

Effect of Crystallinity on Gas Permeation in Miscible Polycarbonate-Copolyester Blends

W. E. PRESTON,* J. W. BARLOW, and D. R. PAUL, *Department of Chemical Engineering and Center for Polymer Research, University of Texas, Austin, Texas 78712*

Synopsis

Permeation rates of helium, methane, and carbon dioxide in miscible blends of polycarbonate and a copolyester were measured at 35°C. The permeabilities for semicrystalline blends having copolyester crystallinity induced by annealing were compared to fully amorphous blends. Crystallinity caused a slightly greater impedance to carbon dioxide transport than it did for helium or methane. The relative rates of permeation of one gas compared to another, an issue important for membrane separations, varied greatly with blend composition; however, the effect of crystallinity was not large.

INTRODUCTION

The physical and chemical behavior of the miscible blends formed from bisphenol-A polycarbonate and a copolyester (composed of 1,4-cyclohexane dimethanol and a mixture of terephthalic and isophthalic acid units) have been described in a series of papers from our laboratory.¹⁻⁷ One of these⁴ papers gave a detailed account of the sorption and permeation of CO₂ in blends which were free of copolyester crystallinity. A more recent paper⁷ has examined the effect of copolyester crystallization, produced by annealing, on mechanical properties of the blends. The purpose of this paper is to explore further the permeation of various gases in these blends and to examine the effect copolyester crystallinity has on gas permeation.

Gas sorption and transport in glassy polymers is a complex process,^{4,8} and characteristic parameters like the permeability coefficient usually are not constant but vary with the magnitude of the driving pressure used. However, since these issues were not the primary focus of this work, the experimental program was simplified by using a single, fixed driving pressure for all three permeants employed, viz., helium, methane, and carbon dioxide.

MATERIALS AND EXPERIMENTAL PROCEDURES

All materials were the same as used previously,¹⁻⁶ viz., copolyester, Kodar A-150 from Eastman Chemical Products, Inc., and polycarbonate, Lexan 131-111 from General Electric Co. Prior to any melt processing, both polymers were dried at 75°C for 24 h and the copolyester was precrystallized at 150°C for 1 h. All melt mixing was executed in a single screw extruder using similar processing

* Present address: Texaco, Inc., P.O. Box 52332, Houston, TX 77052.

conditions described earlier.³ Prior to blending with polycarbonate, 0.1% As₂O₃ was melt-mixed into the copolyester to deactivate residual titanium polymerization catalyst.² Films having thicknesses of 2.8–4.3 mils were extruded from each blend composition using melt draw ratios of 7–10, i.e., the film take-up velocity relative to the average velocity in the die.

Samples of film for each composition were redried and then annealed at constant length for 30 min at 440 K to crystalline the copolyester. Heats of fusion were determined by DSC using computer-aided integration of melting endotherms. If crystallization occurred during the scan, the area of the crystallization exotherm was subtracted from the area of the melting endotherm to determine the sample's original level of crystallinity. The results for the annealed blends are given in Table I. The unannealed blends were found not to be crystalline as prepared.

Permeation rates of helium, methane, and carbon dioxide through annealed and unannealed films were determined at 35°C using an upstream pressure of 1 atm by techniques described previously.^{4,9} The data presented are averages of several determinations.

EXPERIMENTAL RESULTS

The observed permeability coefficients for unannealed and annealed samples are plotted versus overall blend composition in Figure 1 for helium, Figure 2 for methane, and Figure 3 for carbon dioxide. For several cases, a comparison with earlier data⁴ was possible, and the agreement was excellent. Annealing did not affect the permeability of polycarbonate to these gases since this polymer does not crystallize and molecular orientation, which would relax during this thermal treatment, of the extruded film was very low. However, owing to crystallization of the copolyester, the permeability of annealed specimens showed a progressively larger decline relative to the unannealed film as the copolyester content of the blends increased. In all cases, the permeability versus composition relations are slightly concave upward on the semilogarithmic coordinates employed in Figures 1–3. This curvature is consistent with previous observations and theoretical expectations^{4,10,11} for miscible blend systems.

There are two interesting ways to analyze these data in further detail by con-

TABLE I
Characterization of Crystalline Blends

Total wt % copolyester in blend	ΔH_f (cal/g)	Percent crystallinity ^a	Wt % copolyester in amorphous phase
100	7.2	24.2	100
80	6.4	21.5	74.5
60	4.0	13.4	53.7
40	3.3	11.1	32.4
20	1.3	4.4	16.2
0	0	0	0

^a Calculated using a value of 29.8 cal/g estimated⁵ for the heat of fusion of the 100% crystalline material. Percent crystallinities are based on total sample mass.

