



Water sorption in poly(ethylene furanoate) compared to poly(ethylene terephthalate). Part 2: Kinetic sorption



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ABSTRACT

Diffusion coefficients for water in amorphous poly(ethylene furanoate) (PEF) and poly(ethylene terephthalate) (PET) were studied at 35 °C over the entire water activity range. PEF exhibits a ~5× reduction in diffusion coefficient averaged over the entire concentration interval compared to PET. Fickian diffusion was observed for water in both polyesters up to ~0.6 activity, after which the presence of non-Fickian relaxations required treatment using the Berens–Hopfenberg modeling framework. Penetrant plasticization at high activity was found for both PEF and PET, as evidenced by a positive correlation between diffusion coefficient and increasing water concentration. Arrhenius interpretation of diffusion coefficients measured at 15, 25, 35, and 45 °C allowed calculation of the activation energies of diffusion for PEF and PET, which were similar at 47.1 ± 2.8 kJ/mol and 46.4 ± 3.0 kJ/mol, respectively. This study complements prior work pertaining to the equilibrium water sorption properties in both polyesters, and subsequently provides a detailed investigation of the water diffusion process in these materials.

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1. Introduction

Studies involving water transport in polymeric materials are important, since most polymers will realistically encounter humid environments at some point during their usable lifetime. Such transport data are particularly important for materials which will be in direct contact with liquid water, since water at unit activity can cause undesirable plasticization and swelling effects in a wide variety of polymers [1–4].

Recent innovation by Avantium (The Netherlands) has enabled economical, large-scale production of 2,5-furandicarboxylic acid (FDCA), which is one of two monomers needed to manufacture poly(ethylene furanoate) (PEF). Integration of PEF into the global polyester market is desirable, due to renewable sourcing of the monomers and the largely improved barrier, mechanical, and thermal properties compared to PET [5]. Multiple studies have focused on various aspects of PEF synthesis and/or material property characterization [6–11], however, no data exist in the literature regarding the fundamental water transport properties.

Applications of PEF in the beverage and food packaging industry involve high humidity environments, and knowledge of the water transport properties at ambient temperature is therefore required for accurate shelf-life predictions.

In comparison to PET, the current study indicates that PEF exhibits ~5× reduced water diffusion coefficients averaged over the entire concentration interval. This reduction is attributed to fundamental differences in segmental mobility, which originate from the rigid furan moiety in PEF compared to the mobile phenyl moiety in PET [5]. The results from the current work can be compared to the diffusion of water in poly(ethylene naphthalate) (PEN), which exhibits somewhat analogous rigidity to PEF due to hindered flipping of the bulky naphthalene moiety [12]. Rueda and Varkalis report a ~3.2× reduction in diffusion coefficient for PEN compared to PET, where both polymers are amorphous and in the hydrated state [13]. Interestingly, the authors also report a higher equilibrium sorption in PEN compared to PET due to differences in free volume [13,14], although the disparity in equilibrium uptake is not as significant as in the current work comparing PEF to PET [15].

The current study presents a detailed kinetic investigation of water diffusion in amorphous PEF and PET, and complements prior work regarding equilibrium sorption properties for water [15], oxygen transport [16], and fundamental segmental mobility [5]. Similar to the companion work [15], gravimetric sorption

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experiments were performed using three independent techniques, thereby allowing verification of the reported diffusion coefficients. Concentration dependent diffusion coefficients are presented for amorphous PEF and PET at 35 °C over the entire water activity range, and exhibit plasticization type behavior as evidenced by the positive correlation with increasing activity. The presence of non-Fickian relaxations at high activity is consistent with this notion, as is the sorption/desorption hysteresis observed for both polyesters reported in our companion work [15]. Additional measurements of the activation energy of diffusion can be combined with the enthalpy of sorption measurements provided elsewhere [15], thereby allowing a means to estimate the activation energy of water permeation in both polyesters. Similar calculations involving the diffusivity and solubility reveal a reduction in permeability of $\sim 2.8\times$ averaged across the entire concentration interval for PEF compared to PET, which is consistent with the reduction of $\sim 2\times$ for PEF vs. PET reported by Avantium [17]. This work, in combination with the equilibrium sorption counterpart [15], presents the first detailed study of water transport in PEF.

2. Experimental

2.1. Materials and film preparation

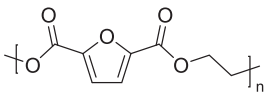
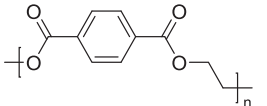
Virgin poly(ethylene furanoate) (PEF) and poly(ethylene terephthalate) (PET) were provided by The Coca-Cola Company, and are characterized in previous works [5,15,16]. Repeat structures for both polyesters are shown in Table 1. Amorphous films were prepared using the same melt-press/quench methodology described in prior work [5]. Nitrogen carrier gas (Airgas, Radnor PA) was utilized by the TA-VTI SA+ sorption instrument, and de-ionized water was used for all sorption experiments.

