Physical aging of polystyrene films tracked by gas permeability

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Abstract
Most studies using gas permeation to characterize physical aging in thin polymer films have focused on polymers of interest as membrane materials, such as polysulfone (PSF) and Matrimid. Many other physical aging studies, using techniques other than gas permeation, focus on polystyrene (PS). In this work, physical aging in bulk PS films and PDMS-coated thin PS films was studied using well-established gas permeation techniques. The ~400 nm PS films aged slightly faster than bulk PS. However, the difference between rates of aging in thin and thick films was much less than that reported in PSF and Matrimid films of similar thicknesses. The ~800 nm films aged in a manner generally similar to bulk PS.

1. Introduction

Physical aging generally refers to spontaneous property changes that occur over time in a non-equilibrium glassy material as it approaches equilibrium via structural rearrangement [1]. In bulk polymer glasses at typical service temperatures, these changes are usually slow and continue almost indefinitely [2]. At elevated temperatures, however, aging is typically more rapid, and equilibration is possible over accessible experimental timescales. Much of the recent literature regarding physical aging in polymers has focused on aging in confined geometries. Interest in this area of study stems from the wide variety of applications that utilize polymers in confined geometries, such as gas separation membranes and nanocomposites, among others [3–8].

A significant portion of the literature on aging in confined polymers has focused on aging in glassy materials that are of interest as gas separation materials, such as polysulfone (PSF) and various polyimides (notably Matrimid) [4,5,9–21]. Typically, the polymers of interest have $T_g$ greater than 150 °C (often much higher) [4,9,11,15]. These studies are normally conducted at near-ambient temperatures (35 °C, most often), and gas permeability is measured over the course of weeks or months. Researchers using gas permeation techniques have generally observed accelerated or enhanced physical aging with decreasing film thickness. The thickness at which noticeable modifications in the aging behavior begin has been observed to be on the order of a few microns, which is much greater than the thickness typically associated with the onset of $T_g$ depression in thin films (by roughly an order of magnitude or more, for many polymers) [22,23].

Huang and Paul used gas permeability measurements to study freestanding PSF, Matrimid, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) films with thicknesses ranging from bulk down to 400 nm [4,16,24–26]. They observed an acceleration of aging with decreasing film thickness in all polymers studied. In a study of the temperature dependence of aging as assessed by gas permeability, Huang and Paul observed that the difference between the aging rates of 400 nm and 3.6 μm PSF films was greater for films aged at 35 °C than for films aged at 45 °C or 55 °C [16]. Increasing the temperature increased the aging rate at each thickness but decreased the sensitivity of aging rate to film thickness. For the thinnest films considered (400 nm), the difference in the aging rates at the three temperatures considered was small. A study of PPO films aged at different temperatures showed similar results [25]. Rowe et al. used a PDMS coating technique to enable gas permeation studies of PSF and Matrimid films as thin as ~18 nm [5]. They observed that the initial permeability decreased as
film thickness was decreased incrementally from 465 nm to 20 nm. For a 20 nm PSF film, the initial oxygen permeability was approximately 30–40% less than that of a bulk or 465 nm PSF film, indicating that the thinner film had already achieved a denser, lower-free-volume state by the time the first measurement could be made [5]. The properties of the ultrathin films strongly deviated from those of bulk films, and these deviations were said to be consistent with the ideas of enhanced mobility of near-surface material and $T_g$ depression in the thinnest films. In general, gas permeation aging studies have observed that by the time the films reach 100 h of aging time, thinner films typically show most of the following characteristics relative to thicker ones: lower absolute permeability values, higher selectivities, faster rates of permeability decline, and slighter greater rates of increase in selectivity [4,5,24]. In some cases, the rate of permeability decline may not continue to increase with decreasing thickness. For example, the thinnest films studied by Rowe et al. (20 nm PSF and 18 nm Matrimid) show a slower rate of permeability decline than some of the thicker films, but they have absolute permeability values that are significantly lower. This finding indicates that, for the thinnest films, which would be expected to have decreased $T_g$, rapid aging occurring in the first hour may result in a highly “aged” film that has a reduced driving force for physical aging and thus a slower rate of permeability decline.

