



# Oxygen sorption and transport in amorphous poly(ethylene furanoate)



Steven K. Burgess<sup>a</sup>, Oguz Karvan<sup>a</sup>, J.R. Johnson<sup>a</sup>, Robert M. Kriegel<sup>b</sup>, William J. Koros<sup>a,\*</sup>

<sup>a</sup> School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

<sup>b</sup> The Coca-Cola Company, Atlanta, GA 30313, USA

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## ABSTRACT

Oxygen transport in amorphous poly(ethylene furanoate) (PEF) was studied at various temperatures using complementary permeation and pressure-decay sorption techniques. A significant reduction in oxygen permeability of  $\sim 11\times$  was observed at 35 °C for PEF compared to poly(ethylene terephthalate) (PET), and is attributed primarily to reduction in chain segment mobility for PEF resulting from a hindrance of furan ring flipping. A custom-built high accuracy sorption system allowed determination of temperature-dependent so-called dual-mode parameters that have not been reported for oxygen in any polyester. Energetic parameters, i.e. the enthalpy of sorption and activation energies of diffusion and permeation, were measured for oxygen in PEF and discussed in the context of PET and related polyesters. The current work presents the first detailed study of penetrant transport in PEF, which demonstrates the impressive performance enhancements of PEF compared to PET.

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## 1. Introduction

Many attempts have been made to improve the barrier properties of poly(ethylene terephthalate) (PET), which has an undesirably high oxygen permeability that hinders juice and vitamin water packaging [1]. Barrier-improvement techniques are diverse and include organic barrier coatings, multi-layered barrier polymers, nanocomposite materials, polymer blends, and vacuum deposited coatings [2]. While the barrier properties of PET can be improved by such techniques, complex processing steps coupled with high capital investment can hinder production on a large scale [1]. As a result, much work has also focused on the development of novel pure-polymer replacements for PET with the goal of providing enhanced performance.

Poly(ethylene furanoate) (PEF) is the recently developed high-barrier polyester synthesized from ethylene glycol and 2,5-furandicarboxylic acid (FDCA). Due to the production of FDCA from renewable sugars [3], PEF also offers a bio-sourced replacement to poly(ethylene terephthalate) (PET) in addition to offering improved mechanical, thermal, and barrier properties [4]. Large-scale production of bio-sourced PEF can significantly reduce

greenhouse gas emissions and non-renewable energy usage compared to petroleum-sourced PET [5]. Multiple studies have focused on small-scale synthesis and subsequent property characterization of PEF and related furan-derived polyesters [6–13]; however, only two brief reports exist regarding the barrier efficacy to oxygen [4,14].

The current work can be motivated by an abbreviated table which compares the oxygen permeability properties in amorphous PET, which is the base case for comparison, to PEF and other analogously rigid polymers to PEF such as poly(ethylene naphthalate) (PEN) and poly(ethylene isophthalate) (PEI). A useful metric to normalize and compare permeability results from different studies is the so-called Barrier Improvement Factor (BIF), which can be defined as the permeability of oxygen in PET divided by the permeability of oxygen in either PEF, PEI, or PEN ( $BIF = P_{PET}/P_{PEF, PEN, PEI}$ ) [15]. Consequently, BIF's greater than unity illustrate barrier improvement compared to amorphous PET. Table 1 provides such permeability data and BIF comparisons between PET and related polyesters.

From Table 1, it is apparent that PEF exhibits largely improved oxygen barrier properties compared to PET as evidenced by the large BIF of 11, while PEN exhibits a smaller BIF of 2.9 and PEI a BIF of 3.6. Although significantly lower than PET, the oxygen permeability for amorphous PEF is still higher than for semicrystalline barrier polymers such as dry Nylon-MXD6 (0.002 Barrer at 35 °C [18]) and dry ethylene vinyl alcohol (EVOH, 0.0003 Barrer at 35 °C

\* Corresponding author. Tel.: +1 404 385 2845; fax: +1 404 385 2683.

E-mail addresses: [sburgess3@gatech.edu](mailto:sburgess3@gatech.edu) (S.K. Burgess), [bill.koros@chbe.gatech.edu](mailto:bill.koros@chbe.gatech.edu) (W.J. Koros).

**Table 1**  
Permeability and Barrier Improvement Factor (BIF) comparison between amorphous PET and amorphous PEF, PEI, and PEN.

Polyester	Temp (°C)	Permeability (Barrer)	BIF (–)	Reference
PET	35	0.114	1	[4], This work
PEF	35	0.0107	11	[4], This work
PET	35	0.103	1	[16]
PEN	36	0.037	2.8	[16]
PET	30	0.054	1	[17]
PEN	30	0.019	2.9	[17]
PEI	30	0.015	3.6	[17]

[18]), however the latter polymers typically exhibit poor oxygen permeability performance in humid environments. Nevertheless, the significant oxygen barrier improvements for PEF compared to PET greatly expand the opportunities for introduction of PEF into markets beyond that of beverage packaging applications. This notion is complemented by PEF exhibiting improved mechanical and thermal properties compared to PET [4], which enhancements can be further improved via transitioning into the semicrystalline domain.