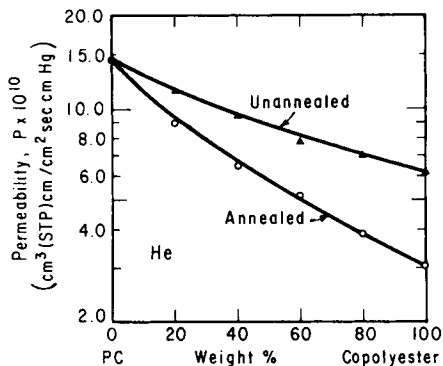


Fig. 1. Helium permeation in amorphous and semicrystalline blends.

structuring various permeability ratios. The first is to examine the effect of crystallization caused by annealing on the rate of permeation of a given gas. This may be done by ratioing the permeabilities to each gas of the semicrystalline and the amorphous film for each blend composition. This ratio is plotted versus the fraction of crystalline material in the annealed blends (see Table I) as shown in Figure 4. To a first approximation, this ratio appears to correlate uniquely with the crystallinity and to be independent of the gas type. This is what one would expect if these materials conformed to a simple two-phase model of the crystalline-amorphous phase composite. However, as shown in the next section, this method of presentation is not an extremely sensitive one, and some subtle features of the data are masked. One factor not accounted for here is the fact that crystallization of the copolyester removes some of this component from the remaining amorphous phase. Hence, the ratios used in Figure 4 compare amorphous phases, through which all permeation occurs, of different compositions. The fourth column in Table I gives the calculated composition of the amorphous phase for the blends which have been annealed.

The second way to look at these data is to compare the relative rates of per-

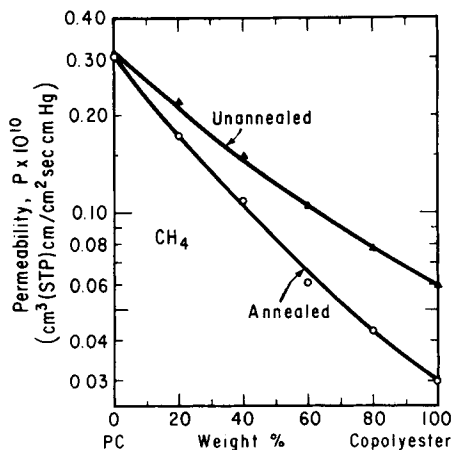


Fig. 2. Methane permeation in amorphous and semicrystalline blends.

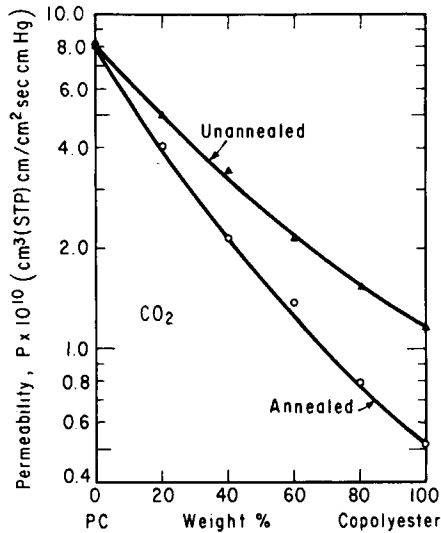


Fig. 3. Carbon dioxide permeation in amorphous and semicrystalline blends.

meation for any pair of these gases, i.e., He/CH₄, He/CO₂, and CO₂/CH₄, for each blend composition in the annealed or unannealed states. The various permeability ratios, equivalent to ideal separation factors for membrane separation processes, are plotted vs. overall blend composition in Figures 5–7. Ideally, for a simple two-phase model of crystalline-amorphous composites, one would not expect any difference between annealed and unannealed film; however, some small differences which grow with copolyester content are seen. This is further evidence of subtle effects on permeation caused by crystallization mentioned above. The copolyester shows more rapid helium permeation relative to both methane and carbon dioxide than does polycarbonate, whereas carbon dioxide transport relative to methane is more rapid in polycarbonate than in the copolyester. Thus, blending of miscible polymers may offer a useful technique for tailoring selectivity characteristics of membranes for gas separations. Note that the ratios

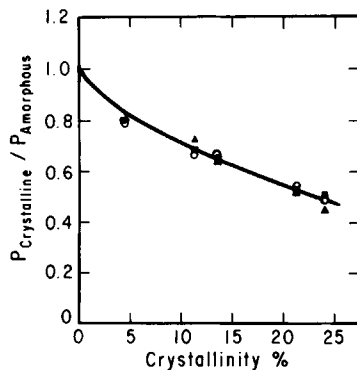


Fig. 4. Comparison of the ratio of permeabilities in crystalline and amorphous blends (without adjustment for changes in amorphous phase composition): (\blacktriangle) CO₂; (\blacksquare) CH₄; (\circ) He.

