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Effect of film thickness on the changes in gas permeability of a glassy polyarylate due to physical aging
Part II. Mathematical model

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Abstract

Part I of this series documented a substantial loss in gas permeability over time for thin films of a glassy polyarylate made from bisphenol-A–benzophenone dicarboxylic acid. The rate of permeability loss, and, thus, aging was found to be dependent on film thickness in a way that suggested that physical aging occurs by two mechanisms. In this paper, a mathematical model was developed to quantitatively describe the physical aging process in terms of the free volume (permeability) loss observed using reasonable physical parameters. The model describes two simultaneous mechanisms of free volume loss: free volume diffusion to the film surface (thickness dependent) and lattice contraction (thickness independent). A step-wise model development is described with comparison to the data and optimization of the model parameters at each step. The final dual-mechanism model describes the experimental data presented in Part I remarkably well. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Physical aging process; Free volume diffusion; Lattice contraction

1. Introduction

The first paper in this series [1] showed that the gas permeability of thin, glassy polyarylate membranes decreases significantly with time after quenching from above the glass transition temperature while selectivity increases modestly. Considerable evidence supports the contention that these effects are due to physical aging or volume relaxation of the glassy polymer film, and that the rate of aging is strongly influenced by the film thickness [1–5]. Knowledge of this phenomenon is relevant to membrane-based gas separation processes [2–4,6–11]. In turn, the observations provide an opportunity to gain a better understanding of how glassy polymers evolve toward an equilibrium state.

Most of the theories of physical aging or glassy state volume relaxation have been developed in response to experimental observations and are mainly phenomenological in nature [12–16]. The literature continues to invoke free volume diffusion as a mechanism, at least qualitatively, for volume relaxation [2–5,12,13,17–20]; however, some have disputed the notion of hole diffusion leading to alternative explanations of volume relaxation [21,22].

The evidence presented in Part I [1] supports the idea that the free volume reduction associated with physical aging occurs by two simultaneous mechanisms: one seems to be independent of thickness and is completed quickly while the other is thickness dependent and seems to scale with thickness as expected for a diffusion process, i.e. the time, t, response for films of different thicknesses, ℓ, collapse onto a single curve when plotted versus t/ℓ^2. The purpose here is to construct a mathematical model based on these two mechanisms to see if it is possible to describe quantitatively the response observed using reasonable physical parameters.

2. Background

When a polymer melt (or a liquid) is cooled, the time scale for volume contraction increases rapidly as the temperature becomes lower, and eventually the polymer is not able to maintain an equilibrium structure on the time scale of the observation; amorphous materials that are trapped in such a non-equilibrium state are commonly referred to as glasses. The actual state of the glass, as judged

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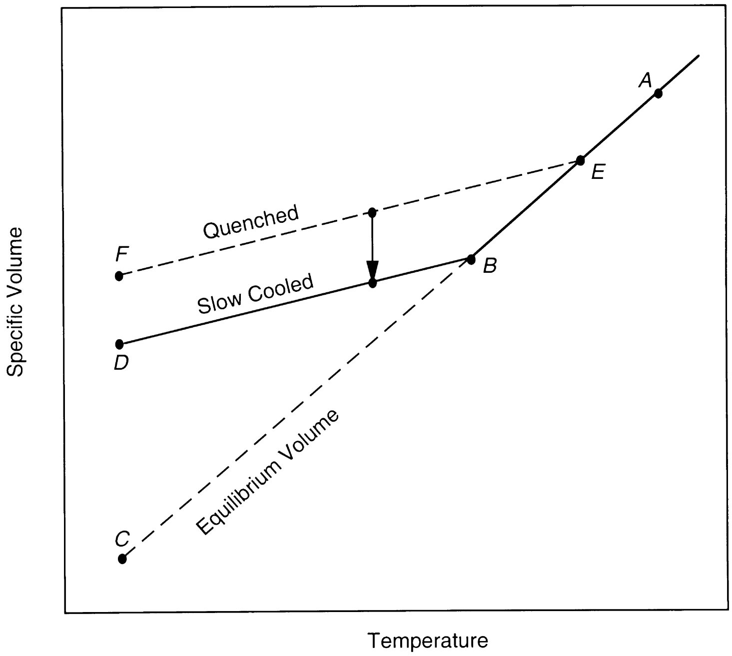

Fig. 1. Schematic temperature–volume relationship for an amorphous polymer. The arrow represents the spontaneous loss in specific volume of a rapidly quenched sample to that of a slow cooled specimen.

for example by specific volume, depends on its history (see Fig. 1). There is a driving force for the glass to relax (physical aging) over time to the equilibrium state, but for most polymer glasses (based on observations of macroscopic samples) the rate of this process is extremely slow (usually imperceptible) except at temperatures slightly below T_g. The kinetics of the relaxation is generally understood to be determined by the rate of segmental motion of the polymer chains. Most of the polymer literature apparently regards the specific volume of a glassy polymer as a bulk property and does not consider sample size effects or the mechanisms by which the volume contraction occurs. However, as mentioned above, there is considerable evidence, albeit mostly indirect, that polymer glasses that are very small in at least one dimension relax much more rapidly than macroscopic specimens. The following subsection considers two mechanisms of volume contraction; one (free volume diffusion) depends on the dimensions of the sample while the other (lattice contraction) does not. The next subsection provides a basis for connecting the observed changes in gas permeability (see Part I [1]) with the volume contraction that accompanies physical aging of a glassy polymer.