2.2. Sorption measurements

Water uptake data between 0 and 0.95 activity were measured during sorption and subsequent desorption for both polyesters using an automated TA VTI-SA+ vapor sorption analyzer (TA Instruments, New Castle, DE). In this system, the desired vapor concentration is obtained via mixing of separate wet and dry nitrogen streams, which are automatically controlled by the instrument via two separate mass flow controllers. Feedback is provided to the instrument from a dew point analyzer, which continually measures the water content in the stream. The sample mass is constantly monitored via a microgram balance, after which equilibrium is realized when no change in mass is observed versus time. Additional details regarding this technique are provided in the companion paper [15].

Two additional gravimetric methods, i.e. the McBain quartz spring technique [18] and gravimetric liquid water method, were

Table 1
Poly(ethylene furanoate) (PEF) and poly(ethylene terephthalate) (PET) repeat structures.

Polymer	Structure
Poly(ethylene furanoate)	
Poly(ethylene terephthalate)	

used to verify and corroborate the measurements recorded by the automated VTI instrument. The former technique is more suitable to testing at low vapor activities, while the latter provides uptake data at unit activity. Additional details are provided in our companion work [15].

3. Results and discussion

3.1. Diffusion model development

Gravimetric water sorption values are typically reported in units of weight percent water (wt%, g H₂O/g dry polymer), and can be converted via Equation 1 to a non-dimensional form useful for extracting kinetic information.

$$\frac{M_t}{M_\infty}(t) = \left(\frac{m(t) - m_{\text{initial}}}{m_{\text{final}} - m_{\text{initial}}} \right) \quad (1)$$

In Equation (1), M_t represents the water uptake at time t , M_∞ is the water uptake at equilibrium (i.e. infinite time), m is the sample mass measured by the balance, *initial* represents the beginning of the sorption interval, and *final* represents the end of the sorption interval. The M_t/M_∞ parameter in Equation (1) therefore represents a normalized, non-dimensional quantity that varies from zero to unity.

Solutions of the time-dependent diffusion equation have been widely tabulated for diffusion cases involving an infinite sheet geometry and a variety of boundary and initial conditions [19]. The simplest solution is obtained via implementing a constant initial concentration throughout the film (i.e. $C = C_0$ at $t = 0$) and a constant concentration at the film surfaces for $t > 0$ (i.e. $C = C_1$ at $x = \pm l/2$ for $t > 0$, where l is the film full-thickness). Solution using these conditions is provided in Equation (2) [19], where the subscript “F” denotes the Fickian solution, D_{Avg} (cm²/s) is the effective diffusion coefficient averaged over the concentration interval, and l (cm) is the film full-thickness.

$$\frac{M_t}{M_\infty} \Big|_F = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D_{\text{Avg}}(2n+1)^2 \pi^2 t}{l^2}\right) \quad (2)$$

Equation (2) accurately describes the kinetic sorption behavior of relatively non-condensable gases in polymer materials (i.e. O₂ in PEF [16]) and some vapors at low activity [20,21], consistent with the validity of the boundary and initial conditions in these applications. Equation (2) can also describe the water sorption data

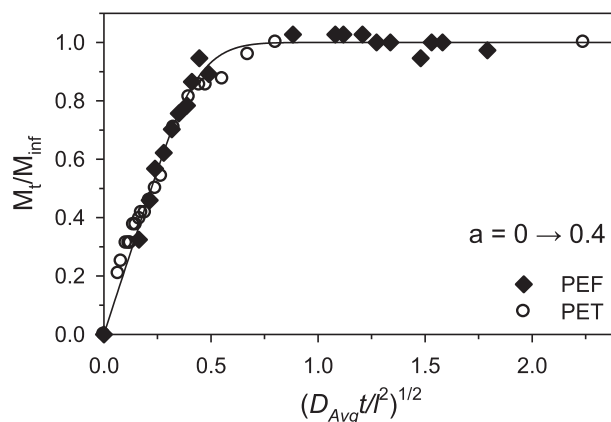


Fig. 1. Water uptake data at 35 °C for PEF (diamonds) and PET (circles) measured during sorption between 0 and 0.4 activity using the quartz spring system. Data are plotted versus a non-dimensional time, with the corresponding Fickian fit from Equation (2). Respective D_{Avg} values are provided in the Supplemental Information.

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