Rowe et al. also characterized the aging behavior of polysulfone (PSF) films using variable energy positron annihilation lifetime spectroscopy (PALS) [27]. The results indicated that free volume decreased throughout the film during physical aging, as expected. A 450 nm film was observed to undergo accelerated aging when compared to a bulk sample, which is in agreement with previous studies of PSF films that used gas permeation techniques [4]. Additionally, Rowe et al. observed reduced ortho-positronium lifetimes at lower implantation energies, suggesting the existence of smaller free volume elements in the near-surface region of the film (within the first 50 nm). In contrast, variable-energy PALS studies of PS films by Cao et al. and Algiers et al. showed an increase in o-Ps lifetime at low implantation energies [28,29]. Rowe et al. suggested that the near-surface regions of PSF films age more rapidly than bulk and that the enhanced mobility offered by a free surface allows that region of the film to reach a lower free volume state more quickly than bulk. Using established correlations, the o-Ps lifetime was used to calculate the fractional free volume (FFV), and the FFV was then used to calculate the oxygen permeability. The permeability values calculated from the PALS aging data (with no adjustable parameters) were then compared to data gathered independently using gas permeability measurements over time. For films of 50 nm, 125 nm, and ~450 nm, there was remarkably good agreement between the two sets of data [27].

Another important body of literature has focused on aging in polymers like polystyrene (PS), which is perhaps the most commonly used polymer in studies of the glass transition and physical aging in confined geometries. In many of these studies, aging has been characterized using ellipsometry, dielectric spectroscopy, fluorescence spectroscopy, or DSC [8,30–36]. These studies often investigate aging at temperatures that are closer to $T_g$ than the temperatures used in the gas permeation studies.

Pye et al. used an ellipsometry procedure developed in their laboratories [32] to study aging in thin PS films and observed that a ~30 nm film aged at a slower rate than a ~2400 nm film at all temperatures considered [31]. The difference between the aging rates of the two PS films depended on the aging temperature. For the aging temperatures they considered, there was generally a larger difference between the aging rates of thicker and thinner films when the aging temperature was a greater distance from $T_g$. The difference in aging rates did not correspond merely to a shift in the aging rates to lower temperatures due to $T_g$ depression in the ~30 nm film, which they found to be consistent with the idea of a gradient in dynamics across the film.

Koh and Simon studied the aging of stacked ultrathin PS films using DSC [37]. They observed that the $T_g$ broadened and decreased with decreasing film thickness. An aging rate was defined as the rate of change in the fictive temperature ($T_f$) with respect to the logarithm of time ($-d T_f/d \log t_o$). When aged at the same distance from $T_g$, bulk and ultrathin films (62 nm) showed similar aging rates, but the time required to reach equilibrium was slightly greater for the 62 nm films than it was for bulk. When aged at the same temperature, however, the ultrathin films had reduced aging rates compared to bulk yet required a shorter time to reach equilibrium. They note that their results suggest the possibility that at aging temperatures that are more than 15 °C lower than $T_g$ (i.e., $T_g - T_o > 15$ °C), the ultrathin films may begin to show greater aging rates and shorter equilibration times than bulk when aged at equivalent distances from $T_g$. Using the equilibration time as the criteria for comparing the aging responses of the various films, the ultrathin films were said to undergo accelerated aging. A recent DSC study by Boucher et al. found that even PS films with thicknesses in the range of hundreds of nanometers demonstrated accelerated aging (as judged by the time required to reach equilibrium) when aged at 358 K or 369 K [35].

Priestley et al. studied the physical aging of PS supported on a non-attractive silica substrate by measuring changes in the peak fluorescence intensity of chromophore-doped PS films [38]. When aged at 32 °C ($T_g$,bulk = 71 °C), the aging response of a 20 nm film was similar to that of a 500 nm film. However, when aged at 93 °C ($T_g$,bulk = 10 °C), the 20 nm film showed no aging while the 500 nm film aged more rapidly than it did at 32 °C. The absence of aging in the 20 nm film aged at 93 °C was said to arise from $T_g$ depression, which caused the 20 nm film to be above its $T_g$ and in equilibrium at 93 °C.