2.1. Prior models for volume contraction

In 1943, Alfrey et al. [23] proposed, in a qualitative discussion, that diffusion of “holes” or free volume from the interior of a glassy polymer to the surface is responsible for volume contraction on isothermal aging below the glass transition temperature, T_g. This type of mechanism has been claimed to be responsible for the elimination of quenched-in excess vacancies in thin metallic films, where the surface acts as a sink for “holes” [24,25]. Curro et al. [13] prompted by the well-known volume relaxation experiments of Kovacs et al. [26] for poly(vinyl acetate), developed a quantitative analysis of the diffusion of free volume in the form of holes or vacancies, limited by chain segmental motion; they described this change in fractional free volume, f, as

$$\partial f/\partial t = \nabla(D\nabla f) \tag{1}$$

where D, the diffusion constant for holes, is a function of fractional free volume, and the driving force for vacancy diffusion is a free volume gradient. The well-known Doolittle equation [27] was used to describe the free volume dependence of the diffusion coefficient

$$D = D_r \exp\left[-B\left(\frac{1}{f} - \frac{1}{f_r}\right)\right] \tag{2}$$

where the reference state is taken as the glass transition temperature and B is a material constant. They proposed values of $D_r = 1 \times 10^{-14}\ \mathrm{cm^2/s}$ and $B = 10.5$; other published values for B range from 1.0 to 10.5 [13,15,28]. Their analysis assumed an arbitrary length scale, ℓ, which they chose not to identify with any physical dimension of the sample but argued in favor of a much smaller, submicron, internal length scale. Of course, use of the thickness of a thin film for this dimension would naturally lead to a thickness dependent aging rate.

Curro et al. [13] coined the term “lattice contraction” to describe the simple mechanism of volume contraction in which segments of the polymer chains uniformly move closer together throughout the sample. That is, if one

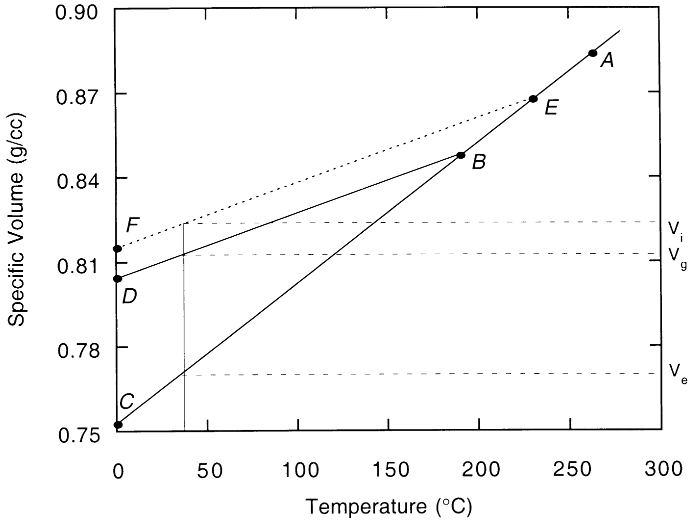

Fig. 2. Experimental PVT relationship of BPA–BnzDCA and the estimates of the specific volume parameters for the model.

imagines a lattice, the overall reduction in volume is caused by a decrease in lattice spacing throughout the specimen; this mechanism is not dependent on sample size. They argued that lattice contraction could possibly be coupled with free volume diffusion to describe the overall volume reduction upon aging. Curro et al. did not propose any mathematical model for the simple mechanism of lattice contraction. However, Hirai and Eyring [22] proposed that volume contraction in a liquid due to an isothermal pressure increase from p_1 to p_2 is described by the following equation:

$$v = v_2 + (v_1 - v_2)e^{-t/\tau} \tag{3}$$

where v_2 is the final volume, v_1 the initial volume, t the time and τ a relaxation time. This equation provides a simple model to describe the kinetics of size independent lattice contraction; however, a more realistic model might require a distribution of relaxation times or more conveniently employ a stretched exponential function [29–33].

2.2. Relationship between gas permeability and specific volume

Diffusional processes in polymers are commonly described within the framework of the concept of free volume; Eq. (2) is a typical example. The permeation of gases in glassy polymers has been successfully correlated in terms of free volume using an analogous relationship

$$P = Ae^{-(B/f)} \tag{4}$$

where P is the gas permeability coefficient, and A and B are constants that depend on the gas molecule type. The fractional free volume, FFV or f, in this relationship is defined as

$$f = \frac{V - V_0}{V} \tag{5}$$

where V is the polymer specific volume and V_0 the volume occupied by the polymer segments; the latter can be calculated by various group contribution schemes like the simple Bondi method [34], the somewhat more complicated scheme suggested by Park and Paul [35], etc. For a given polymer/gas pair, the above provides a relationship between the gas permeability coefficient and the specific volume of the polymer. As the latter changes with sample history, such as during physical aging, so does the gas permeability. To the extent that this relationship is valid, permeation measurements provide a useful and sensitive way to monitor physical aging, especially in thin films where density measurements are difficult to perform with high levels of accuracy.