The large BIF for PEF vs. PET listed in Table 1 and reported in our prior work [4] motivated the current study, which provides a more detailed investigation regarding the oxygen transport characteristics of PEF. Fundamental understanding of the solubility and diffusivity contributions to oxygen transport in PEF will help elucidate the dominant mechanism of barrier enhancement compared to PET and can guide development of increasingly advanced barrier resins. Previous research [4] using NMR methods and dynamic mechanical analysis has revealed that penetrant diffusion in PEF and PET is strongly affected by chain mobility originating from the ring-flipping mechanism. The symmetry about the ring-flipping axis and lack of phenyl ring polarity promotes ring-flipping in PET. On the other hand, the nonsymmetrical axis of ring rotation and polarity in the furan ring hinders ring-flipping in PEF [4] and thus suggested a basis for understanding our limited preliminary oxygen transport data.

The current study utilizes complementary permeation and pressure-decay sorption methods to probe the dissolved and Langmuir sorbed populations in amorphous PEF, thus providing a detailed understanding of the complex transport environment in the glassy polymer. The significant permeability reduction of  $\sim 11\times$  for oxygen in PEF compared to PET is explained primarily by a difference in chain mobility [4], since both polyesters exhibit similar oxygen solubilities at 35 °C. Furthermore, energetic transport parameters derived from permeation and pressure-decay sorption techniques will be shown to have excellent internal consistency between the independently measured parameters.

## 2. Transport background and theory

Steady-state and transient permeation in rubbery materials are described by Equations (1) and (2) for a constant diffusion coefficient when Henry's law sorption behavior applies [19].

$$P = k_D D \quad (1)$$

$$D = \frac{l^2}{6\theta} \quad (2)$$

In Equations (1) and (2),  $P$  is the permeability,  $k_D$  (ccSTP/(ccPoly·atm)) is the Henry's law sorption coefficient,  $\theta$  (s) is the time lag, and  $l$  (cm) is the film thickness, so no pressure dependence is observed; however, temperature dependence does occur [20].

Equations (1) and (2) can also be used to estimate the sorption coefficient from only transient and steady state permeability measurements, viz.,

$$k_D = \frac{6\theta P}{l^2} \quad (3)$$

Transport in glassy polymers is complicated by the non-equilibrium nature of the glassy matrix at sub- $T_g$  temperatures. Sorption contributions in glassy polymers can be viewed as a combination of a dissolved mode (Henry's law,  $C_D$ ) and Langmuir mode (microvoids or "holes",  $C_H$ ) [21], and is represented by the so-called dual-mode model [22] in Equations (4) and (5).

$$C = C_D + C_H \quad (4)$$

$$C = k_D p + \frac{C_H b p}{1 + b p} \quad (5)$$

where  $b$  (atm<sup>-1</sup>),  $C_H$  (ccSTP/ccPoly) and  $p$  (atm) represent the affinity constant, Langmuir capacity constant, and pressure, respectively. Penetrant sorption for glassy polymers described in Equation (5) can be described using a single coefficient in the low-pressure limit, thus providing an "effective" sorption coefficient,  $k^*$ , with contributions from both Langmuir and dissolved populations, viz.,

$$k^* = (k_D + C_H b) \quad (6)$$

In general, transport in glassy polymers is complicated by the presence of the Langmuir environment and cannot be described by the simple pressure-independent relationships in Equations (1)–(3). As such, the concept of partial immobilization of a penetrant within the Langmuir environment has proven successful in representing concentration dependent permeation and diffusion coefficient data in glassy polymers [22,23]. Apparent activation energies of permeation and diffusion can be calculated using the Arrhenius relationships [24] in Equations (7) and (8), respectively, while the apparent enthalpy of sorption can be calculated using the van't Hoff relationship [19] in Equation (9). Cross-verification of the transport parameters can be performed for consistency checks using independent permeation and pressure-decay sorption measurements and combination of the results via Equation (10).

$$P = P_0 \exp(-E_p/RT) \quad (7)$$

$$D = D_0 \exp(-E_D/RT) \quad (8)$$

$$S = S_0 \exp(-\Delta H_S/RT) \quad (9)$$

$$E_p = E_D + \Delta H_S \quad (10)$$

## 3. Experimental

### 3.1. Materials and sample preparation

High molecular weight poly(ethylene furanoate) (PEF) and poly(ethylene terephthalate) (PET) were supplied by The Coca-Cola Company and are the same materials characterized in our previous work [4]. The polymer repeat structures for PEF and PET are given in Table 2. Research-grade oxygen of 99.999% purity was provided by Airgas (Radnor, PA). Amorphous polyester films were prepared using a similar melt-press/quench procedure as in other works [4,15], and the absence of crystallinity was verified through x-ray diffraction and differential scanning calorimetry (DSC). All

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