There has been discussion in the literature about the possibility of fundamental differences in the aging of stiffer-backbone polymers like PSF or Matrimid and that of a polymer like PS, which has a more flexible backbone [32,34,39]. Gray et al. used ellipsometry to compare the aging behavior of PS and PSF films [34]. They measured the change in thickness of PS and PSF films quenched from above $T_g$ in either a supported or freestanding state and then held at a given aging temperature (65 °C for PS, 100 °C for PSF). For both PS and PSF, 400 nm and 1000 nm films that were supported during the quench showed essentially identical aging behavior. The physical aging of PS films quenched while supported was then compared to that of films quenched in a freestanding state (i.e., mimicking the annealing procedure used in many of the gas permeation aging studies). They observed that 1260 nm and 600 nm films quenched in a freestanding state aged more slowly than supported-quenched films of similar thickness, despite undergoing much more rapid cooling through $T_g$. Upon reheating the freestanding-quenched films above $T_g$ and then cooling in a supported state, the subsequent aging behavior was nearly identical to that of a film originally quenched in a supported state. The difference in aging rates between supported-quenched and freestanding-quenched films was much less in the 600 nm film than in the 1260 nm film. The aging rates of freestanding-quenched PS films exhibited a noticeable thickness dependence at these length scales. This finding differs from what was observed in supported films, which did not show any thickness dependence in their study and were observed previously to have thickness-independent aging rates until becoming thinner than 100 nm [31]. They suggest that different quench conditions (i.e., freestanding versus supported) would lead to different types of stresses in the glassy film, which would in turn affect the aging rate.
They further argue that the biaxial stress in supported-quenched films would be independent of thickness, while the uniaxial stress in freestanding-quenched films held by a wire frame would depend on thickness [34].

The diversity of experimental findings in studies using different polymers, experimental techniques, temperature ranges, and experimental durations suggests that there are many questions about physical aging in confinement that remain unanswered, especially when one considers the difficulty of comparing technique-dependent aging rates that are often calculated at different stages of the aging process. In this study, the physical aging behavior of polystyrene films was characterized using the established gas permeation tracking methodology. For the film thicknesses considered here, no significant \( T_g \) depression is expected. We compare the PS films in this work to PSF and Matrimid films for which aging data is readily available in the literature. In contrast to these materials, PS does not show strongly accelerated or strongly thickness-dependent aging in the temperature and thickness regimes considered here. These differences could be due in part to the large differences in quench depth below \( T_g \) and backbone structure for PS as compared to previously studied polymers like PSF and Matrimid.

2. Experimental

2.1. Materials

Polystyrene (PS) from Pressure Chemical (PS80323, \( M_w = 900,000, \ M_n/M_w = 1.1 \)) was used in this study to prepare both bulk and thin films (PS80323 is hereafter referred to as PS900k). Dow Styron 685D (\( M_w = 300,000, \ M_n/M_w = 2.3 \)) was used to prepare bulk films for comparison. The \( T_g \) s of PS900k and Styron 685D are 106 °C and 104 °C, respectively (DSC, heating rate \( 10 \degree C/min \), midpoint method). Both grades of PS are well below their \( T_g \) at the aging temperature (\( T_o \)) used in this work. At \( T_o = 35 °C \), which was the temperature used for all films considered here, PS is roughly 70 °C below its \( T_g \). Most other polymers previously studied using gas permeation techniques have \( T_g \) s significantly higher than PS, and aging experiments thus take place much deeper in the glassy state. For example, PSF and Matrimid aged at 35 °C are approximately 150 °C and 280 °C below their \( T_g \) s, respectively. Table 1 provides the structure, \( T_g \), oxygen and nitrogen permeabilities, and \( O_2/N_2 \) selectivity (\( \alpha \)) for the polymers used in this study.

2.2. Film preparation

Bulk films of PS were cast onto glass substrates from dichloromethane solutions. The films were allowed to dry in a well-ventilated hood for at least 4 days prior to removal from the substrate. After removal, the films were stored at room temperature until needed. Thin films of PS were prepared by spin casting from toluene solutions onto 5-inch silicon wafers. The spin time was 60 s, and the spinning rates were between 500 and 1000 rpm. The thickness of the PS films was measured using a J.A. Woollam M-2000 spectroscopic ellipsometer.