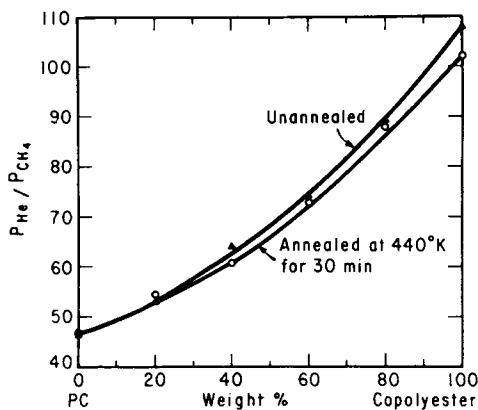


Fig. 5. Relative permeation rates of helium to methane.

of permeabilities are slightly concave upward in every case on these arithmetic coordinates. Note that these ratios for annealed and unannealed film are not being compared at the same composition of the amorphous phases for the reason mentioned above. Correction for this would tend to exaggerate the differences between crystalline and amorphous blends in the cases of He/CO₂ and CO₂/CH₄ but would tend to reduce the differences for He/CH₄.

DISCUSSION

The results described above show, as expected, that crystallization of the copolyester by annealing decreases the permeation rate of various gases through these blend film by an amount that increases as the content of the copolyester in the blend increases. As a first approximation, the factor by which the permeability decreases is a unique function of the fraction of copolyester crystals in the blend and does not depend on the nature of the gas or the composition of the blend except as this affects the fractional crystallinity. This is what one would expect from the ideal two-phase model for semicrystalline polymers; however, as suggested earlier, there does seem to be slight departures from this simple picture which will be developed further at this point by more refined analysis of the data.

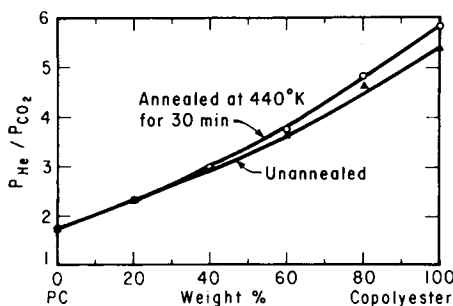


Fig. 6. Relative permeation rates of helium to carbon dioxide.

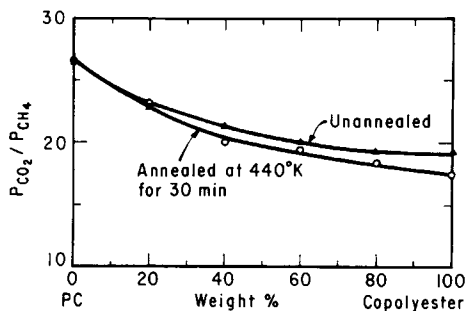


Fig. 7. Relative permeation rates of carbon dioxide to methane.

The two-phase model divides semicrystalline polymers into ideal amorphous and crystalline parts whose intrinsic properties are independent of the relative proportions of these phases. Based on this view, the effective solubility coefficient S for a gas in the semicrystalline polymer is related to that for the purely amorphous phases, S_a , by

$$S = \phi_a S_a \quad (1)$$

where ϕ_a is the volume fraction of the amorphous phase since there is ample evidence for zero solubility of the gas in the crystals¹² and since this model assumes that the characteristics of the amorphous phase do not depend on the presence of crystallites. Thus, the crystallites may be assumed to be impermeable barriers to diffusion much as inert filler particles might be; hence, the effective diffusion coefficient for the semicrystalline polymer, D , can be expressed as a simple proportionality to the diffusion coefficient of the purely amorphous polymer, D_a , i.e.

$$D = \kappa D_a \quad (2)$$

where κ is a structural parameter that depends on ϕ_a plus the shape and orientation of the crystals.¹³⁻¹⁵ Various theoretical predictions for κ are available.^{13,16} When the amorphous phase is glassy, S_a and D_a will depend on the concentration of the gas present.⁸

The effective permeability for a gas in a semicrystalline polymer will be

$$P = DS = \kappa \phi_a D_a S_a = \kappa \phi_a P_a \quad (3)$$

according to this model where P_a is the permeability coefficient for the purely amorphous polymer. Thus, the ratio P/P_a should not depend on the nature of the gas if the simple two-phase model applies. It should only depend on the extent of crystallinity and the morphology or texture of the two-phase mixture. The following will show this is not entirely the case for the present system.

