiring long-term property stability in the presence of high humidity, provided care is taken to minimize thermal degradation during molding and to set the PC content and blend T_g to values sufficiently high to prevent losses of ductility by crystallization and sub- T_g annealing.

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