It is necessary to establish some experimental specific volume–temperature relationships for bisphenol-A–benzophenone dicarboxylic acid (BPA–BnzDCA) since these will be needed in the model to be developed later. First, it is useful to review some general features of glassy polymers that have been widely discussed in the literature for more than 50 years. Fig. 1 schematically illustrates the specific volume–temperature relationship of a typical amorphous polymer [23] where the line AC represents the equilibrium relationship. In the vicinity of the glass transition temperature, equilibrium cannot be reached within the experimental time scale, so the specific volume follows a different relationship on cooling below this temperature. The latter is illustrated for glasses that are rapidly quenched and slowly cooled; it is generally held that the various glassy state lines are approximately parallel to each other. The line labeled “slow cooled”, while not an equilibrium relationship, is representative of glasses made under many conditions. The specific volume of glassy polymers made by many different processes (extrusion, molding, solvent casting, etc.) over a wide range of processing conditions is remarkably reproducible, at least within a certain tolerance; we refer to this as the glassy or “bulk” state. It appears that a quenched sample with a higher specific volume will rapidly approach this state (see arrow in Fig. 1) while

Table 1
Model parameters for BPA–BnzDCA

$P(O_2)_{bulk}$ (Barrer)	V_0[a] (cm^3/g)	f_i[b]	f_g	f_e
1.58	0.692	0.160	0.149	0.102

[a] Occupied volume calculated by the Bondi method [36].

[b] Fractional free volumes were calculated by Eq. (5) from experimental volume–temperature data in Fig. 2.

relaxation from the bulk state towards the equilibrium is much slower.

3. Heuristic model development

In Part I [1] of this series, it was shown that the rate of change in gas permeability coefficients with aging time was strongly dependent on film thickness for very thin films ($\ell < 2.5$ μm) while for thicker films this effect did not seem to be significant. This implies that the loss of free volume with time by physical aging occurs by two mechanisms; one that is thickness dependent (free volume diffusion) and one that is not (lattice contraction). The following is a heuristic approach to developing a mathematical model for describing such a dual mechanism of aging.

The data were separated into two groups, "thick" and "thin", so that the aging mechanisms could be identified and modeled separately. The validity of using a diffusion mechanism to describe the permeability reduction observed in the thin films is tested and the proper diffusion equations identified. This is followed by the development of an empirical thickness independent relationship for the thick films. Finally, relationships that combine both mechanisms are developed, limiting conditions established, values of parameters are optimized and the model output is compared to the entire experimental data set.

3.1. Free volume limits and relationships

The first step in this model development is to define and quantify certain limits of fractional free volume for the subject polymer. In Part I [1], experimental PVT data for the polyarylate BPA–BnzDCA were presented. The line ABD in Fig. 2 summarizes the experimental results extrapolated to zero pressure. The AB segment represents the equilibrium melt line and BC its extrapolation below T_g. The BD segment is the relatively reproducible "slow cooled" line discussed above. Free volume can be calculated via Eq. (5) once a value of V_0 is established; a value of 0.692 cm^3/g was calculated by the Bondi group contribution method [34,36].

In what follows, three fractional free volume values are used, all corresponding to the permeability measurement temperature of 35°C. Specific volume values were obtained as described below and the corresponding free volumes were calculated from Eq. (5) to give the results shown in Table 1.

Values for the glassy or "bulk", f_g, and equilibrium, f_e, fractional free volume were computed from specific volumes obtained from lines BD and BC, respectively, at 35°C. The films were initially heated to $T_g + 35°C = 230°C$ and then cooled. An upper bound on the "initial" free volume, f_i, of the quenched film would be defined by the specific volume taken from line EF drawn parallel to BD that intersects the equilibrium line at 230°C. It is unlikely that the cooling rate experienced by the films could produce such a high f_i, but the data do show that the actual initial fractional free volume is larger than f_g (since the permeability coefficient is initially higher than the "bulk" value). It appears that the model is not extremely sensitive to the exact initial value used.

In the following model development, we need a quantitative relationship between free volume and the permeability coefficient. Eq. (4) provides the form to be used for this purpose. Based on a large database of glassy polymers, Park and Paul [35] reported values of $A = 397$ Barrer and $B = 0.839$ for oxygen. For our system, the value of A_{O_2} was adjusted to 441 while B_{O_2} was held at 0.839 so that the "bulk" oxygen permeability value calculated from Eq. (4) using $f_g = 0.149$ matches the experimental value $P = 1.58$ Barrer. Eq. (4) assumes that the fractional free volume is uniform across the thickness of the film. However, if there is diffusion of free volume as considered in the following model, then there will be a distribution of f across the film. In this case, Eq. (4) is assumed to apply point by point so that the permeability is a function of x and t, i.e., $P(x,t)$, and then it is necessary to integrate the calculated permeability coefficients over the thickness of the film to compare with the experimentally observed values, $P(t)$. The appropriate integration is given by the expression

$$\frac{1}{P(t)} = \frac{1}{\ell}\int_{-\ell/2}^{+\ell/2} \frac{dx}{P(x,t)}. \qquad (6)$$

3.2. Simple diffusion model

The simplest model for volume relaxation by free volume diffusion only may be written in terms of Fick's second law with a constant diffusion coefficient for appropriate initial and boundary conditions, i.e.