One of the most commonly encountered difficulties in aging studies of thin films using gas permeability measurement is the existence of pinhole defects in the film. Such defects obscure the true permeability of the material and cause the measured selectivity to be much lower than it would be in the absence of such defects. Additionally, the thin films are fragile, and preparing a sample for permeation testing requires the film to be handled and manipulated without tearing or otherwise ruining it. The relatively long duration of aging studies (coupled with a practical limit on the number of permeation cells) also requires inserting and removing the film sample from the permeation cell many times. Thus, sample failure is an unfortunate but frequent occurrence, regardless of whether or not the film originally has any defects. Recent studies of aging and CO2 plasticization in thin films have used a PDMS coating technique to mitigate the effects of pinhole defects, thereby increasing success rates in thin film studies [5,19–21]. The PDMS coating layer, which is typically on the order of 3–5 \( \mu m \), also provides mechanical support for the delicate glassy films. It was highly desirable to use PDMS on thin PS films, as it could significantly increase the probability that a given film would be suitable for aging studies via gas permeation techniques. However, the aforementioned studies used solutions of PDMS in cyclohexane to coat films of polysulfone and various polyimides. Cyclohexane, though a rather weak solvent for PS, could still potentially affect the PS thin films in a detrimental way during the PDMS coating step by changing the film thickness, causing non-uniformity of the PS-PDMS interface, or causing stress cracking or crazing. In order to avoid these problems, it was necessary to find a different solvent for the PDMS solutions used in this study.

After initial assessment of the solubility of PS and PDMS in various solvents, iso-octane was identified as the best candidate for our purposes. To verify that the iso-octane would not change the underlying PS layer during the spinning of the PDMS layer, a test was performed using pure iso-octane and the same spinning procedure used for PDMS coating. Iso-octane was deposited onto the PS-coated wafer from a sterile dropper and then spun for 60 s at 1000 rpm. The PS thickness was measured at three locations on three separate wafers both before and after the iso-octane rinse. Fig. 1 shows the results of the test, which indicated that the thickness of the PS layer was essentially unchanged (within 1% of the pre-rinse thickness) at each measurement location. Therefore, iso-octane was used in preparing the PDMS solutions used in this work.

After measurement of the PS layer thickness using ellipsometry, a layer of poly(dimethylsiloxane) (PDMS) was spun atop the previously-deposited glassy layer from a ~12% solution of PDMS in iso-octane. The PDMS solution was prepared by mixing Wacker Dehesive 944 with iso-octane and then adding an appropriate amount of the crosslinker and catalyst solutions supplied with

| Table 1 |
| Typical bulk polymer properties. |

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g )</th>
<th>( P_{O_2} )</th>
<th>( P_{N_2} )</th>
<th>( \alpha_{O_2/N_2} )</th>
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</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>104–106 °C</td>
<td>3.6</td>
<td>0.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane)</td>
<td>−123 °C</td>
<td>800</td>
<td>400</td>
<td>2</td>
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Permeability values reported at 35 °C and in units of Barrers (Ba); 1 Ba = \( 10^{-10} \) \( \text{cm}^3(\text{STP}) \text{cm} / (\text{cm}^2 \text{s} \text{cmHg}) \). 
\( T_g \) values for polystyrene measured via DSC (10 °C/min, 2nd heating, midpoint method).
Annealing oven and quenching to ambient temperature. Using the starting point for the experiment. The aging time is determined by an 800 nm PS upon removal from the annealing oven is estimated to be on the order of 5000 °C/min.

Dehesive 944. After coating with PDMS, the wafer-supported two-layer film was placed under vacuum at ambient temperature for 10–15 min to facilitate the removal of air bubbles and residual solvent from the PDMS layer and to ensure good contact between the PDMS and PS layers. Next, the PDMS was crosslinked at 100 °C for approximately 35 min in a temperature-controlled oven. The thickness of the crosslinked PDMS layer was measured using a Dektak 6M stylus profilometer. For the films discussed here, the PDMS layers were ~5 μm in thickness. We were unable to successfully conduct any aging studies without using a PDMS coating layer, and many of the PDMS-coated PS films also failed during permeation testing. The use of PS900k, which has a higher molecular weight than Styron 685D, increased the yield of usable thin films. The frequent failures were likely due in no small part to the brittleness of PS. According to the manufacturer datasheets, the elongation at break for Styron 685D PS is 3%, whereas for Solvay P-3500 NT LCD PSF (the grade of PSF used in previous thin film aging studies [4,5]), a value of 50–100% is reported. The Izod impact strength of PS is also reported as being roughly 3 times lower than that of PSF (21 J/m for PS, 69 J/m for PSF). PSF is clearly a much tougher and less brittle polymer than PS, so it is perhaps not surprising that many PS films (even those coated with PDMS) failed before sufficient data could be collected, even though permeability measurements on uncoated thin films of PSF have been made in the past [4,17]. PS also has a tendency to craze quite easily, and evidence of this could be seen in thick films that formed semi-opaque white regions when flexed or handled improperly.

