

Barrier Properties of Polyesters – Relationship between Diffusion and Solid State Structure

E. Baer, Y. S. Hu, R. Y. F. Liu, D. A. Schiraldi and A. Hiltner

Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, OH 44106-7202.

INTRODUCTION

Aromatic polyesters, including poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN), are widely used in a range of high barrier application. However, there exists a growing demand to improve the barrier. The barrier properties of polymeric materials are determined by both the chemical and the solid state structures of the system. Here, we will focus on how molecular order influences the oxygen barrier properties of polyesters. The examples emphasize the strong effect of orientation, crystallinity and liquid crystallinity.

METHODOLOGY

The mechanism by which oxygen molecules permeate through polymers has been described by a solution-diffusion process. The permeability coefficient P is the product of solubility coefficient S , a thermodynamic parameter describing the ability of the polymer to dissolve the oxygen and diffusivity coefficient D , a kinetic parameter describing the mobility of the oxygen molecules in the polymer.

Oxygen flux at 0% relative humidity, 1 atm pressure, and 23 °C was measured with a MOCON OX-TRAN 2/20 as described previously.¹ To obtain the diffusivity D and to accurately determine the permeability P , the data were fit to the solution of Fick's second law with appropriate boundary conditions

$$J(t) = \frac{Pp}{l} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{D\pi^2 n^2 t}{l^2}\right) \right] \quad (1)$$

RESULTS AND DISCUSSION

Effect of orientation.² PET, PEN, and a copolymer based on PET in which 55 mol % of the terephthalate was replaced with bibenzoate (PET-BB55) were cold drawn by constrained uniaxial stretching. The processes of orientation and densification correlated with conformational transformation of glycol linkages from *gauche* to *trans*. Oxygen permeability, diffusivity and solubility decreased with the amount of orientation.

Free volume is a useful molecular-scale concept for interpreting transport properties. Permeation of small gas molecules through a glassy polymer is viewed as proceeding by a jumping mechanism whereby a penetrant molecule spends most of the time in free-volume cavities and occasionally jumps into a neighboring cavity. Gas permeation depends on the number and size of cavities (static free volume) and the frequency of jumps (dynamic free volume). Studies of glassy polyesters based on PET demonstrate that oxygen sorption at 1 atm pressure is the process of filling holes of static free volume, and the solubility is proportional to the amount of free volume.³

Figure 1 shows solubility plotted versus specific volume of oriented PET, PEN and PET-BB55. The solid line, with slope β of 3.6 cc(STP) g cm⁻⁶ atm⁻¹ and extrapolated zero-solubility specific volume v_o of 0.722 cm³ g⁻¹ described oxygen solubility of cold-drawn PET. The correlation suggested that cold-drawn PET could be regarded as a one-phase densified glass. Similarly, a linear relationship between solubility and specific volume was observed for PEN and PET-BB55.

The slope β reflected the density of sorbed oxygen. Constant β indicates fundamental similarity in the characteristics of the accessible free volume in glassy polyesters whereas v_o reflects a characteristic of the chemical structure. From proportionality between solubility and amount of accessible free volume, the specific accessible free volume v_f can be obtained from the slope β as

$$v_f = v - v_o = \frac{S}{\beta} \quad (2)$$

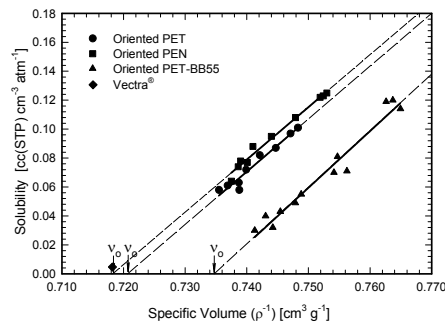


Figure 1. Relationship between S and specific volume ($v = \rho^{-1}$).

Due to the long timescale required for glassy polymers to relax fully, gas transport typically occurs under nonequilibrium conditions wherein the polymer possesses more free volume than it would at equilibrium. Following the concepts of Vrentas and Duda,⁴ the volume of the nonequilibrium glassy polymer is larger than the extrapolated equilibrium volume by the excess-hole free volume, Figure 2. Orientation by cold-drawing is viewed as decreasing the excess-hole free volume and bringing the nonequilibrium polymer glass closer to the equilibrium line.

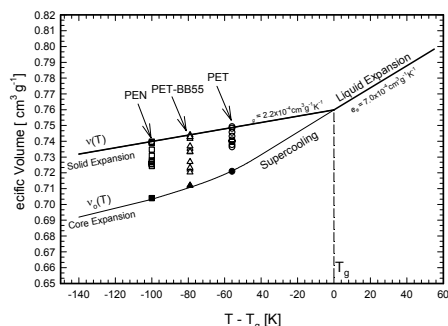


Figure 2. Specific volume-temperature relationship constructed for amorphous PET using oxygen solubility as a measure of accessible free volume and including the effect of orientation.

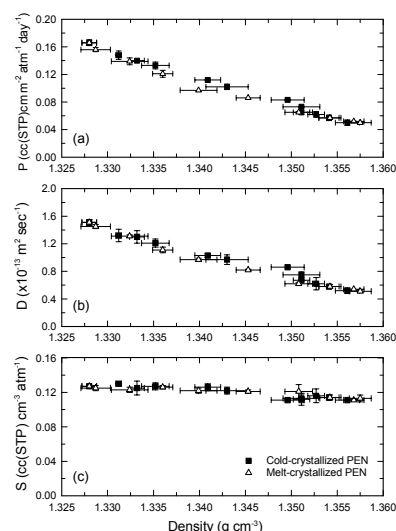


Figure 3. Effect of crystallinity as density on oxygen transport parameters of PEN: (a) permeability; (b) diffusivity; and (c) solubility.