$$\partial f/\partial t = D(\partial^2 f/\partial x^2) \qquad (7)$$

initial condition:

$$f = f_g \qquad \text{at } t = 0 \text{ for } -\ell/2 < x < \ell/2$$

boundary conditions: $f = f_e \qquad \text{at } t = 0 \text{ for } x = \pm\ell/2,$

$$\frac{\partial f}{\partial x} = 0 \qquad \text{for } t \geq 0 \text{ at } x = 0 \text{ (midplane).}$$

The values of f_g and f_e are set at those given in Table 1 while the free volume diffusion coefficient, D, was used as an

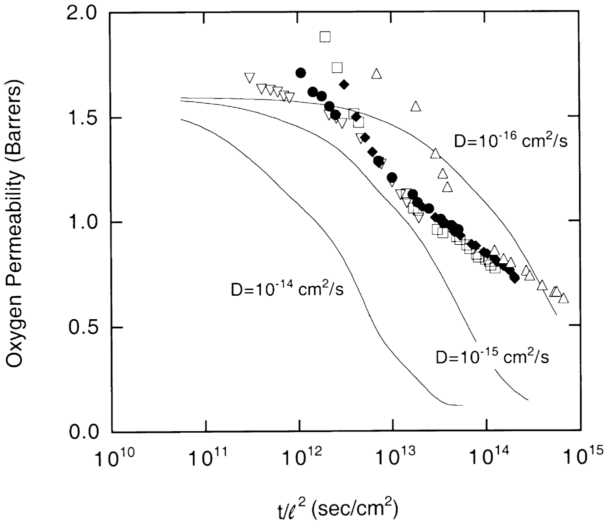

Fig. 3. Comparison of the simple diffusion model (Eq. (7)) calculations (lines) for three free volume diffusion coefficients (D) with the experimental oxygen permeability data for thin BPA–BnzDCA films ($\ell < 2.5$ μm): (▽) 1.85 μm; (●) 0.99 μm; (□) 0.74 μm; (◆) 0.58 μm; and (△) 0.25 μm.

adjustable parameter. This initial condition assumes a uniform distribution of free volume of f_g across the entire membrane before physical aging begins. The boundary conditions assume that after aging starts, the free volume at the surface is at the equilibrium value, f_e, and the profile is symmetrical about the centerline. The glassy fractional free volume, f_g, was used as the upper limit of free volume for comparison with the thin film data because the thickness independent (lattice contraction) mechanism was thought to account for the majority of the initial loss in free volume. The fractional free volume, $f(x,t)$, was calculated from Eq. (7) by PDEase, a computer program that solves ordinary and partial differential equations. These profiles of $f(x,t)$ were used to calculate $P(x,t)$ via Eq. (4). The profile of $P(x,t)$ was integrated over x via Eq. (6) to compute $P(t)$; the well-known analytical solutions of Eq. (7) with these initial and boundary conditions yielded identical curves.

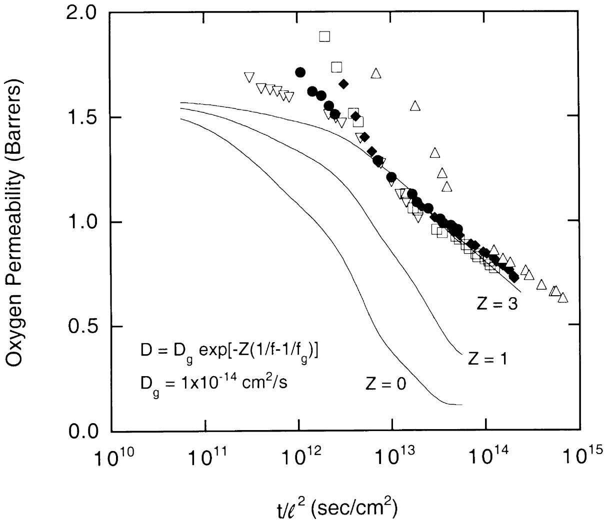

Fig. 4. Comparison of the free volume dependent diffusion coefficient model (Eq. (8)) calculations (lines) for three values of Z with the experimental oxygen permeability data for thin BPA–BnzDCA films ($\ell < 2.5$ μm): (▽) 1.85 μm; (●) 0.99 μm; (□) 0.74 μm; (◆) 0.58 μm; and (△) 0.25 μm.

Fig. 3 compares the oxygen permeability coefficients calculated by this simple model (lines) with the experimental data (symbols) for films with $\ell < 2.5$ μm. Calculations are shown for three diffusion coefficients, spanning three orders of magnitude, for comparison with the experimental data. The shape of the model curves does not closely resemble the data; the model curves always have a higher slope than the data at long times. The experimental data do not entirely collapse onto one curve when P is plotted versus t/ℓ^2 as this simple model would require. At short times, the experimental data lie above the limit predicted by the model.