After crosslinking and thickness measurement, the coated PS film samples were lifted from the wafer using deionized water, collected on rectangular wire frames, and then dried and stored under vacuum at ambient temperature for at least one day prior to beginning an aging experiment. To begin an aging experiment, the film was annealed at 120 °C (~15 °C above the PS Tg) for 20 min, which erases the prior thermal history and provides a well-defined starting point for the experiment. The aging time is defined as the amount of time elapsed since removing the sample from the annealing oven and quenching to ambient temperature. Using the methodology of Gray et al. [34], the cooling rate through Tg experienced by an 800 nm PS film coated with a 5 μm layer of PDMS upon removal from the annealing oven is estimated to be on the order of 5000 °C/min.

Gas permeability coefficients were measured at 35 °C using a constant-volume, variable-pressure permeation cell. Fig. 2 shows a schematic drawing of how film samples are mounted for permeation testing.

The upstream pressure was set at ~20 psia for thin films (to decrease the likelihood of film failure) and ~30 psia for the bulk films (to ensure a readily detectable gas flux through the film, because these films are considerably thicker).

3. Results and discussion

3.1. Calculation of PS permeability

Gas permeability measurements were made on PS–PDMS composite films. However, it is the permeability of the PS layer alone that is of interest. The permeability of the PS layer can be calculated using a model based on mass transfer resistances in series, which is shown in Equation (1).

\[ \frac{P_{\text{composite}}}{P_{\text{PS}}} = \frac{P_{\text{PS}}}{P_{\text{PS}} + P_{\text{PDMS}}} \]

where \( P_{\text{PS}} \) is the thickness of the PS film, \( P_{\text{PDMS}} \) is the thickness of the PDMS coating layer, \( P_{\text{PS}} \) is the permeability of the PS film, and \( P_{\text{PDMS}} \) is the permeability of the PDMS layer. The total film thickness (i.e., the sum of the PS and PDMS layer thicknesses) is given by \( t_{\text{composite}} \) and \( t_{\text{PS}} \) is the thickness of the two-layer composite film. McCaig and Paul have demonstrated that the PDMS permeability (and hence the mass transfer resistance) does not change with time [9]. This method of calculation has been used in other aging studies [5,19,20], and it is based on work by Henis and Tripodi [40]. In this work, the resistance of the PDMS layer was always less than ~6% of the resistance of the PS layer. Previous studies have found that the presence of the PDMS layer does not have a substantial effect on the aging behavior of PSF [5] or a 6FDA-based polyimide [20].

3.2. Gas permeability and aging in PS films

Fig. 3a presents oxygen permeability as a function of aging time for bulk films of PS, PSF, and Matrimid. Bulk films of both grades of PS (PS900k and Styron 685D) are shown, along with data for PSF and Matrimid from Huang [41]. The absolute oxygen permeability of PS900k is roughly 10% higher than that of Styron 685D. The two types of PS are made by different processes (i.e., anionic polymerization for PS900k versus free-radical polymerization for Styron 685D) and have different average molecular weights and molecular weight distributions. Additionally, the commercial material may contain oligomers and/or additives not present in PS900k. Thus, small differences in the permeability values of bulk films of PS900k and Styron 685D are not unexpected. Both grades of PS appear to age similarly, and the bulk PS films, like those of other materials, experience a steady drop in permeability over time. The oxygen permeabilities of two films of Styron 685D show good agreement with one another. Thus, for the sake of clarity, the remaining figures show only one set of data for bulk Styron 685D. Fig. 3b shows the data of Fig. 3a normalized by the permeability value at an aging
time of 1 h Fig. 3b shows that bulk PS films exhibit a more rapid relative decline in oxygen permeability than bulk PSF films do. The relative oxygen permeability decline of PS is similar to that of Matrimid, though perhaps slightly faster.