Effect of crystallinity.⁵ Impermeability of crystals is the basis of the simple two-phase transport model, which consists of an impermeable crystal phase dispersed in a permeable amorphous

matrix. The formulation of the two-phase model was tested for PEN by examining the effect of cold-crystallization and melt-crystallization on oxygen transport properties. The effect of cold and melt crystallization on oxygen barrier properties of PEN is shown in Figure 3, with crystallinity expressed as density. Cold and melt crystallization reduced P by a factor of 3. The improved barrier of crystallized PEN was almost entirely due to a decrease in D . Crystallization had almost no effect on S which remained virtually constant at the value for amorphous PEN of $0.127 \text{ cc(STP) cm}^{-3} \text{ atm}^{-1}$.

It was found previously that amorphous phase density decreased with increasing crystallinity for PET. The fact that the bulk solubility S of PEN does not decrease with crystallinity as measured suggests that PEN falls in the category of PET. De-densification, or the increase in specific volume of the amorphous phase with crystallization, is attributed to constraint on relaxation of amorphous chain segments imposed by their attachment to chain segments in crystals.

Effect of liquid crystallinity.⁶ As compared to most thermoplastics, aromatic liquid crystalline polymers (LCPs) stand out because of remarkably low gas permeability. The extraordinarily low gas permeability of LCPs stems mainly from low solubility rather than from low diffusivity.^{7,8} Two models were put forward to explain the low solubility.^{9,10} One suggests that LC domains exclude permeant in the same way that most 3-dimensional crystals do, and transport is dominated by the small volume fraction of interdomain boundary regions. Alternatively, gas sorption occurs in the LC regions, however ordered arrangement of the chains reduces gas solubility to well below that of a conventional amorphous glass. Most of the speculation is based on results for nematic Vectra[®] and Vectra[®]-like copolymers, and it is generally agreed that the existing data are not sufficient to definitively support either model.

Poly(diethylene glycol 4,4'-biphenylate) (PDEGBB) was chosen for study because the solid state can be systematically varied from an LC glass to a crystallized LC glass. The permeability of the smectic phase was tested by examining the effect of cold crystallization on oxygen transport properties. The morphology of PDEGBB was examined in order to develop a structural model for oxygen transport.

Quenched PDEGBB had oxygen permeability of $0.0318 \text{ cc(STP) cm m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$, more than one order of magnitude lower than that of amorphous PET. The exceptionally low oxygen permeability of PDEGBB and other LCPs resulted mainly from very low S . Crystallization of PDEGBB reduced oxygen transport as shown in Figure 4 with crystallinity expressed as density. Oxygen permeability decreased to $0.0154 \text{ cc(STP) cm m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ due to decreases in both D and S , with S decreasing more than D .

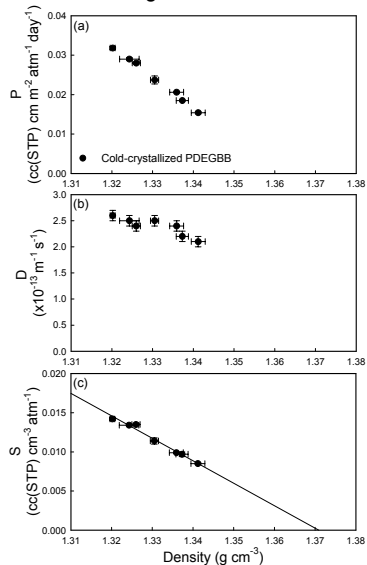


Figure 4. Effect of density on the oxygen transport parameters of PDEGBB: (a) permeability; (b) diffusivity; (c) solubility.

The linear relationship between S and crystallinity measured as density suggests that cold-crystallized PDEGBB also conforms to the two-phase model with

$$S = S_{LC}(1 - \phi_c) \quad (3)$$

where S_{LC} is the oxygen solubility of the quenched LC glass

Two hypotheses have been put forward to explain the low solubility of LCPs. Results for nematic Vectra[®] copolyesters appear to favor the first interpretation.^{9,10} This conclusion is based primarily on the observation that increasing crystallinity as measured from melting enthalpy does not reduce gas solubility. However, in this example, crystallization also does not alter density, suggesting that density of the crystal is close to that of the nematic phase.¹¹ It appears that the crystal of Vectra[®] is highly defective, and likewise can be considered permeable.

In contrast, the density of smectic PDEGBB is demonstratively less than the density of the crystal. Moreover, oxygen solubility decreases linearly with crystallinity as measured by density or melting enthalpy. This behavior is consistent with the second hypothesis as formulated in the 2-phase transport model of impermeable crystallites dispersed in a permeable matrix, with the caveat that the LC matrix possesses much lower gas solubility than a conventional amorphous polymer.

CONCLUSIONS

These studies demonstrated that solid state structure plays a vital role in determining the oxygen barrier properties of polyesters. Oxygen transport can be used as an effective structural probe of these structures. In summary, orientation of glassy polyesters densifies the glass and reduces the accessible free volume. Crystallization of PEN introduces a permeable spherulitic phase with a constrained, de-densified amorphous phase. Oxygen permeability of liquid crystallinity state is intermediate between amorphous glass and 3-dimensional crystal. LC order naturally leads to inherently low oxygen solubility.

ACKNOWLEDGEMENTS

Financial support from the National Science Foundation (DMR 9975774 and DMR 9986467) and KoSa is gratefully acknowledged. Modern Controls, Inc., generously supported the development of a facility for gas transport studies at Case Western Reserve University.

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