3.3. Self-retarding diffusion model

The failure of the simple diffusion model described above to represent the experimental data indicates, as expected, that the diffusion of free volume is a self-retarding process in which the diffusion coefficient for free volume is dependent on the free volume. As free volume is reduced, chain mobility decreases, which in turn causes the rate of aging to decrease [27,37–40]. This is analogous to a concentration dependent diffusion coefficient for sorption of organic vapors by polymers. To incorporate a free volume dependent diffusion coefficient, Eq. (7) was modified as follows:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial f}{\partial x}\right) \tag{8}$$

where D is described by a Doolittle type expression

$$D = D_g \exp\left[-Z\left(\frac{1}{f} - \frac{1}{f_g}\right)\right] \tag{9}$$

and Z is a material constant and D_g is the diffusion coefficient for free volume at $f = f_g$. This partial differential equation was solved with the same boundary conditions as before using the software mentioned earlier. A comparison between the model (lines) and the thin film data (symbols) for three values of Z is shown in Fig. 4. When $Z = 0$, the diffusion coefficient is no longer free volume dependent, and the model reduces to Eq. (7). As Z increases, the diffusion coefficient for free volume becomes more dependent on the free volume, and therefore, the aging rate slows significantly and the slope of the predicted response begins to resemble the shape of the experimental data. For values of $Z = 3$ and $D_g = 10^{-14}$ cm^2/s, the model agrees rather well with the shape and magnitude of the part of the experimental aging data that scale to t/ℓ^2, i.e. the "master curve". The values for D_g and Z will be further optimized when the final model is assembled.

A free volume dependent diffusion coefficient leads to

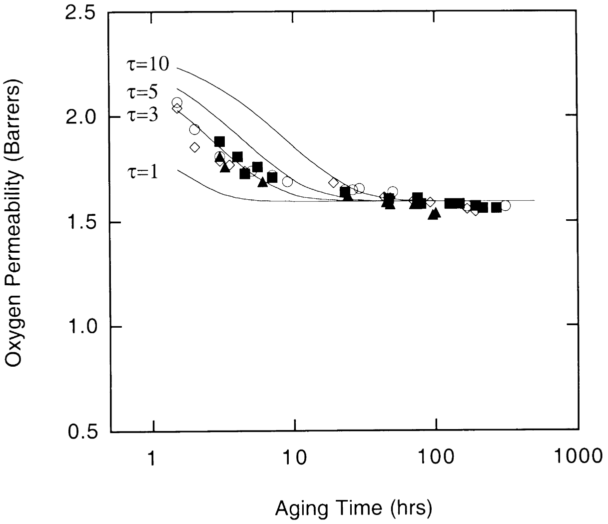

Fig. 5. Comparison of the lattice contraction model (Eq. (10)) calculations (lines) for four values of τ with the experimental oxygen permeability data for thick BPA–BnzDCA films ($\ell > 2.5$ μm): (○) 33 μm; (■) 28 μm; (◇) 9.7 μm; and (▲) 4.4 μm.

much better agreement between the model output and the experimental data. This confirms the expectation that free volume diffusion is a self-retarding process that cannot be described by a constant diffusion coefficient. Next, we address modeling of the rapid initial stage of aging.

However, before doing so it is important to comment on a discrepancy between the experimental data and the models to this point. The initial fractional free volume of the film immediately after quenching, f_i, must be larger than f_g because the initial permeability coefficients reported in Part I [1] of this series are larger than those seen in thick or bulk films where the fractional free volume is f_g. The work of Pfromm and Koros [2] and Rezac and co-workers [3,4] indirectly support the conclusion that the permeability coefficients of thin films begin above the bulk value. They reported that O_2/N_2 selectivity values in thin films begin below the bulk (aged, thick film) values and increase beyond this with time; indicating that the respective permeability coefficients begin above the glassy permeability and decrease with time. They were not able to show this directly because they did not have a sufficiently accurate way to measure the film thickness. For convenience, we have estimated f_i as described earlier using ideas suggested by Alfrey et al. [23] more than 50 years ago; this estimate is clearly only an upper bound on f_i.

3.4. Lattice contraction model

An inspection of the data in Part I [1] indicates that there is a relatively rapid reduction in permeability (hence, free volume) that is more or less independent of film thickness and is, therefore, the only mechanism discernible in thick films. As mentioned earlier, there is evidence that this process begins at a free volume higher than f_g. Based on the work of Hirai and Eyring discussed earlier, the following equation was adapted to describe this aging process:

$$f = f_g + (f_i - f_g)e^{-t/\tau} \tag{10}$$

where $f_g = 0.149$ in the present case, $f_i = 0.160$ (estimated as described above) is the initial fractional free volume, t is the aging time, and τ is a material relaxation time. The name “lattice contraction” given to the mechanism described by Eq. (10) comes from the work of Curro et al. [13]. Since BPA–BnzDCA is a new polymer, there is no information in the literature about the appropriate magnitude of the relaxation times for this material; however, Sandreczki et al. [32] used a relaxation time of 3.5 h for bisphenol-A polycarbonate in another aging study. In Fig. 5, the experimental data from Part I [1] for the thick films are compared with the lattice contraction equation shown above for several values of τ. It is apparent that a value of τ between 3 and 5 h gives good agreement with the data; the value from the study by Sandreczki et al. is within this range.

The lattice contraction expression adequately reflects the shape and magnitude of the initial aging curves. The assumption that the free volume reduction due to lattice contraction stops at the glassy value, f_g, is debatable, but the expression proposed here for this mechanism is phenomenological in nature and appears to be consistent with the available data. Intuitively, one might expect that the free volume should approach the equilibrium value by the lattice contraction mechanism, just as assumed in the diffusion mechanism. An expression representing a large drop in initial free volume over a short time scale followed by an approach to the equilibrium free volume over nearly geological time scales that accurately represents the experimental data could not be found. A stretched exponential function was explored, as it meets some of the requirements, but the shape and magnitude of the curves were not comparable to the experimental data.