Fig. 4 shows the (a) oxygen and (b) nitrogen permeability as a function of aging time for thin and bulk PS films. For thin films (i.e., $t_{\text{PS}} < 1000$ nm), two samples of each thickness were studied. The samples were taken from the same film casting, but they were distinct from one another and were studied using different permeation cells. For films of the same thickness, the aging behavior appears similar. Although there are differences in the calculated absolute permeability values, these differences amount to ~10% or less. Differences in permeation cell calibrations, as well as uncertainties associated with measurements of the area available for gas permeation and the film thickness (for both the PS and PDMS layers), can contribute to discrepancies in the calculated permeability values for nominally identical films. Differences in the permeability values of no more than ~10% are considered reasonably good agreement for two films measured on different permeation cells. The oxygen and nitrogen permeabilities of the 830 nm films are greater than those of either 417 nm film. This finding is similar to what was observed at early aging times by Huang and Paul in both PSF and Matrimid, where initial permeabilities were higher for ~1000 nm films than they were for ~400 nm films [4].

The aging behavior of the thin PS films does not appear to differ as markedly from bulk as that of thin PSF or thin Matrimid films. Past studies on these materials and others have typically observed much greater differences in the aging behavior of thin versus bulk films [4,5,9,24,25]. The $O_2/N_2$ selectivity of PS films as a function of aging time is shown in Fig. 5. The selectivity values for the thin PS films are similar to bulk values, indicating that the PDMS-coated PS layers are behaving like defect-free films. The initial selectivity of the bulk PS900k film is ~15% lower than that of the other films. The lower initial selectivity is due largely to difficulty in fully degassing a thick bulk film when it is first placed into the permeation cell (and in between permeation tests during the initial period of the aging study). This can result in slightly higher permeability values for nitrogen (as can be seen in Fig. 4b) and lower selectivities. As the study progresses and the film is able to be fully degassed between tests and held under vacuum, this problem is eliminated. Thus, one should not over-interpret the fact that the bulk PS films show a slightly higher initial $N_2$ permeability and lower initial selectivity.
than would be expected based on extrapolation from the longer-time aging data. Future studies of PS films using gas permeability tracking will likely address this issue in more depth. As would be expected from the bulk permeability data, the bulk Styron 685D film shows a slightly higher selectivity than the bulk PS900k film. The normalized oxygen permeability as a function of aging time for PS films is shown in Fig. 6. Normalization facilitates comparison among films with different absolute permeability values by showing the relative decline in permeability over time. Fig. 6 shows good agreement between films of the same thickness. The 417 nm films appear to undergo a slightly greater relative decline in permeability over time than either the 830 nm films or the bulk films. The 830 nm films appear to age in a manner that is generally similar to bulk. The relative changes in permeability for PS films are much less than those seen in PSF or Matrimid films of comparable thicknesses that were studied previously [4, 5, 24].

Fig. 7 shows a comparison of normalized oxygen permeability as a function of aging time for films of PS, PSF, and Matrimid that are around 400 nm in thickness (data for PSF and Matrimid are taken from Fig. 17 in Ref. [4]). The permeability decline of the ~400 nm PS films is roughly linear with the logarithm of aging time and is less rapid than that of PSF or Matrimid. In contrast, Fig. 3b shows that bulk PS undergoes a relative decline in permeability that is similar to Matrimid and more rapid than PSF, demonstrating that the thickness dependence of aging is much more pronounced in polymers like PSF and Matrimid than in PS. Perhaps the gas permeation aging behavior of PS films would show greater deviation from bulk behavior if the films were much thinner (on the order of 100 nm or less), but experimental difficulties have prevented this possibility from being explored.

There are many potential reasons why the aging behavior of PS films at 35 °C differs so markedly from that of other polymers. One significant difference between PS and PSF or Matrimid is that at the aging temperature used in nearly all gas permeation studies (35 °C), PS is much closer to its Tg (Tg ~ 70 °C) than PSF or Matrimid, which are ~150 °C and ~280 °C from their Tgs, respectively. Differences in the thickness dependence of aging for these polymers could be due in part to differences in Tg - T. Huang and Paul observed a weakening of the thickness dependence of the aging rate of PSF (based on oxygen permeability data) as the aging temperature was increased (i.e., Tg - T decreased) [16]. Pye et al. also observed a smaller difference between the aging rates of relatively thick (2.4 μm) and ultrathin (29 nm) PS films as the aging temperature was increased [31].