As mentioned earlier, crystallization of the copolyester from the blend removes a portion of this component from the remaining amorphous phase. Estimates of this effect are shown in Table I calculated from the following equation

$$w' = \frac{w - \phi_c}{1 - \phi_c} \quad (4)$$

where w' is the weight fraction of copolyester in the amorphous phase of the

semicrystalline blend, w is the overall weight fraction of this component in the blend, and ϕ_c is the fraction of the blend which is crystalline, $\phi_c = 1 - \phi_a$. It is assumed that the fractional crystallinity is the same on a volume and on a weight basis since the densities of the two phases are only slightly different.⁵ Thus, in eq. (3) we should replace P by P' , where the latter is the permeability in the purely amorphous blend having the same composition as the amorphous phase in the semicrystalline blend, i.e., w' . These values can be read from the graphs of permeability for the unannealed blends shown in Figures 1–3 using the corrected amorphous phase compositions given in Table I. Using the smoothed data represented by the solid lines drawn in Figures 1–3, the following quantity was calculated:

$$1/\kappa = \phi_a P'_a / P \quad (5)$$

where P is the observed permeability for the annealed or semicrystalline film. The results are plotted in Figure 8 versus the fractional crystallinity values deduced from thermal analysis listed in Table I. This structural parameter is essentially the same for helium and methane but is noticeably different for carbon dioxide. Consequently, we conclude that the simple two-phase model is not entirely adequate, as formulated, for this system when the data are inspected more carefully in this way. It should be pointed out that carbon dioxide shows stronger nonlinear or concentration-dependent effects for both sorption and transport in glassy polymers than do helium and methane. For this reason, carbon dioxide may be a more sensitive probe of the physical state of the amorphous, glassy phase than is either helium or methane, and this may be the origin of the effect shown in Figure 8. However, carbon dioxide showed an entirely similar departure from the behavior of other gases like helium, nitrogen, and methane in silicone rubber membranes filled with zeolite particles.¹⁷ Clearly, further research is needed to determine the actual cause of the effect noted.

The dotted line shown in Figure 8 is the theoretical prediction for impermeable

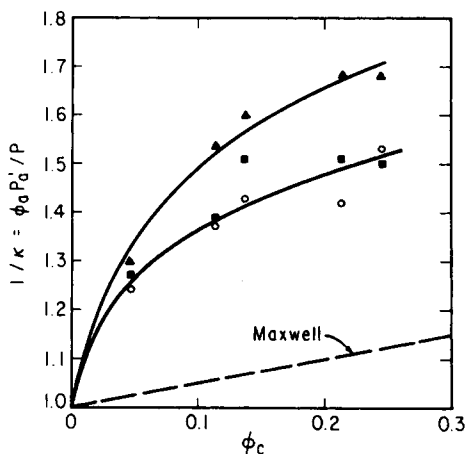


Fig. 8. Detailed analysis of the impedance of permeation caused by copolyester crystallinity: (---) calculated from eq. (6); (▲) CO₂; (■) CH₄; (○) He.

spheres imbedded in a permeable matrix as deduced by Maxwell,¹⁸ i.e.,

$$\kappa = 1/(1 + \frac{1}{2}\phi_c) \quad (6)$$

The experimentally determined factor by which crystallinity reduces permeability for the present system is considerably larger than this estimate. No doubt the cause for this lies in the fact that the crystallites have aspect ratios quite different from unity. Using some simplified models developed by Nielsen,¹⁶ we estimate crystallite aspect ratios as large as 6, and these values evidently depend on the level of crystallinity. However, aspect ratios cannot be uniquely determined from such data if the notion of amorphous phase chain immobilization caused by crystallites as introduced by Michaels et al.^{14,15} exists.

The effect of crystallinity on the mechanical properties of these miscible blends has been reported in a companion paper.⁷

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