3.5. Dual mechanism model

As mentioned at the outset, the data from Part I [1] strongly suggest that free volume is lost by diffusion to the surface and uniformly throughout the film simultaneously. Thus, we attempt here to construct a model that combines both mechanisms in a self-consistent way. We do this by restating the total free volume at any time and position within the film as follows:

$$f = f_i - \Delta f_{LC} - \Delta f_D \tag{11}$$

where Δf_{LC} is the amount of free volume lost due to lattice contraction and Δf_D represents that lost by diffusion. The former is defined by

$$\Delta f_{LC} = f_i - f^*_{LC} \tag{12}$$

where the quantity f^*_{LC} is represented by the following

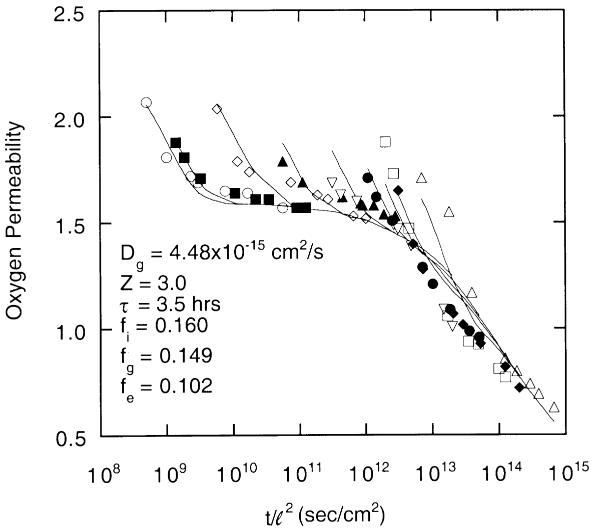

Fig. 6. Comparison of the dual mechanism model (Eq. (11)) calculations (lines) for the experimental oxygen permeability data for thin BPA–BnzDCA films: (○) 33 μm; (■) 28 μm; (◇) 9.7 μm; (▲) 4.4 μm; (▽) 1.85 μm; (●) 0.99 μm; (□) 0.74 μm; (◆) 0.58 μm; and (△) 0.25 μm.

adaptation of Eq. (10):

$$f^*_{\mathrm{LC}} = f_{\mathrm{g}} + (f_{\mathrm{i}} - f_{\mathrm{g}})e^{-t/\tau} \tag{13}$$

The free volume lost to the surface by diffusion is given by

$$\Delta f_{\mathrm{D}} = f_{\mathrm{i}} - f_{\mathrm{D}} \tag{14}$$

where the change in f_{D} is governed by the following diffusion equation:

$$\frac{\partial f_{\mathrm{D}}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial f_{\mathrm{D}}}{\partial x}\right) \tag{15}$$

with the initial condition:

$$f_{\mathrm{D}} = f_{\mathrm{i}} \qquad \text{at } t = 0 \text{ for } -\ell/2 < x < \ell/2$$

and boundary conditions:

$$f_{\mathrm{D}} = f_{\mathrm{e}} + (f_{\mathrm{i}} - f_{\mathrm{g}}) \qquad \text{at } t > 0 \text{ for } x = \pm\ell/2,$$

$$\frac{\partial f_{\mathrm{D}}}{\partial x} = 0 \qquad \text{for } t \geq 0 \text{ at } x = 0 \text{ (midplane)}$$

where D is dependent on the total free volume, f, and described by the Doolittle expression of Eq. (9).

Optimization of the model parameters by comparison to the experimental data for all thicknesses led to values of $Z = 3$ and $D_{\mathrm{g}} = 4.48 \times 10^{-15}$ cm^2/s. The model predictions and the experimental permeability data are shown in Fig. 6 plotted as a function of t/ℓ^2. The predicted lines calculated from the model are in remarkably good, but not perfect, agreement with the experimental data represented by the points. The predicted values are essentially all within 10% of their corresponding experimental values. There is a predicted curve for each thickness since the initial aging modeled by the lattice contraction mechanism is independent of film thickness and does not scale as t/ℓ^2; whereas, the changes predicted by the diffusion mechanism do scale as t/ℓ^2 and this dominates the responses at high values of t/ℓ^2 for thin films. The experimental data do not show the earliest stages of the short-term response that is independent of film thickness; thus, the fit of the data is not very sensitive to the choice of f_{i} used in the model.

It is useful to see how the predicted free volume varies with the time and position within the film. Fig. 7 shows predictions for three thicknesses that differ by an order of magnitude from each other. For the thickest film ($\ell = 1$ mil or 25.4 μm) diffusion of free volume has little effect except at very long times near the free surface. Essentially all of the predicted aging occurs by lattice contraction, and, thus, the free volume has approached the value of f_{g} throughout the film between the times $t = 1$ and 10 h as shown. Levels of f lower than f_{g} develop over an appreciable region near the surface after quite long times relative to the observation times in Part I [1], i.e. $t \approx 1000$ h.