The ellipsometry studies of Gray et al. [34] showed that PS films quenched in a freestanding state had aging rates that depended on thickness (where the aging rate, β, is determined by the change in normalized film thickness, i.e., β = −1/αt(h)h log t). The PS films in their work (Tg ~ 100 °C) were aged at 65 °C (Tg - T = ~35 °C), and the data covered aging times up to ~7 h. In our study, a lower aging temperature was used, and the permeability measurements were made over a longer period of time. The temperature dependence of aging in freestanding quenched PS films is not known. However, had the films of Gray et al. been aged at 35 °C, one could reasonably expect the aging to be slower. The changes in film thickness (which are directly related to density changes, since the film is biaxially constrained on a wafer) over the course of their experiments are quite small. Considering that the expected density changes would be even smaller for a film aged at 35 °C relative to one aged at 65 °C, it is not surprising that the PS films in this work show relatively little thickness dependence in permeation tests. In contrast to the
ellipsometry experiments, permeation experiments may be less able to reliably capture such small differences in aging behavior. Using the aging rate calculation methodology of Gray et al., the ellipsometry data of Huang and Paul for a ~400 nm PSF film aged at 35 °C (see Fig. 6 in Ref. [42]) show that it ages more rapidly than any of the PS films aged at 65 °C that were considered by Gray et al. [34] or Pye et al. [31] (βPS ~ 17 x 10^{-4}, while the largest value of βPS is roughly 10 x 10^{-4}). Thus, both permeation experiments and ellipsometry experiments are in agreement that thin PS films age more rapidly than PS films of comparable thicknesses.

As mentioned previously, there has been discussion in the literature regarding potential differences between the physical aging behavior of the relatively stiff-backbone polymers used in gas permeation studies and that of polymers with more flexible backbones, such as PS or poly(methyl methacrylate) (PMMA). Baker et al. measured the oxygen permeability of PMMA films ranging in thickness from 190 nm to ~6 μm over the course of roughly two months [32]. They observed no noticeable thickness dependence in the aging behavior and saw very little decrease in gas permeability over time. Additionally, Priestley et al. observed similar aging behavior between 500 nm and 20 nm PS films aged at 305 K (32 °C, very similar to the aging temperature in this work) [38]. Although these films were supported on silica and the 20 nm film was much thinner than any considered in this work, it is worth noting that thin PS films aged at nearly the same temperature used in this work have been shown to lack thickness dependence.

3.3. Comparison of aging data to the upper bound

A well-documented tradeoff exists between the gas permeability and permselectivity of polymeric membrane materials [43–47]. This tradeoff is typically discussed in terms of an “upper bound” line, which describes the current performance limits of polymer materials (i.e., the line is defined by the polymers with the highest selectivity at a given permeability, or vice-versa). The O2 permeability and O2/N2 selectivity values for bulk and thin PS films are compared to the upper bound in Fig. 8. Data for a bulk PS film and a 400 nm PSF film from Huang are also included for comparison [4]. The results for PS are similar to what has been observed previously in other gas permeation aging studies, which have shown that aging generally results in movement that parallels or deviates slightly away from the upper bound line [5,48].

4. Conclusions

The physical aging of both thin and bulk PS films was studied as a function of aging time at 35 °C. The aging behavior of bulk films of PS and two samples each of ~400 nm and ~800 nm PS films coated with PDMS was characterized using gas permeation techniques. In contrast to thin films of PSF and Matrimid studied earlier by Rowe et al. [5] and Huang and Paul [4,16,17,24], PS films do not show aging behavior that is strongly thickness-dependent and highly accelerated relative to bulk. The ~400 nm PS films in this work showed slightly faster aging than bulk PS; however, the slight acceleration seen here is much less than that observed in PSF and Matrimid films of similar thicknesses that were also aged at 35 °C. Additionally, comparison of the normalized oxygen permeability of PS, PSF, and Matrimid films of roughly 400 nm aged at 35 °C revealed that a ~400 nm PS film experiences a slower decline in relative permeability than a PSF or Matrimid film does. Bulk films of PS, however, aged more rapidly than PSF and at a rate similar to that of Matrimid (as assessed by their normalized oxygen permeabilities over time). Thus, at the thicknesses and aging temperature considered in this study, the aging behavior of PS shows much weaker thickness dependence than that seen in polymers like PSF and Matrimid. Comparisons to the Robeson upper bound showed that physical aging in PS produced changes with respect to the upper bound (for O2/N2 separation) similar to those reported previously in other polymers. Based on our findings, it would be difficult to use the results of PS aging studies to predict the aging behavior of typical gas separation polymers. Thus, PS, which is not used commercially as a membrane material due to its relatively poor mechanical properties, low chemical resistance, and low Tg, is not a good model for the aging behavior of useful membrane materials.

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References