For the thinnest film, $\ell = 0.254$ μm, diffusion is predicted to be the dominant mechanism of volume contraction over times of the order used in the experimental investigation. However, even after 100 h, the center of this very thin film is still quite far from the expected equilibrium free volume, f_{e}. This is shown in greater detail in Fig. 8 as the value of free volume at the center of the film is plotted versus the aging time for the same three thicknesses as in Fig. 7. There is very little change in the value of f at the center line for the two thicker films ($\ell = 2.54$ and 25.4 μm); for the thinnest film the value of f is about half way between f_{g} and f_{e} after 100 h of aging time. Computational limitations precluded calculating the free volume in the thinnest film for aging times much greater than 100 h. The free volume reduction is predicted to be a mixture of lattice contraction and diffusion for the intermediate thickness, $\ell = 2.54$ μm. The effects of the self-retarding feature of the diffusion mechanism for this intermediate thickness are conveniently seen in Fig. 9 by comparing calculations using $Z = 0$ ($D =$ constant) and $Z = 3$ where D decreases rapidly with a loss in free volume.

The lattice contraction component adequately describes the thickness independent nature of the first mode of aging, and free volume diffusion with a free volume dependent diffusion coefficient rather accurately simulates the self-retarding nature of the second mode of aging. The values of Z and D_{g} in the final model are within the ranges of similar model parameters in other aging studies [13,28], and the value of 3.5 h for τ was based on the study by Sandreczki et al. [32] of the structurally similar polymer BPA–PC.

4. Summary and conclusions

The permeability reduction experienced by BPA–BnzDCA films in Part I [1] of this study was modeled in terms of free volume reduction occurring by two

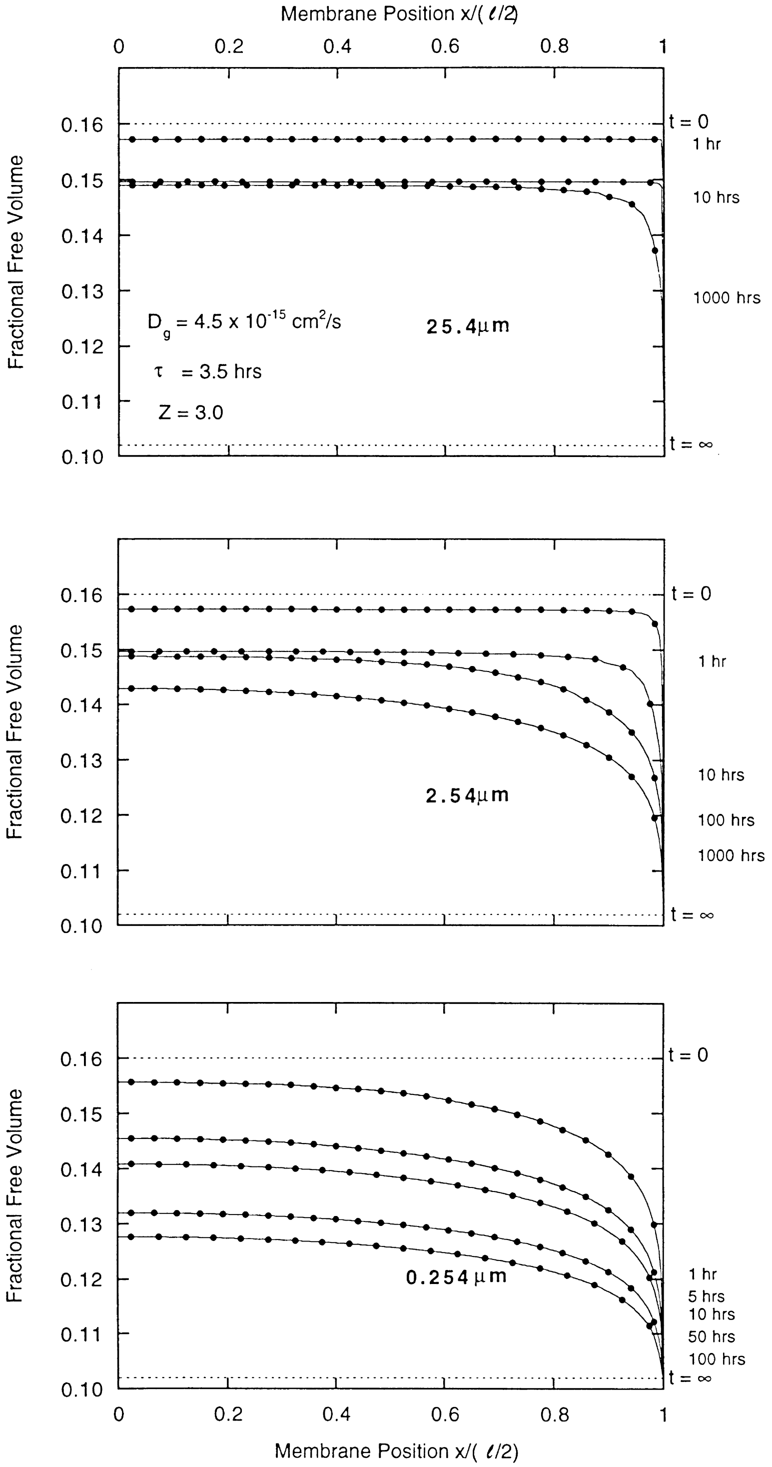

Fig. 7. Effect of film thickness on the free volume distribution predicted from the dual mechanism model for a membrane of thickness $\mathcal{L}$. The response is symmetrical about the center line, i.e. $x/(\mathcal{L}/2) = 0$.

simultaneous mechanisms: lattice contraction and free volume diffusion. The results from the optimized dual-mechanism model compare favorably with the experimental data for both thick and thin films.

One goal for constructing this type of model is to predict the gas transport behavior of any glassy polymer over its lifetime; another is to provide insight into the mechanisms of the aging process. Although many assumptions were made in order to construct this model, the final result is entirely consistent with two mechanisms being responsible for the permeability reduction seen in glassy films. One mechanism, lattice contraction, is independent of thickness

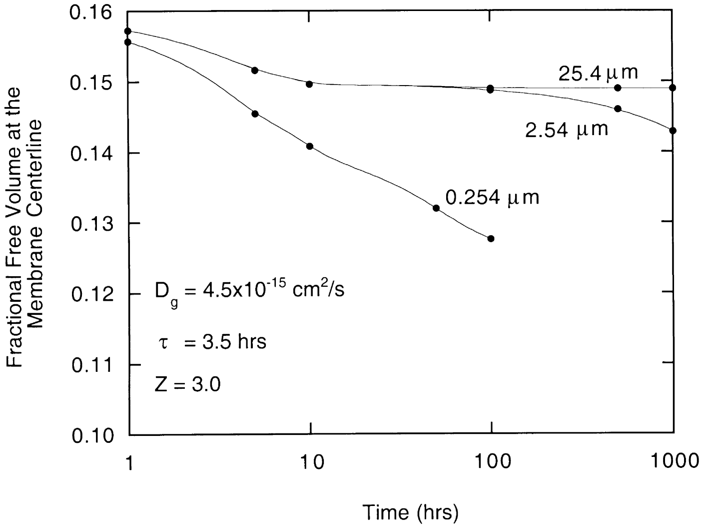

Fig. 8. Effect of film thickness on the value of the free volume at the center line as a function of aging time.

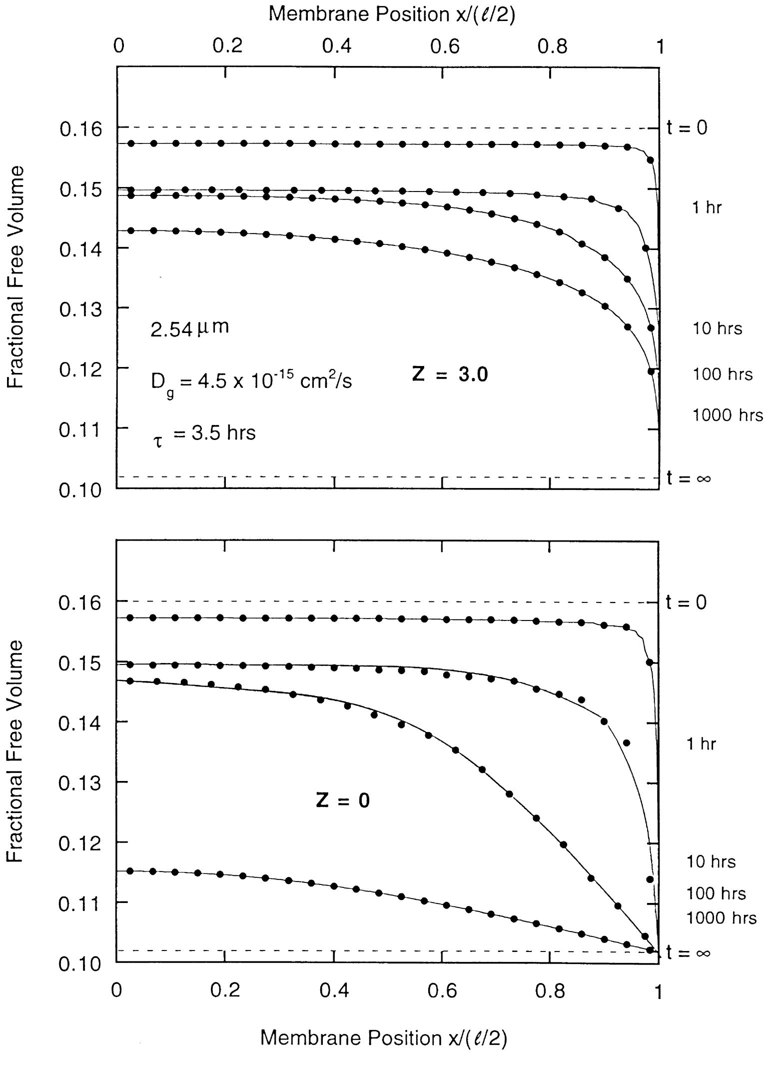

Fig. 9. Effect of the value of Z in the dual mechanism model on the fractional free volume distribution for a membrane of thickness ℓ.

and describes a rapid reduction in free volume following a quench from above T_g. The other mechanism can be successfully modeled as diffusion of free volume out of a membrane, and the limits of free volume diffusion are obtainable by simple PVT experiments. It is hoped that the presentation of this model will stimulate further experimental studies and subsequent refinement of the model or alternate explanations.

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